III-Nitride Nanocrystals for Green Photonics

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Dedication

To Ammu, Abbu, Farz

Table of Contents

Table of Contents	iii
Abstract	vi
Abrégé	viii
Acknowledgment	X
Contribution of Authors	xii
List of Figures	xiv
List of Tables	XX
List of Acronyms	xxi
-	

Chapter 1 Introduction	1
1.1 Motivation towards green photonics	1
1.2 III-Nitride materials as a building block for green photonics	3
1.3 The promises, current status and challenges of InGaN for high efficiency LEDs/lasers and photos	otovoltaic
devices	5
1.3.1 InGaN LEDs	5
1.3.2 InGaN Laser diodes	6
1.3.3 InGaN photovoltaic devices	8
1.4 Current status of GaN-based surface emitting laser diodes	9
1.5 Current status of photoelectrochemical and photochemical CO ₂ reduction	10
1.5.1 CO ₂ reduction to syngas	11
1.5.2 Photochemical CO ₂ reduction to syngas	15
1.6 Advantages of InGaN nanocrystals in green photonics	15
1.6.1 InGaN nanocrystals-based LEDs	15
1.6.2 InGaN nanocrystal-based laser diodes	17
1.6.3 Artificial photosynthesis based on InGaN/GaN nanocrystals	17
1.7 Organization of this thesis	19
Chapter 2 Experimental Techniques	21
2.1 Molecular beam epitaxial (MBE) growth for III-Nitride nanostructures	21
2.1.1 MBE tool details	22
2.1.2 Spontaneous (SP) growth mechanism	24

2.1.3 Selective area growth (SAG) mechanism	24
2.2 Pattering techniques: electron beam lithography	27
2.3 Device fabrication	27
2.4 Device characterization	28
2.5 Structural characterization	28
2.5.1 Scanning Electron Microscopy (SEM)2	28
2.5.2 Transmission Electron Microscopy (TEM)2	29
2.5.3 X-ray Photoelectron Spectroscopy (XPS)	30
2.6 Optical characterization	31
2.7 Photoelectrochemical and photochemical measurement	32
2.7.1 Photoelectrochemical measurement	32
2.7.2 Photochemical measurement	34
2.7.3 Co-catalyst deposition	35
2.8 Conclusions	5
Chapter 3 Demonstration of Stable Light Emission from InGaN Nanowire Photonic Crystal3	6
3.1 Introduction	\$7
3.2 Results and Discussions	39
3.3 Conclusions	.6
Chapter 4 An Electrically Pumped Surface-Emitting Semiconductor Green Laser	7
4.1 Introduction	8
4.2 Results and Discussions	19
4.3 Conclusions	7
Chapter 5 Efficient and Controllable Syngas Generation from Photoelectrochemical CC Reduction using Dual Cocatalysts5) ₂ 58
5.1 Introduction	;9
5.2 Results and Discussions	50
5.3 Conclusions	8
Chapter 6 Photocatalytic CO ₂ reduction to Syngas by III-Nitride Nanostructures6	i9
6.1 Introduction	0'
6.2 Results and Discussions	70

6.3 Conclusions	76
Chapter 7 Conclusions and Future Work	77
7.1 Summary of the work	77
7.2 Future work	78
7.2.1 Micro LEDs	
7.2.2 High efficiency syngas generation	80
7.2.2.1 Band engineering of nanowires	80
7.2.2.2 Integration with molecular and other catalysts	81
7.2.3 The Effect of CO ₂ impurity	82
7.2.4 Implementation of artificial photosynthesis system under natural sunlight	
Appendix A	85
Appendix B	90
Appendix C	102
Appendix D	112
List of Publications	116
References	119

Abstract

Green photonics, *i.e.*, photonic devices and systems that can operate at high efficiency and with reduced energy consumption and minimum environmental impact, holds the key to address the energy and environmental challenges we face. III-nitride semiconductors have unique properties that can be exploited to realize next generation green photonic devices and systems. Their energy bandgap can cover nearly the entire solar spectrum, making them an ideal material for LEDs and lasers operating in the blue, green and red, and for solar energy harvesting. However, conventional III-nitride epilayers have some fundamental issues. It is very difficult to incorporate high indium composition. As a result, the performance of GaN-based green LEDs is much worse than those operating in the blue spectrum, leading to the so-called "green gap" in photonics. On the same circumstances, there has been no demonstration of efficient photovoltaic devices using GaN-based materials. The realization of these devices and systems with high efficiency will address some of the grand challenges we face, including energy generation, reliability, distribution and utilization. Therefore, it is essential to develop novel III-nitride semiconductor materials to realize green photonic devices and systems.

In this thesis, we have investigated the molecular beam epitaxial (MBE) growth and fundamental structural, electrical and optical properties of InGaN/GaN heterostructures for applications in green light emitters and artificial photosynthesis. With the use of selective area epitaxy (SAG), InGaN/AlGaN core–shell dot-in-nanowire arrays have been grown with precisely controlled size, spacing, and morphology. We have demonstrated, for the first time, all epitaxial surface-emitting green laser diodes, which can exhibit a very low threshold current density ~400 A/cm² at room temperature. We have further explored the potential of GaN-based nanocrystals for the development of artificial photosynthesis devices for the conversion of CO₂ to syngas, a combination of CO and H₂ and one of the prominent future solar fuels. We have investigated the design and performance of photoelectrochemical and photochemical cells for syngas production. A new benchmark record of 1.88% efficiency for syngas generation has been achieved by integrating Au/Pt co-catalyst particles on GaN nanowire arrays in a photoelectrochemical cell. In order to utilize the abundant visible solar spectrum, we have designed a multi-band InGaN/GaN nanowire heterostructure, which is decorated with the unique Au/CrO_x core/shell nanostructures.

The engineered InGaN/GaN heterostructures can exhibit a energy conversion efficiency of ~0.91% in a simple, one-step photochemical cell.

This thesis establishes the use of III-nitride nanocrystals for energy efficient green light emitters and solar fuel production.

Abrégé

La photonique verte est la clé pour relever les défis énergétiques et environnementaux auxquels nous sommes confrontés. Les semi-conducteurs III-nitrure ont des propriétés uniques qui peuvent être exploitées pour réaliser des dispositifs et des systèmes photoniques verts de nouvelle génération. Leur bande interdite d'énergie couvre presque tout le spectre solaire, ce qui en fait un matériau idéal pour les LED et les lasers fonctionnant dans les domaines bleu, vert et rouge, ainsi que pour la récupération de l'énergie solaire. Cependant, les épilayers classiques au nitrure III ont quelques problèmes fondamentaux. Il est très difficile d'incorporer une composition à haute teneur en indium. Par conséquent, la performance des LED vertes à base de GaN est pire qu'un fonctionnement dans le spectre bleu, ce qui mène à ce que l'on appelle le fossé écart en photonique. Pour ces mêmes circonstances, l'existence de dispositifs photovoltaïques efficaces utilisant des matériaux à base de GaN n'a pas été prouvée. La réalisation de ces dispositifs et systèmes à haute efficacité répondra à certains des grands défis auxquels nous sommes confrontés, notamment la production d'énergie, la fiabilité, la distribution et l'utilisation. Par conséquent, il est essentiel de développer de nouveaux matériaux semi-conducteurs à base de nitrure III pour réaliser des dispositifs et des systèmes photoniques écologiques.

Dans cette thèse, nous avons étudié la croissance et la structure fondamentale ainsi que les propriétés électriques et optiques des hétérostructures InGaN/GaN par épitaxie de faisceaux moléculaires (MBE) pour des applications dans les émetteurs de lumière verte et la photosynthèse artificielle. Grâce à l'utilisation de techniques d'épitaxie de zone sélective (SAG), les réseaux de points dans le noyau-coquille InGaN / AlGaN ont été développés avec une taille, un espacement et une morphologie précieusement contrôlés. Nous avons démontré, pour la première fois, que toutes les diodes vertes au laser à émission de surface épitaxiale peuvent présenter une très faible densité de courant de seuil ~ 400 A/cm² à température ambiante. Nous avons également exploré le potentiel des nanocristaux à base de GaN pour le développement de dispositifs de photosynthèse artificielle destinés à la conversion du CO₂ en combustibles propres, y compris le syngaz, une combinaison de CO et de H₂, l'un des principaux combustibles solaires du futur. Nous avons étudié la conception et les performances de cellules photoélectrochimiques et photochimiques pour la production de gaz de synthèse. Un nouveau record de référence d'efficacité de 1.88% de l'énergie

solaire par rapport au gaz de synthèse a été atteint en intégrant des particules de co-catalyseur Au/Pt sur des réseaux de nanofils de GaN dans une cellule photoélectrochimique. Afin d'utiliser le spectre solaire visible abondant, nous avons conçu une hétérostructure de nanofils InGaN/GaN multi-bandes, qui est décorée avec les nanostructures uniques noyau/coque Au/CrO_x. Les hétérostructures d'ingénierie InGaN/GaN peuvent présenter un rendement de conversion de l'énergie solaire en gaz de synthèse d'environ 0.91% dans une simple cellule photochimique à une étape.

Cette thèse établit l'utilisation de nanocristaux de nitrure III pour des émetteurs de lumière verte à haute efficacité énergétique et pour la production de combustible solaire.

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Contribution of Authors

This dissertation work includes the contribution from the candidate and many other individuals. The supervisor of the candidate, Professor Zetian Mi, conceived and supervised the projects. The candidate and Professor Zetian Mi worked closely on discussions and manuscript writings. The contribution of individuals to the works presented from chapter 3 to chapter 6 is described as follows:

Dr. Yong Ho Ra and the candidate have equally contributed to work mentioned in Chapter 3. Specific contributions of the authors for Chapter 3 are as follows: Dr. Yong Ho Ra, the candidate, and Prof. Zetian Mi designed the study. The candidate and Dr. Yong Ho Ra did the EBL design and fabrication for Ti-mask-patterned substrate. Dr. Yong Ho Ra and the candidate conducted the InGaN photonic crystal growth along with the various optical characterization such as: photoluminescence and cathodoluminescence measurements. nanowire growth. The theoretical analysis, plane wave expansion method, has been done by Dr. Xianhe Liu. The manuscript was written by Dr. Yong Ho Ra, the candidate and Prof. Zetian Mi with contributions from other co-authors. The candidate has taken consent from Dr. Yong Ho Ra to include the manuscript in this thesis.

For chapter 4, Dr. Yong Ho Ra, the candidate and Professor Zetian Mi conceived the ideas. The candidate and Dr. Yong Ho Ra fabricated the nano-patterned mask substrates and conducted the MBE growths. Dr. Yong Ho Ra and the candidate performed SEM and PL measurements. Dr. Yong Ho Ra and the candidate contributed to the TEM analysis and carried out the device fabrication. Dr. Yong Ho Ra and the candidate performed the electrical and optical characterization. Dr. Xianhe Liu and Kishwar Mashooq contributed to the theoretical simulation. The manuscript was written by Dr. Yong Ho Ra, the candidate and Professor Zetian Mi with contributions from other co-authors. The candidate has taken consent from all the co-authors to include the manuscript in this thesis.

Dr. Sheng Chu, the candidate, Pengfei Ou and Pegah Ghamari have equally contributed to work mentioned in Chapter 5. The candidate did the n-GaN nanowire growth and MBE maintenance by herself. Renjie Wang and Hong Tran helped on growth and maintenance occasionally. The candidate did all the solar cell HF treatment and substrate cleaning for the MBE loading with the assistance of Pegah Ghamari and Hong Tran. The candidate herself did all the cleanroom work and structural characterization of SEM and TEM. Dr. Sheng Chu assisted some TEM sessions and did the XPS analysis. For the PEC experiments, making contacts, solar cell preparation (doing and annealing) were performed by the candidate and Pegah Ghamari. The theoretical DFT calculation and write up was conducted by Pengfei Ou and Prof. Jun Song. The manuscript was written by Dr. Sheng Chu, the candidate, Pengfei Ou, Prof. Jun Song, and Prof. Zetian Mi, with contributions from other co-authors. The candidate has taken consent from all the co-authors to include this manuscript in this thesis.

For chapter 6, the candidate, and Prof. Zetian Mi conceived the ideas. The candidate did the InGaN:GaN nanowire growth and MBE maintenance by herself. Dr. Faqrul Chowdhury assisted on growth related discussions. The PC cocatalyst preparation including the cleanroom work, the experiment plan, PL analysis, SEM, TEM, XPS and the PC experiments had been done by the candidate herself. David Liu from McGill FERM guided the candidate during the TEM session. Dr. Faqrul Chowdhury helped on XPS analysis. For PC experiments, the candidate, Dr. Baowen Zhao and Dr. Sheng Chu discussed on some parts and analysis of the data. The manuscript is currently under preparation.

List of Figures

Figure 1.1: Global energy related Carbon dioxide emission in the period of 1990–20181
Figure 1.2: History and projections of (a) electricity generation from selected fuels and (b)
renewable electricity generation in billion kilowatt hours (for y-axis) between 2010–20502
Figure 1.3: Common platforms of green photonics
Figure 1.4: Band gap energy vs. lattice constant for III-nitrides at room temperature
Figure 1.5: Band edge positions of commonly reported nitride photocatalysts. The oxidation and
reduction potentials of water are also shown (green dotted lines). The red dotted line represents
the band edge positions of $In_xGa_{1-x}N$ with x increasing from left to right (0–1). The reduction
potentials of CO_2 to various value-added products are also shown
Figure 1.6: Summary of key contributions to the efficient blue LED
Figure 1.7: Maximum external quantum efficiency (EQE) of commercial nitride and phosphide
LEDs, illustrating the "green gap" problem
Figure 1.8: Analogy among (a) natural photosynthesis, (b) photoelectrochemical synthesis, and
(c) photochemical synthesis on photocatalysts10
Figure 1.9: Syngas derivatives with reference to their composition (*H ₂ /CO molar ratio)12
Figure 1.10: Possible reaction pathways for electrocatalytic CO ₂ RR on metal electrodes in
aqueous solutions
Figure 1.11: SEM and emission images excited by He-Cd laser from InGaN/GaN nanocolumns
with the diameter of (a) 143 nm, (b) 159 nm, (c)175 nm, (d) 196 nm, (e) 237 nm, and (f) 270
nm16
Figure 1.12: Schematic is showing light absorption, charge separation, diffusion, recombination,
water reduction, and oxidation on nanowire photocatalyst18
Figure 2.1: The Vecco GENxplor Molecular Beam Epitaxy (MBE) system
Figure 2.2: Simplified schematic of the MBE growth chamber
Figure 2.3: Schematic illustration of the spontaneous growth of III-nitride nanowires by molecular
beam epitaxy24
Figure 2.4: The schematic of SAG pattern process, (a) deposited oxide/metal layer on substrate,

(b) coating with a thin functional layer, (c) opening apertures by using e-beam or nanoimprinting lithography, (d) final mask-patterned substrates after RIE etching and functional layer removal, (e) preciously controllable size with the lattice constant *a*, nanowire lateral size *d*......25

Figure 3.2: (a) Photoluminescence spectrum of InGaN/AlGaN dot-in-nanowire photonic crystals measured at room-temperature (red curve). Also shown for comparison is the photoluminescence emission of conventional InGaN/AlGaN nanowires (blue curve) without controlled spacing. (b)

Figure 5.1: Density functional theory calculations. Schematic of reaction paths for (a) CO_2RR to CO and (b) HER. Theoretical predicted volcano plots of (c) CO_2RR and (d) HER activity versus the binding energy of *CO on (*111*) and (*211*) facets of different fcc metals. The black vertical dashed line shows the equilibrium potential of *CO/CO. Red and blue solid lines show the potential-limiting steps for CO_2RR and HER as the *CO binding energy varies on the (*111*) and

List of Tables

Table 1.1 . Standard electrochemical potentials for CO ₂ reduction	12
Table 7.1. The list of most possible ranges of impurity in oxy-fuel combustion	82

List of Acronyms

APS	Artificial Photosynthetic
BEP	Beam Equivalent Pressure
BF	Bright Field
CA	Chronoamperometry
CAR	Continuous Azimuthal Rotation
CBM	Conduction Band Minima
CCD	Charge Coupled Device
CCS	CO ₂ Capture and Storage
CE	Counter Electrode
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CO ₂ RR	CO ₂ Reduction Reaction
CO ₂ RCs	CO ₂ Reduction Catalysts
CL	Cathodoluminescence
CW	Continuous Wave
DBR	Distributed Bragg Reflector
DFT	Density Functional Theory
DH	Double-Heterostructure
EBL	Electron Beam Lithography
EDX	Energy-Dispersive X-Ray Spectroscopy
EIA	Energy Information Administration
EL	Electroluminescence
EQE	External Quantum Efficiency
FE	Faradic Efficiency
FIB	Focused Ion Beam
FWHM	Full Width at Half Maximum
GaN	Gallium Nitride
GC	Gas Chromatograph

GHC	Green House Gas
Gt	Giga-Ton
HECs	Hydrogen Evolution Catalysts
HER	Hydrogen Evolution Reaction
HF	Hydrofluoric Acid
HIT	Heterojunction with Intrinsic Thin layer
HRTEM	High Resolution Transmission Electron Microscopy
IEA	International Energy Agency
InGaN	Indium Gallium Nitride
InGaP	Indium Gallium Phosphide
InN	Indium Nitride
IQE	Internal Quantum Efficiency
ITO	Indium Tin Oxide
I–V	Current-Voltage
KCl	Potassium Chloride
KHCO ₃	Potassium Bicarbonate
LD	Laser Diode
LED	Light Emitting Diode
LOC	Lateral Optical Confinement
MBE	Molecular Beam Epitaxy
MOF	Metal Organic Framework
MOCVD	Metal-Organic Chemical Vapor Deposition
MQD	Multiple Quantum Disk
MQW	Multiple Quantum Well
NC	Nanocolumn
NCSEL	Nanocrystal Surface-Emitting Laser
NW	Nanowire
PAMBE	Plasma Assisted-Molecular Beam Epitaxy
PC	Photocatalytic or Photochemical
PCSEL	Photonic Crystal Surface Emitting Laser
PEC	Photoelectrochemical

PECVD	Plasma Enhanced Chemical Vapor Deposition
PhC	Photonic Crystal
PL	Photoluminescence
PMMA	Polymethyl Methacrylate
PTFE	Polytetrafluoroethylene
PV	Photovoltaic
QCSE	Quantum Confined Stark Effect
QD	Quantum Dot
QW	Quantum Well
RE	Reference Electrode
RF	Radio Frequency
RGB	Red, green, and blue
RHE	Reversible Hydrogen Electrode
RHEED	Reflection High Energy Electron Diffraction
RIE	Reactive-Ion Etching
RTA	Rapid Thermal Annealing
RTCW	Room-Temperature Continuous Wave
SAE	Selective Area Epitaxy
SAED	Selective Area Electron Diffraction
SAG	Selective Area Growth
sccm	Standard Cubic Centimeter per Minute
SCOE	Solar-to-CO Efficiency
SEM	Scanning Electron Microscopy
SP	Spontaneous
SQW	Single Quantum Well
SSL	Solid State Lighting
STEM	Scanning Transmission Electron Microscopy
STS	Solar-to-Syngas
TEM	Transmission Electron Microscopy
TJ	Tunnel Junction
TON	Turnover Number

UHV	Ultra-high Vacuum
VBM	Valence Band Maxima
VCSEL	Vertical Cavity Surface Emitting Laser
WOCs	Water Oxidation Catalysts
WE	Working Electrode
XPS	X-ray Photoelectron Spectroscopy
2D	Two-Dimensional
2D-FEM	Two-Dimensional Finite-Element Method
μLED	Micro-Light Emitting Diode

Chapter 1

Introduction

1.1 Motivation towards green photonics

To date, fossil fuels cause 65% of greenhouse gas (GHC) emissions and disrupt the carbon cycle on the earth. Global energy consumption in 2018 increased at nearly twice the average rate of growth since 2010 and global energy-related CO₂ emissions rose by 1.7% to a historic high of 33.1 Gt CO₂, shown in Figure 1.1 [1]. Global warming and energy crisis may lead to many issues, including global famine in the near future [1, 2].



Figure 1.1: Global energy related Carbon dioxide emission in the period of 1990–2018 [1].

Based on recent International Energy Agency (IEA) report, CO₂ emitted from various fuel combustion was largely responsible for the global average annual surface temperatures above preindustrial levels. Lighting accounts for significant global energy consumption. Significant CO₂ emissions can be reduced with the adaption of LED bulbs, compared to conventional fluorescent and incandescent lighting [3, 4]. Recently, there is also a significant increase in the generation of electricity using renewable energy sources. Shown in Figure 1.2 is the projection based on the U.S. Energy Information Administration (EIA). It is expected that renewable generation will increase from 18% to 31% by 2050 [5]. In this regard, green photonics is positioned to address some of the major challenges we face in this century.



Figure 1.2: History and projections of (a) electricity generation from selected fuels and (b) renewable electricity generation in billion kilowatt hours (for y-axis) between 2010–2050 [5].



Technology Breadth

Figure 1.3: Common platforms of green photonics [6, 7].

Shown in Figure 1.3 is the schematic of some of key components and technologies related to green photonics, based on the report of Opto-Electronics Industry Development Association (OIDA) and Holland High Tech Systems and Materials (HTSM) roadmap [6, 7]. Through engineering photon generation, propagation, modulation, signal processing, switching, amplification, detection and sensing, green photonics will enable more efficient solid-state lighting, photovoltaic, communication systems etc., which will save energy and reduce CO₂ emissions. Broadly speaking, green photonics refers to photonic devices and systems that can operate with high efficiency, reduced energy consumption, and minimum environmental impact. Examples of green photonic devices include LED lighting, photovoltaics, and artificial photosynthesis devices.

1.2 III-Nitride materials as a building block for green photonics

Group III-nitride semiconductor materials ((In, Ga, Al) N and their ternary alloys) have unique electrical, optical, and structural properties. Wurtzite phase III-nitrides have direct bandgaps ranging from 0.7 eV for InN to 6.0 eV for AlN, which can cover nearly the entire solar spectrum [8], making the ideal material for light emitting diodes (LEDs) and lasers operating in the blue, green and red, and for solar energy harvesting. In 2014, Nobel Prize in Physics was awarded to Professors Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura for their invention of GaN-based blue LEDs, which opens the new path for GaN-based compounds are the materials of choice of various optoelectronic and electronic devices.



Figure 1.4: Band gap energy vs. lattice constant for III-nitrides at room temperature [8].

III-nitrides have also emerged as the materials of choice for harvesting solar energy for the generation of solar fuels from water splitting and/or CO_2 reduction. III-nitrides (e.g., InGaN), compared to conventional metal oxide photocatalyst materials, have a narrow bandgap (E_g), due to the negative potential of the N_{2p} orbital compared to the O_{2p} orbital. Moreover, the band edges of III-nitrides straddle the redox potential of water, with sufficient kinetic overpotentials for water redox reactions and CO_2 reduction to various hydrocarbons [9] (Figure 1.5). Because of the strong ionicity of nitrides, the surface states are located mostly near the band edges, which prevent them from being non-radiative recombination centers [10]. Recent studies also suggest nearly defect-free and N-terminated III-nitride photocatalysts are highly stable against photo-corrosion in acidic and neutral pH electrolytes [11, 12]. Hence the defect free and high crystalline quality nitrides can function both as photoanodes and cathodes. Additionally, nitrides possess a high absorption coefficient and large charge carrier mobility, which can lead to strong photon absorption and efficient charge carrier extraction required for efficient solar-fuel conversion [13].



Figure 1.5: Band edge positions of commonly reported nitride photocatalysts. The oxidation and reduction potentials of water are also shown (green dotted lines). The red dotted line represents the band edge positions of $In_xGa_{I-x}N$ with *x* increasing from left to right (0–1). The reduction potentials of CO₂ to various value-added products are also shown [9].

Challenges for conventional III-nitride epilayers include the difficulty in incorporating high indium composition and the presence of extensive defects and dislocations. In this thesis, we will focus on the study of III-nitride nanostructures, which are largely free of dislocations and can be integrated directly on low cost, large area Si wafers.

1.3 The promises, current status and challenges of InGaN for high efficiency LEDs/lasers and photovoltaic devices

1.3.1 InGaN LEDs

LEDs are one of the most vital optoelectronic devices of many applications. Tremendous progress has been made since the first high brightness InGaN-based LED was demonstrated in 1994 by Shuji Nakamura [14]. In the following year, the same group demonstrated efficient yellow, green, and blue InGaN DH QW LEDs by introducing InGaN single quantum well (SQW) structures [15]. Conventional planar InGaN/GaN QW based LEDs, however, suffer from the presence of large dislocation densities, strain-induced polarization field associated and poor light extraction.



Figure 1.6: Summary of key contributions to the efficient blue LED [15].

Although high power InGaN-based optoelectronics have been demonstrated and developed successfully [16, 17], the emission wavelengths of high-efficiency InGaN planar heterostructures devices have been limited in the near-ultraviolet, blue, and blue-green spectral ranges. The realization of InGaN-based deep green and yellow lasers has been limited by the large densities of defects and dislocations due to the large lattice mismatch (~11%) between InN and GaN [9, 15], large strain-induced polarization field and the resulting quantum-confined Stark effect (QCSE), and the difficulty in realizing efficient *p*-type conduction in In-rich InGaN [15, 18, 19]. Moreover, there is no established technology for spatially varying indium compositions in quantum wells to

achieve multi-color emission on the same substrate. Consequently, the current commercial green lasers generally rely on the use of nonlinear optical conversion. Such devices, however, are bulky, heavy and expensive, and are not suitable for on-chip integration [19-21].

GaN-nanocolumn-based InGaN/GaN multiple quantum disk (MQD) LEDs with a novel columnar structure were fabricated on *n*-type (111) Si substrates by Kishino group in 2004 [22]. In 2010, the same group demonstrated controlled In composition and InGaN/GaN multiple quantum well (MQW) nanocolumn arrays with various nanocolumn (NC) diameters, which can exhibit emission from blue to red [18]. In this thesis, we have studied the design, epitaxy, and fabrication of GaN-based nanowire LEDs.



Figure 1.7: Maximum external quantum efficiency (EQE) of commercial nitride and phosphide LEDs, illustrating the "green gap" problem [23-25].

1.3.2 InGaN Laser diodes

Moreover, compared to LEDs, recent studies have shown that lasers offer several unique advantages for these applications. It has been demonstrated that the use of four monochromatic lasers can produce white light with quality comparable to a continuous spectrum [26, 27]. Lasers can also offer better performance than LEDs, including higher efficiency and output power, due to the reduced efficiency droop [26]. Moreover, the operation speed of lasers can be much faster than LEDs, promising ultrahigh speed Li-Fi. White-color lasers will also lead to TV and computer displays with much wider color gamut, significantly higher contrast ratio, and much more vivid colors than any existing technologies, thereby providing unparalleled visual experience.

To date, however, there are no efficient semiconductor light emitters operating in the deep visible spectral range, which is also referred to as the "green gap", illustrated in Figure 1.7. LEDs and lasers operating in the deep visible spectrum are critical for many applications, including high efficiency LED lighting, displays, consumer electronics, heath care, and photosynthesis of green plants, to name just a few. InGaP-based materials have been intensively studied for orange and red-emitting devices [21, 28, 29]. The device performance, however, degrades considerably with decreasing wavelength, due to the poor carrier confinement in the yellow and orange spectral range [21]. InGaN exhibits direct energy bandgap in the range of 3.4 eV to 0.65 eV by varying alloy compositions [30]. Although high power InGaN-based lasers have been successfully demonstrated and developed [27, 31, 32], their emission wavelengths have been limited to the near-ultraviolet, blue, and blue-green spectral ranges [33-36]. The realization of InGaN-based deep green and yellow lasers has been limited by the large densities of defects and dislocations due to the large lattice mismatch (~11%) between InN and GaN [37, 38], large strain-induced polarization field and the resulting QCSE, and the difficulty in realizing efficient p-type conduction in In-rich InGaN [39, 40]. Moreover, there is no established technology for spatially varying indium compositions in quantum wells to achieve multi-color emission on the same substrate. Consequently, the current commercial green lasers generally rely on the use of nonlinear optical conversion. Such devices, however, are bulky, heavy and expensive, and are not suitable for on-chip integration [41, 42]. More recently, white lasing has been demonstrated with the use of multi-segment ZnCdSSe nanosheets [43]. These devices, however, only operate under optical pumping. For organic LEDs, the challenges include limited lifetime of organic materials, relatively expensive manufacturing process [44], low efficiency and brightness, and poor stability [45-47]. Moreover, it has remained difficult to achieve small size devices [48, 49].

Since the invention of blue laser diodes by Nakamura, tremendous progress has been made for GaN-based edge-emitting lasers [50, 51]. To date, however, the operating wavelengths of these devices have been limited to the blue and blue-green spectral range. The world's first InGaN quantum well laser at a true green wavelength was reported in 2010 with the wavelengths at 524 nm and 531.7 nm under continuous-wave (CW) and pulse electrical biasing [52], and its output power reached 50 mW. More recently, an InGaN quantum well laser with longer wavelengths at 535.7 nm was reported under CW electrical biasing and its output was 75 mW [53]. Under CW operation, the threshold current density of InGaN quantum well laser is in the range of ~3.1–18

 kA/cm^2 for lasing wavelengths from 500 nm to 535.7 nm [52-57]. By optimizing semipolar quantum well structure and growth conditions, low-threshold CW lasers were obtained with threshold current densities as low as 5.4 kA/cm^2 at 533.6 nm, 5.2 kA/cm^2 at 527.2 nm, 4.3 kA/cm^2 at 525.6 nm, and 3.4 kA/cm^2 at 511 nm [58]. Some of the extraordinary challenges for achieving low threshold electrically injected InGaN quantum well green, and possibly red-emitting lasers include the presence of large densities of defects and dislocations in the device active region due to the large lattice mismatch (~11%) between InN and GaN. The strong strain-induced polarization fields and the resulting quantum-confined Stark effect further decreases the device efficiency and the maximum achievable gain. Moreover, the quality of InGaN quantum wells has been limited by severe In phase separation, and In-incorporation is often restricted by the high growth temperature of the conventional MOCVD process [23, 59].

1.3.3 InGaN photovoltaic devices

Currently more than 90% of PV market is based on silicon solar cells, and III-V solar cell has demonstrated the highest energy conversion efficiency of 46.5% [60, 61]. Compared with Si, Ge, and the GaAs system, InGaN offers unique advantages for designing full solar spectrum PV devices due to the tunable energy bandgap from 0.64 to 3.4 eV [62-64]. Earlier theoretical calculation has indicated that InGaN-based solar cells can be designed to exhibit a theoretical conversion efficiency of greater than 50% with two-layer multi-junction cell with bandgaps of 1.1 eV and 1.7 eV, and by depositing multiple layers tuned to a wide range of bandgaps an efficiency up to 70% [62, 65, 66]. The calculated efficiency of InGaN/Si tandem solar cells can reach 38.3% using double InGaN junctions [67]. To date the highest experimental PEC efficiency is reported of 7.12% from n-In $_{0.4}$ Gaa. $_{0.6}$ N/p-Si hybrid solar cell on Si [68], which is far below the theoretical prediction. The low efficiency is mainly due to the low In composition and also the poor crystalline quality, due to the large lattice mismatch between InN and GaN, In phase separation/segregation, and high defect and dislocation densities [62, 66].

InGaN nanocrystals such as nanowires (NWs) have shown tremendous promise to improve the efficiency, due to the enhanced light absorption, drastically reduced dislocation densities, and direct path for carrier transport and charge carrier separation and collection [69-74]. In addition, NW arrays can introduce light trapping effect, which can dramatically enhance the light absorption [75]. InGaN NW based solar cells have been studied intensively. For instance, coaxial core-shell

n-GaN/*i*-In_{*x*}Ga_{*1-x*}N/*p*-GaN NW PV devices showed promising open circuit voltages of 1–2 V and short circuit current densities (J_{sc}) in the range of 0.39 to 0.059 mA/cm² for In compositions varying from 0 to 0.27 [76].

1.4 Current status of GaN-based surface emitting laser diodes

Compared to the conventional edge-emitting devices, vertical cavity surface emitting lasers (VCSELs) offer a number of advantages, including lower threshold, circular and low-divergence output beam, single longitudinal mode emission, longer lifetime and easy production of dense twodimensional arrays. To date, however, the realization of a high performance GaN-based VCSELs has remained elusive, and there has been no commercial GaN-based surface-emitting lasers. Some of the earliest demonstrations of GaN-based VCSELs were achieved under optical pumping [77-83], with threshold power in the range of MW/cm². The extremely large threshold is due to the relatively low reflectivity of the distributed Bragg reflectors (DBRs) and the presence of extensive defects and dislocations in the active region. By utilizing a hybrid mirror approach consisting of one semiconductor DBR and one dielectric DBR, Lu et al. demonstrated the first electrically injected GaN-based VCSELs in 2008 [84], which operated at 462 nm at 77 K. Subsequently, by further improving the designs, including the use of dual-dielectric DBRs, room-temperature operational GaN VCSELs have been demonstrated. Monolithically integrated GaN-based VCSELs operating at room-temperature have also been achieved by utilizing nearly defect-free DBRs containing Al_{0.18}In_{0.82}N layers lattice-matched to GaN [85]. Researchers at UCSB have demonstrated the first *m*-plane GaN VCSELs operating at 412 nm at room-temperature [86]. In 2017, Kuo group from NCTU, Taiwan, demonstrated room temperature, CW and low-threshold green lasing from InGaN QD-based VCSELs with wavelengths from 491.8 to 565.7 nm with a threshold current density of 66 kAcm⁻² [47]. Recently, a differential quantum efficiency value of 31% and an enhanced 15.7 mW output power, blue VCSEL with AlInN/GaN DBR has been reported by introducing a novel SiO₂-buried lateral index guide. Lateral optical confinement (LOC) lessen the transverse radiation exhibited by typical VCSELs based on GaN [87].

Alternatively, surface-emitting lasers can be achieved by exploiting the two-dimensional (2D) band-edge resonant effect of a photonic crystal [88-91]. At the band-edge, the group velocity of light becomes zero, and a stable 2D cavity mode (standing wave) is formed in the photonic crystal

structure. The photonic crystal itself serves as a diffraction grating, and the output beam is emitted from the surface. Previously, an output power >1.5 W and slope efficiency ~0.66 W/A has been achieved in an InGaAs photonic crystal surface-emitting laser (PCSEL) operating at 941.5 nm under continuous wave operation at room-temperature by Noda group [91]. However, there have been very few studies on InGaN photonic crystal surface-emitting lasers [92-94]. The first reported electrically injected InGaN photonic crystal surface-emitting lasers developed by Noda group in 2008. It operated in the blue-violet spectral range (λ ~406 nm), with extremely large threshold current density (~67 kA/cm²), due to the large densities of defects in etched planar structures [94].

1.5 Current status of photoelectrochemical and photochemical CO₂ reduction

 CO_2 , the main contributor to the greenhouse gas, can be considered as a valuable *C1* feedstock for fuel or chemical synthesis [95]. The conversion of CO_2 into fuels or value-added chemicals using solar energy is of great significance but has remained a great challenge. The conversion of CO_2 with H₂O using unlimited solar energy and low cost photocatalysts, also known as artificial photosynthesis, can make a significant contribution to the future energy supply. It mimics the natural photosynthesis and transforms atmospheric CO_2 and water to chemical fuels using sunlight [96, 97].



Figure 1.8: Analogy among (a) natural photosynthesis, (b) photoelectrochemical synthesis, and (c) photochemical synthesis on photocatalysts [97].

In the photoelectrochemical (PEC) route, the PEC cells are a photocurrent-generated device composed of proper electrolyte and a photoactive semiconductor electrode [97]. The cathode is for the CO_2 reduction and the anode for the water oxidation. In the photocatalytic or photochemical

(PC) approach, it is the direct wireless approach of the CO₂ reduction. The light absorption, charge carrier separation, and catalytic reactions take place on an integrated system, which includes photocatalyst light absorber and other suitable co-catalysts [12].

To date, studies on artificial photosynthesis are mostly focused on solar water splitting to produce H₂ [9]. In contrast, photocatalytic and photoelectrochemical CO₂ reduction to highenergy-rich fuels is of more interest, which not only produces value added fuels, but also provides a disruptive approach to reduce anthropogenic CO₂ [98]. The first demonstration of photoelectrochemical and photocatalytic CO₂ reduction to hydrocarbons were reported by Halmann [99] in 1978 and Inoue [100] in 1979, respectively. Since then many groups have studied the use of various semiconductors to achieve improved performance. However, the development of visible light photocatalysts has remained challenging, whereas most of the research has been focused on UV light sensitive photocatalysts (e.g., GaN, ZnS, SiC, SrTiO₃, and TiO₂) [101]. As illustrated in Figure 1.5, the bandgaps of nitrides are relatively narrow and can straddle the oxidation potential of water and reduction potential of CO₂. Therefore, the development of nitride based photocatalysts for CO₂ reduction has attracted significant attention and is the focus of part of this thesis.

1.5.1 CO₂ reduction to syngas

 CO_2 reduction requires efficient catalysts and sufficient energy input to active linear CO_2 molecule [102]. PEC and PC CO_2 reduction suffer from poor performance, due to competing reaction pathways and diverse reduction products including carbon monoxide (CO), formic acid (HCOOH), methane (CH₄), ethylene (C₂H₄), and many others depending on the reaction conditions [103]. Furthermore, the hydrogen evolution reaction (HER) is often favored over the CO_2 conversion [104]. Hence, the intrinsic nature of the electrolysis process could be exploited to an attractive strategy by combining CO_2 reduction and HER to produce syngas.

Reaction	E° (V <i>vs.</i> NHE)	
Reduction Potential of CO ₂		
$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	-0.53	
$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$	-0.61	
$CO_2 + 4H^+ + 2e^- \longrightarrow H_2CO + H_2O$	-0.48	
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$	-0.38	
$CO_2 + 6H^+ + 2e^- \longrightarrow CH_3OH + H_2O$	-0.24	
$CO_2 + e^- \longrightarrow CO_2^-$	-1.9	
Oxidation Potential of H_2O		
$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+$	+0.82	

Table 1.1. Standard electrochemical potentials for CO₂ reduction [97, 104].



Figure 1.9: Syngas derivatives with reference to their composition (*H₂/CO molar ratio) [104].

The combination of CO and H_2 , i.e., syngas, can be used to produce hydrocarbons through well-established industrial technologies [104]. Figure 1.9 shows that syngas (synthesis gas, CO+H₂ mixtures) can be employed as feedstock for the generation/production of methanol. The
photoelectrochemical route is one of the most promising methods to produce syngas, with syngas desirable CO/H₂ ratio of 1:2. The CO/H₂ ratio can be tuned in the range of 1.5–2.2, which is desired for methanol synthesis and the Fischer–Tropsch reaction; a CO/H₂ ratio of 3 is suited for the methanation reaction; and a CO/H₂ ratio of 1 is ideal for hydroformylation synthesis.

PEC three electrode cells: The PEC CO₂ -into-syngas conversion often involves two independent electrochemical reactions: the electrocatalytic CO₂ reduction reaction (CO₂RR) and the hydrogen evolution reaction. Studies have been performed for splitting CO₂ to produce syngas with various semiconductor photocathodes, including *p*-Si [105-107], ZnTe [108, 109], CdTe [110], *p*-InP [110], *p*-GaP [99, 111], *p*-GaN [112], Cu₂ZnSnS₄ (CZTS) [113, 114], Cu₂O [115, 116] and *p*-NiO [117]. Molecular metal-complex or metal cocatalyst (e.g., Au, Ag and derivatives) have also been used to realize selective CO production. However, it remains challenging to develop efficient and stable PEC CO₂ reduction devices. This is limited by that after the chemical absorption on the electrode, the first electron transfer to form CO₂⁻⁻ anion radical may not start until -1.90 V is reached (Table 1.1). This intermediate state puts a significant overpotential and is considered as the rate limiting step, leading to a large external bias and a small photocurrent. In this regard, there is a need to develop low cost photocathode with low onset potential and high photocurrents.



Figure 1.10: Possible reaction pathways for electrocatalytic CO₂RR on metal electrodes in aqueous solutions [97].

The state-of-the-art PEC system for the conversion, which occurs at the engineered interface of $Pt/TiO_2/p$ -Si photocathodes and was reported by our group in 2018 with solar-to-syngas conversion efficiency of 0.87% [118]. The unique metal/oxide interface provides the multifunctional combination of metal and oxide catalytic sites with complementary chemical properties, which opens new reaction channels that are not possible with the individual

components. Integrating the Pt/TiO₂ cocatalyst with *p-n* Si junction and efficient electron extraction effect of GaN nanowires enabled the achievement of record half-cell solar-to-syngas (STS) efficiency of 0.87% with desirable CO:H₂ of 1:2. Recently, *a*-Si/TiO₂/Au photocathodes exhibits the syngas efficiency of 0.42% with the desirable CO/H₂ ratios such as 1:2 and 1:1 [119].

PV cell coupled PEC: A photoelectrode-photovoltaic (PV) dual absorber tandem system is an alternative strategy for PEC CO₂ reduction. The photo absorber in PV cells can absorb the remaining photons passed the photoelectrode in PEC cell. In this way, the PV cell will provide an extra photovoltage to reduce CO₂ [109, 120-122]. Grätzel and co-workers employed perovskite photovoltaics to construct a photovoltaic-based tandem electrocatalytic device for CO₂ reduction in 2015 [123]. The device reached a solar-to-CO efficiency (SCOE) exceeding 6.5%. In this study, IrO₂ was used as anode and oxidized Au was used as cathode. Recently, a system composed of a gold decorated triple-layered ZnO/ZnTe/CdTe core–shell nanorod array photocathode and a CH₃NH₃PbI₃ perovskite solar cell in tandem showed a solar to fuel efficiency of 0.43% [109]. By using Cu-Zn cathode and Si HIT cell with Ni foam photoanode a solar-to-syngas conversion efficiency of 4.3% was been reported, where the experiment has performed in special filter-press reactor PEC cell [124]. Very recently in 2019, an artificial photosynthetic (APS) with the *N*-TiO₂ photoanode for the solar-driven conversion of CO₂ into syngas with the conversion efficiency of 0.3.6% with FE of 80%, has been demonstrated. The system is tunable with a wide range of CO:H₂ ratio between 1:2 and 5:1 [121].

Various electrodes have also been explored to achieve tunable CO:H₂ ratio. For instance, metal-organic framework (MOF) coating on the surface of Cu₂O photocathode can offer active sites for CO₂ reduction [125]. By employing Zn-Cu alloyed electrodes with hierarchical porosity, Mougel group demonstrated tunable selectivity for CO₂ versus H⁺ reduction of 0.2 to 3.65 (>9 h) [126]. Porous Pd nanomash could catalyze CO₂-into-syngas conversion with the ideal tunable ratio [127]. In addition, a wafer-scale nanoconed Si arrays substrate with loaded metallic nanoparticles (Au and Cu) has been developed by Ye group [128]. They claimed that at an applied potential of -1.6 V vs. Ag/AgCl, the Cu-Si photocathode exhibited the highest CO₂-to-CO faradaic efficiency of 15.1% and a total efficiency of 43.5% into syngas.

1.5.2 Photochemical CO₂ reduction to syngas

In 2018, A. Li et al. reported that 84.2 μ mol h⁻¹g⁻¹ CO and a desirable CO/H₂ ratio of 1:2 were achieved with solar energy conversion yield of 0.108% by using MnO_x@TiO₂@CuPt alloy mesoporous hollow spheres (MTCP-MSs) [129]. By using non-noble metal catalyst Co(bpy)₂Cl₂, with the photosensitizer Ru(bpy)₃Cl₂, PC reduction of CO₂ and H₂ is achieved with 62.3 and 69.9 μ mol [130]. However, in both cases, the experiments weren't performed solely under the presence of CO₂ and H₂O only, which is the desired platform, instead it's done under various aqueous solution such as in the mix of KHCO₃ and Na₂SO₃ [129] and in MeCN/H₂O/TEOA solution [130], respectively. Several other groups developed various catalysts for PC CO₂ reduction to realize prominent selective CO output, and in most of the cases, H₂ was measured as a byproduct. To date, there have been no demonstrations of efficient and stable photocatalytic CO₂ reduction, which is part of the focus of this thesis work.

1.6 Advantages of InGaN nanocrystals in green photonics

While tremendous advancement has been made in the optoelectronics, the performance and applications of planar devices have been largely limited by the presence of extremely large defect densities. One dimensional (1D) nanocrystals have emerged as the material of choice for green photonics. Nanocrystal can be largely free of dislocations, due to the effective lateral strain relaxation, and can be grown without catalyst, which can ensure high crystal-quality, associated with the large aspect ratio.

1.6.1 InGaN nanocrystals-based LEDs

First InGaN NW based LED was fabricated by Kishino group in 2004 with a typical turn-on voltage of 2.5–3.0V at room temperature, where InGaN/GaN multiple quantum disk (MQD) was used as active region [131]. Following year, Liebar group reported single GaN based NW LEDs using GaN/InGaN/GaN core-multishell NW heterostructures with tunable emission from 365 to 600 nm [15]. Kishino group developed a novel technology, known as selective area epitaxy (SAE) or selective area growth (SAG), to control the In compositions in InGaN QW on the same substrate [18]. Recently Feezell group demonstrated the RF characteristics of electrically injected GaN/InGaN core-shell nanowire-based μ LEDs with a record -3 dB modulation bandwidth ~1.2

GHz at 1 kA/cm². The LEDs showed high IQE (62%), low turn-on voltage (2.9 V) and short carrier lifetime (1–2 ns) [132]. To achieve high performance LEDs, Ra et al. reported coaxial InGaN/GaN QW structures on *n*-GaN core NW-LEDs without polarization [133]. However, the achievement of such devices using conventional InGaN/GaN QW heterostructures has been difficult, due to the presence of large densities of dislocations and polarization fields [134]. To further enhance the carrier confinement in the NW active region, well/disk-in-a-wire LED heterostructures were developed.



Figure 1.11: SEM and emission images excited by He-Cd laser from InGaN/GaN nanocolumns with the diameter of (a) 143 nm, (b) 159 nm, (c) 175 nm, (d) 196 nm, (e) 237 nm, and (f) 270 nm [18].

Significantly improved radiative recombination can be achieved by using InGaN/GaN dot-ina-wire heterostructures. Moreover, the color chromaticity and temperature can be well controlled by varying the compositions and/or sizes of the dots in a single epitaxial growth step. Mi group demonstrated InGaN/GaN dot-in-a-wire heterostructures by MBE growth without using any foreign catalyst, including the highest internal quantum efficiency of about 56.8% for a nonphosphorous white LED [135]. Also, by varying the dot compositions in the NW, strong emission across nearly the entire visible wavelength range can be realized [48]. Ra et. al. demonstrated the monolithic integration of full-color LEDs on a single chip, coupled with the capacity to tune light emission characteristics at the single NW level [136]. InGaN/GaN dot-in-a-wire was further incorporated with n^{++} -GaN/InGaN/ p^{++} -GaN and Al tunnel junction. This structure offers reduced voltage loss and enhanced hole injection and holds promises for high brightness NW LEDs [137, 138].

1.6.2 InGaN nanocrystal-based laser diodes

InGaN laser diodes (LDs), including Fabry-Pérot lasers, plasmonic lasers, photonic-crystal lasers, random lasers, and micro-ring/disk lasers, with lasing wavelengths from the ultraviolet to the near-infrared have been demonstrated. However, almost all these demonstrations of NW lasing were achieved under optical pumping. For practical applications, electrical injection is required. The first report on electrically pumped single-NW lasers were investigated by Lieber group using CdS NWs in 2003 [139]. The demonstrations of electrically injected NW lasers have largely been limited by highly detrimental surface recombination and low resistivity metal contact for efficient current injection. In other cases, the cavity is simply limited by optical losses at the facets. As a result, NW-laser demonstrations to date have large threshold power densities [140-143]. To date, the only reported electrically injected InGaN photonic crystal surface-emitting laser (PCSEL) have operated in the blue-violet spectral range ($\lambda \sim 406$ nm) with an extremely large threshold current density (~67 kA/cm²) due to the large densities of defects in etched planar structures [94].

1.6.3 Artificial photosynthesis based on InGaN/GaN nanocrystals

In_xGa_{1-x}N, one of the group III-nitride compound semiconductors, exhibits direct energy bandgap covering nearly the entire solar spectrum. The band edges of InGaN can straddle proton reduction and water oxidation under visible and part of infrared light. Figure 1.5 shows the band alignments of InGaN alongside with other commonly used photocatalyst materials, depicting the optimum band edge potential for water splitting and CO₂ reduction up to ~50% of indium incorporation. With the advantages of 1D NWs unique features, InGaN/GaN NWs simply uphold the fundamental steps for artificial photosynthesis: light capturing, charge separation and transportation of charges for electrochemical reaction [9] and enhance the light absorption and rapid electron-hole separation, hence improve the solar-to-fuel conversion efficiency.



Figure 1.12: Schematic is showing light absorption, charge separation, diffusion, recombination, water reduction, and oxidation on nanowire photocatalyst [9].

Mi group is one of the pioneers in the discovery of InGaN nanocrystals in the artificial photosynthesis field such as water splitting to get H₂ fuel, CO₂ reduction and hydrocarbon carbon fuels [9, 118, 144-149]. Recently, they demonstrate the first ever artificial photosynthesis system that is capable of direct solar water splitting with the photocatalytic performance of $\sim 2.7\%$ and long-term stability of >580 h [144]. This epitaxial grown GaN/InGaN nanostructures contains up to 25% indium content, which efficiently augment the sunlight absorption. With a double-band ptype GaN/InGaN heterostructures, a solar-to-hydrogen conversion efficiency of ~1.8% [145], and by quadruple-band InGaN NW arrays photocatalyst ~5.2% efficiency was achieved [146]. Consequently, by integrating the multiband InGaN/GaN structures into Si solar cells, tandem PEC device has been introduced. An ideal tandem dual-junction device has the potential to reach a STH of $\approx 27\%$ under AM1.5G illumination [147]. A high applied bias photon-to-current efficiency (ABPE) of 10.7% with long-term stability (>100 h) has been reported by n^+ -GaN NWs incorporated on Si photocathode [148]. Employing a novel InGaN/GaN multi-quantum well (MQW) nanowire heterostructures, Ebaid et. al. got a stable water splitting with solar to hydrogen conversion of 0.21% [150]. Following the same strategy, a tandem InGaN photo-electrode and Si *p-n* junctions converted CO₂ reduction to HCOOH with an energy conversion efficiency of 0.97% using an aqueous photoelectrochemical cell [151]. GaN NWs/ n^+ -p Si with the incorporation of metal-oxide (Pt-TiO₂) interface as co-catalyst, a desirable CO/H₂ ratio of 1:2 with efficiency 0.87% has been demonstrated by Mi group [118]. J. K. Sheu et. al. designed double side InGaN/GaN epitaxial wafers as a working electrode without Si tandem cell for PEC cell to produce H_2 and HCOOH from the same cell with energy conversion efficiency of 5.48% and 1.09% [152]. Bare GaN nanowire showed higher photoactivity for CO production CH₄ by CO₂ photocatalytic reduction [149]. Therefore InGaN/GaN nanowire array holds the imaginable potential for the development of valuable solar fuels (e.g., H_2 , syngas) by the artificial photosynthesis system.

1.7 Organization of this thesis

In this thesis, we have explored the potentials of III-nitride nanocrystals as a building block for green photonics. The study of the molecular beam epitaxy, characterization, and device applications of InGaN/GaN nanocrystals with relatively high indium composition was conducted. We demonstrated InGaN photonic crystals with controllable emission characteristic in the green region. We have further demonstrated relatively efficient artificial photosynthesis, i.e., the conversion of solar energy, carbon dioxide and water into hydrogen and hydrocarbon fuels. Introduction and background and summarization of various techniques used in this thesis were presented in Chapters 1 and 2, respectively. Chapters 3 and 4 present the work on the realization of efficient InGaN nanocrystal LEDs and laser diodes. Chapters 5 and 6 present our recent demonstration of artificial photosynthesis on InGaN nanocrystals.

Chapter 1 provides an overview on the need to develop efficient photonic devices for sustainable, renewable smart energy system. A general overview of III-nitride based optoelectronics devices, especially LEDs, Lasers and solar energy devices is also presented. Finally, the motivation for using one-dimensional InGaN nanowires for optoelectronics and artificial photosynthesis is discussed.

Chapter 2 discusses the growth of III-nitride nanostructures by molecular beam epitaxy (MBE) and characterization techniques used for this dissertation. The study and growth mechanism of (In)GaN nanowires includes spontaneous growth and selective area growth techniques. The InGaN photonic device fabrication, the co-catalyst deposition techniques, photoelectrochemical and photocatalytic experimental methods are briefly summarized. The optical and electrical characterizations of InGaN/GaN nanowire heterostructures are presented.

Chapter 3 demonstrates the unique approach to develop InGaN photonic crystal surface emitting devices which can function as a building block for new generation of photonic crystal devices and systems.

Chapter 4 presents a nanocrystal surface-emitting laser (NCSEL) diode, consists of InGaN/AlGaN nanocrystal arrays with precisely controlled size, spacing and surface morphology. This work is the first demonstration of electrically pumped NCSEL diode that can operate efficiently in the green spectrum. This unique laser concept can be readily extended to achieve monolithic surface emitting laser diodes operating across the entire visible, as well as mid and deep UV wavelengths.

Chapter 5 presents an efficient and stable PEC CO_2 reduction system for syngas production with controlled composition by simply varying the composition of dual cocatalysts of Au/Pt. the CO/H_2 ratio in the syngas mixture can be controllably tuned in a wide range between 1:99 and 10:1 with a total unity Faradaic efficiency.

Chapter 6 introduces the novel approach for the demonstration of efficient photochemical reduction of carbon dioxide CO_2 into syngas using wafer scale multiband InGaN/GaN nanowire structures. Photochemical CO_2 reduction can open a new opportunity for the sustainable renewable source of carbon neutral storable source of energy.

Chapter **7** presents the summary of this thesis work, as well as discussions on future research opportunities.

Chapter 2

Experimental Techniques

This chapter will provide the related basic epitaxial growth mechanism, fabrication process, and characterization principles, which are the foundation for the subsequent chapters on the design and performance characterization of the unique III-nitride nanocrystal green photonic devices, including optoelectronics (LEDs and LASERs) and artificial photosynthesis of CO₂ reduction. In this dissertation, photonic crystal devices have been grown on nano patterned substrate using the special technique of selective area epitaxy by plasma-assisted MBE, followed by fabrication and the structural, optical and electrical characterization techniques. For CO₂ reduction, III-nitride nanocrystals have been grown using spontaneous formation. This chapter will provide the detailed experimental techniques related to our work, including molecular beam epitaxy and device fabrication details. Furthermore, relevant techniques for the structural, optical, and electrical characterization will be described.

2.1 Molecular beam epitaxial (MBE) growth for III-Nitride nanostructures

MOCVD and MBE are the widely used growth techniques for achieving high quality III-nitride materials. Because of better interface control to achieve high quality crystalline materials MBE can provide the highest control of the epitaxial growth of various nanostructures, and the composition and thickness of the epilayer can be controlled precisely to atomic level compared to MOCVD. Furthermore, MBE has ultra-high vacuum environment ($\sim 10^{-8}$ to $\sim 10^{-10}$ Pa), which can reduce the impurity incorporation in the epitaxial layers. The MBE growth technique can lead to high indium content InGaN structures by enhancing indium incorporation as MBE growth temperature is lower than that of MOCVD.

In our work, III-nitride nanowires have been grown by catalyst-free PAMBE under nitrogen rich conditions. A plasma source of high purity inert N₂ gas is used to supply the group element. The active nitrogen plasma includes ionized molecules (N^+_2) , atoms (N), and ionized atoms (N^+) , which are introduced into the chamber for the In(Ga)N deposition. The amount of active nitrogen

plasma can be well controlled by adjusting the nitrogen flow rate and the plasma power. This catalyst-free or self-catalytic growth process is a diffusion induced growth process wherein the differences in diffusion coefficients, surface energies, sticking coefficients cause the growth of nanowires [153]. The length, diameter, shape of nanowires, wire density and uniformity depend on the growth conditions, such as III/V flux ratio, substrate temperature, and growth rate. For instance, nanowire density, and nucleation density can be controlled by adjusting the growth temperature [154], and the III/V flux ratio [155], respectively.

In this dissertation, the III-nitride nanostructures were grown under nitrogen rich conditions without using any foreign catalyst in Vecco GENxplor Molecular Beam Epitaxy (MBE) tool, which is situated in the Electrical Engineering department at McGill University (Figure 2.1). The study has been done using both spontaneous and selective area growth techniques on various substrates to investigate on promising opportunities green photonics applications.



Figure 2.1: The Vecco GENxplor Molecular Beam Epitaxy (MBE) system [156].

2.1.1 MBE tool details

MBE is a versatile tool for achieving semiconductor with high quality, defect-free growth. It is well known as one of the most efficient bottom up approaches to grow nanowires as well. Both nearly defect-free planar structures and nanowires can be grown in an ultra-high vacuum (UHV) ambient conditions in the MBE growth chamber. This UHV ambient condition reduces the impurities in the growth chamber and provides extreme flexibility to characterize the growth in situ. A typical ~ 10^{-12} Torr base pressure is maintained in the growth chamber using a cryo pump and an ion pump. For various III-nitride nanocrystal growth a radio frequency (RF) plasma source of ~350–400 W and ultrahigh pure N₂ flow of 0.45–1 standard cubic centimeter per minute (sccm) is used. The RF power supply dissociates stable N₂ molecules into nitrogen species (neutral atoms, ions, and active molecules). Usually, the atomic nitrogen is very reactive, and reacts readily with Ga, In, and Al to form stable nitride nanostructures.



Figure 2.2: Simplified schematic of the MBE growth chamber.

The MBE systems consist of three main vacuum chambers, an intro chamber (or load lock chamber), a buffer chamber, and a growth chamber. The Veeco GENxplor MBE system at McGill University is equipped with Ga, In, Al, Mg, and Si Knudsen effusion cells. The RHEED gun is a powerful device to monitor the in-situ oxide desorption of the substrate surface. It can probe the topmost layers of the sample rather than the bulk structure. During the nanowire growth, spotty patterns (an array of dots) can be observed on the RHEED screen which can give the general information of the nanowires, such as the size, shape, orientation, and density. However, there are no diffraction patterns on the RHEED screen for an amorphous layer, such as an oxide on the top surface. The substrate heater is designed with a continuous azimuthal rotation (CAR) to provide excellent uniformity for deposition of materials on the substrate.

2.1.2 Spontaneous (SP) growth mechanism

The spontaneous growth of GaN/InGaN nanowires has been performed in MBE without any foreign catalysts' participation in N_2 rich environment. The spontaneous formation of GaN/InGaN nanowires involve a self-catalytic growth process, wherein Ga and In droplets can serve as catalysts to assist the nanowire formation with three essential steps: 1) adsorption, 2) desorption, and 3) diffusion. The major driving force for the spontaneous formation is suggested as diffusion-induced growth [157]. The growth of nanowires is initiated by the differences in surface energies, sticking coefficients, and diffusion coefficients on different crystal planes. As shown in Figure 2.3, adatoms diffuse from the nanowire sidewall to the top, due to the lower chemical potential at the top surface. The sticking coefficient at the tip of nanowires is much higher than that on the sidewalls. As a result, Ga adatoms impinging directly on or within a surface diffusion length of the nanowire tip can be incorporated on the nanowire tip, leading to the axial growth of nanowires. The diffusion-induced mechanism is consistent with the observation that the nanowire axial growth rate increases with the increase of substrate temperature, due to the significantly enhanced adatom surface migration [157, 158].



Figure 2.3: Schematic illustration of the spontaneous growth of III-nitride nanowires by molecular beam epitaxy [157].

2.1.3 Selective area growth (SAG) mechanism

Selective area growth (SAG) is a catalyst-free epitaxial growth technique which combines bottom-up (epitaxy) and top-down (lithography) approach. The substrate is covered with a thin functional layer which is lithographically patterned. This layer is chemically inert and acts as mask where nucleation during growth is strongly suppressed. The regions where the layer has been removed act as nucleation centers. For sufficiently small apertures in the functional layer, this leads to position-controlled epitaxial growth of nanostructures on the substrate. The selective area growth provides a better control over the nanowire position, size, and aspect ratio and hence is capable of growing materials with controlled emission wavelengths. Nanowire growth is largely determined by adatom migration, adsorption, and desorption on the exposed substrate surface as well as the masked region, which can be controlled by varying the growth conditions including the substrate temperature and III/V flux ratios. The size and position of the patterns on the mask can be designed to achieve desired nanowire structures. The simple illustration of the SAG process is shown in Figure 2.4.



Figure 2.4: The schematic of SAG pattern process, (a) deposited oxide/metal layer on substrate, (b) coating with a thin functional layer, (c) opening apertures by using e-beam or nanoimprinting lithography, (d) final mask-patterned substrates after RIE etching and functional layer removal, (e) preciously controllable size with the lattice constant *a*, nanowire lateral size *d*.

SAG growth of nanowires using nanomask patterns contributes the homogenization of the morphology and the composition of the nanostructure. The mask surface is nitrated prior to the growth in the growth chamber. Hence proper pattering is essential to get the right growth output. To do so, thin layer PMMA is coated on the substrate, followed by the lithography process, which can proceed by either e-beam or nanoimprinting and RIE technique. Thus, the opening apertures (holes) of various sizes are created on the same substrate with specific lattice constant a, nanowire lateral size d.

The SAG technique enables the precise control of the size, morphology and position by optimizing the substrate temperature, Ga, In flux, and proper N_2 flow. Show in Figure 2.5 (b), the

neighboring area of a single nanocolumn, Ga adatoms diffuse on the nitride film and are absorbed into the nanocolumn, thus, the diffusion length of Ga can be roughly estimated from the width of the no-nucleation area surrounding a single nanocolumn. Random and spontaneous nucleation on the nitride mask area outside the nanohole patterns was sufficiently suppressed at the high temperature. Hence the enhancement of both the diffusion and desorption of Ga contributed to SAG.



Figure 2.5: The schematic diagram of SAG growth mechanism, (a) before the growth, followed by the nitridation, (b) during the growth.

However, a very high growth temperature may induce an increase in the shape inhomogeneity of the nanocolumns as well as a decrease in column diameter. Nanowire arrays of sufficient uniformity are fabricated in a relatively narrow temperature range around the critical temperature of approximately 900°C in this study [159]. Using appropriate e-beam lithography and dry etching techniques, we can get the desired pattern on the substrate. By single epitaxial MBE growth, precision-controlled nanowire arrays have been grown in this study. The correlated growth details will be provided in chapters 3, and 4.

2.2 Pattering techniques: electron beam lithography

Electron beam lithography (EBL) is one of the most crucial steps for nanolithography on a laboratory scale. The excellent spatial resolution due to the small electron de Broglie wavelength, the small diameter of the focused electron beam, and especially the versatility to vary lithography design parameters are highly desirable for many nanoscale device fabrication [160]. TESCAN MIRA3 XMH has been used in this work, which is placed in McGill Nanotools-Microfab. It is equipped with a Schottky field emission electron gun and an extra-large specimen chamber operating in high vacuum. An EBL resist (typically Polymethyl methacrylate, PMMA) dissolved in organic solvent is spin coated onto a clean substrate, which is prepared by special technique on sapphire substrate. Subsequent electron beam irradiation causes chemical changes of the resist, which changes the solubility of the exposed resist with respect to the developing solvent. The obtained pattern is then transferred to the prepared substrate for epitaxial growth by etching techniques. In our case, the desired pattern is obtained by AutoCad and DesignCad2000 software, which is converted to EBL coding by using NPGS software.

2.3 Device fabrication

For the realization of the green photonic crystal structure devices, the bottom-up InGaN/GaN nanowire heterostructures are fabricated by selective area epitaxy growth using radio frequency plasma-assisted molecular beam epitaxy, as bottom up fabrication provides high crystal quality, material homogeneity, smooth surface faceting, and high-throughput assembly compared to the top-down fabricated structures. To demonstrate high-performance LEDs and LASERs, meticulous fabrication steps have been obtained for surface passivation and contact metallization.

First, a polyimide resist layer was spin-coated to fully cover the nanowires, followed by oxygen plasma etching to reveal the top surface of nanowires, which was monitored by scanning electron microscopy (SEM) precisely (Figure 2.6 (d)). Nanoscale metal electrodes, consisting of Ni/Au metal layers were then deposited on the *p*-GaN top surface of individual nanowires using e-beam lithography and metallization techniques and then annealed in nitrogen ambient. Subsequently, indium tin oxide (ITO) layer was deposited to serve as a transparent electrode. The complete devices with ITO contacts were annealed at 300°C for 1h in vacuum. To facilitate the current injection and device testing, Ni/Au had been deposited on the ITO as the contact metal.

Consequently, a Ti/Au, was deposited as *n*-metal contact on the *n*-type GaN template, followed by the annealing. Depending on the device performance various mask with different openings were used to enhance the device quality. The detailed device fabrication will be presented in chapter 4.

2.4 Device characterization

The device characteristics are studied using photoluminescence (PL) and electroluminescence (EL) study, where we can derive very detailed analysis such as various power dependent measurement, current-voltage characteristics, light-current characteristics etc. The current-voltage (I-V) characteristics have been conducted under various biased conditions. The emission of nanowires has been studied using a micro-PL measurement system with a 405/325 nm laser as the excitation source with continuous wave or pulsed wave mode. For the revelation of the light emission characteristics, the electroluminescence emission was collected using an optical fiber coupled to a high-resolution spectrometer and detected by a charge coupled device (CCD). The In GaN device was placed on a motorized x-y stage (Aerotech's ANT130-XYULTRA), which provided precise spatial mapping. The current-voltage characteristics of the device were performed by a source meter Keithley SMU-2400. The output power was measured using a Si photodiode sensor. Electroluminescence spectra were measured by a liquid-nitrogen cooled CCD attached to an iHR550 spectrometer with 1200 grooves/mm grating. The far-field images were captured by a high megapixel color CCD camera at a distance above the top surface of the device. The polarization was resolved by a Glan-Taylor calcite polarizer (with a High-Precision rotation Mount) installed on the top surface of the device. The device performance such as output power, EQE, linewidth, temperature-dependent characteristics, wall plug efficiency, and far-field radiation pattern profile have been thoroughly investigated.

2.5 Structural characterization

2.5.1 Scanning Electron Microscopy (SEM)

The morphology (dimensions, *i.e.*, height, thickness, diameter and the areal density) of the MBE-grown nanostructures has been analyzed using field emission scanning electron microscopy (SEM). In addition, the sample pattern after solvent cleaning for EBL design, the polyimide

etching in the device fabrication process, the co-catalyst presence after the deposition are investigated by using FEI Inspect F-50 FE-SEM equipment, which is operated at an accelerating voltage of 5–10 KV and emission current of 5–10 μ A. The InGaN/GaN nanowire structures were grown on Ti-mask patterned sample on GaN/Al₂O₃ and for CO₂ reduction analysis. InGaN/GaN nanowires are grown on Si substrate, which are highly conductive. The samples were assessed in both titled view or top view based on the assessments, for instance, a 45° tilted edge view has been done for the nanowire height and width measurement, and a 90° top view image has been taken to check pattern lattice constant.



Figure 2.6: SEM image of (a) spontaneous grown nanowires where (a (i)) grown nanowires and (a (ii)) Au deposited nanowires, (b, c) selective area epitaxial grown nanowire with various diameter and lattice constant (b) 80nm, (c) 150 nm respectively and (b, c (i)) illustrates the top view the nanowire arrays, whereas (b, c (ii)) represents the 45^{0} angled SEM. d (i) and d (ii) demonstrates the SEM of polyimide etching layer of the nanowire array for device fabrication.

2.5.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is based on the electron beam transmission or scattering and transmission, to achieve atomic scale resolution. TEM usually operates in different modes to obtain superior insight of the sample structure such as the precise dimension (length, diameter) of individual nanowire, crystal structure, lattice parameter, defect density, elemental composition etc.

The most common mode TEM operation is the bright field (BF) imaging mode. A high-resolution STEM-BF image of GaN nanowire surface with Cr_2O_3 deposited is shown in Figure 2.7 (a), which revealed high crystallinity of the as-grown wurtzite GaN nanowire grown along the *c*-axis. The distance between the adjacent GaN nanowire lattice fringes is ~0.52 nm, which corresponds to the <0001> direction of GaN [161]. The lattice spacings of 0.24 and 0.26 nm corresponds to the (111) facet of Au and (002) lattice plane of GaN, indicating the preferred nanowire growth along <0001> direction (c-axis) has been illustrated in Figure 2.7 (b) for Au deposited GaN nanowire sample [162].



Figure 2.7: (a) HRTEM image of Cr_2O_3 -deposited GaN sample. It shows Cr_2O_3 coating layer is amorphous and GaN nanowire is single crystalline with the growth direction along the *c*-axis. (b) Au-deposited GaN sample.

2.5.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) or ESCA (Electron Spectroscopy for Chemical Analysis) is surface-sensitive technique for measuring chemical composition, chemical bonds, empirical formula and electronic states by analyzing the surface/near-surface region of a given material. To reveal the elemental compositions of nanostructure surfaces and the chemical bonding between semiconductor (photocatalyst) and co-catalyst, the XPS analysis can be an important technique. The binding energy of the photoelectron relative to the Fermi-level can be measured from the kinetic energy of the photoelectrons. By analyzing the peak position and intensity of the binding energy, one can derive the chemical composition, chemical states/bonds and valence band structure [163]. For highly conductive samples, the standard reference metals (Cu- $2p_{3/2}$, Ag- $3d_{5/2}$, and Au- $4f_{7/2}$ peaks) are equipped on the sample holder to calibrate the binding Energy and for non-conductive or poorly conductive sample, the binding energy calibration needs to be done

thoroughly against carbon C-1*s* peak (284.8 eV). Fisher Scientific K-Alpha XPS system with a monochromatic Al-K α X-ray source (hv = 1486.6 eV) and 180° double focusing hemispherical analyzer has been used for this thesis experiments. The analysis chamber pressure was as low as 10^{-8} Torr. The X-ray source is located at 60° with the surface normal to excite the nonpolar surfaces of nanowire arrays. The high resolution XPS spectra were obtained using an X-ray beam size of 400 µm, pass energy of 50 eV, and a step size of 0.1 eV. The binding energies were calibrated with both Au-4*f* (84.0 eV) and C-1*s* (285.0 eV) peaks and the individual peak fitting was performed using convolution of Lorentzian and Gaussian line shapes (L/G = 30%) with Avantage software of Thermo Scientific.

2.6 Optical characterization

Optical characterization is also known as luminescence studies and in general luminescence is the spontaneous emission of light under excitation. Based on the excitation mechanism, the luminescence studies are categorized in photoluminescence (PL), cathodoluminescence (CL) and electroluminescence (EL). In this study, PL, CL and EL have been used for optical and electrical properties of GaN/InGaN nanostructures.

PL spectroscopy is a useful luminescence analysis technique to assess the fundamental electrical and optical properties of materials, namely, the optical band gap, excitonic states, dopant incorporation, impurity states and recombination mechanism etc. Typically, a light beam with photon energy higher than the band gap of the material is directed onto a sample where it excites electrons from the valence band to the conduction band, leaving behind a hole in the valence band. When a material is excited with above-bandgap photons, the photogenerated electrons and holes thermally relax to the lowest energy states, i.e. conduction band minima (CBM) and valence band maxima (VBM). The optical properties of InGaN/GaN nanowires has been performed with 325 nm and 405 nm lasers He-Cd laser (Kimmon Koha) as excitation source. Zeiss Supra 55 VP field emission gun SEM equipped with a cryogenic stage coupled to a Gatan MonoCL 2 setup has also been used for CL studies.

Electroluminescence study is performed on the fully fabricated device. EL refers to the radiative recombination due to the injection of the minority carriers into a semiconductor p-n

junction. In this thesis work, the EL has been performed by a liquid-nitrogen cooled CCD attached to an iHR550 spectrometer with 1200 grooves/mm grating.

2.7 Photoelectrochemical and photochemical measurement

2.7.1 Photoelectrochemical measurement

The fundamental experimental setup for Photoelectrochemical (PEC) measurements is a threeelectrode configuration, which consists of a PEC cell with three electrodes and electrolyte, a light source (a solar simulator), and a potentiostat. In this study, a quartz ware three-electrode cell from Pine Research Instruments was employed as the three-cell reactor chamber. In addition, the other three-cell configurations for PEC, includes photoactive working electrode (WE), a Pt wire as counter electrode (CE), a single-junction Ag/AgCl (saturated KCl) reference electrode (RE), and 0.5 M KHCO₃ (Fisher Chemical) aqueous solution with a pH of \sim 7.5–8 as the electrolyte solution. The simplified schematic of 3 cell set up has been displayed in Figure 2.8 (d). The photoactive working electrode ($\sim 0.2 \text{ cm}^2$) was prepared in three major steps, which are shown in Figure 2.8 (a) to (c). First, GaN nanowire arrays were grown on p-n Si wafer by PAMBE. Second, the cocatalysts were deposited on GaN nanowires surface in sequential order to provide multiple sites and unique channels to accelerate the CO₂ activation and reaction pathways for syngas production. Third, Ga-In eutectic alloy (99.99%, Sigma-Aldrich) was put on the backside of the Si substrate and subsequently attached to a copper wire with the aid of silver paint (Ted Pella). Then, epoxy resin (PC-Clear) was used to cover the metal and Si surface to avoid any direct contact with the electrolyte solution.

Prior to every CO₂ reduction experiments, electrolyte was saturated with CO₂ (Air Liquid, 99.995%) by sparging the solution for 20 min and then the saturated electrolyte was added into the cell. A solar simulator (Newport Oriel LCS-100) with a calibrated light intensity of 100 mWcm⁻² (1 sun) has been employed as the light source. The current and potential data were collected by an Interface 1000 potentiostat (Gamry Instruments). The recorded potentials vs Ag/AgCl were converted to vs RHE by the following equation:

Where, 0.1976 is a conversion factor from the Ag/AgCl electrode to RHE at 25 °C.



Figure 2.8: Schematic illustration of PEC CO₂ reduction experiment steps: (a) MBE grown GaN nanowires, (b) co-catalyst deposition on GaN nanowires, (c) preparation of nanowire arrays as a photoelectrode, (d) PEC experiment set up.

After the photoelectrolysis, a small fraction of products from the working compartment was sampled by vacuum-tight syringe and analyzed by a thermal conductivity detector (for H₂) and a flame ionization detector (for CO and hydrocarbons) of gas chromatograph. Faradaic efficiency (FE) was calculated by determining the amount of charge needed for each product and then dividing by the total charge passed during the test. The half-cell solar-to-syngas efficiency η_{STS} was calculated using the following equation:

$$\eta_{STS} = \left[\frac{J(mA.cm^{-2}) \times FE_{co}(\%) \times (1.34 - V_{bias})(V) + J(mA.cm^{-2}) \times FE_{H_2}(\%) \times (1.34 - V_{bias})(V)}{P_{in}(mW.cm^{-2})}\right] \dots \dots (2.2)$$

Here *J* is the photocurrent density, and FE_{co} and FE_{H_2} is the faradaic efficiency towards CO and H₂ evolution, respectively, V_{bias} is the applied potential versus an ideal counter electrode for O₂ evolution (+1.23 V vs. RHE), and P_{in} is the light power density (100 mW. cm⁻²).

2.7.2 Photochemical measurement

The schematic experimental setup for photochemical CO₂ reduction is illustrated in Figure 2.9. The CO₂ reduction configuration was performed in an air-tight Pyrex chamber with a quartz lid and wafer sample was fixed its' position at the bottom of the Pyrex reaction by our homemade Polytetrafluoroethylene (PTFE) holder. This simple design works as the assembly of both a reaction system and an evaluation system. The reaction system consists of an external illumination source of 300 W Xe lamp from ILC Tech, CERMAX LX-300. The system was first well evacuated by using a vacuum pump and then filled with pure CO₂ until reaching a pressure of 85–90 kPa. In a separate beaker, distilled water (pH \sim 7.0) was purged with Ar for 20–30 mins before each experiment to remove residual gases dissolved in water. After purging, distilled water was inserted into the reaction cell and wait for 30–40min before the illumination starts. The Xenon lamp was turned on to start the reaction. Various optical filters are also used in some of the experiments. The output products were measured in timely manners by a vacuum tight syringe. For CO evolution, a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector and the gas chromatograph (GC-8A, Shimadzu) equipped with a thermal conductivity detector (TCD) and high purity (99.9999 %) Ar carrier gas is used for H₂ evaluation.



Figure 2.9: Photochemical PEC CO₂ reduction experiment set-up in schematic form.

2.7.3 Co-catalyst deposition

To enhance the carrier extraction efficiency and reduce the overpotential required for CO_2 reduction co-catalysts are frequently required. The deposition of such co-catalysts on the InGaN/GaN nanowire surfaces can be attained through several ways, such as impregnation, adsorption, electron beam, atomic layer deposition or photodeposition. In our study, several co-catalysts have been explored to improve the syngas performance such as Au/Pt, Au/Cr₂O₃, Au/TiO₂. The co-catalyst deposition has been accomplished by e-beam and photodeposition. E-beam has been performed based on physical vapor deposition principle by NexDep ebeam evaporator and photodeposition has been done by homemade PTFE holder with 460 ml Pyrex chamber (Kimble Chase) and quartz lid, using 300 W Xenon lamp (Cermax, PE300BUV) as an outer irradiation source.

2.8 Conclusions

In this chapter, a synopsis of the growth/synthesis and properties of III-nitride nanostructures is introduced with the consideration of the building block – GaN and its ternary alloy, Ga(In)N. The catalyst-free high quality, crystalline InGaN/GaN nanowire heterostructures grown by MBE using an in situ deposited Ga or In seeding layer (prior to growth initiation) for spontaneous growth and the precise control of nanowire morphology by selective area growth have been discussed. Techniques used for characterizing these nanostructures and devices are also discussed.

Chapter 3

Demonstration of Stable Light Emission from InGaN Nanowire Photonic Crystal

To date, there have been no efficient semiconductor light emitters operating in the green and amber wavelengths. This study reports on the synthesis of InGaN nanowire photonic crystals, including dot-in-nanowires, nanotriangles, and nanorectangles with precisely controlled size, spacing, and morphology, and further demonstrates that bottom-up InGaN photonic crystals can exhibit highly efficient and stable emission. The formation of stable and scalable band edge modes in defect-free InGaN nanowire photonic crystals is directly measured by cathodoluminescence studies. The luminescence emission, in terms of both the peak position ($\lambda \approx 505$ nm) and spectral linewidths (full-width-half-maximum ≈ 12 nm), remains virtually invariant in the temperature range of 5–300 K and under excitation densities of 29 W cm⁻² to 17.5 kW cm⁻². To the best of our knowledge, this is the first demonstration of the absence of Varshni and quantum-confined Stark effects in wurtzite InGaN light emitters-factors that contribute significantly to the efficiency droop and device instability under high-power operation. Such distinct emission properties of InGaN photonic crystals stem directly from the strong Purcell effect, due to efficient coupling of the spontaneous emission to the highly stable and scalable band-edge modes of InGaN photonic crystals, and are ideally suited for uncooled, high-efficiency light-emitting-diode operation.

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3.1 Introduction

Highly stable and efficient light emitting devices are essentially required for a broad range of applications including lighting, display, communication, sensing, imaging, and medical diagnostics [164-166]. While GaN-based light emitting diodes exhibit efficient operation in the blue wavelength range, their efficiency and stability degrades considerably with increasing wavelengths, leading to the "green gap" in LED and laser technology [48, 137, 167-170]. The quantum efficiency (η) of a semiconductor light emitter is ultimately determined by,

$$\eta \propto \frac{\tau_r^{-1}}{\tau_r^{-1} + \tau_{nr}^{-1}}$$
(3.1)

where τ_r and τ_{nr} represent the radiative and nonradiative lifetime in the device active region, respectively. In conventional InGaN/GaN green and amber LEDs, the presence of large densities of defects and dislocations, due to the large lattice mismatch (~11%) between InN and GaN, and Auger recombination leads to a small τ_{nr} and therefore low quantum efficiency [171-173]. Moreover, the performance of conventional InGaN light emitters suffers severely from straininduced polarization fields and the resulting quantum-confined Stark effect, which often results in a considerable blueshift in emission wavelengths (up to 30 nm) under high power operation [174, 175]. To date, a clear path to achieve efficient and stable semiconductor light emitters operating in the green, yellow, and amber wavelengths has remained elusive [44, 176].

Emission properties of a semiconductor light emitter are determined not only by the properties of the device active medium but also by the optical density of states surrounding the active region. For example, by exploiting the Purcell effect in an optical microcavity, the radiative lifetime (τ_r) can be significantly reduced, thereby leading to enhanced internal quantum efficiency (η) [177]. To date, however, there has been few demonstrations on the use of Purcell effect to bridge the "green gap" in semiconductor LEDs and lasers [92, 178-181]. The Purcell factor, F_p , is determined by,

$$F_p \propto \frac{Qg}{V}$$
(3.2)

where Q is the quality factor, V is the mode volume of the optical cavity, and g is the mode degeneracy [177]. To enhance the Purcell factor, conventional design considerations are focused

on small optical cavity size (on the order of micron meter) [182-185]. whereas practical LED devices require extended optical mode spread over millimeter scale, i.e. three to six orders of magnitude larger than conventional designs. In addition, previously reported GaN optical cavities, including photonic crystals, are generally fabricated from epilayers using the top-down etching method, which inherently have large densities of defects and dislocations, with emission wavelengths limited to the blue and near-ultraviolet spectral range [93, 94, 186-188].

In this work, we show that such critical challenges can be addressed by using InGaN photonic molecules synthesized via the bottom-up method, wherein the formation of defects and dislocations are minimized due to the efficient surface strain relaxation. With the use of selective area epitaxy, we demonstrate that the size, spacing and morphology of InGaN photonic molecules, including dot-in-nanowires, nano-triangles and nano-rectangles can be precisely controlled, and, as such, spatially extended band edge modes can develop over a large area of such defect-free photonic crystals. It is further observed that InGaN photonic crystals exhibit remarkably stable emission, compared to conventional InGaN light emitters. The luminescence emission, in terms of both the peak position ($\lambda \sim 505$ nm) and spectral linewidths (full-width-half-maximum – FWHM ~12 nm), remained virtually invariant in the temperature range of 5 K to 300 K and under excitation densities of 29 W/cm² to 17.5 kW/cm². To the best of our knowledge, this is the first demonstration of the absence of Varshni and quantum-confined Stark effects in wurtzite InGaN light emitters, factors that contribute significantly to the efficiency droop and device instability under high power operation. Such distinct emission properties of InGaN photonic crystals stem directly from the highly stable and scalable band edge modes, due to the precisely controlled size, position, and morphology of InGaN photonic molecules, and are ideally suited for uncooled, high efficiency LED and laser operation.

3.2 Results and Discussions

Photonic crystal nanostructures synthesized by the bottom-up method often exhibit nonnegligible surface recombination as well as significant variations in size and morphology [189-191]. In this work, we show that these issues can be collectively addressed by selective area epitaxy of GaN photonic crystals on nano-patterned substrate using plasma-assisted molecular beam epitaxy, wherein InGaN/AlGaN quantum dots are incorporated as the active medium to suppress surface recombination. Schematically shown in Figure 3.1 (a), a thin (10 nm) Ti layer was used as a growth mask on a GaN/Al₂O₃ substrate, and various nanoscale patterns were created on the Ti mask by e-beam lithography and reactive dry-etching techniques [136, 192-199]. Each GaN photonic molecule, schematically shown Figure 3.1 (b), consists of 400 nm *n*-GaN, ten vertically aligned InGaN/AlGaN quantum dots, and 80 nm p-GaN layer. Under such conditions, Ga adatoms are only nucleated in the opening apertures, and no epitaxy takes place on the Ti mask. As such, the size and morphology of GaN photonic molecules are precisely determined by the opening apertures in the Ti mask. The incorporation of AlGaN barriers, instead of GaN barriers, leads to the formation of an AlGaN shell surrounding the InGaN quantum dot active region, due to the smaller Al adatom migration length compared to Ga and In adatoms. The resulting core-shell like nanostructures, schematically shown in Figure 3.1 (b), can effectively suppress nonradiative surface recombination [39, 200].

The photoluminescence emission was measured using a 405 nm laser at room temperature. Shown in Figure 3.2 (b), it is seen that the photoluminescence intensity is enhanced by nearly a factor of eight, compared to InGaN/GaN nanostructures without the formation of AlGaN shell. Detailed structural characterization of the InGaN/AlGaN core-shell dot-in-nanowire structures is described elsewhere [39, 200, 201]. Shown in Figure 3.2 (c) and (d) are the scanning electron microscope images of InGaN/AlGaN hexagonal dot-in-nanowire, dot-in-nanotriangle, and dot-in-nanorectangle arrays, which exhibit straight sidewalls and uniform size distribution [179]. The photonic crystals can be arranged in various lattice structures, including rhombic and triangular lattices, with different orientations, illustrated in Figure 3.2 (c). Take the dot-in-nanowire array shown in Figure 3.2 (d) as an example, the nanowire photonic crystals are arranged in a triangular lattice with a lattice constant of 250 nm. The nanowires have lateral sizes of 215 nm and length of

560 nm. The air gap between neighboring nanowires is 35 nm. The uniformity of InGaN nanowire photonic crystals across a large area is further shown in Figure A1 in the Appendix A.



Figure 3.1: (a) Schematic illustration of hole-patterned Ti thin film mask for the selective-area epitaxy of InGaN photonic crystals. SEM image of various nanoscale patterns formed on the Ti mask is shown in the right panel. (b) Illustration of bottom-up InGaN/AlGaN core–shell dot-in-nanowire array grown on pattered substrate. Photoluminescence spectrum of InGaN/AlGaN core–shell dot-in-nanowires measured at room-temperature (red curve) is shown in the right panel. Also shown for comparison is the photoluminescence emission of InGaN/GaN dot-in-nanowires without AlGaN shell (blue curve). (c) Top-view SEM images of InGaN/AlGaN hexagonal dot-in-

nanowire, nanotriangle, and nanorectangle arrays. (d) 45°-tilted-view SEM image of the nanowire photonic crystals arranged in a triangular lattice with a lattice constant of 250 nm. The top-view SEM image is shown in the inset.

Significantly, InGaN/AlGaN dot-in-nanowire photonic crystals exhibit distinctly different emission characteristics, compared to conventional InGaN emitters. Shown in Figure 3.1 (b), strong emission was observed at 505 nm with a relatively narrow spectral linewidth of 12 nm for the photonic crystals illustrated in Figure 3.1 (d). The emission is highly uniform across a large nanowire photonic crystal structure (see Figure A2 in the Appendix A). For comparison, conventional InGaN nanowire arrays or epilayers exhibit broad spectral linewidths (35–50 nm), [168, 201-203], which are limited by the large inhomogeneous broadening associated with indium compositional variation and the presence of defects and strain field [39, 135]. Variations of the light intensity versus excitation power are further shown in Figure 3.2 (b). The integrated luminescence intensity is nearly three times higher than InGaN/AlGaN dot-in-nanowire arrays grown under identical conditions but without the control of the nanowire spacing. The unique dependence of the luminescence emission on the nanowire spacing and height, as well as the impact of optical confinement of photonic crystals on the temperature and power-dependent emission characteristics of InGaN, is described next.



Figure 3.2: (a) Photoluminescence spectrum of InGaN/AlGaN dot-in-nanowire photonic crystals measured at room-temperature (red curve). Also shown for comparison is the photoluminescence emission of conventional InGaN/AlGaN nanowires (blue curve) without controlled spacing. (b) Variations of the light intensity versus excitation power density measured at room-temperature.

First, to understand the effect of optical confinement on the emission characteristics of InGaN, the photonic band structure of InGaN hexagonal nanowire arrays was calculated using the plane wave expansion method. Shown in Figure 3.3 (a) and (b), InGaN nanowires are arranged in a hexagonal lattice with a lattice constant a and lateral dimension d = 0.85a, which is also shown in the structural characterization in Figure 3.1 (d). The refractive index of InGaN nanowires is 2.37. The normalized frequency of the band-edge mode is ≈ 0.49 , which corresponds to $\lambda = 505$ nm for a = 250 nm. By adjusting the flat bands of leaky modes, e.g., frequencies around 0.49 to match the emission wavelengths of the active region, the luminescence efficiency can be significantly enhanced, due to the Purcell effect. The group velocity is determined by the slope of the dispersion curve in the photonic band structure. At the band edge, a low group velocity is achieved, i.e., dw/dk $\rightarrow 0$ for frequencies around 0.49 near the Γ point, thereby leading to the formation of a stable and large cavity mode [204]. The low group velocity and the resulting long interaction time between radiation field and active material lead to a considerably enhanced spontaneous emission rate. Moreover, due to Bragg scattering, the light extraction efficiency will also be enhanced. Shown in Figure 3.4 (c) is the electric field profile of the band edge mode calculated by the finite-element method for areal sizes of $5 \times 5 \mu m$. The calculated mode is TM polarized with electric field in parallel with the *c*-axis. Perfectly matched layer was used for the boundary condition, which can minimize any reflection at the simulation boundary.

The formation of stable and scalable optical modes in such bottom-up photonic crystals is further revealed by cathodoluminescence (CL) studies. Illustrated in Figure 3.3 (d) is the cathodoluminescence image taken at 505 nm at room-temperature. The areal size being excited by the e-beam is $5 \times 5 \mu m$. It is seen that the band edge mode spreads across the entire photonic crystal structure, which is in excellent agreement with the calculation shown in Figure 3.3 (c). Strong light confinement occurs near the center region of nanowire arrays by the scattering of the band edge mode. Moreover, it is interesting to observe that strong photon confinement can also be achieved for photonic crystals with areal sizes as small as $2 \times 2 \mu m$ and $1 \times 1 \mu m$, shown in Figure 3.3 (e) and (f), respectively, confirming the scalability of the band edge modes [204]. Detailed cathodoluminescence measurements were also performed for InGaN photonic crystals with different design parameters and at different emission wavelengths, shown in Figure A3 in the Appendix A. These studies provided unambiguous evidence for the formation of strongly confined, highly uniform, and scalable band edge modes of InGaN photonic crystals, thereby offering a viable approach for realizing both small and large scale efficient light emitters.



Figure 3.3: (a) Schematic diagram of the simulated photonic crystals, including the lattice constant *a*, nanowire lateral size *d*, and the reciprocal lattice vectors. (b) Calculated photonic band structure of the 2D hexagonal array of nanowires (the corresponding SEM is shown in Figure 3.1 (d). (c) The electric field profile of the band edge mode calculated by the 3D finite-difference time-domain method for a bands-edge mode ($\lambda = 505$ nm). (d) Cathodoluminescence mapping image of an areal size of $5 \times 5 \ \mu\text{m}^2$ measured at a wavelength of 505 nm. Cathodoluminescence mapping images over (e) $2 \times 2 \ \mu\text{m}$ and (f) $1 \times 1 \ \mu\text{m}$ regions, respectively. (g) Variations of the integrated luminescence intensity and FWHM of InGaN photonic crystals versus nanowire spacing.

We have further performed extensive studies of InGaN photonic crystals with different design parameters. Shown in Figure 3.3 (g) are variations of the luminescence intensity and spectral linewidth with nanowire spacing while keeping a constant. Epitaxy conditions were optimized to have similar spontaneous emission from the quantum dot active regions when the nanowire spacing is varied. It is seen that the emission characteristics, in terms of both the spectral linewidth and integrated intensity, depend critically on the nanowire spacing. The highest luminescence intensity and narrowest spectral linewidth occurs for a nanowire spacing of 35 nm. A decrease, or increase in nanowire spacing, leads to a reduction in the luminescence intensity, accompanied by a significant increase in the spectral linewidth, which suggests a reduced or minimal level of coupling between the quantum dot spontaneous emission and the band edge mode. Since the light extraction efficiency of leaky modes does not change significantly for such small variations of nanowire spacing [177, 205], the measured variations of luminescence emission may be primarily attributed to the change of the Purcell effect. Based on the measured internal quantum efficiency of 20-30% at room-temperature for the InGaN photonic crystals and assuming a constant light extraction efficiency, the magnitude of Purcell enhancement factor (F_p) is estimated to be in the range of 3 for the spatially extended band edge mode, which is comparable to that for the very small mode in a nanocavity [179]. The relatively large Purcell factor is partly related to the large mode degeneracy factor g shown in Equation (3.2) associated with the large modal volume [177]. The extreme sensitivity of the Purcell effect on the nanowire spacing (radius), compared to the conventional slab photonic crystals [177, 205], is partly related to the quasi 3D nature of InGaN nanowire photonic crystals, due to the presence of planar GaN substrate as well as the finite length of InGaN nanowires. This observation is further supported by the critical dependence of the emission characteristics of InGaN nanowire photonic crystals on the height of nanowires (see in Figure A4 of the Appendix A).

Due to the presence of quantum-confined Stark effect, conventional InGaN light emitters generally exhibit significant blueshift with increasing pumping power [206-208]. Moreover, the emission characteristics also vary considerably with temperature, due to the Varshni's effect. By contrast, we have measured remarkably stable emission characteristics for InGaN nanowire photonic crystals. Shown in Figure 3.4 (a) are the normalized photoluminescence emission spectra of InGaN photonic crystals measured at excitation power from 29 W cm⁻² to 17.5 kW cm⁻² at room temperature. It is seen that the emission spectra remain nearly identical. Shown in Figure 3.5 (b), the peak emission wavelengths (\approx 505 nm) and spectral linewidths (FWHM \approx 12 nm) are virtually invariant versus pumping power. Luminescence emission spectra of InGaN dot-innanowire photonic crystals measured in the temperature range of 5–300 K are further shown in Figure 3.4 (c), which was measured under 8.7 kW cm⁻² continuous wave pumping condition.

Figure 3.4 (d) shows variations of the emission peak and spectral linewidth versus temperature. It is seen that both the emission wavelengths (\approx 505 nm) and spectral linewidths (\approx 12 nm) remained nearly constant in the temperature range of 5–300 K. For comparison, conventional InGaN nanowire arrays without photonic crystal effect exhibit significant variations in the photoluminescence emission properties with increasing temperature and pumping power, shown in the insets of Figure 3.4 (b) and (d). The remarkably stable emission characteristics of InGaN photonic crystals stem directly from the efficient coupling of InGaN quantum dot emission to the robust band edge modes of InGaN photonic crystals, which is virtually independent of device operating conditions and largely determines the emission characteristics.



Figure 3.4: (a) Photoluminescence emission spectra of InGaN photonic crystals measured at excitation power from 29 W cm⁻² to 17.5 kW cm⁻² at room-temperature. (b) Variations of the

emission peak and spectral linewidth versus excitation power in the InGaN photonic crystal. Inset: variations of the emission peak and spectral linewidth in conventional InGaN nanowire arrays without the photonic-crystal effect. (c) Photoluminescence emission spectra of InGaN photonic crystals measured in the temperature range of 5–300 K under 8.7 kW cm⁻² continuous-wave pumping conditions. (d) Variations of the emission peak and spectral linewidth versus temperature in the InGaN photonic crystal. Inset: variations of the emission peak and spectral linewidth in the conventional InGaN nanowire arrays without photonic-crystal effect.

3.3 Conclusions

In summary, we have demonstrated the bottom-up synthesis of InGaN nanowire photonic crystals with precisely controlled size, spacing, and morphology, which can serve as the fundamental building blocks of a new generation of photonic crystal devices and systems. By coupling the light emission into the band edge mode of InGaN photonic crystals, significantly enhanced emission efficiency and reduced spectral broadening was measured. Moreover, the luminescence emission exhibits remarkable stability: there are virtually no variations in the emission characteristics, in terms of both the emission peak and spectral linewidth in the temperature range of 5–300 K and for pumping power variations from 29 W cm⁻² to 17.5 kW cm⁻². To our knowledge, this is the first demonstration of the absence of quantum-confined Stark effect and Varshni's effect in InGaN light emitters. These unique characteristics, together with the scalable band edge optical mode [209], high light-extraction efficiency [210], on-demand beam characteristics [211, 212], and full-color emission [18, 136], render bottom-up GaN nanowire photonic crystals well suited for ultrahigh-efficiency, large-area LED and laser devices, as well as integrated nanophotonic circuits in the ultraviolet and visible spectral range.

Chapter 4

An Electrically Pumped Surface-Emitting Semiconductor Green Laser

Surface-emitting semiconductor lasers have been widely used in data communications, sensing, and recently in Face ID and augmented reality glasses. Here, we report the first achievement of an all-epitaxial, distributed Bragg reflector (DBR)-free electrically injected surface-emitting green laser by exploiting the photonic band edge modes formed in dislocation-free gallium nitride nanocrystal arrays, instead of using conventional DBRs. The device operates at ~523 nm and exhibits a threshold current of ~400 A/cm², which is over one order of magnitude lower compared to previously reported blue laser diodes. Our studies open a new paradigm for developing low-threshold surface-emitting laser diodes from the ultraviolet to the deep visible (~200 to 600 nm), wherein the device performance is no longer limited by the lack of high-quality DBRs, large lattice mismatch, and substrate availability.

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4.1 Introduction

Vertical cavity surface-emitting laser (VCSEL) diodes, first presented in 1979 [213], emit a coherent optical beam vertically from the device top surface and offer a number of advantages compared to conventional edge-emitting lasers, including lower threshold [214], circular and lowdivergence output beam [215], single longitudinal mode emission [216], longer lifetime [217] and easy production of dense two-dimensional (2D) arrays [218-223]. Commercial VCSELs are fabricated on GaAs and InP substrates [224, 225], which emit light mostly in the near-infrared wavelengths [226, 227]. Gallium nitride (GaN) based semiconductors are the material of choice for lasers operating in the visible and ultraviolet (UV) spectral ranges, and substantial efforts have been devoted to developing GaN-based VCSELs in the past decade [77-79, 81-83]. However, the operation wavelengths have been largely limited to the blue spectral range [34, 84, 85, 228]. To date there has been no demonstration of all epitaxial surface emitting laser diodes operating in the green wavelength region, to which eyes are most sensitive. To the best of our knowledge, the only previously reported room temperature continuous wave (CW) surface-emitting green laser diode relied on the use of dual dielectric distributed Bragg reflectors (DBRs) and wafer bonding to a copper plate for low thermal resistance [47]. The realization of a low-threshold, high-efficiency, all-epitaxial surface-emitting green laser diode will enable many exciting applications including projection displays such as pico projectors, plastic optical fiber communication, wireless communication, optical storage, smart lighting, and biosensors [93, 229-231].

An essential component of a VCSEL is distributed Bragg reflectors, which consist of multiple alternative layers of materials with a relatively large difference in refractive index to provide very high reflectivity. DBRs with nearly lattice matched layers can be readily formed in GaAs and InP based materials systems [224] but have remained a critical challenge for GaN-based materials. The large lattice mismatch between GaN and AlN (~2.5%) and between GaN and InN (~11%) [232, 233], together with the difficulty in achieving efficient *p*-type conduction [234], leads to GaN-based DBRs with high electrical resistivity [235], large densities of defects and dislocations [236, 237], and relatively low reflectivity. In addition, the presence of strong polarization field and the resulting quantum-confined Stark effect (QCSE) of conventional *c*-plane GaN devices further reduces the rate of radiative recombination, resulting in higher threshold and instable operation [174]. To address these issues, GaN-based blue VCSELs have been reported by utilizing
AlInN/GaN DBRs [85] or dual-dielectric DBRs [238], and by growing on *m*-plane GaN substrate [86]. The resulting devices, however, still exhibit very large threshold current density ($J_{th} > 10$ kA/cm²) at room-temperature, with the operation wavelengths limited to 400–460 nm [85, 94].

In this work, we propose and demonstrate, for the first time, a nanocrystal surface-emitting laser (NCSEL) diode, which is free of DBRs and can operate efficiently in the green spectrum. Schematically shown in Figure 4.1 (a), the NCSEL consists of InGaN/AlGaN nanocrystal arrays with precisely controlled size, spacing and surface morphology. Due to the efficient strain relaxation, such nanostructures are free of dislocations [239]. Multiple InGaN quantum disks are incorporated on the semipolar planes of the active region, which can significantly reduce QCSE [240]. A unique AlGaN shell structure (Figure 4.1 (c)) is formed surrounding the active region of the NCSEL to suppress surface recombination. By exploiting the photonic band-edge resonant effect of the nanocrystal array, we have demonstrated an electrically injected surface-emitting green laser diode without using conventional thick and resistivity DBRs. The device operates at 523.1 nm and exhibits a low threshold current density ~400 A/cm² and highly stable operation at room-temperature. The achievement of coherent lasing oscillation is further confirmed by the farfield emission pattern and by detailed polarization measurements. This work demonstrates a viable approach to realize high performance surface-emitting laser diodes from the deep UV to the deep visible (~210–600 nm) that were previously difficult to achieve.

4.2 Results and Discussions

Schematically shown in Figure 4.1 (a), (b) and (c) are the design of the InGaN NCSEL, which consists of *n*-type GaN cladding layer (~370 nm thick), an InGaN multiple quantum disk active region, and *p*-type GaN cladding layer (190 nm thick). The nanocrystals have hexagonal shape and are arranged in a triangular lattice. The diameter and lattice constant of the nanocrystals are denoted as *d* and *a*, respectively (Figure 4.1(c)). The design and simulation, including energy band diagram and mode profile, was performed using two-dimensional finite-element method (2D-FEM) simulation with Maxwell's equations (also find in Appendix-B). Shown in Figure 4.1 (d), the reciprocal lattice of a photonic crystal structure has six equivalent Γ' points which are coupled together by the Bragg grating vectors, *e.g.*, *K*₁ and *K*₂. The corresponding wavelength light can therefore form a standing wave resonant in the photonic crystal without any additional dielectric

mirror [241, 242]. Besides such in-plane coupling, there is also out-of-plane coupling between the six Γ' point and the Γ point which has zero in-plane wave vector [243]. The wavevector is essentially vertical, thereby leading to surface emission (Figure 4.1 (d)). In this design, the nanocrystals have a spacing of ~30 nm, and the lattice constant is 250 nm.



Figure 4.1: Design of InGaN nanocrystal surface emitting laser (NCSEL) diodes operating in the green wavelength. (a) Schematic of the InGaN nanocrystal arrays for the surface-emitting laser diode. (b) The diameter and lattice constant of the nanocrystals denoted as *d* and *a*, respectively. (c) Schematic of InGaN/AlGaN nanowire heterostructure, which consists of an *n*-GaN cladding layer, a core-shell InGaN/AlGaN multiple quantum disk active region, and a *p*-GaN cladding layer. (d) The reciprocal lattice of a photonic crystal structure has six equivalent Γ' points, which are coupled together by the Bragg grating vectors *K1* and *K2*. (e) Calculated photonic band structure

for transverse magnetic (TM) polarization from 2D finite-element method (2D-FEM) simulation. (f) The electric field profile of the band edge mode ($\lambda = 523$ nm) calculated by the 3D finitedifference time-domain method. (g) PL spectrum of an InGaN/AlGaN calibration sample showing spontaneous green emission. a.u., arbitrary units. (h, i) The top-view and titled-view scanning electron microscopy (SEM) images of an InGaN nanocrystal array.

The resulting photonic band structure for transverse magnetic (TM) polarization ($E \parallel c$ -axis) from 2D-FEM simulation is shown in Figure 4.1 (e). The Γ point in the 4th band is located at ~0.48 a/λ which corresponds to λ ~520 nm. The group velocity is determined by the slope of the dispersion curve in the photonic band structure. At the band edge, the low group velocity is achieved when the slope of dispersion curve become zero, *i.e.*, near the Γ point the group velocity of light becomes zero ($dw/dk \rightarrow 0$), thereby leading to the formation of a stable and large single-cavity mode [91, 244-247]. The mode profile is simulated and shown in Figure 4.1 (f). The mode intensity is mostly distributed in the nanocrystals. The extremely low group velocity leads to the long interaction time between radiation field and active material and consequently gives rise to a strong gain enhancement. Photons are also confined around the active region in the vertical direction, due to the higher average refractive index in the active region. The mode intensity profile in the vertical direction shown in Figure B1, and the simulation details are described in Appendix-B, text B2.

The realization of NCSELs requires a precise control of the nanocrystal size, spacing, and uniformity across a relatively large area. The fabrication of such nanocrystal arrays is achieved by the special technique of selective area epitaxy using plasma-assisted molecular beam epitaxy (MBE) (see Appendix-B, Figure B2, and text B1 and B3) [136]. An AlGaN shell structure was incorporated in the active region to reduce surface recombination [39, 200]. Figure 4.1 (g) shows the photoluminescence (PL) spectrum for a calibration sample without significant photonic band edge resonant effect. The peak emission wavelength is ~523 nm. Significantly enhanced photoluminescence emission intensity was measured for InGaN/AlGaN core-shell structure, compared to similar structures but without AlGaN shell (Appendix-B, Figure B6, and text B4 and B8). Shown in Figure 4.1 (h) and (i) are the top-view and tilted-view SEM images of the InGaN nanocrystals for a 6 μ m × 6 μ m area. The nanocrystal arrays have a triangular lattice with a pitch of 250 nm, lateral size of 230 nm, height of ~600 nm, and gap between neighboring nanocrystals

of ~30 nm. The nanocrystals exhibit uniform length, smooth sidewalls, and near-perfect hexagonal shape and high (depth to width) aspect ratio, which correlate well with the design parameters described above.

We further performed detailed structural characterization of InGaN nanocrystals using scanning transmission electron microscopy (STEM) (Appendix-B, Figure B7 and text B5). We prepared a cross-sectional sample using a focused ion beam system. Figure 4.2 (a) shows the high-angle annular dark-field (HAADF) atomic number contrast image of a representative InGaN nanocrystal. The InGaN/AlGaN heterostructures were formed as a cone shape. This is due to the formation of *n*-GaN nanocrystals that have a Ga polarity and pyramid-like morphology (Appendix-B, Figure B4 and text B6). The resulting unique structure takes advantage of the semipolar effect in the active region to reduce the polarization field in GaN wurtzite structure [248]. Shown in Figure 4.2 (b) is a high-magnification image taken from the marked region in Figure 4.2 (a). The sloping multiple quantum disk layers can be more clearly observed. The formation of multiple quantum disk heterostructures on semipolar planes of (0113) orientation is further supported by the representative selected-area electron diffraction pattern analysis (Figure 4.2 (c)).

From the wide-thickness layers with the bright contrast in the middle region, it can be seen that multiple quantum disk structures are formed as a cone-like shell structure (Figure 4.2 (c)). The formation of such cone-shaped active layer is further supported by the formation of the *n*-GaN structure as shown in Appendix-B. The unique 3D structure provides an emission area that is much larger than that of the typical quantum disk/dot active regions aligned vertically with the same diameter. Figure 4.2 (d) shows the high-magnification HAADF image of InGaN/AlGaN active region. The presence of highly uniform multiple quantum disk layers can be clearly identified by different contrast. No noticeable extended misfit dislocations or stacking faults were observed. The thicknesses of the InGaN disks and AlGaN barriers are ~2.5 nm and 1.5 nm, respectively. To further confirm elemental distribution of the active region, an energy dispersive X-ray spectrometry analysis was performed along the growth direction of InGaN/AlGaN quantum disks, which is labeled with "1" in Figure 4.2 (d). The qualitative variations of In and Al across different disks and barriers are displayed in Figure 4.2 (e). Because the atomic number of Al is smaller than the atomic number of In, it appears as dark contrast in the STEM image. The In signal exhibits a maximum in the bright regions and drops in the dark regions. In contrast, the Al signal shows clear

peaks in the dark regions, confirming the formation of InGaN/AlGaN quantum disk heterostructures. The presence of Al-rich AlGaN shell layer formed spontaneously on the sidewall of the InGaN quantum disk is also confirmed by the EDXS point analysis (Figure 4.2 (f)). The spontaneously formed AlGaN shell structure can effectively suppress nonradiative surface recombination, a primary limiting factor for the performance of conventional nanostructured devices [200]. Moreover, the semi-polar InGaN/AlGaN core-shell heterostructure further offers several distinct advantages, including significantly reduced polarization fields [240] and enhanced light emission efficiency [249], as well as significantly improved carrier injection efficiency [39] and luminescence efficiency [250], compared to conventional quantum disk/dot structures (Appendix-B, Figure B6 and text B8). It is also worthwhile mentioning that such a unique structure cannot be fabricated by the conventional top-down approach because the active region is predefined by the film structure.



Figure 4.2: Structural characterization of InGaN/AlGaN core-shell quantum disk heterostructures. (a) STEM-HAADF image of a representative core-shell InGaN/AlGaN multiple quantum disk (MQD) heterostructure nanocrystal. (b) High-magnification image taken from the region marked in Figure 4.4 (a) and (c) Schematic illustration for quasi-3D structure of the semi-polar active region and selective area electron diffraction pattern of the InGaN/AlGaN core-shell

heterostructure. (d) High-magnification HAADF image of the InGaN/AlGaN quantum disk region. (e) EDXS line-profile of the InGaN/AlGaN quantum disks along the line labeled with "1" in Figure 4.2 (d). (f) EDXS point analysis of AlGaN shell region marked as "A" and "B" in Figure 4.2 (b).

We fabricated InGaN NCSEL diodes using planarization, polyimide passivation, contact metallization, and photolithography techniques (Appendix-B, Figure B7 and text B9). Schematic illustration of the fabricated device is shown in Figure 4.3 (a), and an optical microscopy image of the device after metallic contact grids is also shown in the inset. Shown in Figure 4.3 (b) is a representative current-voltage (*I-V*) curve for a device with surface contact area of ~25 μ m², which clearly shows rectification characteristics with a sharp turn-on voltage of ~3.3 V at room temperature. The leakage current is negligible under reverse bias (the inset of Figure 4.3 (b)). The device exhibited excellent *I*–*V* characteristics, which is partly due to the significantly reduced defect density and enhanced dopant incorporation in nanocrystal structures (*58, 59*).



Figure 4.3: Fabrication and characterization of InGaN NCSEL diodes. (A) Schematic illustration of the fabricated NCSEL device. Inset: Optical microscopy image of the device after metallic contact grids and electroluminescence (EL) image of the green lasing. (B) Current-voltage (*I-V*) characteristics of the NCSEL device. Inset: The *I-V* curve on a semi-log scale. (C)

Electroluminescence spectra measured from different injection currents under CW biasing conditions at room temperature (R.T.). (D) Variations of the output power versus injection current. It shows a clear threshold of ~400 A/cm². SP, spontaneous emission. (E) Variations of spectral linewidth (FWHM, full width at half maximum). (F) Peak wavelength position measured under different injection current densities.

The electroluminescence characteristics were measured under CW biasing conditions at room temperature. The emitted light was collected from the top surface of nanocrystal (Appendix-B, Figure B8 and text B10). Figure 4.3 (c) shows the electroluminescence spectra of the nanocrystal device measured under different injection currents. At low injection current density of ~200 A/cm², the device exhibits a broad emission spectrum centered at ~524 nm, with a full-width-at-halfmaximum of ~ 30 nm, which corresponds to the spontaneous emission and may be limited by nonuniform current injection. A sharp lasing peak at ~523.1 nm wavelength was observed with increasing injection current, with a narrow linewidth of ~0.8 nm. The strong lasing spot is shown in the inset of Figure 4.3 (a), which was recorded at a current density ~1 kA/cm². Variations of the output power vs. injection current were further measured, which exhibits a clear threshold at ~400 A/cm² (Figure 4.3 (d)). The measured lasing threshold is significantly lower compared to previously reported GaN VCSELs [47, 85, 93, 94, 251, 252]. An output power of ~12 µW was measured at an injection current density of ~1 kA/cm² under CW operation. The output power shows a saturation with further increasing the injection current, due to heating effect. The measured output power is significantly higher than previously reported values of GaN-based VCSELs operating at 460 nm and 500 nm [253] and can be further improved by optimizing the design and fabrication process.

Variations of spectral linewidth (FWHM) and wavelength peak position are investigated under different injection current densities (Figure 4.3 (e) and (f)). The spectral linewidth decreased from ~30 nm to 0.8 nm at the threshold. It is also seen that the lasing peak position stays nearly constant at ~523 nm above threshold, suggesting highly stable lasing of the core-shell nanocrystal lasers. The low threshold current density and highly stable emission are directly related to the robust photonic band edge mode of nanocrystal optical cavity, the dislocation-free bottom-up nanocrystal structure, and the reduced nonradiative surface recombination and suppressed polarization-field with the extended emission area in InGaN/AlGaN cone-like shell active region.

The far-field radiation pattern of the nanocrystal laser structure was simulated using the 3D finite-difference time-domain (FDTD) method, shown in Figure 4.4 (a) (also Appendix-B, text B1 and B11). Because the wavelength near Γ point has very small in-plane wavevector component, the wavevector is expected to be almost vertical. Because of this unique property of the Γ point, the far-field pattern exhibits a spot in the center with a very small divergence angle, which corresponds to highly collimated vertical emission. The far-field patterns measured below and above threshold of the InGaN NCSEL are shown in Figure 4.4(b) and 4.4(c), respectively (Appendix B, Figure B9 and text B12). Below threshold, the far-field image shows emission without any interference fringes, with the uniformity partly limited by the current spreading and injection at relatively low current densities. When the current density is above threshold, the lasing emission shows the presence of interference fringes that indicate coherent emission [183, 254-257]. Such results provide strong evidence that the coherent lasing oscillation has been achieved in InGaN nanocrystal arrays.



Figure 4.4: Far-field and polarization emission properties of InGaN NCSEL diodes. (a) Far-field radiation pattern of the nanocrystal laser structure simulated using the 3D FDTD method. Electroluminescence image of the far-field pattern observed below the threshold current density

 (200 A/cm^2) (b) and slightly above the threshold current density (c) of the InGaN NCSEL recorded using a high-resolution charge-coupled device (CCD) camera above the device top surface. (d) Polarized electroluminescence spectra of the InGaN NCSEL measured under a current density of 1 kA/cm². The polarization ratio is ~0.86. (e) The measured electroluminescence intensity as a function of the emission polarization angle (0° to 360°).

We have further studied the polarization properties in the far-field of light emission of InGaN NCSELs. The degree of polarization is defined as $\rho = (I_{0^{\circ}} - I_{90^{\circ}}) / (I_{0^{\circ}} + I_{90^{\circ}})$ (Appendix B, Figure B10 and text B13), where $I_{0^{\circ}}$ and $I_{90^{\circ}}$ are the electroluminescence emission intensity, corresponding to the electric field along 0° and 90° direction, respectively. Figure 4.4 (d) shows the electroluminescence spectra measured under a current density of 1 kA/cm² for different polarizations. It is seen that the electroluminescence emission is highly polarized. The degree of polarization is as large as 0.86. Variations of electroluminescence intensity *vs.* polarization angle (θ) are further plotted in Figure 4.4 (e), showing a high degree of polarization at $\theta = 0^{\circ}$. It is worthwhile mentioning that this is a remarkably stable and directional polarized emission compared to conventional photonic crystal laser devices [243, 258]. These studies also provide unambiguous evidence for the achievement of a surface-emitting laser.

4.3 Conclusions

A new generation of surface-emitting laser diodes using bottom-up InGaN nanocrystals has been demonstrated. The presence of a clear threshold, sharp linewidth reduction, distinct far-field emission pattern, and polarized light emission provides unambiguous evidence for the achievement of coherent lasing oscillation. Significantly, compared to the conventional GaN VCSELs, lasing and surface emission are achieved without using thick, resistive, and often heavily dislocated DBRs. This unique laser concept can be readily extended to achieve all-epitaxial, DBRfree surface-emitting laser diodes operating across the entire visible, as well as mid and deep UV wavelengths, and to realize such lasers on low-cost, large-area Si wafers. Our studies therefore open a new paradigm in the design and development of surface-emitting laser diodes, wherein the performance is no longer limited by the availability of DBRs, lattice mismatch, and substrate availability.

Chapter 5

Efficient and Controllable Syngas Generation from Photoelectrochemical CO₂ Reduction using Dual Cocatalysts

Photoelectrochemical conversion of aqueous CO₂ into syngas (a mixture of CO and H₂) provides a promising route to mitigate greenhouse gas emissions and store intermittent solar energy into value-added chemicals. Design of photoelectrode with high energy conversion efficiency and controllable syngas composition is of central importance but remains challenging. Herein, we report a decoupling strategy using dual cocatalysts to tackle the challenge based on joint computational and experimental investigations. Theoretical calculations indicate the optimization of syngas generation using a combination of fundamentally distinctive catalytic sites. Experimentally, by integrating spatially separated dual cocatalysts of a CO-generating catalyst and a H₂-generating catalyst with GaN nanowires on planar Si photoelectrode, we report a record high half-cell solar-to-syngas efficiency of 1.88% and a high turnover number of 58,800 under one-sun illumination. Moreover, by simply varying the composition of dual cocatalysts, the CO/H₂ ratio in the syngas mixture can be controllably tuned in a wide range between 1:99 and 10:1 with a total unity Faradaic efficiency. This work provides a modular approach to design efficient and adjustable photoelectrochemical syngas generation to meet various downstream thermocatalytic processes.

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5.1 Introduction

Photoelectrochemical (PEC) CO₂ reduction represents a promising route to store intermittent solar energy into clean and sustainable chemical fuels, while simultaneously reduce atmospheric carbon emissions at ambient conditions [259-262]. In aqueous solutions, CO₂ reduction reaction (CO₂RR) is difficult to compete with hydrogen evolution reaction (HER), which is kinetically more feasible due to a two-electron transfer process and the high proton concentration in aqueous environment [263-265]. In this context, the generation of syngas (a mixture of CO and H₂) from a combination of CO₂RR and HER renders the opprotunity to utilize side product H₂ and leverages well-established industrial processes (e.g., Fischer-Tropsch technology) for synthesizing long hydrocarbons and liquid fuels [266].

In practical applications to upgrade syngas into downstream products, the ratio of CO/H_2 plays a key role in tuning the product selectivity (e.g., 1:1, 1:2 and 1:3 for hydroformylation, methanol synthesis and methanation reaction, respectively) [104, 267-270]. In industrial technology, the CO/H₂ ratio was adjusted by use of the (reverse) water-gas shift reaction, which is an energyintensive and costly process. Therefore, it is desirable to develop efficient PEC syngas generation system that can deliver controllable CO/H_2 ratio. To date, a variety of photocathodes, such as p-Si [107, 118, 271-273], ZnTe [108, 274], and Cu₂O [125, 275], usually in conjunction with a CO₂RR cocatalyst (e.g., Au, Ag and molecular metal-complex), have been developed for PEC CO₂ reduction into CO/syngas. However, it remains challenging to develop efficient syngas production with widely controllable CO/H₂ ratio, as a single catalyst with a monofunctional site usually cannot provide balanced and simultaneously optimized CO₂RR and HER activity. Herein, we report a decoupling strategy using spatially separated dual cocatalysts to tackle the challenge, on the basis of theoretical calculation and experimental verification. By rationally assembling a Au COgenerating site and a Pt H_2 -generating site at the tip and side of GaN nanowires respectively, a record high solar-to-syngas (STS) efficiency of 1.88% and a benchmark turnover number (TON) of 58800 were achieved on planar Si photoelectrode. In addition, the CO/H₂ ratio in the syngas product can be controllably tuned in a wide range between 1:99 and 10:1 by simply varying the composition of dual cocatalysts.

5.2 Results and Discussions

DFT studies were conducted first to gain insight into the design of high-performing catalyst for syngas generation from CO₂ reduction on an atomic level. CO₂RR to CO proceeds via reaction intermediates of *COOH and *CO that bind metal surfaces through a carbon atom (Figures 5.1 (a)), whereas HER takes place via H* intermediate (Figure 5.1 (b)). The binding energies of key reaction intermediates, *COOH and *CO in the CO₂RR to CO, and *H in HER are reaction descriptors to determine the corresponding catalytic activity [276, 277]. In addition, two *CO protonation steps to form *COH and *CHO were also considered as they are possible potentialdetermining steps that compete with CO desorption step [278]. The volcano plot can be obtained according to the Sabatier principle, since the optimal catalyst binds the reaction intermediates neither too strongly nor too weakly [279-281]. Figure 5.1 (c) and (d) show the theoretical predicted volcano plots of CO₂RR and HER activity versus the binding energy of *CO for eight facecentered cubic (fcc) transition metals, including H₂-generating ones (Pt, Ir, Rh, Ni, Pd), COgenerating ones (Au, Ag) and hydrocarbon-generating one (Cu) [282]. The uniformity of fcc crystal structure allows us to perform a better comparison of catalytic activity among various metals. In addition, we consider both (111) and (211) facets to represent terrace and step sites, respectively. The detailed fitting data of scaling relations are available in Appendix-C. The free energy corrections for adsorbed and non-adsorbed species are listed on Table C1 in Appendix-C.

Among the fcc metals screened, it is found that Au and Ag locate on the right of *CO/CO equilibrium line (black vertical dashed line), indicating facile CO desorption due to the weak binding energy of *CO. In contrast, Ir, Pt, Rh, Pd, Ni and Cu favor further reduction of *CO to other downstream products due to a stronger binding with *CO. In addition, compared to Ag, Au is predicted to be more active for the CO evolution from CO₂RR owing to a smaller energy barrier for CO₂ hydrogenation to *COOH. As for HER, Pt (*111*) locates very near the top of the volcano plot with optimal binding of the potential-determining *H intermediate ($|\Delta G_{*H}| = 0.02 \text{ eV}$), suggesting the best-performing catalyst for HER, whereas Au displays a low activity as its binding with *H is too weak. The above findings demonstrate that it is challenging to develop efficient PEC syngas generation with optimal activity for both CO and H₂ evolution using a single monofunctional site, suggesting the necessity to decouple the two reactions using dual cocatalysts.



Figure 5.1: Density functional theory calculations. Schematic of reaction paths for (a) CO_2RR to CO and (b) HER. Theoretical predicted volcano plots of (c) CO_2RR and (d) HER activity versus the binding energy of *CO on (*111*) and (*211*) facets of different fcc metals. The black vertical dashed line shows the equilibrium potential of *CO/CO. Red and blue solid lines show the potential-limiting steps for CO₂RR and HER as the *CO binding energy varies on the (*111*) and (*211*) facets, respectively, whereas dashed lines show associated elementary steps for CO₂RR and HER.

Experimentally, we integrated spatially separated dual cocatalysts of a Au CO-generating site and a Pt H₂-generating site with a material platform of GaN nanowire arrays on n^+-p Si (abbreviated as AuPt_x/GaN/ n^+-p Si, where x denotes the Pt/Au molar ratio). The schematic design and energy band diagram of AuPt_x/GaN/ n^+-p Si are illustrated in Figure 5.2 (a) and (b). The GaN/ n^+-p Si platform takes advantage of the strong light-harvesting of Si (bandgap of 1.1 eV) and efficient electron extraction effect as well as large surface area provided by GaN nanowires [148, 283]. The nanowires allow high mass loadings of electrocatalyst and enhance the light absorption with decreased light reflection [284]. Significantly, the optical absorption and electrochemical reaction are decoupled spatially and functionally in the multi-dimensional structure, providing a unique platform to tune the product distribution by simply varying the cocatalyst composition. Under light illumination, the narrow-bandgap of n^+-p Si junction is readily photoexcited by the major portion of solar spectrum to generate electron-hole pairs for the reactions. The light absorption of GaN nanowires is negligible due to its large bandgap of 3.4 eV. Because the conduction band edges of GaN and Si are closely aligned and both Si and GaN are heavily *n*-type doped, which facilitate the electron migration from Si to GaN [148].

The sample was synthesized in two main steps. First, GaN nanowire arrays were grown on n^+ p Si wafer by molecular beam epitaxy. Next, Au nanoparticles were decorated at the tip of GaN nanowires using e-beam evaporation followed with thermal annealing, and Pt nanoparticles were anchored on the side of GaN nanowires by photodeposition using H₂PtCl₆ as Pt precursor (see Appendix C, text C2 for synthesis and details). The spatial separation of dual cocatalysts, i.e., Au on the polar surface (top surface) and Pt on the nonpolar surface (side surface) of GaN nanowires, could controllably align the CO evolution rate and H₂ evolution rate in a balanced manner to achieve tunable syngas composition.

The morphology and chemical component of AuPt_{0.2}/GaN/ n^+ -p Si sample were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX) mapping, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The cross-sectional SEM image (Figure 5.2 (c)) indicates an average length of 350 nm and a diameter of 40 nm for the GaN nanowires, and a size ranging from 20 to 40 nm for Au tips. TEM image (Figure 5.2 (d)) indicates the Au-tipped structure and 1–2 nm Pt nanoparticles on the side surface of GaN nanowire. High-resolution (HR) TEM images in Figure 5.2 (e) and (f) show the (111) facets of Au and Pt, and (002) lattice plane of GaN, indicating the nanowire growth along the caxis direction. XRD results confirmed the (111) plain of Au and (002) plane of GaN (presents in Appendix C). The absence of XRD peaks of Pt nanoparticles is likely due to its low content and small crystalline size of 1-2 nm. The scanning transmission electron microscopy EDX (STEM-EDX) elemental mapping of a single nanowire (Figure 5.2 (g)) confirmed the Au-tipped structure and Pt distributed uniformly on the lateral surface of nanowire. The XPS analysis in Figure 5.2 (h) and (i) indicates metallic Au (Au⁰) and Pt (Pt⁰). ICP-AES analysis reveals the loading amounts of Au and Pt in AuPt_{0.2}/GaN/ n^+ -p Si were 8.5 and 1.7 nmol cm⁻² respectively with Au/Pt molar ratio of 5. By varying the introduced amount of Pt precursor, $AuPt_x/GaN/n^+$ -p Si samples with different cocatalyst ratios (AuPt_{0.1}, AuPt_{0.2}, AuPt_{0.4}) were prepared, with the loading amounts determined

by ICP-AES analysis (Table C2 in Appendix-C). The TEM images of $AuPt_x/GaN/n^+-p$ Si with different cocatalyst compositions are shown in Appendix-C, Figure C4, showing Au located at the tip and the well dispersion of Pt nanoparticles across the nanowire.



Figure 5.2: Schematic illustration and sample characterization. (a) Schematic and (b) energy band

diagram of AuPt_x/GaN/ n^+ -p Si photocathode (not drawn to scale), showing the generation of syngas under sunlight illumination. (c) 45°-tilted SEM, (d) TEM, (e) and (f) HRTEM images of AuPt_{0.2}/GaN/ n^+ -p Si sample. The HRTEM images of (e) and (f) are obtained from the blue and yellow boxed areas in (d), respectively. (g) STEM-EDX elemental mapping images. XPS of (h) Au-4f and (i) Pt-4f.

PEC studies of AuPt_x/GaN/ n^+ -p Si photocathodes were investigated in CO₂-saturated 0.5 M KHCO₃ solution (pH 7.5) under air mass 1.5 global (AM 1.5G) standard one-sun illumination (100 mW cm⁻²) in a three-electrode configuration (Figure 5.3 (a)). Figure 5.3 (b) shows the Faradaic efficiencies (FEs) for CO and H₂ on AuPt_x/GaN/ n^+ -p Si photocathodes with different cocatalyst compositions at an applied potential of +0.17 V vs reversible hydrogen electrode (RHE). Hereafter, all the PEC potentials are reported with respect to the RHE unless otherwise specified. The corresponding chronoamperometry data are shown in Figure C6 (a) in Appendix-C. Dominant CO evolution and H₂ evolution were detected on Au/GaN/ n^+ -p Si and Pt/GaN/ n^+ -p Si, respectively. With the increase of x from 0.1 to 0.4 in AuPt_x/GaN/ n^+ -p Si, a linearly increased FE for H₂ evolution with concurrently decreased FE for CO evolution was observed. By systematically tuning the cocatalyst composition, the ratio of CO/H₂ could be tailored in a wide range from 1:99 to 10:1. In particular, AuPt_{0.2}/GaN/ n^+ -p Si produced syngas with a CO/H₂ ratio of 1:2, which is a desirable composition for methanol and hydrocarbon fuels synthesis [266]. As for all the samples, a unity FE was obtained for the cogeneration of CO and H₂, with no other products detected.

Figure 5.3 (c) shows the current-potential (*J*-*V*) curves of different photocathodes. Compared to the negligible photocurrent density of bare GaN/n^+-p Si, Au/ GaN/n^+-p Si displays a photocurrent density of 21 mA cm⁻² at -0.2 V with an onset potential of ~0.4 V. With the incorporation of Pt, the onset potential shifts gradually to ~0.5 V, and the photocurrent increases due to high activity of Pt for HER. The partial current densities of CO and H₂ at +0.17 V are shown in Figure 5.3 (d). With the increase of Pt content, the partial current density for H₂ increases, while CO was kept nearly unchanged with the increase of Pt/Au ratio up to 0.2, indicating the access of balanced and simultaneously high CO₂RR and HER activity in AuPt_{0.2}/GaN/ n^+-p Si sample.



Figure 5.3: Tunable syngas generation. (a) Schematic illustration of three-electrode PEC cell for syngas generation. WE: working electrode, RE: reference electrode, and CE: counter electrode. (b) FEs for CO (purple bars) and H₂ (red bars), and CO/H₂ ratio of AuPt_x/GaN/ n^+ -p Si photocathodes at +0.17 V vs RHE. (c) *J*-*V* curves. (d) Partial current density for CO (purple bars) and H₂ (red bars) of AuPt_x/GaN/ n^+ -p Si photocathodes at +0.17 V vs RHE. Experimental conditions: CO₂-saturated 0.5 M KHCO₃ aqueous solution (pH 7.5), AM 1.5G one-sun illumination (100 mW cm⁻²).

It is worth noting that the spatial separation of CO evolution and H₂ evolution sites is critical to controllably tune syngas composition with a wide ratio of CO/H₂. A control experiment using Pt(NH₃)₄Cl₂ as Pt precursor obtain sample with Pt nanoparticles located on the polar surface of GaN nanowire in close proximity to Au (Figure C5 (a) in Appendix-C). In contrast to the spatially separated dual cocatalysts, the mixture of cocatalysts produces a dominant H₂ evolution with FEs over 90% and low controllability of syngas composition as a function of cocatalyst composition

(Figure C7 (b) in Appendix-C). It is a highly competitive process between adjacent Pt and Au for electron transfer, which favors the HER on Pt due to its kinectically feasibility. The different photodeposition behaviors using different Pt precursors are ascribed to the stronger adsorption of $PtCl_6^{2-}$ anions on GaN surface than $Pt(NH_3)_4^{2+}$ cations (Figure C7 (a) in Appendix-C). Pt nanoparticles were preferentially deposited on the sidewall of GaN nanowires using H₂PtCl₆ as Pt precursor due to a sorption-detemined deposition mechanism [285]. In contrast, Pt were photodeposited on the tip of nanowire in close proximity with Au where electrons reside when using Pt(NH₃)₄Cl₂ as Pt precursor due to negligible adsorption of Pt(NH₃)₄²⁺ cations on nanowire [286, 287].



Figure 5.4: Photoelectrochemical performance. (a) FEs for CO (purple bars) and H₂ (red bars), and solar-to-syngas efficiency of AuPt_{0.2}/GaN/ n^+ -p Si as a function of applied potential. (b) Performance comparison of AuPt_{0.2}/GaN/ n^+ -p Si with state-of-the-art photocathodes for PEC CO₂ reduction into CO/syngas. (c) Chronoamperometry data and FEs for CO and H₂ of AuPt_{0.2}/GaN/ n^+

 n^+ -p Si photocathode at +0.17 V vs RHE. The dashed lines indicate cleaning of photoelectrode with DI water and purging of PEC chamber with CO₂. (d) *J*-*V* curves. Experimental conditions: CO₂-saturated 0.5 M KHCO₃ aqueous solution (pH 7.5), AM 1.5G one-sun illumination (100 mW cm⁻²).

Figure 5.4 (a) shows the FEs for CO and H₂ on AuPt_{0.2}/GaN/ n^+ -p Si at an applied potential between +0.37 V and +0.07 V. The CO/H₂ ratio was kept at nearly 1:2 in the PEC potential range investigated. The STS efficiencies at different applied potentials were calculated according to the measured photocurrent density and FEs for CO and H₂ (Equation C(7) in Appendix-C). The STS efficiency reached a maximum of 1.88% at +0.17 V, which is more than two times higher than that of state-of-the-art photocathodes (Figure 5.4 (b), and the details including the reference sources can be found in Appendix-C, Table C3).

The durability of AuPt_{0.2}/GaN/ n^+ -p Si photocathode was also investigated, as shown in Figure 5.4 (c). Both the photocurrent density and product selectivity remain unchanged for a period of 10h. In addition, the SEM, TEM, and XPS analysis of AuPt_{0.2}/GaN/ n^+ -p Si sample after the PEC reaction show no change of GaN nanowires and Au-Pt cocatalysts (see in Appendix-C). The total TON, defined as the ratio of the total amount of syngas evolved (120 µmol) to the amount of Au-Pt catalyst (2.04 nmol, calculated from the catalyst loadings and electrode sample area of 0.2 cm²), reached ~58,800, which is the highest reported value to date for PEC CO/syngas production from CO₂RR to our knowledge [118, 288, 289]. The mass activity of syngas production for AuPt_{0.2}/GaN/ n^+ -p Si photocathode at +0.17 V was calculated ~4.7 A/mg, which is one or two orders of magnitude higher than conventional planar Au-based CO/syngas generation system [273, 290, 291]. The large surface-to-volume ratio of GaN nanowire allows high-density catalytic sites with a significantly reduced loading amount compared to the planar structure.

To understand the role of GaN nanowires, control experiments using $AuPt_{0.2}/n^+-p$ Si planar sample in the absence of GaN nanowires were performed. *J*-*V* curve of $AuPt_{0.2}/n^+-p$ Si planar sample displays a low photocurrent density (0.5 mA cm⁻² at +0.17 V) and a poor onset potential of 0.25 V (Figure 5.4 (d)). Meanwhile, the FE for CO of $AuPt_{0.2}/n^+-p$ Si is 9% at +0.17 V, which is much lower than that of 32% for $AuPt_{0.2}/GaN/n^+-p$ Si (Appendix-C, Figure C9). These results indicate the critical role of GaN nanowires as a superior structural scaffold to enhance the PEC performance and product selectivity. To demonstrate that the generated CO from CO₂ reduction, isotopic experiment using ¹³CO₂ was conducted. The signal at m/z = 29 assigned to ¹³CO appeared in the gas chromatography-mass spectrometry analysis and no signal of ¹²CO was detected (Appendix-C, Figure C10). In addition, blank test performed in Ar-purged Na₂SO₄ aqueous solution showed no formation of CO, confirming the CO product is originated from the reduction of CO₂.

5.3 Conclusions

In summary, we have demonstrated the decoupling of CO₂RR and HER using dual cocatalysts to overcome the efficiency bottleneck and composition uncontrollability of PEC syngas generation from aqueous CO₂. By spatially assembling a Au CO-generating cocatalyst and a Pt H₂-generating cocatalyst on the polar and nonpolar surfaces of GaN nanowires, respectively, a record half-cell STS efficiency of 1.88% and a benchmarking TON of 58,800 are achieved on Si photoelectrode. In addition, the CO/H₂ ratio in the syngas mixture can be controllably tuned in a wide range between 1:99 to 10:1 with a total unity Faradaic efficiency, by simply varying the composition of dual cocatalysts. This work provides a promising route for the rational design of high-performance PEC syngas generation with controllable composition from aqueous CO₂ reduction.

Chapter 6

Photocatalytic CO₂ Reduction to Syngas by III-Nitride Nanostructures

To date, there have been no efficient and stable catalysts for photocatalytic CO₂ reduction to mimic the natural photosynthesis solely using CO₂ and H₂O as the feedstocks. Syngas has been widely used in industry to produce other chemicals and fuels. Therefore, the ability to generate syngas directly from sunlight, CO₂ and H₂O will significantly impact the future chemical industry. Here we report the demonstration of relatively efficient photochemical reduction of carbon dioxide into syngas using wafer scale multiband InGaN/GaN nanowire structures. This work establishes the potential use of III-nitride nanowire arrays as a highly efficient photocatalyst and the engineered core/shell co-catalysts in improving the selectivity towards tunable syngas production.

^{*} This chapter is based on a manuscript under preparation: R.T. Rashid et. al. (except for primary authors: R.T. Rashid, and Z. Mi, other co-authors and their orders are to be determined).

6.1 Introduction

In the exigency of mitigating the global crisis instigated by greenhouse CO₂ emission, harvesting the intermittence renewable energy by recycling CO₂ reduction with lower carbon contents than fossil fuels and non-sustainable sources, can be a winning way to cope with global warming and energy demand. Photocatalytic CO₂ reduction into syngas is one of the promising sustainable routes of artificial photosynthesis for direct conversion of solar energy into chemical fuel and onwards the carbon-neutral energy. Photocatalytic CO₂ reduction into syngas is one of the promising sustainable routes of artificial photosynthesis for direct conversion of solar energy into chemical fuel and onwards the carbon-neutral energy. Photocatalytic CO₂ reduction into syngas is one of the promising sustainable routes of artificial photosynthesis for direct conversion of solar energy into chemical fuel. Syngas (synthesis gases), the combination of CO and H₂, is the critical *C1* feedstock to produce methanol and various synthetic liquid fuels by tuning the CO/H₂ ratios (1:2 and 1:1 for methanol and dimethyl ether, respectively) [104, 272]. In addition, photochemical (PC) synthesis is the wireless version of photoelectrochemical CO₂ reduction, where no external bias and circuitry is required, which makes the system simple, accessible and cost effective [9].

PC CO₂ reduction has been more uncontrollable than solar hydrogen generation [9, 292]. The state-of-the-art advances in materials and reactors for PC CO₂ has been lagged far behind those in solar water splitting because of the complicated multielectron reduction kinetics, low reduction efficiency, photostability and selectivity of photocatalysts [293-296]. So far, PC CO₂ reduction has often been performed with the presence of sacrificial reagents [129-130]. However, the desired platform of artificial photosynthesis, the solely operation under the presence of CO₂ and H₂O only, with efficient and stable photocatalytic CO₂ reduction has not been demonstrated yet.

Indium gallium nitride is the only material among all the known photocatalysts whose energy bandgap can be tuned across nearly the entire solar spectrum and can straddle water and CO_2 to CO redox potentials [145]. In this work, we present a detailed study of PC CO_2 reduction into syngas with the desirable H₂ and CO ratio of 1:2 to 1:4 by introducing engineered InGaN:GaN nanowires and controlled Au/Cr₂O₃ core/shell co-catalyst.

6.2 Results and Discussions

The vertically aligned InGaN/GaN NWs were grown on Si substrate by radio frequency plasma-assisted Molecular Beam Epitaxy under nitrogen-rich conditions. To enhance the light

absorption and efficient harness of solar photons, multi-stacked GaN:Mg/InGaN:Mg NW photocatalyst has been introduced along the GaN NW growth direction. The InGaN/GaN NWs grown in this present work are based on extensive studies on the growth and characterization of Mg doped InGaN nanostructures, which includes careful optimizations of the III/V flux ratio, doping concentration, growth temperature, and growth duration for maintaining high photocatalytic activity [145]. InGaN nanowire arrays were grown on top of a GaN nanowire template for controlled formation of InGaN nanowires to achieve superior structural and optical properties. As shown in the schematic of Figure 6.1 (a), several segments of InGaN ternary nanowires, capped with a thin GaN layer were incorporated to minimize the formation of misfit dislocations [135, 297]. A forward plasma power of ~ 350 W with the nitrogen flow rate of 1.2 standard cubic centimeters per minute (sccm) was used during the full structure growth. The beam equivalent pressure of Ga, and In are in the range of ~3.9 × 10⁻⁸ Torr, and ~6.25 × 10⁻⁸ Torr, respectively. The Mg effusion cell temperature was varied from 290°C to 320°C.

The nanowire arrays are vertically aligned along the growth direction (*c*-axis) grown directly on Si (111) substrate with an average length of 600–750 nm and a diameter of 70–90 nm, as shown in the cross-sectional scanning electron microscopy image (Figure 6.1(b)). The nanowires are spontaneously grown on the substrate with high uniformity, which is shown in the Figure D1 in Appendix D. The photoluminescence spectrum measured at room-temperature is shown in Figure 6.1 (c), with a single band-to-band optical emission peak at ~507 nm, corresponding to a bandgap of 2.45 eV.

Structural properties of the InGaN/GaN nanowires were further analyzed by scanning transmission electron microscopy and energy dispersive X-ray spectrometry spectrum imaging (EDXS-SI), which were acquired using FEI Tecnai G2 F20 microscope operated at 200 keV. Figure 6.2 (a) shows a high-angle annular dark field image of InGaN nanowire, illustrating the atomic number contrast between GaN (darker) and InGaN (brighter) regions. The nanowires are tapered, with the diameter increasing from the bottom to top. As can be seen, the nanowires consist of four segments of InGaN (each ~70–80 nm long). The elemental distribution in the nanowire was analyzed by EDXS. Variations of the In $L\alpha$, Ga $K\alpha$, and N $K\alpha$ signals along the nanowire axial direction (white line in Figure 6.1 (d)) are plotted in Figure 6.2 (d), clearly showing the InGaN /GaN multi-stacked nanowire structure. It can also be noted that the GaN outer shell is very thin

and is likely to be less than ~10–15 nm. The formation of InGaN/GaN nanostructure is attributed to the enhanced surface desorption of In at the growth temperature and the difference in formation enthalpies between InN and GaN [298]. At the growth temperature (~750°C), the surface desorption of In atoms is significant, compared to Ga atoms. Due to the shadowing effect of the surrounding nanowires, impinged In flux may not readily arrive at the lateral surfaces of the nanowires to compensate for the desorbed In atoms during the MBE growth process. The tapered nanowire morphology, on the other hand, is directly related to the enhanced lateral growth, due to the reduced substrate temperature and enhanced indium incorporation.



Figure 6.1: (a) Schematic of Mg-doped InGaN/GaN (active/capping layer) nanowire structures grown on GaN nanowire template. (b) A 45⁰ tilted SEM image of InGaN/GaN nanowires grown on Si (*111*) substrate. (c) Room temperature photoluminescence spectrum of as grown nanowires. (d) High-angle annular dark field image (HAADF) showing InGaN/GaN multi-stacked nanowire.

(e) Energy dispersive X-Ray (EDX) line scan showing the distribution of In, Ga and N along the blue line in (d).

To facilitate syngas generation, Au/Cr₂O₃ core/shell co-catalyst was deposited on nanowire surfaces in sequential order using e-beam evaporation and photodeposition process, respectively. The details of the co-catalyst deposition are shown in Appendix D. Transmission electron microscopy image (Figure 6.2 (c)) confirmed the core-shell structure with Au particle diameter of 5–10 nm and Cr₂O₃ shell thickness of 2–3 nm. High-resolution (HR)TEM image in the inset of Figure 6.2 (c) shows the (*111*) facet of Au and amorphous structure of Cr₂O₃ shell. The scanning transmission electron microscopy EDX elemental mapping of a single nanowire (Figure 6.2 (b)) confirmed the Au and Cr₂O₃ distributed uniformly across the nanowire. Also, the relative line scan elemental plot and EDAX curve have been presented in Appendix D. The XPS of the co-catalyst has been investigated, which is presented in Figures 6.2 (d) and (e) as the Au-4*f* Cr-2*p* of Au/Cr₂O₃/NW sample, accordingly. The Au-4*f*_{7/2} binding energy at 88.0 eV are assigned to metallic Au (Au⁰). Cr-2*p*_{3/2} binding energy at 576.9 eV and Cr-2*p*_{1/2} binding energy at 586.6 eV corresponds to Cr^{III} state from Cr₂O₃.



Figure 6.2: (a) High-angle annular dark field (HAADF) image of Au/Cr₂O₃ decorated InGaN/GaN nanowire sample. (b) STEM-EDX elemental mapping images of the element of Ga, In, N, Au, Cr

with overall mapping. (c) TEM image of Au/Cr₂O₃/NW sample. The inset is HRTEM image of Au/Cr₂O₃ core/shell structure on nanowire surface. XPS of (d) Au-4*f* and (e) Cr-2*p* of Au/Cr₂O₃/InGaN sample.

The Au/Cr₂O₃ core/shell co-catalyst decorated InGaN nanowire photocatalyst was used for photochemical CO₂ conversion into syngas and O₂ in the absence of any sacrificial reagents in a gas-phase reactor under concentrated sunlight irradiation. With gas-phase approach, the issue of low solubility of CO₂ in water is addressed. Oxidation of H₂O takes place on NW surface, whereas reduction of CO₂ occurs on co-catalyst. By effective adsorption and hydrogenation of CO₂ molecules on Au/Cr₂O₃, a significant syngas generation rate of 1.03 mol/h/g_{cat} (0.39 and 0.64 mol/h/g_{cat} for CO and H₂, respectively) was yielded with the best experimental conditions, as shown in Figure 6.3 (c). No other gaseous products except a trace amount of CH₄ was detected. The CO/H₂ ratio in the syngas product was generated at nearly 1:2 ratio, which is a desirable syngas composition for producing methanol and hydrocarbon fuels. Compared to bare InGaN nanowire, the modification of Au/Cr₂O₃ cocatalyst enhances the CO and H₂ evolution rate by factors of 80 and 15, respectively.

By adjusting the various ratios of the co-catalysts, the performance has been improved accordingly. In these photochemical experiments, H^+ was formed via the oxidation of water molecules, where OH^- species can be formed on the surface of InGaN/GaN [9, 145]. Water oxidation occurred on the nanowire surfaces. InGaN/GaN has been previously reported to have excellent water oxidation and reduction activity. In this context, the oxidation of water occurs on the NW surface while the reduction of protons occurs on the metal cocatalyst. The H⁺ formation on the surface plays an important role in these reactions, providing the feedstock for the formation of syngas. Therefore, the overall mechanism for CO₂ photoreduction to syngas is the result of a sequential combination of H₂O oxidation and CO₂ reduction. For these reactions to occur photocatalytically, the valence band (VB) energy position of the photocatalyst must be greater than the electrochemical potential of the H₂O oxidation. Furthermore, the conduction band (CB) position of the photocatalyst should be lower than the electrochemical potential for a CO₂ reduction into CO. Related mechanism is schematically illustrated in Figure 6.3(a). The experimental results of gas evolution with initial calibration studies are presented in Figure 6.3(b). More detailed understanding of the reaction mechanism will be studied in the future.



Figure 6.3: (a) Schematic illustration of the overall CO₂ reduction reaction on a nanowire. (b) The output gas evolution for calibration studies performed on nanowires with various co-catalyst deposition. (c) The evolution rate of H₂ and CO over similar nanowire samples with or without Au/Cr₂O₃. The inset shows a typical nanowire sample used for these experiments. Variations of the co-catalyst deposition leads to changes in the H₂ and CO ratio. (d) Time courses of H₂ and CO evolution over Au/Cr₂O₃/InGaN sample. The dashed lines indicate the evacuation of photoreactor and restart of the test.

The durability of Au/Cr₂O₃/NW photocatalyst was also investigated. There is no appreciable degradation after 4 consecutive runs (Figure 6.3 (d)), indicating the high photostability of the photocatalyst. The isotopic experiment using ¹³CO₂ has also been performed to demonstrate the output CO evolution is from the CO₂ reduction. The signal at m/z = 29 assigned to ¹³CO appeared

in the gas chromatography-mass spectrometry analysis. In order to confirm the photocatalytic CO_2 reduction activity under visible light illumination, a 420 nm long pass filter was placed in front of the Xe lamp. Repeated cycles for the output gas evolution of H₂ and CO from the Au/Cr₂O₃ decorated *p*-type GaN/InGaN nanowire heterostructures has been observed.

6.3 Conclusions

In conclusion, we have demonstrated one-step photocatalytic CO_2 reduction, which can open new opportunities for the sustainable production of syngas with minimum environmental impact. Combining our engineered InGaN/GaN nanowire structures with core-shell Au/Cr₂O₃ co-catalyst, we have achieved relatively efficient solar-to-syngas conversion directly from CO_2 . The presented work offers a new approach for addressing future increased energy demand while helping combat environmental challenges associated with greenhouse gas emissions.

Chapter 7

Conclusions and Future Work

7.1 Summary of the work

This thesis presents a detailed study of MBE grown III-nitride nanocrystals and their application in green photonics. The unique III-nitride nanowire properties offer distinct advantages for energy efficient light emitters and solar fuel production. The presented work in this thesis has been focused on the design, MBE growth, and structural, optical and electrical characterization of InGaN/GaN nanowires and their device applications.

Chapter 1 presented an overview on the current global energy challenge and the impact of green photonics, followed by the promises, challenges and prospects for the development of novel InGaN/GaN nanocrystals for LEDs/lasers and artificial photosynthesis devices/systems. The basics of InGaN based light emitters and artificial photosynthesis systems PEC and PC systems were presented as well. Chapter 2 described the experimental and characterization techniques used in this thesis work which includes MBE growth, device fabrication, PEC-PC experimental details, cocatalyst deposition technique, and structural/optical/electrical characterization of InGaN/GaN nanowire arrays.

The potential of InGaN nanocrystals for future green optoelectronics has been explored in Chapters 3 and 4. Precisely controlled InGaN nanowire has been epitaxially grown by using the special technique of selective area epitaxy. This unique single step epitaxy of InGaN photonic crystals delivers controllable stable emission characteristic in the green region. We have further demonstrated, for the first time, an all epitaxial surface-emitting green laser diode. Our laser diode operates at room temperature with a low threshold current density ~400 A/cm² at 523.1nm.

Chapters 5 and 6 discussed on the solar fuel devices, including syngas generation over InGaN/GaN nanowires in PEC and PC cells. We have established a new syngas benchmark halfcell solar-to-syngas efficiency of 1.88% by integrating GaN nanowire arrays with Au/Pt cocatalyst in a PEC cell. Along with the variable dual cocatalysts combination, our simple experiment route has been fine-tuned in a wide range of 1:99 to 10:1 with a near unity Faradaic efficiency. In addition, we have demonstrated, for the first time, one-step photochemical conversion of CO_2 to syngas using wafer scale multiband InGaN/GaN nanowire structures.

7.2 Future work

With careful engineered nanostructures, improved fabrication techniques and exploration of different earth abundant co-catalysts, III-nitride nanocrystal based green photonic devices can exhibit further improved performance and enhanced efficiency. We are currently working on some of the promising strategies that can lead to a viable approach for full color nanowire pixel and further improve the efficiency and stability of artificial photosynthesis. In what follows, we describe some of the proposed future work.

7.2.1 Micro LEDs

Micro-light emitting diode (μ LED) has emerged as next generation display technologies where each individual red, green and blue subpixel can be independently tuned and controlled. This display gadget is still in its early stage [298-300]. The acquirement of high-performance emission for green and red has remained challenging for III-nitrides. With the use of nanowire photonic crystal structures, it is possible to develop large area micro-display consisting with nanowire LED pixels. Based on the nano-patterned substrates described in Chapters 3 and 4, we will develop the epitaxial growth of multi-color InGaN/GaN dot-in-nanowire LED arrays on the same substrate. In this approach, the position and diameter of nanowires will be precisely controlled, and the emission characteristics can be engineered by the nanowire diameter. A fundamental advantage of this approach is that multi-color emission can be achieved on the same wafer through a single epitaxial growth process, since the emission wavelengths can be controlled by varying nanowire diameters through the patterning process. Schematic illustration for the formation of the multi-color nanowire LED arrays and light emitters in the single epitaxial growth step is shown in Figures 7.1 (a) and (b).



Figure 7.1: Simplified illustration of proposed multicolor micro LED: (a) By varying the nanowire position, arrays and sizes, the various nanowire photonic crystal structures can be readily controlled on same substrate. (b) Schematic illustration of the epitaxy of full-color InGaN nanowire arrays and photonic crystal surface-emitting lasers monolithically integrated on a single chip.

During the initial study, yellow LED pixels of 4 μ m × 4 μ m size are successfully formed as schematically shown in Figure 7.2. In order to get higher definition display of the nanowire micro-LED pixels, we did some initial investigation on InGaN/GaN nanowire LED pixel arrays with pitch sizes of 20 μ m and 40 μ m, respectively. The size of the nanowire LED pixels for all samples is 4 μ m × 4 μ m. Such nanowire LED displays has the potential to exhibit excellent light emission characteristics. Obtaining the red nanowire micro devices in the same epitaxial growth is one of the future goals to realize full color display.



Figure 7.2: Schematic illustration of nanowire LED pixel arrays, inset the top-view electroluminescence (EL) images of nanowire micro-LED display. Each pixel has a size of 4 µm

 \times 4 µm. The pitch sizes vary from 20 µm to 40 µm (from top to bottom).

7.2.2 High efficiency syngas generation

For the selective CO₂ reduction into valuable carbon-based chemicals and fuels, we need to rationally develop high-performance syngas generation systems. Study on advanced engineered InGaN/GaN nanostructures for the development of various effective co-catalyst on the same InGaN/GaN structures were described in Chapters 5 and 6.



Figure 7.3: Streamlined strategies for highly efficient syngas generation.

7.2.2.1 Band engineering of nanowires

To get an efficient syngas system, careful engineering of the InGaN:GaN nanostructures is the most important task with some challenges as well. These nanostructures with large surface area can provide a new avenue to develop the ideal light absorbers, with broad absorption in the solar spectrum, stable excited states and high charge carrier mobility. Multiband InGaN:GaN is a promising platform for artificial photosynthesis. With the tunnel junction interconnect in nanowires, dopant interaction can be significantly enhanced which will improve carrier agility as well and AlGaInN barriers will assist to reduce the electron overflow and to suppress nonradiative surface recombination. Hence tunnel junction and multiple quantum well in the nanostructures presents in the Figures 7.4 (c) and (d) as the future implemented structures. In addition, the bottom absorber (Si p-n junction and substrate) will be incorporated to integrate with the nanowires. Doping concentration and conditions, annealing temperature, introducing tunnel junction by changing doping states, texturing the Si surface are some of the proposed optimizations for future directions.



Figure 7.4: Schematics of (a) multiband nanowire arrays and (b, c, d) different engineered nanowires.

7.2.2.2 Integration with molecular and other catalysts

The development of the proper co-catalysts on InGaN:GaN nanowires can provide multiple sites and unique channels to accelerate the CO_2 activation and reaction pathways for syngas production. One of our future research works is to develop efficient and stable PEC/PC catalytic system that can activate inert CO_2 molecule at low overpotential or even spontaneously, and selectively produce syngas with controlled composition in a wide range to meet different downstream products. Molecular catalyst is one promising way to enhance the performance of artificial photosynthesis systems.



Figure 7.5: Schematic illustration for the development stages of active applicable catalysts. Inset: the table of transition metals, as potential catalyst.

To date, various molecular catalysts have been utilized because of its abundance and low cost. When these catalysts are synthesized on InGaN:GaN nanostructures, they can enhance the number of active sites and improve the intrinsic activity of each active site. The enhancement of activity from increasing the number of active sites can be achieved through increased loading of catalysts or by modifying catalyst structures [281]. These catalysts can also perform as CO₂RCs (CO₂ reduction catalysts), HECs (hydrogen evolution catalysts) and WOCs (water oxidation catalysts).

7.2.3 The effect of CO₂ impurity

Globally CO₂ capture and storage (CCS) technology is an emerging technology to mitigate climate change [301-304]. The CO₂ sources generally contain a range of different types of impurities [304-306]. The CO₂ impurities from different CO₂ capture technologies are listed in various reports [306, 309]. Table 7.1 shows the most possible impurities in the oxy-fuel combinations. The study of CO₂ impurities is one important future work.

Table 7.1. The list of most possible ranges of impurity in oxy-fuel combustion [304, 307]

Gas Composition	Composition (mol %)
CO_2	76
O_2	6 (±3%)
N_2	15 (±7%)
Ar	2.5 (±2%)
SO_2	0.5 (±0-1.5%)

We have done some initial studies to check our sample reliability with various impurities. This feasibility test was done with the Au/GaN/ n^+ -p Si in the tested impurity gases of 0.1% nitric dioxide (NO₂), 1% Sulfur Dioxide (SO₂) and 1% oxygen (O₂) and compare the performance with pure CO₂ gas. The study reveals comparable result with the Faradic efficiency of around 90% at +0.27 V vs RHE. A thorough investigation of high impurity gas mixtures needs to be studied in the future.



Figure 7.6: (a) *J-V* curves of Au/GaN/ n^+ -p Si photocathode and (b) Faradaic Efficiency comparison at different CO₂ impurity gas conditions.

7.2.4 Implementation of artificial photosynthesis system under natural sunlight

Over the past decades solar hydrogen production has been brought to a level closer to commercialization [144, 308, 309]. We have demonstrated a natural sunlight outdoor prototype for H_2 generation by solar water splitting. Figure 7.7 shows the outdoor setup, where InGaN:GaN structures on 3-inch Si wafer were employed.



Figure 7.7: Outdoor experiment set up for solar fuel generation under natural sunlight.

Large-scale implementation of PEC/PC CO2 reduction is hindered by the manufacturing costs

and scalability. Our developed nanostructures using GaN and Si will be an excellent choice as light absorbers. InGaN:GaN can be scaled up on 300 mm Si wafer. The avenue of CO_2 reduction to syngas still needs further investigation and development, including studies on impurity gas conditions, light intensity, temperature, pressure, moisture, etc. Illustrated schematic shown in the figure below presents our vision and prediction for the future sustainable fuel community.



Figure 7.8: A schematic illustration of the future solar fuel process.
Appendix A

A.1 Experimental Section

Ti-Mask-Patterned Substrate

A 10 nm Ti layer was used as the mask layer for selective area growth, which was deposited on GaN $(4 \ \mu m)/Al_2O_3$ (0001) substrate by e-beam evaporator system. Subsequently, a poly(methyl methacrylate) layer was selectively exposed by e-beam lithography. Thereafter, the exposed Ti thin film area was etched using reactive dry-etching technique. The nanohole patterned substrate was cleaned by hydrogen chloride prior to loading into the MBE growth chamber.

Molecular Beam Epitaxial Growth

The bottom-up InGaN/AlGaN nanowire heterostructures were fabricated using radio frequency plasma-assisted MBE. The growth process included a surface nitridation of the Ti mask layer for 10 min at 400°C. The growth conditions for Si-doped GaN nanowires included a growth temperature of 800°C, with a nitrogen flow rate of 0.6 standard cubic centimeter per minute, a forward plasma power of 350 W, and Ga beam equivalent pressure (BEP) of 3.5×10^{-7} Torr. In order to introduce the formation of the AlGaN shell structure in the active region, the InGaN dot with a thickness of ≈ 3 nm is first grown at the center region of GaN nanowire. Due to the strain induced self-organization, the size of the InGaN dot becomes smaller than the GaN nanowire diameter. The incorporation of AlGaN barriers, instead of GaN barriers, leads to the formation of an AlGaN shell surrounding the InGaN quantum dot active region, due to the smaller Al adatom migration length compared to Ga and In adatoms [199, 136]. As a consequence, the entire growth front including the top and sidewalls of the InGaN core region can be covered by AlGaN layer, thereby leading to the spontaneous formation of Al-rich large band-gap shell structures [315]. Growth conditions for the InGaN/AlGaN quantum dot active region included a substrate temperature of $\approx 600^{\circ}$ C, Ga BEP of 9×10^{-9} Torr, in BEP of 7.5×10^{-8} Torr and Al BEP of 4.5×10^{-8} 10⁻⁹ Torr. By repeating this process, vertically aligned InGaN/AlGaN multi quantum dot layers can be formed with highly uniform AlGaN shell structure surrounding the active region. Growth conditions for the Mg-doped GaN layer included a Ga BEP of 3.5×10^{-7} Torr and Mg BEP of $2 \times$ 10^{-9} Torr with substrate temperature of 750°C.

PL Measurement

A 405 nm laser was used as the excitation source for the PL measurement of the InGaN/AlGaN nanowire heterostructures. A visible neutral density filter was used to adjust the laser excitation powers in range of 29 W cm⁻²–17.5 kW cm⁻². The emitted light was spectrally resolved by a high-resolution spectrometer and was detected by a high sensitivity and low noise liquid nitrogen cooled CCD in the visible range. Temperature-dependent PL measurements were carried out using a helium closed-loop cryostat.

CL Measurement

CL measurement was performed using a Zeiss Supra 55 VP field emission gun SEM equipped with a cryogenic stage coupled to a Gatan Mono CL 2 setup. A gold thin film layer was deposited on the substrate in order to suppress charging effect induced by the electron beam. The accelerating voltage used in the CL characterization is 10 keV. The emission was collected by a parabolic mirror and detected using a dry-ice cooled photomultiplier tube.

A.2 Illustration of the uniformity of InGaN photonic crystal molecules across a large area



Figure A1: 45° tilted-view SEM image of the InGaN nanowire photonic crystal molecules arranged in a 25 μ m × 25 μ m area, showing extremely high uniformity across a large area.

A.3 The emission stability of InGaN nanowire photonic crystal structures across a large area

We have investigated the emission characteristics, including the uniformity and yield of InGaN nanowire photonic crystal structures fabricated in a large area. As illustrated in Figure A2 (a), six different points were measured in an areal size of 100 μ m × 100 μ m using a 405 nm laser as the excitation source at room temperature. The emission wavelengths remain nearly invariant at 505 nm with a narrow spectral linewidth of 12 nm for various regions of the nanowire photonic crystal structure, shown in Figure A2 (b). The extremely high yield and uniformity is attributed to the well-controlled nanowire size and position of the unique selective area epitaxy.



Figure A2: (a) Schematic of the InGaN nanowire photonic crystal structure fabricated in an areal size of 100 μ m × 100 μ m and six different positions for the photoluminescence measurement. (b) Variations of the emission peak and spectral linewidth vs. measurement point.

A.4 Cathodoluminescence (CL) mapping measurement spectrally resolved at different emission wavelengths and with different design parameters.



Figure A3: (a) Spectrally resolved CL mapping images collected at various wavelengths of 370, 450, 505 and 520 nm, respectively, showing the presence of band edge mode and strong optical confinement effect only at an emission wavelength of 505 nm. (b) CL mapping image at a wavelength of 505 nm for InGaN nanowire arrays with a relatively large spacing compared to the optimum design shown in (a), showing the absence of the band edge mode. Due to the weaker emission for the image shown in (b), the measurement was performed with a relatively long integration time to clearly show the light distribution.

To further confirm the formation of stable band edge modes in InGaN photonic crystals, we have performed more detailed spectrally resolved CL mapping measurements at different wavelengths. Figure A3 (a) shows the CL mapping images collected at wavelengths of 370, 450, 505 and 520 nm, respectively. The CL image at 370 nm exhibits highly uniform contrast in the entire region. It was also noticed the spacing between nanowires shows brighter emission, which is due to the light emission from the underlying GaN template. No emission was observed at 450 nm wavelength since there is no light emission from the nanowires in this wavelength. At 505 nm, strong optical confinement effect at the center region of nanowire arrays was clearly observed. Significantly weaker emission was also measured at 520 nm. These studies provide unambiguous evidence for the direct measurement of the band edge mode in defect-free nanowire photonic crystals. We have further performed CL wavelength mapping measurement of InGaN nanowire

arrays with a relatively larger spacing compared to the optimum design. The image taken at a wavelength of 505 nm is shown in Figure 3.4 (d), and no optical confinement effect was observed.

A.5 Emission characteristics of InGaN nanowire photonic crystals vs. nanowire height

We have also studied the dependence of the emission characteristics of InGaN nanowire photonic crystals on the height of nanowires. Five InGaN/AlGaN dot-in-nanowire photonic crystals, schematically shown in Figure A4 (a) were investigated, which have identical designs except the height of the *n*-GaN segments were varied from ~380 nm to 460 nm. Each nanowire, schematically shown in Figure A4 (a), consists of the *n*-GaN segment, ten vertically aligned InGaN/AlGaN quantum dots, and 30 nm *p*-GaN layer. PL emission of the InGaN nanowires was measured at room temperature with a 405 nm laser as the excitation source. Strong emission was observed at a wavelength of ~510 nm with a relatively narrow spectral linewidth of ~6 nm for nanowire arrays with heights varying from ~550 to 590 nm, shown in Figure A4 (b). However, the light intensity showed a significant decrease when the nanowire height was reduced below 550 nm, accompanied by a significantly broadened linewidth. These studies show that the band edge mode and the Purcell effect depends critically on the nanowire height, in addition to the nanowire diameter and spacing.



Figure A4: (a) Illustration of bottom-up InGaN/AlGaN core-shell dot-in-nanowire structure. The *n*-GaN segment length was varied from 380 to 460 nm. (b) PL emission spectra of InGaN nanowire structures measured at room-temperature for nanowire heights of ~510, ~530, ~550, ~570 and ~590 nm, respectively.

Appendix B

B.1 Materials and Methods

InGaN NCSEL design and simulation

The band structure for nanocrystal arrays with a triangular lattice was firstly calculated by 2D-FEM simulation using the radio frequency (RF) module in the commercial software package COMSOL Multiphysics 4.3b. The refractive index of nanocrystals was assumed to be 2.56. The filling material (polyimide) between the nanocrystals has a refractive index of 1.75. The simulation was performed for a unit cell with Floquet periodic boundary condition to solve for different points in the *k* space. The lattice constant and nanocrystal diameter were subsequently varied to tune the Γ point of the fourth band to be ~520 nm. Then, the same lattice constant and nanocrystal Due to larger refractive diameter were used to simulate a nanocrystal array with dimensions of about 5 µm by 5 µm. The in-plane mode profile was also calculated by 2D-FEM simulation. The boundary conditions were impedance boundary conditions with a refractive index of 1.75, which is the same as the filling material. Possible modes around the Γ point of the fourth band were computed, and the one exhibiting profile that is characteristic of the Γ point was identified.

MBE growth

The nanocrystal arrays were grown on an *n*-type GaN template on a sapphire substrate by the RF plasma-assisted MBE (Veeco GENxplor) system. *n*-GaN:Si nanocrystal arrays were first grown with a substrate temperature of 850°C, a nitrogen flow rate of 0.4 standard cubic centimeters per minute (sccm), and a Ga beam equivalent pressure (BEP) of ~ 2.9×10^{-7} torr. The growth conditions for the vertically aligned InGaN/AlGaN quantum disk active region included a substrate temperature of 650°C, a nitrogen flow rate of 1.2 sccm, a Ga BEP in the range of 1.8×10^{-8} torr, an In BEP of approximately 8.1×10^{-8} torr, and an Al BEP in the range of 4.2×10^{-9} torr, respectively. For the top *p*-GaN:Mg nanocrystals, Mg cell temperatures of 330°C were used with a Mg BEP of ~ 1.5×10^{-9} torr and a nitrogen flow rate of 0.6 sccm. A forward plasma power of ~ 350 W was used during the full structure growth.

Optical and structural characterization

PL measurement was carried out using a 405 nm laser as the excitation source with a visible neutral density filter. The optical emission was spectrally resolved using a high-resolution iHR550 imaging spectrometer and detected by a high-sensitivity liquid nitrogen-cooled charge-coupled device (CCD). SEM images were taken using a FEI Inspect F50 FE-SEM system. The measurements were performed with a 90° (top view) and a 45° tilted angle from the cross section of the sample. An accelerating voltage of 10 kV was used for imaging. STEM measurement was performed using a JEOL JEM-2100F equipped with a field-emission gun with an accelerating voltage of 200 kV. STEM-HAADF imaging was measured with an electron beam diameter of approximately 0.1 nm. A silicon drift detector of a 60 mm² was used for STEM-EDXS analysis.

Laser device fabrication

The NCSEL devices were fabricated by the following steps. The nanocrystal arrays were first planarized by a spin-coating system using a polyimide layer, followed by O₂ plasma etching to expose the top surface of the nanocrystals. A SiO_x passivation layer (~ 50 nm thick) was further deposited by plasma-enhanced chemical vapor deposition at 300°C, and the device active region area is defined by the opening aperture on the SiO_x layer. A metal electrode consisting of Ni (8 nm)/Au (8 nm) was deposited on the *p*-GaN top surface by an e-beam evaporator with an e-beam lithography technique and then annealed at ~ 550°C for 2 min in N₂ gas ambient. Subsequently, an 80-nm-thick indium tin oxide (ITO) layer was deposited to serve as a transparent electrode and current spreading layer. The ITO contact was also annealed at 300°C for 1 hour in vacuum. Ni (20 nm)/Au (100 nm) and Ti (20 nm)/Au (100 nm) contact layers were deposited on the surrounding ITO top surface and *n*-GaN template to serve as the *p*- and *n*-metal contacts, respectively. The fabricated devices with metal contacts were annealed at ~ 550°C for 2 min in N₂ gas ambient.

Laser device characterization

For electrical injection measurements, the InGaN device was placed on a motorized *x-y* stage (Aerotech's ANT130-XYULTRA), which provided precise spatial mapping. The current-voltage characteristics of the device were performed by a source meter Keithley SMU-2400. The output power was measured using a Si photodiode sensor. Electroluminescence spectra were measured by a liquid nitrogen–cooled CCD attached to an iHR550 spectrometer with 1200 grooves/mm grating. The far-field images were captured by a high megapixel color CCD camera at a distance

above the top surface of the device. The polarization was resolved by a Glan-Taylor calcite polarizer (with a High-Precision Rotation Mount) installed on the top surface of the device.

B.2 Simulation for photon confinement in the vertical direction

Due to larger refractive index for InGaN compared to GaN, the effective refractive index is higher around the active region. In order to calculate the effective refractive index, the nanocrystals are assumed to have flat top morphology. The lattice constant is 250 nm and the spacing between nanocrystals is 30 nm. The refractive index is 1.75 for the filling material (polyimide), 2.69 for InGaN, 2.35 for AlGaN, and 2.38 for *n*-GaN and *p*-GaN [310-313]. The diameter at root of the nanocrystals is approximated to grow from 170 nm to 255 nm within a height of 50 nm. Due to the high viscosity of the filling material and small spacing between nanocrystals, air gaps exist near the root of GaN nanocrystals. Considering the lengths of the segments in Figure 4.1 (a) in the main text, the variation of effective refractive index in the vertical direction and the corresponding TM polarized mode are calculated as shown in Figure B1. It is observed that the mode is mostly confined near the active region due to higher refractive index.



Figure B1: Variation of the effective refractive index along the growth direction and the TM polarized mode intensity profile.

B.3 Nano-hole patterned Ti mask substrate for selective area epitaxy

Nano-hole masks for the selective area growth were fabricated on *n*-type GaN (4 μ m thick) template on Al₂O₃ (0001) substrate. Firstly, a 10 nm thin Ti layer was deposited by e-beam

evaporator system. A positive Polymethyl methacrylate was used as a resist layer with spin-coating technique. The e-beam lithography process was optimized to obtain uniform arrays of nano-holes with a diameter of ~ 180 nm and a lattice constant of 250 nm in triangular lattices. The lateral growth effect was taken into account in the pattern design. Subsequently, a MIBK:IPA (1:3) solution was used for development process. Thereafter, the exposed Ti thin film area was etched down by reactive ion dry-etching technique using CF₄/O₂ plasma gas. The nano-hole patterned substrate was cleaned by Hydrogen Chloride acid (37%) prior to loading into the MBE growth chamber. Prior to the GaN nanocrystal SAG, a nitridation step was performed at 400°C with a plasma power of 380 W and a nitrogen flow rate of 1 sccm. Consequently, the thin Ti film was converted to TiN film which prevents the formation of cracks and degradation at elevated temperature. Figure B2 shows the FE-SEM image of the patterned hexagonal shape Ti mask with an opening hole size of ~180 nm.



Figure B2: Schematic illustration and FE-SEM image of the patterned Ti thin film nano-hole mask fabricated on *n*-type GaN template substrate.

B.4 Epitaxial growth of InGaN/AlGaN core-shell heterostructures

The InGaN/AlGaN core-shell heterostructures were incorporated in the laser active region. First, the core InGaN disk layer was grown on the top surface region of *n*-GaN nanocrystal. Due to the strain induced self-organization effect, the size of the InGaN disk becomes smaller than the *n*-GaN nanocrystal diameter. The incorporation of AlGaN barrier layers, instead of GaN barrier layers, leads to the formation of an AlGaN shell structure surrounding the InGaN quantum disk active region, due to the smaller Al adatom diffusion length compared to Ga and In adatom diffusion [314]. As a consequence, the growth fronts including the top and sidewalls of the InGaN region can be covered by AlGaN layers, thereby leading to the spontaneous formation of large

band-gap AlGaN shell structures [200, 315]. The growth conditions of InGaN/AlGaN multiple quantum disk layers included a substrate temperature of 650°C, a nitrogen flow rate of 1.2 sccm, a forward plasma power of ~ 350 W, In BEP ~ 8.1×10^{-8} Torr, Ga BEP ~ 1.8×10^{-8} Torr, and Al BEP ~ 4.2×10^{-9} Torr, respectively. By repeating the growth process, coaxially aligned cone-like AlGaN shell layers can be fabricated surrounding the InGaN multiple quantum disk structures.

B.5 TEM specimen preparation using a FIB system

The cross-sectional TEM sample preparation was performed in a FIB instrument (FEI Helios Nanolab 660 DualBeam) incorporating a gallium (Ga) liquid metal ion source and in-situ scanning electron microscopy imaging using a field emission source. The preparation of TEM lamella by the FIB lift-out technique was carried out as follows: a thick Cu layer was firstly deposited on the substrate to protect the top surface of the nanocrystals. Thereafter, the milling for lamella was processed to remove only regions A and B of the hexagonal shape nanocrystal as shown in Figure B3 (a), and after milling the GaN lamella has <100 nm thickness. Lastly, the cross-sectional surfaces of lamella were cleaned in low voltage mode by FIB to remove the beam damage and contamination layers. For the TEM measurement, the *a*-plane ($2\overline{110}$) zone-axis orientation of TEM lamella was used to observe the InGaN/AlGaN multi-quantum disk layers in the active region, shown in Figure B3 (b).



Figure B3: (a) Top-view FE-SEM image of the milling region for TEM lamella preparation of the nanocrystal. (b) Schematic illustration of the hexagonal GaN structure for zone-axis orientation of TEM measurement.

B.6 Ga-polar *n***-GaN nanocrystal structure**

A polarity generally refers to the direction in which GaN grows considering Ga-N bonds that are collinear with the *c*-axis of the wurtzite crystal structure. The vector from Ga to N-direction defines [0001], which is the positive direction of the c-axis [316]. When the growth direction is [0001], i.e., Ga-polarity, the formation of pyramidal geometry is often observed for GaN nanowires. Conversely, the structure has *N* polarity when the growth direction is [000 $\overline{1}$], which often exhibits a flat top surface [317, 318]. In the case of GaN wurtzite crystal structure, it is already well known that the polarity depends critically on the growth kinetics, buffer layers, substrates, and growth systems [319, 320]. In this study, we first performed the epitaxial growth for only *n*-GaN segment. As shown in Figure B4, the *n*-GaN nanocrystals were formed as a pyramid shape with the Ga-polarity because of the Ga-terminated GaN template on Al₂O₃ substrate [317]. Consequently, this Ga-polar crystal geometry leads to the formation of a cone-shaped semipolar multi-quantum disk layers in the active area.



Figure B4: (a) Schematic illustration of the Ga-polar *n*-GaN nanocrystal structure grown on GaN template. (b) FE-SEM image of the *n*-GaN nanocrystals which possess the Ga-polarity with a pyramid shape.

B.7 Projection effect image and quasi-3D structure of InGaN/AlGaN quantum disk layers

The 3D cone-like structure is expected from n-GaN nanocrystal structure as shown in Figure B5. Intriguingly, due to the quasi-3D structure of InGaN/AlGaN multi-quantum disk layers, the TEM images have different projection effects from the different layers, shown in Figure B5 (a).

Figure B5 (b) shows different TEM images from different projection effects by the overlapped layers and single layers.



Figure B5: (a) Schematic illustration of the FIB milling region and TEM lamella structure and projection effects of quasi-3D structure of InGaN/AlGaN quantum disk layers in the active region.(b) Different projection effects in the InGaN/AlGaN quantum disk layers.

B.8 Properties of semi-polar InGaN/AlGaN core-shell heterostructures

Optical properties of the semi-polar InGaN/AlGaN core-shell heterostructure were studied using photoluminescence spectroscopy. Shown in Figure B6 is the PL spectra measured at room temperature using a 405 nm laser as the excitation source. It is seen that the PL intensity of the

semi-polar InGaN/AlGaN core-shell is enhanced by nearly a factor of eight, compared to InGaN/GaN heterostructure without the formation of AlGaN shell. To examine the effect of an AlGaN shell on the optical emission properties, this study was performed on calibration samples under conditions without significant photonic band edge resonant effect. The shell structure spontaneously formed on the sidewalls of the active region can lead to drastically reduced non-radiative surface recombination due to the effective lateral confinement offered by the large band-gap AlGaN shell [200]. Moreover, unique quasi 3D structure exhibits massively enhanced surface emission and improved carrier injection efficiency, due to the much larger active area [249]. It is also well known that such semi-polar structure can effectively suppress the quantum-confined Stark effect due to the reduced polarization fields [248-250].



Figure B6: Photoluminescence emission spectra of InGaN/AlGaN core-shell multi-quantum disk nanocrystals (green curve) and InGaN/GaN multi-quantum disk nanocrystals without AlGaN shell (blue curve) measured at 300 K.

B.9 NCSEL device fabrication

In order to achieve stable and low resistivity ohmic contact, we have performed extensive optimization of the thickness of Ni and Au and annealing process. Upon annealing, Ni may form NiO_x and becomes nearly transparent [16, 17]. The thin Au layer, however, does partially block the emitted light. It is estimated that the transmittance of the Au metal layer is about 60–70% in the green wavelength region [17-19], which leads to non-negligible optical loss and limits the

optical power. There is significant room to further optimize the fabrication process to improve the current injection and spreading and to enhance the device output power. For example, nonuniform current injection, particularly at low current densities, may significantly affect the photonic band edge resonance mode.

Exposed top surface p-i-n nanocrystals Polyimide 2. Polyimide passivation / Surface etching 1. Nanocrystals grown on substrate 5102 ПO Au Opening aperture 3. Opening aperture 4. Thin metal contact / ITO deposition by SiO₂ passivation layer Ni/Au ITO 5 µm Au Ni/Au Ni SiO₂ Ti/Au Polyimide p-i-n nanocrystal arrays Ti/Au Substrate 5. Metallic electrode contact grids Laser device structure

The nanocrystal surface-emitting laser device was fabricated by the following steps.

Figure B7: Schematic illustration of the full device fabrication, including passivation, planarization, photolithography and contact metallization techniques.

B.10 Electroluminescence measurement

The EL spectrum measurement involves the use of an objective lens and an iHR550 spectrometer with a CCD detector. The emitted light was collected from the top surface of the device, shown in Figure B8. The output power was measured using a Si photodiode sensor placed directly on top of the device.



Figure B8: Schematic illustration of the measurement setup for EL spectra.

B.11 Calculation of far-field radiation pattern

The far-field radiation pattern of the nanocrystal laser structure is calculated by 3D-FDTD simulation using the commercial software package Lumerical FDTD Solutions 8.6. The nanocrystals are modelled to have flat top surface rather than pyramid top surface. The nanocrystals are arranged in a hexagonal region with a side length of ~ 3.5μ m. The nanocrystal diameter and the lattice constant are the same as designed by 2D FEM simulation. The nanocrystals have three layers, including 370 nm *n*-GaN, 40 nm active region, and 190 nm *p*-GaN. The refractive index is 2.38 for *n*-GaN and *p*-GaN. The 40 nm active region has an effective refractive index of 2.56. A broadband TM polarized dipole source was used to fully excite all possible modes in the structure. Perfectly matched layer boundary condition was applied to minimize reflection at the simulation boundary. The simulation was performed for sufficiently long time to reach steady

state. Only the data in the last 600 fs of the simulation was used for calculation to avoid misinterpretation due to the transient stage. The near field of 50 nm above the nanocrystal array was used for calculating the far field radiation pattern.

B.12 Measurement of far-field radiation pattern

For the far-field measurement, the light emission was collected by a high megapixel color charge coupled device camera with a magnification zoom lens, which was placed at a distance from the top surface of the device. The arrangement was completely perpendicular to the NCSEL device surface, shown in Figure B9.



Figure B9: Schematic illustration of the far-field measurement setup with a CCD camera at a distance above the NCSEL device.

B.13 Polarization measurement of the light emission of InGaN NCSELs

The polarizer was installed on the top surface of the InGaN NCSEL, shown in Figure B10. The polarization was resolved by a Glan-Taylor calcite polarizer with a high-precision rotation mount system. The polarization angle was defined based on the nanocrystal structure as shown in Figure B10.



Figure B10: Schematic illustration of the polarization angle measurement.

Appendix C

C.1 Computational methods

DFT calculations

The density functional theory (DFT) calculations were performed with BEEF-vdW [321] exchange-correlation functional and projector augmented wave (PAW) pseudopotential [323, 324] within the Vienna Ab-initio Simulation Package (VASP) [324, 325]. A cut-off energy of 400 eV was chosen, and structural optimization were achieved until the residual force of each atom was smaller than 0.01 eV Å⁻¹. A (3 × 3) and (3 × 1) surface unit with a four-layer slab were modeled for the (*111*) and (*211*) facets of fcc metals respectively, both containing 9 surface metal atoms per supercell. All slabs were spaced more than 20 Å perpendicular to the slab surface to avoid interaction due to periodicity. A 4 × 4 × 1 Monkhorst-Pack mesh of *k*-points [326] was used both for (*111*) and (*211*) facets. When relaxing the geometries, adsorbates and the top two layers were allowed to relax, while the bottom two layers were fixed to their initial bulk positions.

The reaction mechanism of CO_2 reduction to CO in an aqueous solution is suggested to include the following steps [327]:

$$CO_2+H^++e^-+* \rightarrow *COOH \qquad \dots \qquad \dots \qquad \dots \qquad (C-1)$$

$$*COOH + H^+ + e^- \rightarrow *CO + H_2O \dots \dots \dots \dots \dots \dots (C-2)$$

$$*CO \rightarrow *+CO$$
 (C-3)

where * denotes either a surface-bound species or a vacant catalytic active site. The HER consists of two consecutive proton-electron pair transfer steps:

$$H^++e^-+* \rightarrow *H$$
 (Volmer step) ... (C-4)

$$*H + H^+ + e^- \rightarrow * + H_2$$
 (Heyrovsky step) ... (C-5)

Or $*H + *H \rightarrow *+H_2$ (Tafel step) (C-6)

Absorbate energies: The CO₂RR and HER activity maps were calculated by computational hydrogen electrode (CHE) model suggested by Nørskov et al. [328]. By employing the CHE model, a proton/electron (H⁺ + e⁻) in solution can be directly treated and the effect of a bias can be applied by shifting by ΔG by +neU, where n is the number of proton-electron pairs transferred, e is the elementary positive charge, and U is the applied potential. The free energy change (ΔG) is calculated as $\Delta G = \Delta E + \Delta ZPE + \int C_p dT$ - T ΔS , where ΔE is the total energy directly obtained from DFT calculations, ΔZPE is the change in zero-point energy, C_p is the heat capacity, T is temperature, and ΔS is the change in entropy. The temperature is set to 298.15 K to compare current DFT results with the experimental data. The contributions to the free energy for each adsorbate involved in the lowest-energy pathways are listed in Table C1. As indicated in previous study [330], the reaction intermediates would be stabilized by the hexagonal water overlayer above them, therefore the solvation correction was also employed by applying a *COOH and *CO stabilization of 0.25 and 0.1 eV, respectively.

Table C1: Contributions to the adsorbate free energy from the zero-point energy correction, enthalpic temperature correction, entropy, and the total free energy correction, respectively. The assumed fugacity for each non-adsorbed species are also included. H_2 (ref) is used for the computational hydrogen electrode model as described in Computational Methods Section.

Species	Fugacity	ZPE	∫CpdT	-TS
	(P a)	(eV)	(eV)	(eV)
*СООН	-	0.62	0.10	-0.27
*CO	-	0.19	0.08	-0.16
*Н	-	0.16	0.01	-0.01
$H_2(ref)$	101325	0.27	0.09	-0.42
СО	101325	0.14	0.09	-0.67
H_2O	3534	0.58	0.10	-0.65
CO_2	101325	0.31	0.10	-0.65

Non adsorbed species and gas phase correction: DFT calculations of non-adsorbed species were performed using the same techniques as described above for adsorbed species, except with a Fermi level smearing of 0.01 eV. The components of the energy calculations for all non-adsorbed species are also listed in Table C1.



Figure C1: Scaling relations between the *CO binding energy and basic reactions in CO_2RR and HER on transition metal fcc(*111*) facet. The fitted equations are shown in the insets.



Figure C2: Scaling relations between the *CO binding energy and basic reactions in CO_2RR and HER on transition metal fcc(*211*) facet. The fitted equations are shown in the insets.

C.2 Experimental methods

Nanowire growth

GaN nanowire arrays were grown on planar p-n Si wafer Veeco GEN Explore radio frequency plasma-assisted molecular beam epitaxial (PA-MBE) growth system. Prior to loading into the MBE chamber, the n^+ -p Si substrate was cleaned with acetone and methanol to remove any organic contaminants. Subsequently, Si substrate was immersed in 10% BHF (used in industrial cleaning of Si wafers) to remove native oxide. The nanowires were formed spontaneously under nitrogenrich conditions without using any external metal catalyst on Si substrate. The growth conditions included a substrate temperature range of 850°C with the Ga beam equivalent pressure of 5.9×10^{-8} torr, nitrogen flow rate of 1 standard cubic centimeter per minute (sccm) and plasma forward power of 350 W. *n*-GaN nanowire arrays are grown for 1.5 hours.

Fabrication of *n*⁺-*p* Si substrates

To fabricate the n^+ -p Si substrate, several steps has been conducted. First, the double side polished p-type Si (100) wafer (WRS Materials, thickness: 254–304 µm; resistivity: 1–10 Ω ·cm) was spin-coated with liquid phosphorous dopant precursor (Futurrex, Inc.) on one side to form the n^+ -Si emitter, followed by liquid boron dopant precursor (Futurrex, Inc.) on the other side to form the p^+ -Si back field layer. Next, the thermal diffusion process was performed around 950°C for 6 hr under argon gas flow in a typical furnace. Lastly, the residue of the precursor was carefully removed by buffered oxide (BHF) etch solution.

Sample synthesis

Au nanoparticles were deposited on GaN nanowires using an e-beam at a deposition rate of 0.1 Å/s for 500 s, followed with thermal annealing in Ar at 650°C for 2 min. During the annealing process, small Au nanoparticles migrated and coalesced to form large Au nanoparticles on GaN nanowires for decreasing the surface energy [330]. Au was favourable to grow on the *c*-plane of GaN nanowires as a tipped heterostructure. This can be explained by the smaller formation energy for Au on *c*-plane GaN, partly due to the smaller lattice mismatch between Au (*111*) and *c*-plane GaN compared to *m*-plane GaN (0.24, 0.26 and 0.28 nm, respectively) [331]. Prior to the Au e-beam deposition, the GaN nanowires on p-n Si substrate was pretreated with concentrated HCl solution for 30 s to remove native oxide. Pt nanoparticles were deposited on GaN nanowires by

photodeposition using H₂PtCl₆ (99.9%, Sigma Aldrich) as precursor from an aqueous methanol solution (15 mL methanol and 60 mL deionized water) [332]. 2, 5 and 12 μ L of 0.2 M H₂PtCl₆ were used for the preparation of AuPt_{0.1}/GaN/n⁺-*p* Si, AuPt_{0.2}/GaN/n⁺-*p* Si and AuPt_{0.4}/GaN/n⁺-*p* Si, respectively. Pt nanoparticles were preferentially deposited on the sidewall of GaN nanowires due to a sorption-determined deposition mechanism as reported previously [285]. For comparison, AuPt_{0.2}/n⁺-*p* Si was prepared by following the same protocol by depositing Au and Pt nanoparticles directly on planar *n*⁺-*p* Si wafer.

Characterization

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed on a Thermo Scientific iCAP 6000 Series inductively coupled plasma atomic emission spectroscopy instrument to determine the loading amount of metal cocatalysts. The samples were digested in aqua regia (HNO₃:HCl = 1:3) at 95°C for 3 h before the analysis. The morphology of samples was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were acquired from an Inspect F-50 FE SEM system at an accelerating voltage of 5 keV. TEM images were attained on FEI Tecnai G2 F20 microscope at 200 keV, with energy dispersive X ray spectroscopy (EDX) attached. The nanowires were scratched off from the Si substrate onto a Cu TEM grid. Surface chemical compositions of samples were analyzed by X ray photoelectron spectroscopy (XPS) in a Thermo Scientific K Alpha XPS system with a monochromatic Al K α source (h ν = 1486.6 eV). The binding energies were calibrated using the C-1*s* peak at 284.8 eV as the reference.



Figure C3: SEM, and TEM images of Au/GaN/ n^+ -p Si before (a, b) and after (c, d) annealing process.

Sample	Au/GaN/ n ⁺ -p Si	AuPt _{0.1} /GaN/ n ⁺ -p Si	AuPt _{0.2} /GaN/ n ⁺ -p Si	AuPt _{0.4} /GaN/ n ⁺ -p Si	Pt/GaN/ n ⁺ -p Si
Au (nmol-cm ⁻²)	8.5	8.8	8.5	8.6	-
$Pt (nmol-cm^{-2})$	-	0.9	1.7	3.4	3.7

Table C2: ICP-AES analysis of Au and Pt loading amounts of different samples.



Figure C4: TEM images of (a) Au/GaN/ n^+ -p Si, (b) AuPt_{0.1}/GaN/ n^+ -p Si, (b) AuPt_{0.2}/GaN/ n^+ -p Si, (b) AuPt_{0.4}/GaN/ n^+ -p Si and (b) Pt/GaN/ n^+ -p Si.



Figure C5: (a) TEM image of AuPt_{0.1}/GaN/ n^+ -p Si using Pt(NH₃)₄Cl₂ as Pt precursor. (b) XRD patterns of GaN/ n^+ -p Si and AuPt_{0.2}/GaN/ n^+ -p Si.

PEC measurements

PEC CO₂ reduction was performed in a three electrode configuration with AuPt/GaN/ n^+ -p Si as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The electrolyte was 0.5 M KHCO₃ saturated with CO₂ (pH 7.5) by purging the PEC cell for 30 min. The light source was a solar simulator (Newport Oriel LCS-100) with a calibrated light intensity of 100 mW cm⁻² (1 sun) on the sample surface. The PEC data were collected by a potentiostat (Gamry Instruments, Interface 1000). The current-potential (J-V) curve was obtained at a scan rate of 20 mV/s. Chronoamperometry for product analysis was performed at a certain potential for 100 min. Gas products after the photoelectrolysis were analyzed by a gas chromatograph (Shimadzu GC-8A) with a thermal conductivity detector (for H_2) and a gas chromatograph (Shimadzu GC-2014) with a flame ionization detector (for CO and hydrocarbons). Liquid products were analyzed afterwards by nuclear magnetic resonance (NMR, Bruker AV-500) using 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS, Sigma Aldrich) as an internal standard. Faradaic efficiencies (FEs) were calculated from the amount of charge needed to produce each product divided the total charge passed during the test. To confirm the origin of the product, ¹³Clabeled isotope experiment was performed in ¹³CO₂ (99%, Sigma Aldrich)-saturated 13Cbicarbonate solution (NaH13CO3, 98%, Sigma Aldrich) under otherwise identical conditions. The gas products were analyzed by gas chromatography mass spectrum (GC-MS, Agilent 5975).

The half-cell solar-to-syngas efficiency η_{STS} (also named applied bias photon-to-current efficiency, ABPE) was calculated using the following equation:

$$= \begin{bmatrix} J(mA. cm^{-2}) \times FE_{co}(\%) \times (1.34 - V_{bias})(V) + J(mA. cm^{-2}) \times FE_{H_2}(\%) \times (1.34 - V_{bias})(V) \\ P_{in}(mW. cm^{-2}) \end{bmatrix} \dots \dots (C7)$$

where J is the photocurrent density, FE_{co} and FE_{H_2} are faradaic efficiency to produce CO and H₂ respectively, bias V is the applied potential versus an ideal counter electrode for O₂ evolution (+1.23 V vs. RHE), and in P is the light intensity (100 mW.cm⁻²).



Figure C6: (a) Chronoamperometry data of $AuPt_x/GaN/n^+-p$ Si photocathodes at +0.17 V vs RHE in CO₂-saturated 0.5 M KHCO₃ (pH 7.5) under AM 1.5G one-sun illumination. (b) *J-V curve of* $AuPt_{0.2}/GaN/n^+-p$ Si and $AuPt_{0.2}/n^+-p$ Si in CO₂-saturated 0.5 M KHCO₃ (pH 7.5) under AM 1.5G one-sun illumination.



Figure C7: (a) The adsorption amount of Pt precursor on Au/GaN/ n^+ -p Si sample. 3 cm² of wafer sample was immersed in 50 mL H₂PtCl₆ or Pt(NH₃)₄Cl₂ aqueous solution (0.01 mmol/L) overnight. The Pt concentration in the solution was analyzed by ICP-AES, and the adsorbed Pt amount was calculated. The results show the stronger adsorption of PtCl₆^{2–} than that of Pt(NH₃)₄²⁺. (b) FEs for CO (purple bars) and H₂ (red bars) of AuPt_x/GaN/ n^+ -p Si with different cocatalyst compositions at +0.17 V vs RHE using Pt(NH₃)₄Cl₂ as Pt precursor.



Figure C8: (a) SEM and (b) TEM images of AuPt_{0.2}/GaN/ n^+ -p Si photocathode after PEC stability test. XPS analysis of (c) Au-4f and (d) Pt-4f of AuPt_{0.2}/GaN/ n^+ -p Si photocathode before and after PEC stability test.



Figure C9: FEs for CO (purple bars) and H₂ (red bars) of AuPt_{0.2}/ n^+ -p Si and AuPt_{0.2}/GaN/ n^+ -p Si at +0.17 V vs RHE.



Figure C10: Mass spectrometry chromatogram of the gas phase analysis after ¹³C-labeled isotope experiment.

Table C3: Performance comparison of photocathodes for PEC CO₂ reduction into CO/syngas at underpotential (more positive than the equilibrium potential $E^{\circ}(CO_2/CO) = -0.11$ V vs RHE).

Photocathode	Light intensity (mWcm ⁻²)	Onset potential (V vs RHE) ^[a]	FE _{co} (%) ^[b]	Solar to syngas efficiency (%) ^[c]	References
Cu-ZnO/GaN/n ⁺ -p Si	800	+0.07	70	~0.01	[272]
Au ₃ Cu/ n^+ - p Si	20	-0.09	80	0.07	[271]
Au/n^+ -p Si	100	+0.22	91	0.12	[334]
Au/ZnO@ZnTe@CdTe	100	+0.3	67	0.18	[335]
$Ag_2P/Al_2O_3/n^+$ -p Si	100	+0.2	67	0.3	[336]
Au/TiO ₂ /a-Si	100	+0.4	50	0.42	[273]
Pt-TiO ₂ / n ⁺ -p Si	800	+0.47	78	0.87	[118]
Cu ₃ (BTC) ₂ /Cu ₂ O	100	$-1.77 V vs F_C / F_C^+$	95	0.83	[337]
AuPt/GaN/ n ⁺ -p Si	100	+0.4	91	1.88	Current work

^[a] Defined as the reported most positive potentials for CO generation. The potentials were converted to RHE values by the following equation: $V_{\text{RHE}} = V + (0.059 * \text{pH}) + V_{\text{Ref}}$, Where, $V_{\text{Ref}} = 0.244$ and 0.197 for SCE and Ag/AgCl respectively,

^[b] The highest FE reported in the system.

^[c] calculated value using equation (C7).

Appendix D

D.1 Experimental methods

Co-catalyst deposition

The Au/Cr₂O₃ co-catalyst were deposited on the NW using two steps, where Au was deposited by e-beam and photo deposition from liquid precursors has been used for Cr₂O₃, respectively. First, the Au nanoparticles were deposited on InGaN:GaN nanowires using an e-beam evaporator. Later Cr co-catalyst was deposited by photodeposition process, which was performed in a sealed Pyrex chamber with a quartz lid [332]. The sample was fixed in a Teflon holder and placed in the chamber. Then, 60 mL deionized water (purged with Ar for 20 min before use), K₂CrO₄ (\geq 99.0%, Sigma Aldrich), and 15 mL methanol (99.8%, ACP Chemicals) as the sacrificial electron donor were added in sequence. The reaction chamber was then evacuated and irradiated for 30 min.

Photocatalytic experimental procedures

The CO₂ reduction and product evaluation experiments were performed an airtight gas circulation system (~450 mL). The sample placed on a homemade polytetrafluoroethylene holder in a Pyrex chamber with a quartz lid. After system is well evacuated and then filled with pure CO₂ (Air Liquid, 99.995%) until reaching the pressure of around 55–60 kPa. 2.5 milliliters of distilled water were inserted into the reaction cell, which was purged with Ar for 20–30 min before each experiment. After the photocatalysis reaction, the gas products were analyzed by a GC (Shimadzu GC-8A) with a thermal conductivity detector (for H₂ evolution) and for CO evolution, a GC (Shimadzu GC-2014) with a flame ionization detector. The absence of carbon residues on the samples was confirmed by control experiments. The experimental error in the evolution of H₂, CO and O₂ is estimated to be ~ 10% due to manual sampling of the evolved gases and leakage through the septum.

The solar-to-syngas efficiency η_{STS} is calculated using the following equation:

$$\eta_{STS} (\%) = \left(\left[\frac{Output \ energy \ of \ hydogen \ (H_2) evolved}{Energy \ of \ incident \ solar \ light} \right]_{AM \ 1.5G} + \left[\frac{Output \ energy \ of \ carbon \ monoxide \ (CO) \ evolved}{Energy \ of \ incident \ solar \ light} \right]_{AM \ 1.5G} \times 100$$

$$= \left(\left[\frac{(mmol H_2 s^{-1}) \times 237 (KJ mol^{-1})}{p_{in} (MW cm^{-2}) \times area (cm^2)} \right]_{AM 1.5G} + \left[\frac{(mmol CO s^{-1}) \times 257 (KJ mol^{-1})}{p_{in} (MW cm^{-2}) \times area (cm^2)} \right]_{AM 1.5G} \right) \times 100$$

D.2 Structural and optical characterizations of grown nanowires

SEM images were carried out using a FEI Inspect F50 FE-SEM system with a 45-degree tilted angle from the cross section of the sample. The grown nanowire is spontaneously grown all over the substrate, shown in Figure D1. The PL measurement was performed using a 405 nm laser as the excitation source. The laser beam was focused on the sample through a $\times 60$ objective, with a circular beam size of ~ 5 µm.



Figure D1: 45° tilted-view SEM image of the InGaN:GaN spontaneously grown nanowire array on Si substrate.

STEM measurements [STEM-secondary electron, STEM-BF and STEM-HAADF imaging] were acquired using FEI Tecnai G2 F20 microscope operated at 200 keV, with an electron beam diameter of approximately 0.1 nm. The nanowires were scratched off from the Si substrate onto a copper grid prior to TEM measurements. X-ray photoelectron spectroscopy (XPS) measurements

were performed in a Thermo Scientific K-Alpha XPS system with a monochromatic Al $K\alpha$ source (hv = 1486.6 eV). The binding energies were calibrated using adventitious C-1s peak at 284.8 eV.

The relative line scan with element profile plot and EDAX curve of Au/Cr₂O₃ decorated InGaN/GaN nanowire sample are shown in Figures D2 and D3. Figure D2 shows the Energy dispersive X-Ray (EDX) line scan with the distribution of In, Ga, N, Au, Cr along with the line scan and Figure D3 presents the EDXS for identifying and quantifying elemental composition of the sample area.



Figure D2: The line scan and elemental plot of Au/Cr₂O₃ decorated InGaN/GaN nanowire sample.



Figure D3: EDXS of Au/Cr₂O₃ decorated InGaN/GaN nanowire sample. Inset shows the corresponding elemental analysis by eZAF Smart Quant Results Table.

List of Publications

Patent Applications:

1. **Roksana Tonny Rashid**, Yong-Ho Ra, Xianhe Liu, Zetian Mi, "Electrically Pumped Surface-Emitting Semiconductor Green Laser", University of Michigan, OTT Ref. No.: 2020–213, filed on Dec. 2, 2019.

2. Zetian MI, Yong-Ho RA, **Roksana RASHID**, Xianhe LIU, "Core-Shell InGaN/AlGaN Quantum Nanowire Photonic Structures", U.S. No. 16 /044, 337, filed on Jul. 24, 2018.

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1. **Roksana Rashid**, Zetian Mi, "Photocatalytic CO₂ reduction towards tunable Syngas by III-Nitride Heterostructures", Manuscript in progress.

 Yong-Ho Ra, Roksana Tonny Rashid, Xianhe Liu, Sharif Md. Sadaf, Kishwar Mashooq, Zetian Mi, "An Electrically Pumped Surface-Emitting Semiconductor Green Laser", Sci. Adv. 2020; 6: eaav7523.

3. Baowen Zhou*, Pengfei Ou*, **Roksana Rashid***, Srinivas Vanka, Kai Sun, Lin Yao, Haiding Sun, Jun Song, Zetian Mi, "Atomic iron layer for hydrogen evolution from water by photoelectrocatalysis", Submitted to Nano Letters, Manuscript ID: nl-2020-00580k [*Equal Author Contribution].

4. Shaobo Cheng, Zewen Wu, Brian Langelier, Xianghua Kong, Toon Coenen, Sangeetha Hari, Yong-Ho Ra, **Roksana Rashid**, Alexandre Pofelski, Hui Yuan, Xing Li, Zetian Mi, Hong Guo, Gianluigi A. Botton, "Nanoscopic understanding of the boomerang shape of InGaN/AlGaN quantum disks", Submitted to Nano Letters, Manuscript ID: nl-2020-00520t.

5. Sheng Chu*, Pengfei Ou*, **Roksana Tonny Rashid***, Pegah Ghamari, Renjie Wang, Hong Nhung Tran, Songrui Zhao, Jun Song, Zetian Mi, "Controllable Syngas Generation from Photoelectrochemical CO₂ Reduction with Dual Cocatalysts", submitted to JACS (Journal of the American Chemical Society) [*Equal Author Contribution].

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7. Mingxin Liu, Lida Tan, **Roksana Rashid**, Yunen Cen, Shaobo Cheng, Gianluigi A. Botton, Zetian Mi, Chao-Jun Li, "Clean and transition metal free radical coupling reaction of carbonyl catalyzed by gallium nitride nanowire under black light", submitted to ACS Nano.

8. Xu Hai, **Roksana Rashid**, Zetian Mi, Songrui Zhao, "Light emission properties of AlGaN nanowire deep ultraviolet light emitting diodes", submitted to PSSA (Physica Status Solidi A: Applications and Materials Science).

9. Xu Hai, **Roksana Rashid**, Zetian Mi, Songrui Zhao, "On the longer wavelength components in AlGaN nanowire deep ultraviolet light emitting diodes", submitted to SST (Semiconductor Science and Technology).

10. Sheng Chu, **Roksana Tonny Rashid**, Xuedong Liu and Zetian Mi, "Photodeposition of a conformal metal oxide nanocoating", Chemical Communications, 2019, 55, 6305-6308.

11. Shaobo Cheng, Brian Langelier, Yong-Ho Ra, **Roksana Tonny Rashid**, Zetian Mi, and Gianluigi A. Botton, "Structural origin of the high-performance light-emitting InGaN/AlGaN quantum disks", Nanoscale, 2019, 11, 8994.

12. Mingxin Liu, Yichen Wang, Xianghua Kong, **Roksana T. Rashid**, Sheng Chu, Chen-Chen Li, Zoë Hearne, Hong Guo, Zetian Mi, Chao-Jun Li, "Direct Catalytic Methanol-to-Ethanol Photoconversion via Methyl Carbene", Chem, 2019, 5(4), 858-867.

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1. **Roksana T. Rashid**, Yong H. Ra, Xianhe Liu, Zetian Mi, "Efficient Light Emitter by Scalable InGaN Nanowire Photonic Crystal", MRS Fall Meetings 2019, Boston, Massachusetts, Nov. 29-Dec. 3, 2019.

2. **Roksana T. Rashid**, Faqrul A. Chowdhury, Sheng Chu, Zetian Mi, "Photochemical Artificial Photosynthesis of CO₂ Reduction into Syngas Production", MRS Fall Meetings 2019, Boston, Massachusetts, Nov. 29-Dec. 3, 2019.

3. **R.T. Rashid**, S. Chu, F. A. Chowdhury, Z. Mi, "Artificial Photosynthesis of CO₂ Reduction into Syngas Using InGaN Nanowires", Photonics North, PN 2019, Quebec City, Quebec, May 21-23, 2019.

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5. Yong-Ho Ra, **Roksana Rashid**, Ishiang Shih and Zetian Mi, "Bottom-up InGaN Nanowire Photonic Crystal Structures", The 11th International Symposium on Semiconductor Light Emitting Devices, ISSLED 2017, Banff, Canada, Oct. 8-12, 2017.

6. Zetian Mi; Yong-Ho Ra; Renjie Wang; **Roksana Rashid**, "Multi-color nanowire LEDs on a single chip", 30th Annual Conference of the IEEE Photonics Society, IPC 2017, Orlando IL, United States, Oct. 1-5, 2017.

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