Graphene quantum dots and their applications in bioimaging and catalysis

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**GRAPHENE QUANTUM DOTS AND THEIR
APPLICATIONS IN BIOIMAGING AND CATALYSIS**

CHEN JIE

SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2019

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

A thesis submitted to the Nanyang Technological University

in partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Prof. CHEN PENG

Authorship Attribution Statement

This thesis contains material from three papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as J. Chen, A. Than, N. Li, A. Ananthanarayanan, X. Zheng, F. Xi, J. Liu, J. Tian, P. Chen, Sweet Graphene Quantum Dots for Imaging Carbohydrate Receptors in Live Cells, FlatChem 5 (2017) 25-32. DOI: 10.1016/j.flatc.2017.08.006

The contributions of the co-authors are as follows:

- Prof. Chen Peng provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Ananthanarayanan and Dr. Than.
- I co-designed the study with Prof Chen Peng and performed most of the laboratory work at the School of Chemical and Biomedical Engineering. Dr. Ananthanarayanan and Dr. Li Nan helped me with experiments on material preparation. I also analyzed the data.
- Dr. Than assisted in biological experiments particularly in operations of confocal microscopy and image analysis.
- Dr. Zheng conducted XPS characterization for me. Dr. Xi and Dr. Liu provided suggestions and guidance on the experimental practices and academic writing

Chapter 4 is published as K. Li*, J. Chen*, Y. Yan, Y. Min, H. Li, F. Xi, J. Liu, P. Chen, Quasi-homogeneous carbocatalysis for one-pot selective conversion of carbohydrates to 5-hydroxymethylfurfural using sulfonated graphene quantum dots, Carbon 136 (2018) 224-233. DOI: 10.1016/j.carbon.2018.04.087 (*Co-first author)

The contributions of the co-authors are as follows:

- Prof. Chen Peng provided the initial project direction and edited the manuscript drafts.
- Dr. Li Kaixin and I co-designed the study with Prof. Chen Peng.
- I performed all the materials synthesis and purification, catalytic reactions, collected samples for high-performance liquid chromatography analysis and material characterization such as atomic force microscopy and transmission electron microscopy, and conducted data evaluation.
- Dr. Li Kaixin performed the acidic strength analysis, Fourier-transform infrared spectroscopy, density functional theory calculations and analyze the data.
- Dr. Li Kaixin wrote the drafts of the manuscript.
- Dr. Yan, Mr. Li and Dr. Min advised on the experiments set-up and operations.
- Dr. Xi and Dr. Liu provided suggestions and guidance on the experimental practices and academic writing.

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The contributions of the co-authors are as follows:

- Prof. Chen Peng provided the initial project direction and edited the manuscript drafts.
- Dr. Yan Yibo co-designed the study with Prof. Chen Peng.
- Dr. Yan performed all the laboratory work at the School of Chemical and Biomedical Engineering and also analyzed the data.
- I performed the characterization like transmission electron microscopy, photoluminescence and UV-Vis adsorption spectra, et al. I also

assisted Dr. Yan in the materials preparation, catalytic experiment set-ups and data analysis.

- Dr. Yan wrote the drafts of the manuscript.
- Dr. Li Nan, Li Kaixin and Dr. Tian advised on the material synthesis, catalytic theory and laboratory operations.
- Dr. Liu and Dr. Tian provided suggestions and guidance on the experimental practices and academic writing.

02-Aug-2019

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Date

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List of Abbreviations

GQD: Graphene quantum dot

PL: Photoluminescence

QY: Quantum yield

SGQD: Sulfonated graphene quantum dot

5-HMF: 5-hydroxymethylfurfural

DFT: Density functional theory

QD: Quantum dot

GO: Graphene oxide

GOQD: Graphene oxide quantum dot

DMF: Dimethylformamide

HRTEM: High-resolution transmission electron microscopy

XRD: X-ray powder diffraction

AFM: Atomic force microscopy

0-D: Zero-dimensional

CD: Carbon dot

XPS: X-ray photoelectron spectroscopy

FTIR: Fourier-transform infrared spectroscopy

UV: Ultraviolet

Vis: Visible

TDDFT: Time-dependent density functional theory

FWHM: Full width at half maximum

HOMO: Highest occupied molecular orbital

LOMO: Lowest unoccupied molecular orbital

N-GQD: Nitrogen doped graphene quantum dot

N, S-GQD: Nitrogen and sulfur co-doped graphene quantum dot

S-GQD: Sulfur doped graphene quantum dot

rGQD: Reduced graphene quantum dot

GQD-PEG: graphene quantum dot passivated with polyethylene glycol

FITC: Fluorescein isothiocyanate

NIR: Near infrared

GM: Göppert-Mayer units

ASPL: Anti-Stokes photoluminescence

CND: Carbon nanodot

ECL: Electrochemiluminescence

rGO: Reduced graphene oxide

MTT: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide

AST: Aspartate aminotransferase

ALT: Alanine aminotransferase

MRI: Magnetic resonance imaging

AuNP: Gold nanoparticles

FRET: Fluorescence resonance energy transfer

PEC: Photoelectrochemical

DOX: Doxorubicin

HA: Hyaluronic acid

PLA: Poly(L-lactide)

FA: Folic acid

ROS: Reactive oxygen species

Ce6: Chlorin e6

PDT: Photodynamic therapy

PBS: Phosphate-buffered saline

RTI: Reverse transcriptase inhibitors

IAPP: Islet amyloid polypeptide

OER: Oxygen evolution reaction

ORR: Oxygen reduction reaction

CO₂RR: Carbon dioxide reduction reaction

HER: Hydrogen evolution reaction

B-GQD: Boron doped graphene quantum dot

VA: Veratryl alcohol

CNT: Carbon nanotube

WGQD: White fluorescent GQD

WLED: While light emitting diode

CIE: Commission Internationale de l'Enclairage

ODA: Octadecylamine

OLED: Organic light emitting diode

CNF: Cellulose nanofiber

SiNW: Silicon nanowire

DUV: Deep ultraviolet

ASGPR: Asialoglycoprotein receptor

Gal-GQD: Galactose-functionalized graphene quantum dot

Man-GQD: Mannose-functionalized graphene quantum dot

FBS: Fetal bovine serum

PS: Penicillin streptomycin

DMEM: Dulbecco's Modified Eagle Medium

CLSM: Confocal laser scanning microscope

TIRFM: Total internal reflection fluorescence microscope

PLE: Photoluminescence excitation

STEM-EDX: Scanning transmission electron microscopy-energy dispersive X-Ray spectroscopy

TPD: Temperature programmed desorption

MWCO: Molecular weight cut-off

MTS: Methoxytrimethylsilane

Da: Dalton

HPLC: High performance liquid chromatography

RID: Refractive index detector

HB: Hydrogen bond

BSSE: Basis set superposition error

NH₃-TPD: Temperature programmed desorption of ammonia

EDS: Energy-dispersive X-ray spectroscopy

DMSO: Dimethyl sulfoxide

MIBK: Methyl isobutyl ketone

MTS: Methoxytrimethylsilane

OPD: O-phenylenediamine

DNPT23: 2,3-diaminonaphthalene

DNPT18: 1,8-diaminonaphthalene

BNPTL: 1,1'-bi(2-naphthylamine)

Anln-OCH₃: Panisidine

Anln-OCF₃: 4-(trifluoromethoxy) aniline

Anln-OCCL₃: 4-(trichloromethoxy)aniline

MS: Mass spectrometry

AQY: Apparent quantum yield

CBM: Conduction band minimum

VBM: Valence band maximum

VB: Valence band

CB: Conduction band

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Abstract

Graphene quantum dot (GQD) is an emerging zero-dimensional material and the latest addition to the family of carbon materials. Owing to its unique and intriguing properties, GQD promises a wide spectrum of novel applications. For example, its tunable photoluminescence (PL), high photostability, excellent biocompatibility and molecular size make GQD a desirable candidate for bioimaging. In the first result chapter of this thesis, we have successfully synthesized single-crystalline GQDs by using a bottom-up approach. The as-prepared GQDs have a high quantum yield (up to ~31 %), a small average size (~5.4 nm) and sufficient exposed carboxyl groups. Subsequently, for the first time in the world, they are conjugated with monosaccharide moieties, galactose and mannose, respectively. Further, the GQD-sugar conjugates are employed to reveal the distribution and dynamic trafficking of carbohydrate receptors on live cells.

GQD has an excellent dispersity in aqueous solutions due to its abundant oxygen-containing groups and molecular sizes. Taking advantage of that, we for the first time demonstrate the use of GQDs and sulfonated GQDs (SGQDs) as a quasi-homogeneous catalyst for chemo-catalytic biomass conversion. Specifically, we demonstrate that GQDs can selectively and effectively degrade carbohydrates (e.g., fructose, glucose, and cellulose) into 5-hydroxymethylfurfural (5-HMF). For example, dehydration of fructose (up to 20 wt% concentration) to 5-HMF is catalyzed by SGQDs with a product yield of 51.7 % and a conversion rate of 91.8 %. The high catalytic performance is attributed to unique physicochemical and

structural properties of GQDs, i.e., they uniquely combine the merits of homogenous catalysts and heterogeneous catalysts. On one hand, highly dispersive SGQDs resemble homogenous catalysts in the reaction. On the other hand, they can be recycled for reuse like heterogeneous catalysts. The DFT calculations reveal that intra-molecular hydrogen bonded hydroxyl groups and the adjacent sulfonic groups on SGQDs play a synergistical role in their high catalytic efficiency. This study suggests the potential of SGQD as an efficient and green carbon catalyst for one-pot biomass transformation and more generally the unique potential of functionalized GQDs as novel quasi-homogeneous catalysts for various reactions.

Furthermore, we have designed two different functionalization strategies to systematically tailor the bandgap structures of GQDs whereby making them snugly suitable for particular applications. Specifically, we conjugate GQDs with poly aromatic molecules to enlarge π -conjugated sp^2 -carbon systems thus narrow the GQD bandgap by lowering the π^* orbital. We also introduce the intermediate n orbital between π and π^* orbitals by coupling GQDs with electron-donating functional groups. The functionalized GQDs with a narrow bandgap form a unique intramolecular Z-scheme structure, which consists of p-type oxygenated groups, n-type conjugates, and sp^2 ohmic contact (mediator) in between. Then, the GQDs are employed as the efficient photocatalysts for water splitting and carbon dioxide reduction under illumination of visible light. GQDs as photocatalysts have several advantages. They are made from coal, an earth-abundant and cheap material. Besides, they are very small, and their large surface area allows more exposed active sites to intimately contact with the substrates.

Chapter 1 Introduction

1.1 Background

Carbon materials, including coal, graphite, diamond, activated carbon, carbon black, carbon nanotube, et al., play a crucial role in history of humankind. The utilization of carbon materials can be traced back to antiquity, Stone Age, when antient humans used charcoal as heat sources. Recently, the new addition of graphene makes this family more prosperous and attractive. Due to its many intrinsic properties, graphene has been envisioned as a most promising carbon-based material for myriad applications in energy storage and conversion, electrochemical and photochemical catalysis, wearable and stretchable devices et al. The beginning of graphene-related research can be dated back to early twentieth century. In 1947, a pioneering Canadian theoretical physicist, P. R. Wallace, published his work in regard to the band structure of graphite.¹ In 1962, German chemists, Hanns-Peter Boehm and co-workers, discovered the individual-layered structure from the reduction of graphite oxide and found their ability to absorb gases and other small molecules.²⁻³ The production of high-quality and single-layered graphene has not been realized until 2004, when Konstantin Novoselov and Andre Geim declared their successful preparation of atomically thin graphene sheets from graphite by using a scotch tape and studied their electrical properties.⁴ This breakthrough has opened a new era and the past 15 years has witnessed an explosion in the development of materials sciences and engineering. In recognition of their immense achievement, both Novoselov and Geim were awarded Nobel Prize in Physics in 2010.

However, despite its ultra-large specific surface area ($\sim 2630 \text{ m}^2\text{g}^{-1}$), excellent electric and thermal conductivity, superior mechanical strength and chemical inertness,⁵ pristine graphene sheets are often limited in biological, biomedical and bio-photonic applications due to aggregation and their poor dispersity and in aqueous solutions.⁶ In the past decade, scientists have designed and developed new strategies to produce functional graphene-based materials by either functionalization or modification of their dimensions.⁷⁻¹² Among many of these materials, graphene quantum dots (often abbreviated as GQDs) have emerged as the latest addition to nanocarbon family and received ever-increasing attentions nowadays. GQDs are essentially zero-dimensional form of graphene. Their extremely small size, typically less than 10 nm in diameter, endows them with more intriguing properties.

Foremost, in this scale (less than 10 nm), the quantum confinement effect and edge state become significant, leading to bandgap opening.¹³⁻¹⁵ As a result, GQDs exhibit a distinctive photoluminescence (PL), in which case GQD molecule can absorb photons of certain wavelength and then emit photons of different wavelength. Molecules with PL emitting property are generally known as fluorophores. Currently, the commonly used fluorophores include fluorescent proteins, organic dyes, and inorganic semiconducting quantum dots (QDs). These commercially available fluorescent materials have widespread applications in the areas of biology, medicine, biophotonics and biosensing.¹⁶⁻¹⁸ However, they are suffering from many natural flaws. For example, fluorescent organic dyes tend to undergo photobleaching of luminescence upon continuous or repeated light exposure. Their excitation range is often narrow, making them undesired candidates in long-

term imaging uses. Fluorescent proteins are specifically expressed together with the proteins of target while their synthesis and purification require a long time and multiple procedures. Inorganic semiconducting QDs have been developed and emerged as an alternative to conventional organic dyes and fluorescent proteins. QDs have been employed for applications in optoelectronics and microelectronic devices, while lately they have attracted more interests in the biological and biomedical fields. They have inherent advantages over organic dyes and fluorescent proteins, such as resistance to photobleaching, high quantum yield, complex surface chemistry and tunability in both excitation and emission wavelengths. However, they also raise concerns because most of the QDs consist of heavy metal elements, like cadmium, which are toxic to organisms and environment. GQDs, however, show clear advantages over above counterparts. Just like QDs, they are resistant to photobleaching, chemically stable, small in sizes and tunable in PL properties. Additionally, they have many functional groups on edges and basal plane, making them easier to be tailored or functionalized. Most importantly, they are genetically safe on account of their carbon-based nature.

Structural and chemical properties of GQDs also promise a wide spectrum of novel applications in photo/electro/chemical catalysis. GQDs have a large surface area and excellent dispersity, and through practices like heteroatoms doping, GQDs suggest more active sites than conventional catalysts.

Currently, although the enormous potentials have been increasingly demonstrated in numerous studies, the field of GQDs is still full of vitality and abundant opportunities. This thesis attempts to contribute to the expanding filed of

GQDs by optimizing the synthesis methods to avoid tedious procedures and expensive equipment and developing new strategies for functionalization, bandgap engineering and property control, eventually making GQD a competent candidate for a variety of applications in bioimaging, biosensing, chemical conversion, photochemical and electrochemical catalysis.

1.2 Objectives

Owing to their intriguing properties and unique advantages over traditional functional materials, GQDs have sparked significant excitement as a new class of nano-carbon materials. However, their potentials in different fields have not been fully derived as it is riddled with challenges to fully understand and exploit this material. At present, open debates are still existing among the scientists around the world when it comes to identifying the PL origins of GQDs. Besides, new synthetic methods are required to be created to precisely control the properties of GQDs, such as ultra-high quantum yield, red/infrared emission, uniform sizes and morphologies. These challenges still hinder the widespread use of GQDs. Therefore, it is of extreme importance to continue ongoing research to harness the potentials of GQDs in applications such as bioimaging, photoluminescent sensing, photoelectrochemical and chemical catalysis. Keeping in mind this thesis will extensively focus on the modification of synthetic methods, functionalization and bandgap engineering of GQDs and their novel application in the fields of selective intracellular imaging, photoluminescent sensing and exploration of acidic catalysis and electrochemical catalysis.

The specific objectives of this thesis are:

1. To develop, optimize and modify the synthesis routes for GQDs. The as-synthesized GQDs shall possess desired properties such as specific functional groups and high quantum yield for specific applications.
2. Synthesis and surface modification of GQDs aiming to render specificity towards selective cellular imaging and target molecular fluorescent sensing.
3. To explore the use of GQDs in chemical catalysis. The large surface areas and fully exposed functional groups of GQDs allow abundant active sites and intimate contact with substrates. A much higher catalytic performance is highly anticipated compared to conventional heterogeneous catalysts.
4. Systematic bandgap engineering to narrow down the bandgap of GQDs through different strategies. Narrow bandgap alters light absorption properties of GQDs, which could be further explored as photo-excited catalysts.

1.3 Outline of this dissertation

Chapter 1 of this dissertation highlights the history of GQD and the urgent need for an alternative fluorophore which combines merits of currently available ones while minimizes their drawbacks. The aims of this thesis and outline of the dissertation will also be described.

Chapter 2 reviews the current development of the nanocarbon material, GQD. Two main synthetic routes will be firstly summarized, followed by their structural,

chemical and physical properties. Their applications in biomedical area, catalysis and energy conversion/storage will be highlighted.

In chapter 3, a new optimized and modified synthesis approach is addressed. The as-prepared GQD has a high quantum yield and further been functionalized with sugar moieties for specific labeling of cancer cells and real-time tracking of receptors on the cellular membrane.

GQDs possess large surface areas and through post-synthesis treatment, specific functional groups can be attached to GQD edges/surfaces. We use sulfonated carbon black derived GQD as our model material and demonstrate its use in biomass conversion to value-added products. Experimental results and theoretical calculations both prove its high performance, which is comparable to some homogeneous catalysts. Most importantly, they can be recycled for reuse. This part is highlighted in chapter 4.

In chapter 5, two strategies are proposed and applied for the narrowing of GQD bandgap. One strategy is to conjugate GQDs with poly aromatic moieties to enlarge π conjugated sp^2 -carbon systems (by lowering of π^* orbital). The other is to introduce the intermediate n orbital between π and π^* orbitals after conjugation with some electron-donating functional groups. The resulting GQDs are further explored as photocatalysts for the water splitting and carbon dioxide reduction reactions.

Chapter 6 summarizes the general conclusions from the above chapters that contribute to the thesis. It also discusses several open challenges for GQD and provides an outlook on the GQD utilization in the future.

Chapter 2 Literature Review

It is indisputable that deep understanding the current research progress of GQDs' preparation, modification, physiochemical properties and a plethora of applications is of great significance for advancing the further exploration of this zero-dimensional materials. In this chapter, the synthesis approaches of GQDs will be firstly introduced and discussed, followed by the summary of surface/edge functionalization, heteroatom doping and property regulation of GQDs. Lastly, recent progresses and advances of applications in biological and biomedical fields as well as chemistry and physics will also be described and discussed.

2.1 Synthesis

The synthetic strategies are normally classified into two categories based on the types of precursor materials, namely “top-down” and “bottom-up” methods. The former involves cutting/cleaving/exfoliation/oxidation of bulk or larger carbonaceous precursors. The latter is usually realized through the pyrolysis/fusion/carbonization of small molecular chemicals.¹⁹

2.1.1 Top-down methods

Acidic oxidation is the most commonly used way to synthesize GQDs from cheap and bulky graphitized carbon materials such as coal,²⁰ graphite,²¹⁻²² carbon black,²³ carbon fiber,¹⁴ graphene,⁷ graphene oxide (GO).²⁴ It is worth mentioning that GQDs prepared from graphene oxide are sometimes called graphene oxide QD (GOQD) or reduced graphene oxide QD. We here call them GQDs to avoid misunderstanding.

Figure 2-1. Top-down synthesis methods for GQDs from (a) coal, (b) graphene oxide, and (c) graphite. (a) Reproduced with permission.²⁰ Copyright 2013, Springer Nature. (b) Reproduced with permission.²⁵ Copyright 2013, The Royal Society of Chemistry. (c) Reproduced with permission.²⁶ Copyright 2016 Wiley-VCH.

Among all the starting materials, coal is the most widely used owing to its availability and low price. It was firstly reported by Ruquan Ye et al.²⁰ In their study, concentrated sulfuric acid and nitric acid (3:1 volume ratio) were mixed and used as oxidant and cutting agent (Figure 2-1a). Since coals have many tiny graphitic subdomains which are linked by amorphous carbon, they can be easily cleaved by the mixed acids and thus coal derived GQDs can be obtained. Nonetheless, the most challenging part is the post-preparation procedures because of the acidic wastes,

especially sulfuric acid. Similarly, mixture of acids was also utilized by Zhiming Luo et al. to exfoliate graphite.²² To assist exfoliation and cutting, they also applied microwave and sonication treatment. In practice, nitric acid alone is also able to serve as cutting oxidant. Carbon black is a cheap paracrystalline carbon material and can be easily cut into GQDs only by 6 M nitric acid solution. It is noteworthy that the scale-up of GQDs production is now a hot topic in the industry and the cheap coal and carbon black are more likely to accomplish this goal than any other carbon materials. Besides strong acids, other oxidants, like hydrogen peroxide^{25, 27} and oxone,²⁸ have also been reported to prepare GQDs (Figure 2-1b). These oxidants are more environmentally friendly than strong acids. GQDs from acidic or other oxidant cutting are inevitably bear oxygenated groups on the surfaces and edges, such as hydroxyl, carboxyl, and epoxy groups. The introduced oxygen content contributes a lot to GQDs' excellent dispersity in aqueous. The amount/ratio of oxygen element varies in different GQDs mostly based on the oxidants used.

On the other hand, reductive agents are also applied to synthesize GQDs. The commonly seen agents include ammonia,²⁹⁻³⁰ hydrazine hydrate,³¹⁻³² dimethylformamide (DMF),³³ and primary amines³⁴ et al. The cleavage mechanism relies on the breaking down of epoxy group (C-O) by as-mentioned reductive agents.^{33, 35} Generally speaking, during reductive cutting, the nitrogen groups will be introduced yet the amount of oxygenated groups will be compromised. The cutting and cleavage efficiency of the process depends on the reductive agents and the abundance of the epoxy groups in the sample. It is worth noting that the supercritical water was reported to be used for the preparation of GQDs from a hydrothermal

treatment of graphene oxide.³⁶ This approach is completely green and produces no hazardous waste. The production yield of GQDs, however, is unclarified.

Alternatively, electrochemical cutting is another common way to produce GQDs. Graphene,³⁷⁻³⁸ graphene paper,³⁹ graphite,⁴⁰⁻⁴² carbon nanotubes,⁴³ and coke⁴⁴ have been reported to be electrochemically cut into GQDs. Compared with the above oxidative cleavage, the electrochemical cutting usually has a relatively high production yield and more uniform size distribution.⁴⁵ In some studies,^{39, 43} organic solvent and/or alkaline/acidic solution was used as electrolyte and thus their proper disposal could be a major concern.

In addition to the chemical exfoliation/cleavage, physical grinding and/or ultrasonication are also two possible routes to produce GQDs. In a typical experiment, Hyewon Yoon et al. has reported a GQD synthesis method using sonication as cutting force.²⁶ They firstly mixed potassium sodium tartrate tetrahydrate powder with graphite and harshly grinded the mixture, followed by heat treatment at 250 °C when the intercalation salts entered graphite layers. Subsequently, ultrasonication was applied and the graphite was broken down to small GQDs (Figure 2-1c). GQDs from physical methods are of low abundance of functional chemical groups and surface defects compared to those from chemical routes.

2.1.2 Bottom-up methods

The bottom-up method is the other way to synthesize GQDs. Bottom-up approach has several advantages over top-down method, for example, a much higher production yield, more uniform GQD sizes and easier control of property. Based on

the types of bottom-up pathways and precursors, they can be further classified into several categories, stepwise wet-chemistry molecular synthesis, molecular carbonization/pyrolysis and opening of other nanocarbon materials respectively.

Figure 2-2. Bottom-up synthesis methods for GQDs from (a) Hexa-*peri*-hexabenzocoronene (HBC), (b) glucose and (c) citric acid. (a) Reproduced with permission.⁴⁶ Copyright 2011, American Chemical Society. (b) Reproduced with permission.⁴⁷ Copyright 2013, Wiley-VCH. (c) Reproduced with permission.⁴⁸ Copyright 2012, Elsevier.

Synthesis of GQDs through a wet-chemistry fusion approach is firstly demonstrated by Müllen's group.^{46, 49} They obtained mono-dispersed fluorescent GQDs of ~60 nm in diameter and 2~3 nm in thickness based on a combined processes of carbonization, oxidization, surface functionalization, and reduction of hexa-*peri*-hexabenzocoronene (Figure 2-2a). Yan et al. have proposed a stepwise organic synthesis of large colloidal GQDs with uniform and tunable sizes through a wet-chemistry pathway by using small-molecule precursors such as 3-iodo-4-bromoaniline.⁵⁰ The as-prepared GQDs contain 168, 132 and 170 conjugated carbon

atoms, respectively. The advantages of this method are the high production yield and precise control of size and compositions. However, like a coin has two side, GQDs from this method also tend to re-stack and aggregate in various solutions due to the low abundance of oxygenated groups and consequent π - π attraction between graphene layers. Therefore, attempts to maintain a good dispersity in solvents especially in water come along with the synthesis routes. This could be realized during or after synthesis processes. In a typical study, Xin Yan et al. have reported to covalently attach 1,3,5-trialkyl-substituted phenyl moieties to the edges of the GQDs in order to increase distance between particles, reduced the attraction force and thus significantly prevent aggregation.⁵¹

More recently, GQD synthesis under hydrothermal or solvothermal conditions is now becoming popular because it is quick, less tedious and easy to introduce heteroatoms. Lau group has reported a microwave-assisted hydrothermal method to synthesize GQDs (Figure 2-2b).⁴⁷ The relationship between quantum yields and the GQD sizes has been systematically studied and negative correlation was deduced. Wang Liang et al. have demonstrated a gram-scale synthetic route for the GQDs using a hydrothermal treatment.⁵² They firstly prepared 1,3,6-trinitropyrene from nitration of pyrene molecules and subsequently added different alkaline solutions of sodium hydroxide, ammonia or hydrazine hydrate. Then, the GQD solutions were simply prepared by hydrothermal treatment of the mixture. This is a promising strategy to scale-up the production and the resultant GQDs have different groups and heteroatomic groups when different alkaline solutions were used.

Pyrolysis or carbonization of small chemical molecules is the other frequently reported method for the GQD preparation. The formation of GQD relies on the melting of starting materials under thermal treatment and then condensation or nucleation, leading to the GQD formation. The precursors are usually small molecules, for example, citric acid^{48, 53} and L-glutamic acid.⁵⁴ By changing the carbonization time of citric acid, Yongqiang Dong has prepared GQDs and even graphene oxide which contain numerous tiny sp^2 -hybridized carbon (Figure 2-2c).⁴⁸

GQDs from the cage-opening of fullerene was demonstrated by Loh's group in 2011.⁵⁵ They used C_{60} molecules as a precursor and ruthenium (Ru) as the substrate. In the synthesis process, the strong attraction between C_{60} molecules and Ru surface led to surface vacancies in the Ru single crystal and subsequently, the fullerene molecules were embedded into the vacancies. When a high temperature was applied, a process of fragmentation, diffusion and aggregation occurred and thus a GQD molecule is formed. The shape and size of GQD can be readily modulated by changing the annealing temperature and the density of carbon clusters. This templated growth of GQDs on Ru surface is a new guide light for the development of nanoelectronics or other relevant fields.

2.2 Properties

2.2.1 Structural property and elemental component

GQDs are typically nanometer-sized crystals consisting of single to a-few layers of sp^2 hybridized graphene sheet (Figure 2-3a).⁵⁶ They are usually single-atom-thick and a few nanometers in diameter, though larger size (up to 60 nm) has been reported.⁴⁶ The shape of GQDs is either circular or elliptical, though other

shapes such as triangle, quadrangle and hexagon were reported.⁵⁵ The height of GQDs does not have a specific relationship to their size, while mostly depends on the synthetic methods. The reported heights are usually less than 3 nm (Figure 2-3b), though thicker GQD has been reported.⁵⁷⁻⁵⁸ Accordingly, most of the as-reported GQDs are composed of 1~5 layers of graphitic sheets.

The crystalline properties of GQDs can be revealed by high-resolution transmission electron microscopy (HRTEM), X-ray powder diffraction (XRD) and Raman spectroscopy. By HRTEM, the lattice structure of GQDs can be visualized (Figure 2-3c).⁵⁹ The in-plane lattice spacing is measured to be between 0.18 and 0.24 nm, corresponding to (1 0 0) lattice fringe.^{19, 60-61} XRD is an equipment which can reflect the interlayer spacing of GQDs. The commonly reported value is 0.334 nm (or greater when more functional groups are present). From Raman spectroscopy measurement, graphitic peak of GQDs located at $\sim 1580\text{ cm}^{-1}$ can be viewed and the value of I_D/I_G ratio depends on the synthetic routes and functionalization.

Figure 2-3. (a) A depiction of GQD, (b) the thickness of GQD characterized by atomic force microscopy (AFM), (c) the lattice structure characterized by high-resolution transmission

electron microscopy (HRTEM). (a) Reproduced with permission.⁵⁶ Copyright 2012, The Royal Society of Chemistry. (b) Reproduced with permission.⁶² Copyright 2013, American Chemical Society. (c) Reproduced with permission.⁵⁹ Copyright 2012, American Chemical Society.

It may be difficult for people to distinguish GQDs and another 0-D material, carbon dots (CDs). Typically, CDs are spherical or quasi-spherical nanoparticles with a size less than 10 nm.⁶³ Some of CDs are consisting of amorphous sp^3 hybridized carbon atoms while some partially have a crystalline graphitic structure. The lattice, sometimes, is not easy to be seen by HRTEM due to the presence of amorphous sp^3 hybridized carbons.⁶⁴

Theoretically speaking, GQDs are just like graphene, only composed of carbon and hydrogen elements. While in fact, due to the aggregation tendency (attribute to π - π stacking) and synthetic methods (such as oxidization, hydrothermal cutting), GQDs always possess oxygenated groups.⁶⁰ These oxygen groups generally refer to carbonyl, hydroxyl, epoxy/ether groups which are present on the surface and/or edges of GQDs. To identify these elements, X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR) are two commonly adopted techniques. The atomic ratio of C/O varies with different GQDs. For example, GQDs from a top-down hydrothermal treatment has an O/C ration of 66.23%;⁶⁵ the O/C ratio reached up to 1.31 through a nitric acid exfoliation method.²³ Apart from carbon and oxygen, heteroatoms, such as nitrogen,^{13, 33, 65} boron,⁶⁶⁻⁶⁸ sulfur,⁶⁹⁻⁷² fluorine⁷³ and selenium⁷⁴ elements are also commonly doped into GQDs. Their content is usually small, less than 10% in atomic.

2.2.2 Light absorbance

GQDs exhibit light-harvesting property especially in short wavelengths such as ultra-violet (UV) region. Because of the π - π^* transition of sp^2 hybridized C=C bonds, GQDs show a predominant absorption peak between 230 and 260 nm, along with a long tail extending into the visible range (Figure 2-4).^{14, 60-61} There is a noteworthy shoulder at ~285 nm which is assigned to the n - π^* transition of C=O bonds.⁷⁵ The absorption feature of GQDs is largely determined by factors such as preparation method, oxygen content, surface functionalization et al.^{19, 60}

Figure 2-4. UV-vis spectra of GQDs A, B, and C, from different reaction temperature at 120, 100 and 80°C. Insert is the digital photos of GQDs under a UV lamp. Reproduced with permission.¹⁴ Copyright 2012, American Chemical Society.

2.2.3 Photoluminescence

One of the most distinguished and alluring features of GQDs is their photoluminescence (PL) (Figure 2-4 insert). During last decade, various GQDs have been synthesized *via* different routes and reported with different emission colors, ranging from ultraviolet (UV)⁵⁷ to red region.⁷⁶ Further, GQDs also show a unique excitation-dependent emission, that is, emission peak position shifts along with

excitation wavelength. Generally, the emission spectra of GQD are quite broad due to the poor control of GQD sizes and morphologies.¹⁹

PL mechanism

Understanding the fundamental PL mechanism of GQDs is still an open challenge, and a definite and convincing conclusion has not been drawn yet. The main reason is that PL of GQDs is affected by a great many factors, ranging from physical morphologies (size, height, zigzag/armchair edge, defects) to chemical components (oxidization degree, heteroatom doping). While experiments which can precisely control the above factors have not been demonstrated yet. For example, the PL emission peak of GQDs does not shift monotonously with their sizes.⁵⁹ Therefore, a controllable synthesis of GQDs of desired properties is the key to unveil the underlying PL mechanism. Nevertheless, efforts by theoretical modelling and calculations have been devoted to study the correlation between PL and properties of GQDs. Mahasin Alam Sk and his co-workers, for the first time, investigated the PL of GQDs by use of density-functional theory (DFT) and time-dependent DFT (TDDFT).⁷⁷ They have confirmed that the PL of GQDs originates from the embedded small sp^2 carbon clusters and can be modulated through changes of size, shape, surface defects, doped heteroatoms and functionalized groups. Further, Jin et al. have functionalized GQDs with amino groups and by using DFT, they revealed the bandgap tuning mechanism and the existence of charge transfer between GQD molecule and functional groups.³¹ In recent years, scientists around the world have proposed and summarized many of the PL origins. Currently, the widely accepted opinion is that PL arises mainly from quantum confinement effect,^{38, 78} which related

to sizes of π -conjugated domain of GQDs which is smaller than Bohr radius. Aside from this, other opinions such as recombination of localized electron-hole (e-h) pairs in localized electronic states,⁷⁹⁻⁸⁰ edge/surface state,^{7, 14, 61} defect effect (energy traps)^{24, 78, 81} have also been proposed by many scientists. Shoujun Zhu and Bai Yang et al. have summarized and stated that the PL of GQDs comes from two origins: the intrinsic state and defect state.⁸² The former mainly refers to quantum confinement effect of π -conjugated domains in GQDs and latter usually includes surface/edge states and defect states.⁸³ Though many of the above hypotheses have been proven by experiments, efforts are still in urgent demand for systematic clarification of the ambiguous GQD PL mechanism.

Bandgap engineering

GQDs feature tunable PL properties mostly owing to their alterable bandgap attributed to the pronounced quantum confinement effect and edge states. Bandgap engineering can be realized through control of size/shape, oxidative degree, surface functional groups and heteroatom doping. As depicted by Mahasin Alam Sk et al., the emitted color (corresponding to the bandgap) of GQDs is largely determined by its size and shape.⁷⁷ Experimentally, size control during top-down synthesis is not easy to be realized, but mostly relies on experience, or expensive and advanced equipment.^{15, 46} Normally, for same preparation method, i.e. oxidative cutting, higher concentration of oxidant, longer treatment time and higher temperature (if necessary) can result in a small size. As for post-synthesis treatment, size-dependent separation is widely used to filter out GQDs with desired sizes. Dong et al. synthesized GQDs from one-pot acidic cutting of carbon black and *via* centrifuge, GQDs with two

average sizes (15 and 18 nm respectively) have been successfully prepared.²³ On the contrary, bottom-up approaches are more reliable in size and shape control. Liu et al. demonstrated that the size, shape and morphologies of GQDs can be precisely controlled by using a stepwise bottom-up approach using different aromatic molecules as precursors.⁴⁶ Secondly, tuning oxidative degree can also alter the PL properties (PL emission color and quantum yield). Oxidation degree of GQDs usually indicates the condition of localized sp^2 carbon clusters and surface defects, which closely related to their PL properties.^{60, 84-85} Zhu et al. have synthesized different GQDs with different oxidative states and found that with a lower degree of oxidation, the emission spectra of GQDs exhibit blue shifting and narrower full width at half maximum (FWHM).⁸⁴ Min-Ho Jang et al. performed an in-depth study, demonstrating how optical properties including the bandgap of GQDs are affected by content of oxygen groups.⁸⁵ Variation of oxidation degree is a factor which determines the brightness of GQDs (QY), usually lower oxidative degree implying higher brightness. This part will be further discussed in the below section. Additionally, bandgap alteration can also be modulated by surface modification of GQDs. This is because chemical groups with either electron-donating or electron-accepting properties could impact the electronic characteristics of GQDs.^{45, 60} It has been reported by Zhu et al. that by programmable modification using alkylamines, the PL peak of GQDs shifted from 516 nm (green) to 446 nm (blue), indicating a change in bandgap.⁸² Yan et al. have systematically conjugated GQDs with a series of aromatic moieties and as a result, their bandgaps varied from 1.88 eV to 2.40 eV.⁸⁶ Similarly, Hiroyuki Tetsuka et al. fabricated molecularly designed GQDs with

different energy levels and gaps by convenient attaching of functional groups.⁸⁷ The mechanism relies on the effective orbital resonance of chemical moieties and GQD highest occupied and lowest unoccupied molecular orbitals (HOMO and LOMO). Doping GQDs with heteroatoms can effectively tune the electronic properties. It has been widely reported that nitrogen doping on GQDs causes blue shift on PL spectra because of the electron-withdrawing nature of nitrogen atoms.^{13, 77, 88-90} Tam et al. synthesized a nitrogen doped GQDs (N-GQDs) from a facile bottom-up approach.⁸⁹ Compared with the non-doped GQDs, they have a similar diameter and height, while the PL intensity increased a lot on N-GQDs and a clear blue shift in the PL spectra was observed. The authors attributed these observations to the change of electronic characteristic due to the introducing of N atoms. Mondal et al. fabricated nitrogen and sulfur co-doped GQDs (N, S-GQDs) and PL emission blue shifted a lot, even more than N-GQDs and S-GQDs, probably attributed to a larger number of localized energy levels produced near conduction band.⁹¹

Quantum yield

Quantum yield (QY) is an important parameter for fluorophores, especially when they are used for sensitive detection or bioimaging. It indicates how efficient a luminescent material can emit light upon absorption of photons. It, by definition, is the ratio of the number of photons emitted to the total number of photons absorbed,⁹² as described below.

$$\text{Quantum Yield } (\varphi) = \frac{n \text{ (number of photons emitted)}}{n \text{ (number of photons absorbed)}} \times 100\%$$

Quantum yield can be directly measured by a fluorescence microscopy equipped with an integrating sphere. Alternatively, relative measurement is also commonly reported in which a fluorophore of known quantum yield (such as quinine sulfate,^{46, 93-94} rhodamine B^{67, 95}) is used as reference.

Quantum yield of GQDs varies significantly and is dependent on many factors such as precursors, synthetic methods and surface chemistry & defects et al. Untreated and undoped GQDs normally have a relatively low quantum yield (< 15% in most cases⁵²). GQDs with more oxygenated groups (e.g. carboxyl, epoxy) which can be non-radioactive electron-hole recombination centers usually have a lower quantum yield.⁷⁹ Therefore, the removal of these groups can reduce the non-radioactive relaxation of excited electrons, resulting in a higher quantum yield. This can be realized either by reduction⁹⁶⁻⁹⁸ or by surface passivation^{81, 99}. For example, Zhang et al. prepared GQDs from oxidative cutting of carbon fibers, followed by reduction using concentrated NaBH₄ solutions to obtain reduced GQDs (rGQDs), and PL quantum yield of GQDs increased more than three times, from 2.6% to 10.1%.⁹⁸ Shen and Li et al. passivated GO derived GQDs with polyethylene glycol (GQDs-PEG), consequently increasing their PL QY from 13.1% to 28%.⁸¹ In addition, heteroatom dopant can alter the electronic characteristics of GQDs thus change the PL QY. Jian Ju and Wei Chen have fabricated nitrogen-doped GQDs (N-GQDs) and the quantum yield of such GQD is much higher than that of undoped ones (4.8 % vs 23.3 %).⁸⁸ All the studies suggest that QY of GQDs can be tuned in order to meet requirements for various applications.

Stability

As mentioned in the first chapter, over traditional organic or inorganic fluorophores, the primary advantage of GQD is its outstanding photostability. Zhu et al. have demonstrated that the fluorescent intensity of GQDs prepared by using a one-step solvothermal route showed no distinct decrease under the illumination of UV lamp or mercury lamp (with low power).⁷⁸ Wu and co-workers have compared photostability between GQDs and an organic fluorophore, Fluorescein isothiocyanate (FITC), and the result manifested the PL of GQDs remained 53% of the original intensity under the illumination of confocal laser for 18 min. However, for FITC, the fluorescence completely bleached after just 2 min's exposure of the same laser (Figure 2-5).⁵⁴ The excellent photostability of GQDs permits long-term and continuous real-time imaging.

Figure 2-5. The photostability of two fluorescent materials, GQD and Fluorescein isothiocyanate (FITC). Reproduced with permission.⁵⁴ Copyright 2013, The Royal Society of Chemistry.

2.2.4 Up-conversion photoluminescence

Up conversion of photon is a process where a fluorophore emits photons at shorter wavelength upon sequential absorption of more photons at a longer wavelength. It has been widely reported that GQDs exhibit PL up-conversion property at a much higher efficiency than conventional fluorophores.^{54, 82, 100} The photoluminescent property discussed in the above section is actually down-conversion PL. Generally, down-conversion PL is not desired for *in vivo* bioimaging because the excitation wavelength is shorter, normally in UV or visible range and cannot efficiently penetrate the animal tissues. While on the other hand, excitation wavelength for up-conversion PL usually locates at near infrared (NIR) region, and NIR light has an excellent penetration ability through deep tissues. This distinct property of GQDs allows high spatial resolution bioimaging with low background noise and low photon-induced toxicity.¹⁹

Qian Liu et al. have reported nitrogen-doped GQDs (N-GQDs) prepared from a solvothermal route as biocompatible two-photon PL probes.³³ The two-photon absorption is the absorption of two low-energy photons to excite a molecule from a lower energy level to a higher one. As reported by Liu, the two-photon cross section of N-GQDs reached up to 48,000 GM, which is two orders of magnitude higher than that of organic dyes. They also reported that the GQDs can achieve a PL imaging depth of 1.8 cm, which was the world record of fundamental imaging depth limit by two-photon microscopy, demonstrating their great potential in both cellular and deep-tissue imaging applications. Besides, up-conversion PL arisen from multi-phonon active process has also been widely reported.^{84, 101} In this case, more than

two photons are absorbed simultaneously. Shen and co-workers, however, believed that multi-photon active process is not enough to explain the upconverted PL behavior of GQDs.⁹⁵ They speculated that the upconverted PL of GQDs is more like the anti-Stokes photoluminescence (ASPL). When several photons are absorbed and excite the electrons from π -orbital to a higher energy level, and subsequently the excited electrons transition back from the higher energy level to a much lower energy level (which is even lower than π -orbital), such as σ -orbital, thus the upconverted PL occurs (Figure 2-6a and b). Their theory was illustrated by an established energy level structural model and explained the reason why there is a constant energy gap between up-conversion excitation and emission wavelength. Contrary to the common sense, Wen et al. have proposed that the up-conversion PL property of GQDs and carbon nanodots (CNDs) is not actually existing based on their observation of five different kinds of CNDs and GQDs.¹⁰² They claimed the observed upconverted PL is essentially the normal down-conversion PL, which is excited by the leaking part of the second diffraction in the monochromator of the photoluminescence spectrometer. Therefore, regarding the up-conversion PL, careful experimental practices and cautious observation is very important.

Figure 2-6. (a) PL spectrum excited at 980 nm laser. Inset: photograph of the GQD aqueous solution taken under a 980 nm laser, (b) A schematic illustration of various typical electronic transitions processes of GQDs, (c) PL ($\lambda_{\text{ex}} = 340 \text{ nm}$) and ECL spectra for the GQDs, (d) an illustration of the ECL mechanism of GQDs. (a) and (b) Reproduced with permission.⁹⁵ Copyright 2011, The Royal Society of Chemistry. (c) and (d) Reproduced with permission.⁹⁶ Copyright 2012, Wiley-VCH.

2.2.5 Electrochemiluminescence

Electrochemiluminescence (ECL), also known as electrogenerated chemiluminescence, is a process in which luminescence is produced during the electrochemical reactions in solutions. Electrons are excited during a highly exergonic reaction and finally generate luminescence upon relaxation to lower energy states. GQDs have been reported to exhibit ECL properties by a great number of studies.^{96, 103-107} Compared with other ECL fluorophores, they have a more stable ECL intensity and their onset potential is closer to 0 V.¹⁹ This unique property of

GQDs have been frequently explored for sensing applications because they have many merits including a high sensitivity, excellent selectivity and wide detection range.⁶⁰ For example, Li et al. have prepared two-color ECL GQDs from a microwave-assisted route using graphene oxide (GO) as starting materials.⁹⁶ The quantum yield of as-synthesized greenish yellow PL GQD reached 11.9 % and further increased up to 22.9 % upon reduction by sodium borohydride (NaBH₄) at room temperature. The ECL behavior of such GQDs were observed and its underlying mechanism was discussed by the authors (Figure 2-6c and d). Briefly, electrochemical reduction of GQD molecules and S₂O₈²⁻ electrolytes produces GQD^{•-} and SO₄^{•-} radicals. Shortly after, GQD^{•-} and SO₄^{•-} radicals could react with each other *via* an electron transfer annihilation pathway, producing a higher energy state (denoted as GQD*) and thus emitting luminescence *via* relaxation.⁹⁶ Based on their ECL property, Li developed a sensing platform for detection of cadmium (II) ions. Recently, Zhang et al. proposed an ECL-based biosensor based on electrochemiluminescent GQDs.¹⁰⁶ They have demonstrated the high performance of realized ECL sensor for targeted miRNA with a linear detection range of 2.5 fM to 50 pM and an extremely low limit of 0.83 fM.

2.2.6 Electrochemical properties

The electrochemical property (especially charge transfer ability) of GQDs depends on a complex interaction between multiple intrinsic properties of GQDs, such as elemental composition (oxygen groups and heteroatoms), the crystalline structure, number of GQD layers et al. Benefiting from their large surface area and sp² hybridized carbon core, GQDs could serve as efficient charge transfer carriers.¹⁹

Besides, their molecular size can help to trap single electron in the quantum well between GQD and surface coating.¹⁰⁸ When a large amount of O-containing groups are present on the GQDs, the electrochemical property will be impaired due to the disruption of conductive π -conjugated carbon networks, which is similar to that of GO or reduced GO (rGO). However, the edge oxygenated groups could endow GQDs with catalytic activity towards substrates like hydrogen peroxide (H_2O_2). Zhang et al. have developed a GQD/gold (Au)-based electrode for high-performance and stable sensing of H_2O_2 , which is better or comparable to other enzyme-immobilized electrodes.¹⁰⁹ Doped heteroatoms (e.g. nitrogen, boron, sulfur) can also alter electrochemical characteristics of GQDs. Many studies have demonstrated enhanced electrochemical catalytic activity by introduction of heteroatoms.^{13, 110-112}

2.2.7 Biocompatibility

Owing to their superior properties and unique advantages over traditional fluorophores, GQDs shown immense potentials for bioimaging, biosensing and other biomedical applications. Therefore, their toxicity to cells and organisms is a natural concern.⁶⁰ Carbon is fundamental constitutional element so GQDs should be safer than any other nanomaterials which contain metal elements. However, their polyaromatic structure raises concerns as some small aromatic molecules are very toxic, i.e. benzene,¹¹³ naphthol.¹¹³ Toxic evaluation studies have been reported by many researchers using a plethora of GQDs, revealing that they appear to be insignificantly toxic.^{14, 23, 42, 52, 65, 75, 78, 82, 114-115} Peng et al. have prepared GQDs from carbon fiber and tested their cytotoxicity against human breast cancer cell lines, MDA-MB-231 and T47D respectively, using a 3-(4,5-dimethylthiazol-2-yl)-2,5-

diphenyltetrazolium bromide (MTT) assay. Results indicated that a low dose of GQDs at 50 $\mu\text{g}/\text{mM}$ negligibly affects cell viability compared to controlled groups.¹⁴ Zhu and co-workers added up to 400 μg of GQDs into 150 μL cell culture medium while the MG-63 cells (human osteosarcoma) showed no significant loss of viability.⁷⁸ Another study conducted by Wang et al. evaluated the cytotoxicity of GQDs from pyrene *via* a bottom-up synthesis approach, revealing that under 100 mg/L concentration against a mouse breast cancer cell line (4T1 cells), GQDs did not exhibit a significant toxicity after incubated with cells for 48 hours.⁵² A more detailed research was investigated by Zhang et al., demonstrating that GQDs can penetrate into stem cells directly and readily without compromising cell viability, proliferation and differentiation.⁴² Similarly, Shang and co-workers further proved cellular metabolic activity and self-renewal ability would not be affected a lot after incubation with GQDs at 250 $\mu\text{g}/\text{mL}$.¹¹⁴

In vivo toxicity of GQDs were investigated by Md Nurunnab et al. They fabricated carboxylate GQDs and performed toxicology studies on mice. Results revealed no appreciable toxicity from such GQDs to the treated mice and no obvious blood or organ damage after 21 days of administration of GQDs at 10 mg/kg .¹¹⁶ Specifically, Kim et al. have evaluated the hepatotoxicity of GQDs. No significant change in aspartate aminotransferase (AST), alanine aminotransferase (ALT), and bilirubin levels in serum were observed after 48 hours, indicating a good biocompatibility of GQDs and feasibility as cell tracking agents in *in vivo* applications.¹¹⁷

All the studies suggest an excellent biocompatibility and great potentials of GQDs for biological and biomedical applications either *in vitro* or *in vivo*. One noteworthy point is biocompatibility may be different for different GQDs. Careful experiments need to be performed before clinical uses.

2.3 Applications

2.3.1 Biomedical applications

It is not surprising that biocompatible GQDs are widely used for a variety of biomedical applications, including cellular and *in vivo* imaging, photoluminescence/electrochemiluminescence sensing, photothermal and dynamic therapies et al. This section will summarize and discuss the typical and latest applications in biomedical fields.

Imaging

As stated above, traditional and commercially available organic fluorophores or luminescent proteins are not desirable for long-term imaging or tracking as they tend to undergo photobleaching over continuous illumination. Alternatively, inorganic quantum dots are designed to overcome this problem while they are generally bigger than molecular size thus, they would change target dynamics or characteristics and cause artificial clusters.⁴⁵ Meanwhile, most of them contain heavy metals which could raise safety concerns. GQDs, on the contrary, have the potential to tackle above issues because they offer numerous key merits for bioimaging applications. They are molecularly small, easy to be chemically modified and internalized by cells. Most importantly, they have a tunable and stable PL property.

The successful PL tracking of small biomolecules in live cells was firstly demonstrated by Zheng et al. in 2013.⁶² They synthesized carboxyl-rich GQDs and subsequently functionalized them with insulin. The insulin conjugated GQDs can serve as specific labels for dynamic tracking of corresponding receptors in live 3T3-L1 adipocytes (Figure 2-7a).⁶² They are the first team to visually unveil the internalization and recycling of insulin receptors and they have demonstrated the feasibility of use of GQDs as universal fluorophores. Since then, GQDs labeled with specific molecule for target and long-term imaging have been further developed and some are of importance to be highlighted here. Recently, Li et al. functionalized GQDs with a chelated redox $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple which is sensitive to the redox environment and they utilize this platform to monitor the dynamic change of intracellular redox condition with a quick response and high sensitivity (Figure 2-7b).¹¹⁸ Later, a GQDs-based PL probe was devised by the same group for live imaging of trace H_2S triggered by stimuli in a breast cancer cell line (MCF-7).¹¹⁹ Similar to the previous work, the fluorescence on and off probe relies on the charge transfer between GQD molecule and target molecule. Another noteworthy advantage of the GQD-based real-time monitoring probe is its reversibility, in which the charge transfer between functionalized molecule and GQD could be induced and cleaved in the presence or absence of target molecules, without significant loss of fluorescent intensity.

Figure 2-7. (a) Tracking the dynamics of insulin receptors in living adipocytes using GQD. Reproduced with permission.⁶² Copyright 2013, American Chemical Society. (b) Dynamic monitoring of redox state in live HeLa cells using a GQD-DFOB-Fe³⁺/Fe²⁺ probe. Reproduced with permission.¹¹⁸ Copyright 2016, American Chemical Society. (c) Bright field (left) and visible light excitation (Ex/Em = 465/620 nm) (right) images on mice with saline (left mouse) and GQD injection (right mouse). Reproduced with permission.¹²⁰ Copyright 2015, The Royal Society of Chemistry. (d) In vivo MRI of mice receiving boron doped GQDs. Reproduced with permission.⁶⁷ Copyright 2017, Wiley-VCH.

In vivo imaging was not easy to be achieved because most of the reported GQDs emitted UV-visible light. Recently, with the fast development of this 0D materials, more and more GQDs with longer wavelength emission were reported and successfully applied for *in vivo* imaging. It is widely accepted that longer wavelength, typically larger than 650 nm, is more favorable for *in vivo* imaging as light with long wavelength can penetrate deeper into animal tissues while light with short wavelength could die out very quickly. Roy et al synthesized a GQD from hydrothermal treatment of neem leaf extract and devised an GQD-antibody

conjugate which can specifically track apoptotic cells.¹²¹ They managed to observe strong red fluorescence from GQDs in zebrafish with excitation of green light. In another work, Zhu et al. prepared GQDs from a top-down method using graphite powder as precursors.¹²⁰ The GQDs showed long wavelength emission and have been utilized as fluorescent probes for *in vivo* imaging of a nude mouse with negligible autofluorescence interference and high contrast (Figure 2-7c). Ge et al. prepared GQDs from polythiophene, which showed a deep-red emission peak at 680 nm.¹²² They observed red fluorescence of GQDs in a mouse and further demonstrated their application in photodynamic therapy. Though GQDs with red emission have been demonstrated for *in vivo* imaging by several studies, the synthesis of GQDs with red or NIR emission at a high quantum yield is still challenging. The main reason is that precise control of GQD size and morphologies during synthesis cannot be realized till today. Alternatively, up conversion properties of GQDs can be utilized for *in vivo* imaging, which has already been discussed in the above section.

Another noteworthy highlight regarding GQDs for imaging is their paramagnetic property realized by doping of boron atoms.⁶⁷ The GQDs were synthesized from fusion of 4-vinylphenylboronic acid and showed a strong paramagnetic behavior. Considering no metal elements are included, the GQDs can serve as a safe contrast agent for magnetic resonance imaging (MRI) both *in vitro* and *in vivo* (Figure 2-7d).

Sensing

The size of GQDs are extremely small, and they can intimately react with some chemicals or biochemicals in a molecular level. Therefore, GQDs based sensors provide much higher sensitivity than conventional ones.^{45, 123} Luminescence of GQDs is the most useful and frequently used indicant when a sensing platform was devised. Various studies have been demonstrated and published, most of which are based on the common sense that the PL intensity of GQDs is dependent on many factors, for example, the dispersity of GQD molecules (aggregation),^{37, 124} the presence of energy-accepting chemicals/particles,¹²⁵⁻¹²⁶ the pH value of the solution,^{125, 127-128} et al. Li and coworkers have devised a sensing probe for ultrasensitive profiling of multiple metabolites in blood samples with high specificity by using tyramine-functionalized GQDs.¹²⁴ The detection mechanism relies on two facts, that are, GQDs have a hydrogen peroxidase mimic activity and the PL can be quenched upon GQD aggregation (Figure 2-8a). Shen et al. proposed a facile and scalable preparation method for N, S-co-doped GQDs and demonstrated their application in sensitive parallel determination of Fe^{3+} , Cu^{2+} and Ag^+ ions.⁷² The fluorescence quenching was aggregation-induced due to the coordination interaction between GQDs and metal ions. Their detection limit reached as low as 8 nM, 250 nM and 50 nM for Fe^{3+} , Cu^{2+} and Ag^+ ions, respectively. Shi et al. developed a sensor based on GQDs and gold nanoparticles (AuNPs) for detection of specific gene sequence of *Staphylococcus aureus*.¹²⁹ The GQDs were modified with capture probe and AuNPs were functionalized with reporter probe. When target gene sequence was present, it would connect both capture and reporter probes and form a sandwich

structure, where GQDs and AuNPs reach a close proximity to allow the occurrence of fluorescence resonance energy transfer (FRET), consequently leading to fluorescence quenching (Figure 2-8b).

GQDs present ECL properties as discussed in the above chapter, which can be utilized as ECL sensing probes for detection of a variety of targets, such as nucleic acids,^{106, 130} antigens,¹³¹ metal ions,^{96, 132} et al. In a typical example, Lou et al. designed a novel strategy for ECL sensing of target DNA molecules with a high sensitivity and selectivity.¹³⁰ This system is based on the site-specific cleavage of *Bam*HI endonuclease (Figure 2-8c). Simply put, ECL intensity decreases when target DNA was present because *Bam*HI breaks off the double-strained DNA fragments.

In addition, there are a few studies demonstrating GQDs in electrochemical by making use of their unique abilities, e.g. π - π interaction with aromatic chemicals, electrostatic interaction with small molecules, facilitated charge transfer.¹³³⁻¹³⁶ For example, a novel electrochemical sensor based on GQDs was developed by Pang et al.¹³⁴ The synthesized GQDs have abundant carboxyl groups and thus a negative charge distribution on the surface which can help to interact with amino groups of dopamine *via* electrostatic attraction. Their sensing platform has a very high selectivity and sensitivity, with a detection limit of 0.45 nM. GQDs in Photoelectrochemical (PEC) sensing have also been explored.¹³⁷⁻¹³⁸ The photocurrent can be enhanced by GQDs due to their light-harvesting ability and electronic interaction between GQDs and photocatalysts. For instance, an iodine doped BiOCl surface decorated with nitrogen doped GQDs (I-BiOCl/N-GQD heterojunction) was fabricated. Based on the specific coordination interaction

between Bi(III) surface and chlorpyrifos, the PEC sensor was constructed, and the detection limit for chlorpyrifos was estimated as 0.01 ng/mL. The N-GQDs used in the system enhance the light harvesting and prolong the lifetime of photogenerated electrons.

Figure 2-8. Applications of GQDs in sensing and drug/gene delivery. (a) A fluorometric sensor based on tyramine functionalized GQDs. Reproduced with permission.¹²⁴ Copyright 2016, American Chemical Society. (b) The mechanism of GQDs–AuNPs FRET biosensor for *S. aureus* gene detection. Reproduced with permission.¹²⁹ Copyright 2015, Elsevier. (c) Schematic illustration of the ECL biosensor based on GQDs. Reproduced with permission.¹³⁰ Copyright 2015, American Chemical Society. (d) Target delivery of GQDs using HA and subsequent release of the Drug from the surfaces of GQD in a tumor cell environment. Reproduced with permission.¹¹⁵ Copyright 2013, American Chemical Society.

(e) GQDs-based cellular imaging and gene delivery. Reproduced with permission.¹³⁹
Copyright 2015, American Chemical Society.

Drug/gene delivery

Owing to the large surface area, GQDs can serve as carriers for delivery of molecular drugs/genes. GQDs can interact with cargo molecules through π - π stacking, hydrophobic interaction, hydrogen bonding, electrostatic attraction, or physisorption.¹⁹ Compared with other commonly used drug carriers, GQDs show clear advantages, such as their small size, PL property and minimum cytotoxicity. Their molecular size and chemical properties allow them to be readily internalized by cells without damaging the cells (biocompatibility), while their PL property can make them visually trackable under fluorescence microscopes.

Wang et al demonstrated a GQD passivated with polyethylene glycol (GQD-PEG) as drug carriers. Their GQDs had a high PL brightness (with QY to 18.8%) and showed an excellent drug loading capability (2.5 mg/mg) for doxorubicin (DOX).¹⁴⁰ To enhance the targeting specificity, Abdullah et al. anchored GQDs with hyaluronic acid (HA) which can target and easily bind to CD44 receptor in A549 cells with high affinity (Figure 2-8d).¹¹⁵ The HA-functionalized GQDs were applied to tumor bearing mice and their effectiveness of targeting was confirmed by fluorescence distribution measurement using a confocal laser scanning microscope. The kinetics of drug loading and releasing was studied and results showed ~75% of the DOX loading efficiency at pH 7.4, and 60% of the drug release after 12 hours under mild acidic environment (pH 5). This pH-dependent loading and releasing behavior is advantageous as tumorous region is slightly acidic as compared to normal

tissues.¹¹⁵ Further, Chong Wang demonstrated huge enhancement of drug delivery efficiency and anti-cancer activity using GQDs as DOX carriers.¹⁴¹ They proved the GQD-DOX conjugates can increase the nuclear uptake efficiency and improve the DNA cleavage ability of DOX. Most impressively, the conjugates showed improved chemotherapy efficacy of some anti-cancer drugs against drug-resistant cells.

Other than drug delivery, gene delivery has also been demonstrated by several scientists. Dong et al. proposed a simple and multifunctional platform based on poly(L-lactide) (PLA) and polyethylene glycol (PEG)-grafted GQDs (f-GQDs) for fluorescent cellular imaging and microRNA (miRNA) delivery.¹³⁹ PLA and PEG ligands improved PL property and biocompatibility of GQDs. It was also discovered that simultaneous loading of gene-targeting agents on GQDs can further enhance the therapeutic efficacy (Figure 2-8e). These findings demonstrated the tremendous potential of GQDs in the biomedical fields.

Therapeutic applications

Owing to biocompatibility, excellent aqueous dispersibility, fast body clearance, biodegradable, long-term stability, broad light absorption and ability to produce radicals, GQDs are widely used for therapeutic application, such as photothermal and photodynamic therapies.^{45, 122}

Xuan et al prepared nitrogen doped GQDs from citric acid with a high quantum yield and low cytotoxicity.¹⁴² The as-synthesized GQDs showed a high photothermal conversion efficiency up to 62.53%, which is a new record for carbon-based nanomaterials. Further, they also found the GQDs had the ability for photoacoustic imaging. They demonstrated the imaging and cellular photothermal

therapy on HeLa cells after coupling GQDs with folic acid (FA). The IR780 iodide is a commercially available theragnostic agent while its clinical application is highly limited due to poor solubility in aqueous environment. As pioneers, Li et al. proposed a new route to load the IR780 iodide onto the surface of FA functionalized GQDs (GQDs-FA) through strong π - π interactions and hydrophobic force.¹⁴³ The platform showed great water solubility, 2400-fold better than IR780 only, and most importantly, the improved photothermal conversion efficiency is measured up to 87.9%. Upon irradiation of 808 nm laser, the IR780/GQDs-FA hybrid could produce enough hyperthermia to kill cancer cells and eliminate tumor tissues (Figure2-9a).

GQDs have also been utilized as photodynamic agent as they can generate radicals under light illumination.¹⁴⁴⁻¹⁴⁶ Tabish et al. reported graphite flack derived GQDs with enhanced yield of singlet oxygen and associated reactive oxygen species (ROS) and demonstrated their potential as a smart and promising photodynamic agent.¹⁴⁷ Nitrogen doping can further enhance the generation of ROS, which was firstly discovered by Kuo et al in 2017.¹⁴⁸ They found a limited quantity of N-GQDs (1 $\mu\text{g/mL}$) with N1s/C1s=0.051 can eliminate 100% of the bacterial *E. coli* while nitrogen-free GQDs only killed 52% of the same bacterial. In addition to their PL emission in the NIR region (E_m :780 nm), these GQDs can be utilized as contrast probes to track and monitor bacterial as well as photodynamic agents. GQD conjugated with a photosensitizer chlorin e6 (Ce6) *via* a reduction cleavable disulfide has been demonstrated to significantly improve the accumulation in the tumor site and successfully suppress the growth of tumor tissues when treated with a cleavable linker (Figure 2-9b).¹⁴⁹ Ge et al. prepared a new PDT agent based on

GQDs which can generate singlet oxygen ($^1\text{O}_2$) with a high quantum yield at ~ 1.3 through a multistate sensitization.¹²² *In vitro* and *in vivo* studies demonstrated its successful photodynamic anti-cancer effect, simultaneously allowing deep-red imaging (Figure 2-9c).

Figure 2-9. GQDs for therapeutic applications. (a) Tumor-bearing mice treated with saline and IR780/GQD, tumor volume and total weight comparisons over time. Reproduced with permission.¹⁴³ Copyright 2017, American Chemical Society. (b) *In vivo* and *ex vivo* distribution of photosensitizer in nude mice with tumors (mice from left to right were treated with PBS, Ce6 only, GO-Ce6 and GQD-Ce6). Reproduced with permission.¹⁴⁹ Copyright

2016, American Chemistry Society. (c) Tumor-bearing mice treated with GQDs + light irradiation (top), GQDs without light irradiation (middle) and light irradiation without GQD injection. Reproduced with permission.¹²² Copyright 2014, Springer Nature.

Besides photothermal and photodynamic applications, other therapeutic applications using GQDs have also been demonstrated. For example, Iannazzo et al. studied the antiviral activity of multiwalled carbon nanotubes derived GQDs conjugated with the reverse transcriptase inhibitors (RTI) CHI499.¹⁵⁰ Their results, for the first time, showed that this GQD-based nanocomposite exerted inhibition of reverse transcriptase activity and binding of virus to the cells, thus providing a new strategy for HIV therapies based on carbon materials. GQDs have been discovered to be able to treat Parkinson's disease through inhibition of α -synuclein fibrillization and direct interaction with natural fibrils, consequently triggering their disaggregation.¹⁵¹ Furthermore, Wang and co-workers have demonstrated the use of GQDs from an electrochemical cutting pathway for the treatment and prevention of human islet amyloid polypeptide (IAPP) induced diseases.¹⁵²

In conclusion, owing to many intrinsic and unique properties in the scope of biomedical areas, e.g. small size, excellent biocompatibility, chemical inertness, enhanced permeation and retention effect in biological tissues, et al., GQDs have ignited massive interests from all over the world. Their potentials in bioimaging, biosensing and therapeutic/diagnostic applications have been demonstrated by numerous studies. However, their development space is still very huge, and some critical issues need to be resolved, such as the low production scale, non-precise control of their synthesis, poor understanding of PL mechanism et al. Nevertheless,

a growing number of scientists from chemistry, materials science, biomedicine or interdisciplinary areas are focusing on this distinct carbon-based nanomaterial and it can be envisioned that the wide spectrum of applications of GQDs will be further expanded to overcome more and more intractable biomedical problems in the future.

2.3.2 Catalysis

Functional groups and doped heteroatoms confer GQDs with excellent catalytic properties. Through size and morphology control, light absorption enhancement, synergic effect, bandgap alignment, GQDs can further improve the catalytic performance of many materials. Besides, due to their chemical stability, or chemical inertness, GQDs can also improve the lifetime of other catalysts. GQDs excellent aqueous dispersibility also provides a new strategy as quasi-homogenous catalysts, which can maintain the high catalytic performance as well as be recycled like heterogenous catalysis.

Photocatalysis

It has been demonstrated by many studies that GQDs can be employed as good photocatalysts for hydrogen (H_2) evolution,^{86, 153-160} carbon dioxide reduction,^{86, 161} and pollutants degradation.¹⁶²⁻¹⁶⁶ All these photocatalytic applications are making use of GQDs' intrinsic properties, such as their accessible surface and edge, good dispersibility, high photostability and their ability to interact with other materials (heterojunction). Most importantly, the band gap of GQDs are large enough to drive redox reactions yet not too large to allow broad photo absorption. In addition, by forming heterojunctions or heterostructures with other

light absorbing materials, their light harvest range and exciton separation can be further enhanced.

GQDs with both electron-accepting atoms or groups (e.g. carboxyl groups) and electron-donating moieties (N, S elements or amino groups) can induce both p-type and n-type conductivity, while the carbons on the basal plane serves as Ohmic contact between them. This network can be considered as the unique intramolecular Z-scheme structure⁸⁶ or p-n type photochemical diode.¹⁶⁰ This type of structure enables separation of photogenerated electron-hole pairs and thus the occurrence of both oxidation and reduction reactions simultaneously at n-type and p-type domains respectively. In a typical example, an engineered GQD with narrow band gap formed a intramolecular Z-scheme structure which has been utilized as photocatalyst for both H₂ evolution and CO₂ reduction.⁸⁶ Chen et al. have studied the mechanism of how nitrogen-containing groups affect the transition and transfer of photogenerated electrons in graphene derived materials.¹⁶⁷ They found the photocatalytic H₂ generation activity increased about 30% by ammonia treated N-doped GQDs (A-NGQD) compared with normal un-doped ones due to the repairment of defects on the basal plane by N functionalities (Figure 2-10a). GQDs are also been used as photo absorbers or electron acceptors in a heterojunction, for example, an S and N co-doped GQD was fabricated and exhibited unique optical properties, with three absorption bands locating at 338, 467 and 557 nm. Then the GQDs were integrated with TiO₂ and the composites showed much improved H₂ evolution catalytic performance under visible light (>420 nm).¹⁵⁷ A functionalized GQD coupled with

dehydrogenase as visible-light-driven photocatalyst was demonstrated by Yadav et al. for a boosted and exclusive conversion of CO₂ to formic acid (Figure 2-10b).¹⁶¹

Figure 2-10. GQDs in catalytic applications. (a) An illustration of overlap of the N lone pair orbital and the π -system and boosted photocatalytic H₂ production. Reproduced with permission.¹⁶⁷ Copyright 2016, Wiley-VCH. (b) An illustration of GQDs as photocatalysts for the conversion of CO₂ to formic acid. Reproduced with permission.¹⁶¹ Copyright 2016, Wiley-VCH. (c) An illustration of GQD-assisted fabrication of nickel-cobalt oxide/GQD nanosheet arrays. Reproduced with permission.¹⁶⁸ Copyright 2018, Elsevier. (d) Schematic diagram of GQD-AuNPs assemble. Reproduced with permission.¹⁶⁹ Copyright 2018, The

Royal Society of Chemistry. (e) GQD functionalized nanowires for photoelectrochemical water splitting. Reproduced with permission.¹⁷⁰ Copyright 2013, Wiley-VCH. (f) An illustration of Au/GQD and its catalytic mechanism for veratryl aldehyde oxidation. Reproduced with permission.¹⁷¹ Copyright 2015, The Royal Society of Chemistry.

Doped GQDs have also been demonstrated to catalyze the organic synthesis process. Jeon et al. fabricated N and S co-doped GQDs for the photocatalysis for aerobic oxidative coupling reactions of various amines. The N, S-GQDs exhibited much higher catalytic performance (100% conversion) than N-GQDs or un-doped GQDs owing to their broad light absorption, increased Fermi level and prolonged lifetime of excited singlet state to convert oxygen to superoxide.¹⁷² Fe (III) porphyrins (FeTSPP) supported on S and N co-doped GQDs were fabricated by Mahyari et al. and utilized as photocatalysts for high-performance oxidation of alcohols to targeted carbonyl compounds at room temperature with a high selectivity.¹⁷³

GQDs also show potentials in the photocatalytic degradation of various pollutants. For example, Hao et al. have synthesized GQDs from graphene nanosheets and used them as co-catalysts for a mesoporous photocatalyst (Bi_2MoO_6). The resulting hybrid photocatalysts showed high charge separation efficiency and broad-spectrum photocatalytic activity from UV to NIR region. The catalytic results confirmed that the addition of GQDs greatly improved the photo-degradation for a variety of pollutants, e.g., bisphenol A, methylene blue, phenol et al.¹⁶⁵ In another work, a hydroxyl-rich GQD modified mesoporous C_3N_4 composites were fabricated by Liu et al. for high-performance photocatalysis.¹⁷⁴ Verified by experimental data, the GQD/ C_3N_4 composites can produce more radical species and a small fraction of

electron holes for enhanced photo-driven degradation of rhodamine B and tetracycline hydrochloride.

Electrocatalysis

GQDs are widely used for many electrocatalytic reactions, e.g., oxygen evolution reaction (OER),^{168, 175-177} oxygen reduction reaction (ORR),^{112, 178-182} CO₂ reduction reaction (CO₂RR)¹⁸³⁻¹⁸⁴ and hydrogen evolution reaction (HER).^{177, 185-186} Nitrogen doped GQDs are more favorable electrocatalysts for OER as the doped N atoms redistribute the charge arrangement of GQDs *via* π - π delocalization, consequently reducing the HOO* thermal dynamic energy barrier.¹⁷⁵ However, GQDs are more frequently hybridized with other intermetallic materials to catalyze OER.⁴⁵ Typical examples include Nickel subsulfide¹⁷⁷, Co₃O₄¹⁷⁶ and nickel-cobalt phosphide.¹⁶⁸ It has been reported recently that the unique nanosized planar structure of GQDs can help to engineer nano catalysts into nanosheet morphologies (Figure 2-10c). As a result, both OER and HER were boosted by this hybrid nanosheet owing to the enhanced charge transfer and transport and improved catalytic kinetics.¹⁶⁸ GQDs have also been used as co-catalysts for the modification of other catalysts such as MoS₂,¹⁸⁶⁻¹⁸⁷ Ni₃S₂¹⁷⁷ and CoP¹⁸⁵ et al. Guo and co-workers devised a GQD-decorated MoS₂ electrocatalyst.¹⁸⁷ Compared with bare coral-shaped MoS₂, GQDs further enhanced the electrocatalytic activity and long-term stability towards HER by electronic band engineering. They confirmed the band gap was reduced by GQDs close to zero, thus leading to a much-improved electrical conductivity and outstanding catalytic performance, according to their first-principle calculation results. Similarly, Wang et al. have synthesized CoP nanoparticles supported on

pristine graphene sheets by dynamically self-assembled GQDs as HER catalysts, with a high performance comparable to those of most reported non-noble-metal catalysts.¹⁸⁵ The GQD-mediated synthesis process increases the dispersion of graphene and promotes the in situ growth of uniformly distributed CoP nanoparticle. The addition of GQD molecules significantly improved the electrocatalytic activity by increasing the number of active sites and promoted carrier nobility.

Heteroatom doped GQDs have been employed as effective electrochemical catalysts for the oxygen reduction reactions. As a typical example, Favaro et al. have investigated the origin of single and multiple heteroatoms doped GQDs for OER catalysts.¹⁸⁰ They synthesized N-GQDs, B-GQDs and B, N-GQDs through an electrochemical route and found a distinct decrease of the overpotential of the above 3 GQD samples. They rationalized that the best performance of B, N-GQDs attributed to the more concentrated active sites and an enhanced positive charge on B atoms caused by the electron-withdrawing nature of N atoms. In addition, Liu and Wu have devised a metal-free electrocatalysts for ORR based on a GQD hybrid with N- and O-rich functional groups.¹⁸⁸ The architecture of the hybrid created more active sites on the surface and the introduced N atoms could induce its molecular orbital resonance with the delocalized π orbital of GQDs, thereby improving the catalytic activity. Nitrogen-doped GQDs was reported to have electrochemical catalytic activity towards CO₂ reduction reactions.¹⁸⁴ The N-GQDs fabricated by Wu et al. through a exfoliation and cutting method have substantially enriched density of N-doping defects at edge sites, which exhibits high catalytic performance in the

reduction reaction of CO₂ to valuable products, such as multi-carbon hydrocarbons and/or oxygenates at a high conversion rate (up to 90%).¹⁸⁴

GQDs are also employed for electrocatalytic synthesis of organic compounds and fuel cells.¹⁶⁹ Zeng et al. have proposed a controllable layer-by-layer structural design of a series of well-defined metal (Au, Ag and Pt) and GQD hybrids *via* electrostatic attraction (Figure 2-10d). Owing to the cooperative synergy between metal nanocrystals and GQDs, the novel multilayered thin films showed significantly improved electrocatalytic performance towards the selective transformation of toxic aromatic nitro chemicals, oxidation of methanol and water splitting.

Photoelectrocatalysis

GQDs also can be utilized as photosensitizer,^{169-170, 189-190} electron donor¹⁹¹ and/or hole extractor¹⁹¹⁻¹⁹² in the photo-induced electrochemical reactions. Guo et al. prepared a green sensitizer based on carbon black derived GQDs and immobilized them onto ZnO nanoarrays (GQDs@ZnO) *via* covalent bonding (Figure 2-10e).¹⁷⁰ The enhanced light absorption property of GQDs@ZnO can be modulated by the amount of GQDs. Most importantly, the hybrids provided a much higher photo-induced open-circuit voltage and short-circuit current density in comparison with the bare ZnO nanoarrays. Other than enhanced light absorption, GQDs in the hybrids also promote efficient charge separation due to their favorable energy levels between GQDs and ZnO nanowires, resulting in a much higher photoelectrochemical catalytic performance. Another work done by Zeng et al. also demonstrated the GQDs-deposited and Au clusters-anchored TiO₂ nanotubes with a remarkable

photoelectrochemical catalytic efficiency towards water splitting.¹⁹⁰ The ternary structure of the hybrids and the synergic effect of GQDs and Au promote charge transfer and charge carrier separation, contributing to the improved water splitting performances.

Chemical catalysis

As mentioned above, GQDs also have been showed to act as peroxidase mimics to catalyze hydrogen peroxide into hydroxyl radicals. Sun et al. have in-depth investigated the origins of the intrinsic peroxide activity in the GQD molecules. They depicted that the -C=O groups in GQD were the catalytic active sites, whereas the O=C-O- groups were the major binding sites while -C-OH groups were able to inhibit the catalytic activity.¹⁹³ Making use of GQD's high intrinsic peroxidase mimic activity, a number of applications have been demonstrated, sensing in particular.^{124, 194-196}

Au/GQD composites were synthesized as catalysts for the ultra-selective conversion of veratryl alcohol (VA) to veratryl aldehyde or veratric acid.¹⁷¹ The GQDs in the hybrid absorb VA *via* π - π stacking and generate singlet oxygen in the presence of H₂O₂ which helps to accelerate the oxidative reaction of VA (Figure 2-10f).¹⁷¹

2.3.3 Energy storage and conversion

Owing to the large surface area, molecular size, tunable band gap, unique sp² hybridized carbon network and their capability to promote charge transport and transfer, GQDs are promising in a wide range of applications, including energy-related storage and conversion.

Batteries and supercapacitors

GQDs have been employed as energy storage materials in rechargeable lithium or sodium batteries. They can improve the electrical conductivity through enhanced charge transfer and simultaneously act as binders to stabilize the improved cyclic stability. In addition, the unique structural property of GQDs can relieve the volume expansion and assist the Li^+ intercalation. As a result, a boosted lithium storage performance was evidenced when utilizing MoS_2/GQD composites as anode materials.¹⁹⁷ GQDs were reported to have the capability to enhance the Li^+ ions' mobility in a gel polymer electrolyte.¹⁹⁸ In this specific study, Chen et al. demonstrated a lithium battery with a 100 % of retention after 500 cycles of charging and discharging processes. Authors attributed the improved performance and lifespan of batteries to GQDs as they can inhibit the formation of ion-solvent clusters and immobilize PF_6^- anions in the electrolyte. In another work, GQDs were coated onto Vanadium oxide (VO_2) surfaces as cathode in order to boost the electrochemical properties of Li and Na batteries. The GQD layer acted as highly efficient surface sensitizer and protector (Figure 2-11a). The as-designed integrated electrode showed a Na storage capacity of 306 mAh/g at 100 mA/g and more than 110 mAh/g after 1500 cycles at 18 A/g.¹⁹⁹

GQDs have also been integrated into supercapacitors to further improve the performances, utilizing GQD's large surface area and special 0D structure.²⁰⁰ Hu et al. have fabricated a GQD/CNT hybrid arrays with a 3D aligned composite structure and integrated into a supercapacitor (Figure 2-11b), with a high capacitance of 44 mF/cm, which is as twice as that of the bare CNT electrode.²⁰⁰ The size effect of

GQDs on the electrochemical properties was investigated by Liu et al.²⁰¹ They firstly prepared GQDs with different size distributions and elucidated that the specific capacitance of all samples increases along with their sizes (Figure 2-11c). The smallest GQDs (with average size of 4.8 nm) showed a highest scan rate of 5000 V/s, ultra-fast power response ($t_0 = 63.3 \mu\text{s}$), and the least specific capacitance with only 3.3 F/g. This work provided insights on the porous graphene materials used for supercapacitor applications. Another work based on GQDs as superior micro-supercapacitors has been reported by Liu and Xue.²⁰² They applied a simple electro-deposition approach to prepare the GQDs//GQDs symmetric micro-supercapacitors and results showed the superior rate capability up to 1000 V/s, excellent power response with very short relaxation time constant and excellent cycle stability. Further, they upgraded the positive electrode with MoS₂ nanoneedles and the performance of this asymmetric GQD//MoS₂ micro-supercapacitor in terms of capacitance and energy density has been improved two times higher.²⁰² They claimed that the excellent capacitive performance of GQDs was attributed to the large specific surface area, and accessible edges and abundant active sites.

Figure 2-11. GQDs as energy conversion and storage materials. (a). GQD-coated VO_2 arrays as electrodes for Li and Na ion batteries. Reproduced with permission.¹⁹⁹ Copyright 2015, American Chemical Society. (b) Fabrication of GQD/CNT-based supercapacitors. Reproduced with permission.²⁰⁰ Copyright 2013, IOP Publishing. (c) The relationship between specific capacitance and sizes of GQDs. Reproduced with permission,²⁰¹ Copyright 2015, The Royal Society of Chemistry. (d) GQD-based WLED structure and CIE1931 coordinates of white emission applied with 11-14 V. Reproduced with permission.²² Copyright 2016, Wiley-VCH.

Light-emitting Diodes

GQDs have been used in applications in light-emitting diodes because of their electroluminescence property, tunable band gap et al. Luo et al have applied a microwave-assisted hydrothermal approach for the synthesis of white fluorescent

GQDs (WGQDs), subsequently constructed a white-light-emitting diodes (WLEDs) based on WGQDs as light-emitting phosphors. The as-prepared WLEDs were featured with a high current density and brightness at 11-14V applied voltage, and more importantly, the Commission Internationale de l'Enclairage (CIE) of WLEDs was very close to the pure white light (Figure 2-11d).²² Similarly, octadecylamine (ODA)-GQDs based LEDs were devised by Kim et al. with high current and external quantum efficiency of 6.51 cd/A and 2.67 cd/A, respectively.²⁰³ This was the highest value among the reported GQD-based LEDs. The high performance originated from the superior optical properties of the as-prepared ODA-GQDs, which were improved due to an increase in the number of holes injected from anode to the active layer.²⁰³

GQDs can act as dopants on the organic LEDs (OLEDs).³⁴ Kwon et al. have prepared GQDs with different sizes through a top-down cutting of tattered graphite exhibiting colorful photoluminescence from blue to brown. The as-synthesized GQD series showed excellent organic stability and a proper band gap structure, subsequently were successfully embedded into OLEDs as a dopant.

GQDs can also be utilized as color conversion materials in LEDs. For example, Tetsuka et al. prepared amino-GQDs from graphene sheets, wrapped them with cellulose nanofiber (CNF) and incorporated CNF-wrapped GQDs into a flexible clay host (GQD@CNF-clay film). The resulting film was further employed as a light color convertor for the conversion of blue light from a blue LED to white light. This GQD@CNF-clay film-based LEDs showed a CIE coordinate value of (0.33, 0.37), indicating a pure white light.²⁰⁴

Photodetectors, photovoltaics and others

The tunable optical and electrical properties of GQDs endow them the ability to fulfill the requirements for photodetectors.²⁰⁵⁻²⁰⁷ For example, Mihalache et al. have fabricated GQDs with yellow PL emission along with a large band gap and an intermediate electronic state.²⁰⁷ They further functionalized the GQDs with poly(ethyleneimine) (PEI) and incorporated them with silicon nanowires (GQD/SiNW) as photodetectors (Figure 2-12a), which exhibited a high photocurrent to dark current ratio and a much improved external quantum efficiency. In the other similar work, a fast-response and highly sensitive deep ultraviolet (DUV) photodetectors were demonstrated by Zhang et al.²⁰⁵ The proposed photodetector was based on GQDs and showed a remarkably high performance with an on/off ratio reaching up to ~6000 and an excellent stability.

GQDs in photovoltaics have also been intensively demonstrated.²⁰⁸⁻²¹² GQDs can be employed as hole transport layer due to their band structure for efficient separation of photo-induced electron-hole pairs as well as electron blocking layer to inhibit recombination of carriers at anode.²¹² By integrated with GQDs in the GQDs/silicon nanowire heterojunction solar cells (Figure 2-12b), the cell power conversion efficiency under AM 1.5G irradiation was estimated as 12.35%, highest among this new solar cells.²¹² Few-layered GQDs with size of ca. 4 nm and abundant carboxyl groups can serve as hole extraction layer in a polymer solar cells.²¹⁰ Compared with GO, the nanoscale GQDs presented a high work function, good film-forming property, and high transmittance, resulting in a remarkable enhancement of device performance with power conversion efficiency of 7.9 %.²¹⁰

Figure 2-12. GQDs for photodetectors, photovoltaics and other applications. (a) A PEI-functionalized GQD/silicon nanowire heterostructure as photodetector. Reproduced with permission.²⁰⁷ Copyright 2017, American Chemical Society. (b) An illustration of GQD/silicon-based solar cell coated with transparent graphene as electrode. Reproduced with permission.²¹² Copyright 2017, Elsevier. (c) Illustrated structure and photo of the flexible memory thin film transistor based on reduced GOQD. Reproduced with permission.²¹³ Copyright 2017, American Chemical Society. (d) An illustration of an electrolyte-free and flexible electrochromic device. Reproduced with permission.²¹⁴ Copyright 2014, Wiley-VCH.

GQDs are demonstrated to have the capability to transfer a series of nanoparticles from non-polar to polar solvent for the thermoelectric devices.²¹⁵ Liang et al. have utilized GQDs for capping nanoparticles to limit the particle sizes

and obtained an enhanced thermoelectric performance with a considerable ZT value of 0.46.²¹⁵ Meanwhile, GQDs were reported to be able to function as charge carrier in a flexible memory device (Figure 2-12c).²¹³ In another study, Hwang proposed an electrolyte-free and flexible electrochromic device with N,N'-dimethyl-4,4'-bipyridinium (MV²⁺) (methyl viologen) as a cation and conductive GQDs as an anion. They formed together *via* strong electrostatic interaction and π - π stacking, leading to a table electrochromic performance (Figure 2-12d).²¹⁴

In conclusion, as a prominent nanomaterial, GQD offers many merits, such as their small size, exceptional mechanical strength, flexibility, tunable optical and electronical properties and high catalytic performance. However, their uses in various applications in energy and catalysis are still in early stage. Compared with other counterparts in specific applications, GQDs are still developing and there is much room for improvement. For example, the presence of defects, which originate from oxygenated groups and incomplete graphene crystalline structure, results in a compromised conductivity thus limits their vast applications in electrochemical applications. Moreover, because of the lack of precise property control, the bandgap structure of GQD is hard to manipulate, which limits their applications in photovoltaics and photocatalysis. Therefore, more efforts are in high demand, especially in terms of precise control of size, morphologies and dopants distributions. We envision that GQDs will play a more vital role in modern electronics and energy-related devices.

Chapter 3 Sweet Graphene Quantum Dots for Imaging Carbohydrate Receptors in Live Cells

GQDs are typically atomically thin carbon sheet with a diameter usually <10 nm. They are emerging as a new class of zero dimensional nanomaterials which promise a wide spectrum of applications including imaging,^{62, 216} optical sensing,^{124, 217} photocatalysis¹⁷² and display,²¹⁸⁻²¹⁹ et al. In particular, GQDs have unique advantages in bioimaging because of several key merits including tunable photoluminescence (PL) properties, high photo-stability, good biocompatibility, and molecular size.¹⁹ Many studies have shown the feasibility of GQD based cellular imaging via nonspecific cellular internalization of GQDs.^{78, 220} A few studies have demonstrated the specific imaging of proteinaceous membrane receptors in cells by functionalizing GQDs with corresponding ligand proteins.

Cell membrane is not only populated with proteins but also saccharides and their respective receptors which are involved in many biological processes including cellular signaling, recognition, adhesion, and immune responses.²²¹⁻²²² In pathological cells (e.g. cancer cells), certain saccharide receptors are overexpressed.²²³⁻²²⁴ Semiconductor quantum dots have been used to visualize the distribution of these receptors.²²⁵⁻²²⁷ However, these quantum dots are intrinsically toxic and much larger than the target molecules (hence potentially causing artificial clustering or altering trafficking dynamics of the targets). We thus envision that GQDs shall be better fluorescence reporters to reveal the distribution and dynamics of carbohydrate receptors.

GQDs can be synthesized using top-down exfoliation from larger carbon precursors (e.g., graphite powder, coal, carbon black, carbon fiber) based on chemical, electrochemical, or physical methods. These top-down methods however produce GQDs with large heterogeneity. Alternatively, GQDs can be synthesized using “bottom-up” approaches based on fusion and carbonization of small organic molecules, which often can offer better production yield and homogeneity as compared to the top-down methods. Recently, Wang et al. demonstrated a bottom-up method using pyrene as the precursor to produce GQDs with good crystallinity and high production yield.⁵² However, the obtained pyrene derived GQDs bear mainly –OH groups, which cannot be easily functionalized with biomolecules.

In this chapter, we synthesize pyrene derived GQDs with COOH groups which exhibit excitation independent green fluorescence, small and uniform size, higher photoluminescence (PL) quantum yield (QY) and ease to be functionalized as compared with pyrene derived OH-GQDs (Scheme 3-1). For the first time, GQDs are conjugated with monosaccharides (galactose and mannose) for specific imaging of carbohydrate receptors on cell membrane. Overexpression of mannose receptor (c-type lectin) in human breast cancer cells, overexpression of galactose receptor (asialoglycoprotein receptor, ASGPR) in human liver cancer cells as well as the endocytosis and exocytosis of activated ASGPR complexes are revealed. This study suggests the unique potential of GQDs in research of glycobiology.

Scheme 3-1. Synthetic route of sugar functionalized GQDs.

3.1 Materials and methods

3.1.1 GQD synthesis and functionalization

The precursor, pyrene (0.5 g, Sigma-Aldrich) was refluxed with hot nitric acid (40 mL, 65%, Merck), and vigorously stirred for 12 h at 80 °C. After cooling to room temperature, the yellowish cloudy mixture was diluted with deionized water (1 L) and filtered through a membrane filter (0.22 mm, Millipore) to remove the acid, followed by drying in a vacuum chamber to obtain 1,3,6- trinitropyrene powder. The yield of trinitropyrene was calculated as ca. 54%. Subsequently, 80 mg of the above

product was dispersed in a NaHCO_3 solution (0.08 M, 15 mL) and the dispersion was ultrasonicated for 1 h. The resultant yellow suspension was then transferred into a 20 mL poly(tetrafluoroethylene) (Teflon)-lined autoclave and heated at 200 °C for 10 h. After cooling to room temperature, the obtained dark brown solution was filtered with a syringe filter (0.22 mm, Millipore) to remove large particles, and further dialyzed in a dialysis bag (with cut-off molecular weight of 500 Da, Spectrum) for 2 days to remove ions and small molecules. Then the obtained solution was further ultra-filtered with a centrifuge filter (10 kDa cut-off, Amicon-Ultra, Millipore) to remove large-sized pieces or aggregations. The remaining GQDs were freeze-dried into powders.

To prepare galactose-functionalized GQDs (Gal-GQDs), 1-ethyl-3-(3-(dimethylamino) propyl) carbodiimide hydrochloride (EDC, 15 mM, Sigma-Aldrich) and N-hydroxysuccinimide (NHS, 22.5 mM) were successively added to GQD solution (5 mg/mL, diluted with phosphate buffer saline, pH 7). After 20 min, the above solution was mixed with galactosamine (25 mM, Sigma-Aldrich) under mild shaking for 4 h. Subsequently, the mixture was dialyzed with a dialysis bag (cut-off molecular weight of 500 Da, Spectrum) for 48 h to remove the unreacted reactants and ions. The same protocol was applied to conjugate mannosamine (25 mM, Sigma-Aldrich) with GQDs (Man-GQDs).

3.1.2 Materials characterization and measurements

The structure of GQDs were analyzed with atomic force microscopy (MFP-3D AFM microscope, Asylum research) and high-resolution transmission electron microscope (HRTEM, JEOL 2100). Their chemical compositions were revealed by

X-ray photoelectron spectroscopy (VG ESCALAB 220I-XL) and Fourier transform infrared spectroscopy (Perkin Elmer FTIR Spectrum GX 69233). The UV–vis absorption and photoluminescence properties of GQDs were characterized by a UV-2450 spectrophotometer (Shimadzu) and a Fluorolog[®] PL spectrometer (Horiba), respectively.

3.1.3 Cell culture and imaging

Human breast cancer cells (MCF-7, ATCC), human liver cancer cells HepG2, ATCC) and human cervical cancer cells (HeLa, ATCC) were cultured with Dulbecco's Modified Eagle Medium (DMEM, Lonza) supplemented with 10% fetal bovine serum (FBS, Gibco) and 1% penicillin streptomycin (PS). Human breast epithelial cells (MCF-10A, ATCC) were cultured with DMEM/F12 supplemented with 20% FBS and 1% PS. All the cells were incubated in an incubator at 37 °C in an air atmosphere containing 5% CO₂. To conduct the imaging experiments, cells were seeded onto a Lab-Tek II chambered cover glass (Nunc) for overnight growth. Then Gal- /Man-GQDs (dispersed in DMEM, 120 mg/mL) were applied to the cells 1 h before imaging. Then the cells were rinsed and incubated with FluoroBrite DMEM (Thermo Fisher Scientific). Confocal images were obtained using a confocal laser scanning microscope (CLSM, Zeiss LSM 710) with a 63x oil objective lens. The time-lapse images (80 frames in 2 min) were also recorded using an inverted total internal reflection fluorescence microscope (TIRFM) system (Zeiss) with a 100x/1.45 oil objective lens, after the cells were incubated with Gal-GQDs for 20 min. All the images were processed with ImageJ.

3.1.4 Cell viability tests

The MTT (3- [4, 5-dimethylthiazol-2-yl]-2, 5-diphenyltetrazolium bromide) assay was applied to justify the cytotoxicity of prepared GQDs. Three different cell lines were transferred into a 96-well plate at a cell density of around 5×10^3 cells/well. After 24 h' incubation in DMEM, cells were introduced with various concentrations of GQDs (100, 200, 300, and 400 mg/mL) for 24 h. Subsequently, after removing old media, the MTT solution (0.5 mg/mL) was added to the wells for another 4 h' incubation. Then the solution was discarded, and 100 mL of isopropanol was added to each well to dissolve the formazan crystals. After 20 min shaking in darkness, the optical density (OD) of each well was recorded by a microplate reader at 570 nm. The cell viability was calculated by following the equation:

$$\text{Cell viability (\%)} = \frac{\text{OD of the cells treated with GQDs}}{\text{OD of controls}} \times 100$$

Where controls are the cells with no GQDs added and the cell viability of controls is recorded as 100%.

3.2 Results and discussion

Wang et al. has demonstrated a bottom-up synthesis of GQDs in NaOH (0.2 M) using 1,3,6-trinitropyrene as the precursor, which fuses into single-layered graphene crystalline structure under hydrothermal condition. But such GQDs enriched with –OH groups cannot be readily functionalized. Here, we replaced NaOH with NaHCO₃ (0.08 M) to obtain GQDs with active –COOH groups. In the nucleophilic substitution reaction under hydrothermal condition, the positively charged –NO₂ groups from trinitropyrene are substituted by alkaline groups (e.g.,

HCO^{3-} , CO_3^{2-} , OH^-), thus leading to grafting of COOH groups onto the GQD. As shown in Figure 3-1a and b, transmission electron microscopy (TEM) reveals that the average diameter of the obtained COOH -GQDs is $\sim 5.4 \text{ nm}$ (± 0.91 , $n = 103$) which is larger than the originally reported OH -GQDs ($3.5 \pm 0.6 \text{ nm}$). The high-resolution TEM (HRTEM) resolves the lattice spacing of $\sim 0.21 \text{ nm}$ corresponding to graphene (1 0 0) planes. The atomic force microscopy (AFM) shows that the average GQD thickness is $\sim 1.1 \text{ nm}$ (± 0.46 , $n = 157$), indicating that most of them are single- or double-layered (Figure 3-1c and d).

Figure 3-1. (a) TEM images of GQDs (scale bar = 10 nm). High-resolution TEM image is shown in inset (scale bar = 2 nm). (b) Diameter distribution of GQDs ($n = 103$). (c) AFM images of GQDs. Inset shows the height profile along the red line. Scale bar = 50 nm. (d) Height distribution of GQDs ($n = 157$).

The Fourier transform infrared (FTIR) spectrum of COOH-GQDs (Figure 3-2a) demonstrates the characteristic peaks originated from the stretching vibration of O–H/N–H bonds ($\sim 3500\text{ cm}^{-1}$), C=O/C=C bonds ($\sim 1631\text{ cm}^{-1}$), C–H/N–O bonds ($\sim 1364\text{ cm}^{-1}$), and C–O bonds (1092 cm^{-1}). X-ray photoelectron spectroscopy (XPS) analysis indicates the abundant existence of oxygenated groups (Figure 3-2b). COOH-GQDs are highly stable in aqueous solutions (no obvious aggregation is observed even after 6 months). The high-resolution C1s spectrum (Figure 3-2c) can be well-fitted with the characteristic peaks from C=C bonds (284.5 eV), C–O/C–N (285.6 eV) and O–C=O (288.7 eV), while the high-resolution O1s spectrum (Figure 3-2d) can be de-convoluted into C=O (532.6 eV) and C–O (531.6 eV) peaks. A small fraction ($\sim 1.55\%$) of nitrogen is originated from C–NH₂, C–NH–C and C–O bonds at 399.6 eV, 400.2 eV and 403.1 eV respectively (Figure 3-2e).²²⁸⁻²²⁹ Taken together, we can conclude that the obtained GQDs bear abundant –OH groups, some –COOH groups and few –NH₂/–NO₂ groups at the edges.

Figure 3-2. FTIR spectrum (a) and XPS analyses (b–e) of the prepared GQDs.

The aqueous dispersion of as-prepared GQDs appears brownish yellow under daylight (Figure 3-3a, inset) and shows bright green fluorescence under 365 nm UV illumination (Figure 3-3b, inset). The UV–Vis absorption spectrum of GQDs (Figure 3-3a) exhibits three shoulder peaks at ~240 nm (5.2 eV), ~380 nm (3.3 eV) and ~450 nm (2.8 eV), which are produced by π - π^* transition of aromatic C=C bonds in the GQD basal plane, n_1 - σ_1^* transition of C=O bonds at the edges, and n_2 - σ_2^* transition of C-O bonds at the edges, respectively (Figure 3-3c).⁸⁰ The maximum emission of COOH-GQD is attained at ~535 nm while being excited at ~488 nm (Figure 3-3b). The emission at 535 nm is originated from radiative relaxation of excited electron from π^* to n_1 orbital (Figure 3-3c). In the other words, the emission property of COOH-GQD is dictated by the bandgap between π^* and n_1 orbitals. In comparison, OH-GQDs have a maximum emission peak at 520 nm with 485 nm excitation, corresponding to the bandgap between π^* and n_2 orbitals.⁵² Our observation is consistent with the previous theoretical calculation which suggests that COOH group causes slightly more red-shifts than OH group at edges.⁷⁷ Notably, COOH-GQD not only can be easily conjugated with biomolecules but also exhibits significantly higher absolute quantum yield than that of OH-GQDs (31% vs. 23%). It is also noteworthy that the emission peak is essentially excitation independent (Figure 3-3d), indicating the high homogeneity of pyrene-derived COOH-GQDs. The PL decay lifetime of COOH-GQDs is determined to be 3.7 ns (Figure 3-4). Furthermore, the as-prepared GQDs show low cytotoxicity to various cell types (MCF-7, HepG2 and HeLa), even at a high concentration of 0.4 mg/mL which is much higher than the needed for bioimaging (Figure 3-5).

Figure 3-3. (a) UV-vis absorption spectrum. Inset is the photograph of the aqueous dispersion of GQDs under ambient light. (b) Photoluminescence excitation spectrum (PLE, emission at 535 nm) and emission spectrum (PL, excited at 488 nm) of GQDs. Inset: Aqueous dispersion of GQDs under a UV lamp illumination (365 nm). (c) Energy band diagram. (d) Emission spectra of GQDs excited with different wavelengths.

Figure 3-4. Time-resolved decay profile of GQDs.

Figure 3-5. Cell viability tests based on MTT assay.

Taken-together, the pyrene-derived COOH-GQDs are highly desirable for bioimaging because of high brightness, small size and molecular weight, excellent biocompatibility, and good photo-stability. A number of efforts have been made to functionalize GQDs with proteins in order to fluorescently enlighten the protein binding targets (e.g., protein receptors on cell membrane). We for the first time functionalize GQDs with monosaccharides aiming to specifically label carbohydrate receptors on cell membrane which play important physiological functions. Specifically, galactosamine or mannosamine is covalently conjugated to the COOH-GQDs via amide bonding. Subsequently, FTIR and UV-Vis absorption were conducted to verify the successful conjugation. In the FTIR spectrum (Figure 3-6a), two peaks at 1568 and 1250 cm^{-1} appear after conjugation, indicating the presence of CO-NH and C-O-C bonding. In the UV-Vis absorption spectrum (Figure 3-6b), a distinguished peak at around 260 nm also appeared, which may originate from the

n-r* transition of N-C=O bonds, testifying the successful conjugation of monosaccharide moieties. Notably, both the photoluminescence excitation and emission spectra of GQDs don't significantly alter after conjugation except slight redshift in emission (~8 nm) (Figure 3-7).

Figure 3-6. (a) FTIR and (b) UV-vis absorption spectra of GQDs before and after conjugation with galactose and mannose.

Figure 3-7. Photoluminescence excitation and emission spectra of GQDs before and after conjugation with galactosamine and mannose.

Cancer cells often overexpress certain types of carbohydrate receptors (lectins). It is known that galactose receptors in hepatocytes involve in binding, internalization, and subsequent clearance of asialoglycoproteins (bearing galactose terminal) from the circulation. But their functions are still not completely understood. These receptors are more abundantly expressed in hepatoma cells (cancer liver cells).²²⁴ Galactose tagged QDs (Gal-QDs) can specifically interact and fluorescently lighten up the galactose receptors. Confocal fluorescence imaging reveals that indeed galactose receptors populate the membrane of HepG2 cells (human liver cancer cell line) whereas they are much less present in MCF-7 cells (human breast cancer cell line) and rarely found in Hela cells (human cell line derived from cervical cancer) and MCF-10A cells (non-tumor human breast epithelial cell line) (Figure 3-8). Mannose tagged QDs (Man-QDs) can selectively label mannose receptors which are found in several cell types (e.g., macrophages) and play a role in both the innate and adaptive immune systems. It has been found that mannose receptors are overexpressed in human breast cancer cells.²³⁰⁻²³¹ Consistently, confocal imaging confirmed that mannose receptors are much expressed on plasma membrane of MCF-7 cells but not HepG2, Hela and MCF-10A cells. These experiments testify that sugar conjugated QDs can be used to uncover the expression and distribution of carbohydrate receptors as well as to identify certain types of cancer cells (Figure 3-8).

Figure 3-8. Confocal fluorescence imaging of Gal-GQD and Man-GQD stained HepG2, MCF-7, HeLa and, MCF-10A cells excited with 488 nm laser. Scale bar = 5 μ m.

Just like protein receptors, binding with the corresponding ligand (here, or sugar residue) will trigger internalization of carbohydrate receptors through endocytosis. And after undertaking some trafficking steps, endocytosed receptors, if not being degraded, will eventually be recycled back to the cell membrane be ready for another round of stimulation. Although the trafficking (recycling) dynamics of many protein receptors has been extensively investigated, the dynamics of carbohydrate receptors is barely studied. Herein, we employed total internal reflection fluorescence microscopy (TIRFM) to reveal the dynamics of galactose receptors. With TIRFM, only the thin section (<200 nm thick) including the cell membrane or the immediately adjacent subplasmalemmal region is illuminated and

imaged. Therefore, it is a powerful tool to investigate membrane receptors and their turnover dynamics. The TIRFM images in Figure 3-9a and b show the galactose receptor clusters labeled by Gal-GQDs on the plasma membrane of a HepG2 cell. As shown by the time-lapse imaging, the receptor cluster indicated by the arrow in Figure 3-9a is endocytosed (vesicular retrieval into the cell and hence moving away from the thin illumination zone, Figure 3-9e) as evidenced by fluorescence dimming and disappearance over time (4s or so). Time-lapse imaging in Figure 3-9e shows that the cluster indicated by the arrow in Figure 3-9b is exocytosed from a previously internalized receptor-containing vesicle as evidenced by fluorescence increase over time as the vesicle approaches the thin illuminated subplasmalemmal region and eventually fuses with the plasma membrane.

Figure 3-9. (a) and (b) TIRF images of HepG2 cells applied with Gal-GQDs (scale bar = 5 μm). (c) and (d) Time-lapse TIRFM images of endocytosis (c) and exocytosis (d) of Gal-

GQD labeled galactose receptors (ASGPR). The images and video were recorded under excitation with a 488 nm laser. (e) Schematic illustration of the trafficking and recycling of galactose receptors.

3.3 Conclusions

In summary, we synthesized a new GQD via a modified hydrothermal route using pyrene as the precursor. The obtained GQDs are bright (QY ~31%), small size (~5.4 nm), easy to be covalently conjugated with biomolecules via its COOH groups, biocompatible, and highly soluble. For the first time, we functionalize GQDs with sugar moieties (galactose and mannose). Such sweet GQDs are instrumental to specifically label carbohydrate receptors and track their dynamics in real-time. This study opens a new perspective in the application of GQDs for bioimaging. While inheriting some intrinsic features from its 2D counterpart (graphene), GQDs with a number of new properties add a new dimension for graphene applications. Many 2D materials other than graphene are emerging.²³²⁻²³⁴ Their 0D forms similarly shall provide vast new opportunities in electronics, energy, catalysis, imaging and sensing.²³⁵

Chapter 4 Quasi-homogeneous Carbocatalysis for One-pot Selective Conversion of Carbohydrates to 5-Hydroxymethylfurfural Using Sulfonated Graphene Quantum Dots

Acid catalysis is one of the most routine operations in both industrial processes and laboratorial research. The production of platform chemicals, synthetic plastics, pharmaceuticals, as well as alternative fuels from biomass is usually realized through acid catalysis. Conventionally, liquid acids (such as sulphuric acid, hydrochloric acid, and hydracids) are used as the homogeneous catalysts to ensure high efficiency because reactants and catalysts can fully interact in the same phase. Nonetheless, they are corrosive and non-recyclable. And their disposal is costly and environmental unfriendly. Therefore, much effort has been spent to develop recyclable heterogeneous acid catalysts, including cation exchange resins,²³⁶ solid superacids,²³⁷ supported metal oxides,²³⁸ zeolites,²³⁹ and natural clays.²⁴⁰ But they usually suffer from poor catalytic efficiency due to limited accessible active sites and high mass transfer resistance. In addition, they are prone to deactivation due to fouling and environmental issues associated with the leakage of metal species. Carbon nanomaterials, which function as earth-abundant metal-free catalysts, hold promise to tackle the abovementioned challenges.²⁴¹⁻²⁴⁷

Qi et al. reported a cellulose-derived sulfonated amorphous carbon as the catalyst for dehydration of fructose to 5-hydroxymethylfurfural (5-HMF).²⁴⁸ The

catalyst is stable and easily recoverable after reaction. However, a good yield of product was obtained only when ionic liquid was used as the reaction solvent, which is expensive and not readily available. SO₃H-functionalized carbon nanotubes were employed in the acid-catalyzed transesterification of triglycerides.²⁴⁹ But the synthesis method involves a complicated process for SO₃H-functionalization. Zhao et al. demonstrated the use of graphene oxide (GO) sheets with diameter ranging from 2 to 10 mm for hydrolyzing cellulose to glucose with a production yield of 49.9%. But as GO sheets aggregate easily, the recyclability is not satisfactory.²⁵⁰

Herein, we employ GQD and sulfonated GQD (SGQD) in the onepot selective conversion of carbohydrates existed in biomass to 5-HMF (Scheme 4-1). 5-HMF is a versatile platform molecule pivotal to biorefinery engineering and several industries like packaging, construction, textile, for example, they can be served as formaldehyde replacement in resins, adhesives and coatings. They are also building blocks of Furan-2,5-dicarboxylic acid and polyethylene furanoate. In this study, GQD and SGQD are discovered to act as quasi-homogeneous acidic catalysts in the reaction and SGQD even show exceptionally higher catalytic activity compared with some homogeneous catalysts. After reaction, they can be readily separated for reuse. That is, SGQD is able to unify the merits of heterogeneous and homogeneous catalysts as a novel carbocatalyst. The high efficiency of SGQD is further explored by DFT calculations. This study suggests the unique potential of such emerging zero-dimensional materials as a new class of catalysts for chemical processes.

Scheme 4-1. Synthesis of SGQD and its quasi-homogeneous behavior in one-pot carbohydrate transformation to hydroxymethylfurfural.

4.1 Materials and methods

4.1.1 Materials and characterization

Fructose ($\geq 99\%$, Alfa Aesar), Glucose (99.5%, Sigma-Aldrich), sucrose (99%, Sigma-Aldrich), cellobiose ($\geq 98\%$, Sigma-Aldrich), xylose ($\geq 99\%$, Sigma-Aldrich), ZSM-5 (Si/Al = 30, Alfa Aesar), Nafion (Sigma-Aldrich), Amberlyst-15 (hydrogen form, Sigma-Aldrich), inulin from chicory (Sigma-Aldrich), cellulose powder (Sigma-Aldrich), 5-HMF ($\geq 99\%$, Sigma-Aldrich), chlorosulfonic acid (98%, Sigma-Aldrich), methoxytrimethylsilane (99%, Sigma-Aldrich), carbon black (Cobat Corporation), carbon nanotube (Sigma-Aldrich), activated carbon (Johnson Matthey, United Kingdom) and other chemicals are commercially available. All the

chemicals were used without further purification. Brønsted ionic liquid was prepared according to the previous report.²⁵¹

FT-IR measurements were performed on a Bruker Tensor spectrometer. The TEM images were taken by JEOL 2100F ultra-high transmission electron microscope with a ZrO/W Schottky Field Emission Gun with an accelerating voltage of 200 KV. Scanning TEM-energy-dispersive X-ray (STEM-EDX) spectrometry with high-angle annular dark field was used for element mapping. Atomic force microscopic (AFM) images were collected from Bruker Dimension Icon system. Raman spectroscopy (Renishaw InVia Reflex Raman) was obtained at an excitation wavelength of 633 nm.

The acidic sites on GQDs and SGQDs were determined by pyridine adsorption characterized by FTIR. In this experiment, FTIR spectra were recorded by Nicolet-6700 FT-IR spectrophotometer with a resolution of 4.0 cm⁻¹. A self-supported wafer of tested sample was placed inside a quartz IR cell equipped with CaF₂ windows. The samples were pretreated under vacuum (0.01Pa) at 350 °C for 2 h. The background spectra were recorded after cooling down to room temperature, IR spectra of adsorbed pyridine on the samples were collected after exposure of the wafer to excess pyridine vapor at room temperature for 0.5 h. Excess of pyridine was desorbed by evacuating the samples at 150 °C and 300 °C respectively for 0.5 h. The spectra of pyridine adsorption were obtained by subtraction of the background spectrum from the sample spectrum.

The acidic strength of GQDs and SGQDs was measured by temperature programmed desorption (TPD) of ammonia on a MicromeriticsAutoChem 2910

instrument. Before adsorption, the samples were pre-treated under Argon stream at 300 °C. Subsequently, they were cooled down to 100 °C at an Argon flow rate of 20 cm³/min before the ammonia adsorption started. The adsorption step was carried out by allowing small pulses of ammonia in Argon at 100 °C until saturation (normally 1 h). The samples were exposed to an Argon flow of 50 cm³/min for 2 h at 100 °C. Finally, the desorption was performed from 100 °C to 600 °C at 10 °C/min and maintained at 600 °C for 10 min under Argon stream of 50 cm³/min. (the adsorbate was completely desorbed under this conditions).

The content of carbon, oxygen and sulfur on the surface of GQDs/SGQDs were determined by X-ray photoelectron spectroscopy (XPS, Escalab MK II spectrometer), using an Al X-ray excitation source ($K\alpha = 1487.6$ eV). The amount of the functional groups bonded to SGQDs was estimated by elemental analysis (vario EL cube, ELEMENTAL) and cation-exchange analysis.²⁵²⁻²⁵³ The density of -SO₃H groups were calculated based on sulphur content obtained from element analysis. Subsequently the contents of SO₃H + COOH and SO₃H + COOH + OH were determined by the exchange of Na⁺ in aqueous solutions of NaCl and NaOH, respectively. The proportions of each functional group were estimated based on the analysis results.

4.1.2 Catalyst preparation

GQDs were synthesized according to the previous procedure,²³ using carbon black as raw material. To achieve sulfonation, 1 g of GQDs were pretreated by calcination under N₂ at 300 °C for 1 h to form a dark solid, which is subsequently dispersed in chloroform containing 5 mL of chlorosulfonic acid. The mixture was

continuously refluxed under N₂ with vigorous stirring for 24 h at 70 °C. After cooling down to room temperature, the suspension was centrifuged, diluted with DI water and neutralized with concentrated NaOH solution. The mixture was further filtered with a 0.2 mm syringe membrane followed by dialysis for 3 days (with 500 Da MWCO) to remove salts. The catalyst powder was finally obtained after freeze drying. Other sulfonated carbon materials (e.g. sulfonated carbon nanotube, sulfonated activated carbon) are synthesized following the same procedure.

To identify the effect of -OH groups in SGQDs on the catalytic performance, methoxytrimethylsilane (MTS) was used to block the groups via condensation of -OH in SGQDs with MTS.²⁵⁴ In a typical procedure, 1.0 g of SGQDs was dispersed in 50 ml of toluene to form a suspension. 1.65 mmol MTS was added to the suspension and the resulting mixture was treated under refluxing at 70 °C for 12 h and then cooled to room temperature. After filtration, the solid was washed three times with anhydrous ethanol, and finally dried overnight at 100 °C. MTS-modified SGQDs (designated as SGQDs-MTS) was finally obtained.

4.1.3 Catalytic reactions and analysis techniques

The catalytic reaction was performed in a 10 ml capacity flask equipped with a low-temperature condenser at 1 °C. In a typical run, fructose, catalyst and solvent were charged into the flask. The mixture was then heated to 170 °C under stirring. After 2 h, the reaction was quenched in an ice bath. The 5-HMF product predominately stays at the upper phase (organic phase) while the catalyst and the unreacted hydrophilic reactants remained in the lower phase (aqueous phase). SGQDs are separated from the aqueous phase by dialysis using a 500 Da MWCO

dialysis bag for reuse. 5-HMF in both organic phase and aqueous phase were sampled and analyzed by HPLC apparatus (Agilent 1100 Series) equipped with XDB-C18 column and a UV detector at 320 nm, using a 2:8 v/v methanol: water as the mobile phase. While the sugars/sugar derivatives in both phases were analysed by the Bio-Rad Aminex HPX-87H pre-packed column (300mm $\times$ 7.8 mm) and refractive index detectors (RID) equipped on the HPLC apparatus. 5mM H₂SO₄ was employed as the mobile phase.²⁵⁵ An external standard method was used for quantifying the products. The identities of the compounds were authenticated by comparing their retention times with those of pure compounds. The carbohydrate conversion and the molar yield of 5-HMF, as well as the molar yield of other products were calculated from the product concentration in both two phases.

4.1.4 Calculation methods

The optimizations were performed using density functional theory (DFT) with the popular Becke's three-parameter hybrid functional (B3LYP) method and the 6-311++G(d) basis set.

Atoms in molecule theory (AIM) analyses were performed for the optimized structures, which has been widely used for analyzing the hydrogen bond (HB) containing systems and proved to be useful and successful tools for interpreting hydrogen-bonding interactions.²⁵⁶ The interaction energies refer to the energy differences between the pairs and the corresponding isolated compound. The basis set superposition errors (BSSEs) produced in the calculations was evaluated by the Boys-Bernardi counterpoise technique. In the AIM analysis, the electron density (ρ), the Laplacian of electron density ($\nabla^2 \rho$), and the energy density (H) at the bond

critical point (BCP) were used to quantify the Hydrogen-bonding interaction. All the calculations were performed using the Gaussian 09 computational package while the AIM topological analysis was performed using Multiwfn 3.3.9.

4.2 Results and discussion

Previously, Wang et al. reported three-step sulfonation of graphene oxide microsheets involving thermal annealing (800 °C), reduction of graphene oxide by n-butyllithium and sulfonation of reduced graphene oxide by chlorosulfonic acid.²⁵⁷ In contrast, we obtained sulfonated GQDs (SGQDs) by a facile synthesis which is more practical and readily engineered.

Figure 4-1. (a) FTIR spectrum, (b) Raman spectra, (c) XPS spectra, and (d) acidity characterization of GQDs and SGQDs.

Figure 4-1a shows the FTIR spectra of GQDs and SGQDs respectively. The vibrational peaks originated from epoxides (C-O-C at ~ 1280 - 1330 cm^{-1}), sp^2 -hybridized C=C (in-plane vibrations at $\sim 1580\text{ cm}^{-1}$), and edge groups such as carbonyls or carboxyls (C=O or COOH at ~ 1650 - 1750 cm^{-1}) are observed in GQDs. In comparison, the epoxide peak significantly declines in SGQDs. The appearance of vibrational bands at 1130 cm^{-1} , 1215 cm^{-1} , arisen from S=O asymmetric and symmetric stretching of $-\text{SO}_3\text{H}$, further confirms successful grafting of sulfonic groups onto SGQDs. The broadband at 2300 - 2700 cm^{-1} is assigned to an overtone (Fermi resonance) of the bending mode of $-\text{OH}\cdots\text{O}=\text{}$ originated from a strong hydrogen bond, which is often found in strong liquid Brønsted acids such as $\text{CF}_3\text{SO}_3\text{H}$.²⁵² This observation implies that -OH groups in proximity on SGQDs are responsible for strong HBs.

In the Raman spectra depicted in Figure 4-1b, GQDs display a D band (A_{1g} breathing mode) at 1368 cm^{-1} and a G band (E_{2g} G mode) at 1590 cm^{-1} , resulting from sp^3 hybridized carbon atoms from the defects and sp^2 hybridized carbon atoms in the graphitic hexagonal lattice, respectively.⁸⁰ In comparison, the D to G ratio is increased, suggesting disruption of graphitic structure upon introduction of SO_3H groups. In addition, a blue shift of G band is observed from SGQDs, probably due to the formation of single-double bond alternation within the sp^2 hybridized carbon domains when two hydroxyl groups are grafted adjacently on the basal plane.²⁵⁸

As seen from the X-ray photoelectron spectroscopy spectra in Figure 4-1c, in addition to the common C1s peak at 284.5 eV and O1s peak at 530.8 eV as observed in GQDs, additional S2s peak at 233.1 eV and S2p peak at 169.8 eV arise

in SGQDs, indicative of the successful conjugation of SO_3H groups. The atom percentages of carbon, oxygen, and sulphur in SGQDs are 60.53%, 34.71%, and 4.76%, respectively. The sulphur content is much higher than other sulfonated carbon material,²⁵⁹⁻²⁶¹ implying that SGQDs should have stronger Brønsted acidity. The total O/S atomic ratio ($\sim 7:1$) of SGQD is much higher than the O/S atomic ratio of $-\text{SO}_3\text{H}$ groups (3:1), suggesting that many oxygen-containing groups (e.g. $-\text{COOH}$, $-\text{OH}$) remain after GQD being sulfonation.

Figure 4-2. The XPS spectra for the deconvoluted C1s peak, O1s peak, and S2p peak.

The high-resolution C1s XPS peak of original GQDs can be deconvoluted into C=C (graphitic carbon) at 284.7 eV, C-C (sp³-hybridized carbon) at 285.4 eV, C-O-C/C-OH (epoxy/hydroxyl) at 286.8 eV and C(=O)-OH (carboxylic group) at 289.5 eV (Figure 4-2). In comparison, the 286.8 eV peak decreases in SGQDs, indicating that many epoxy groups on basal plane (which are more vulnerable to reduction as compared with hydroxyl groups) are removed after the thermal annealing.²⁶² This is consistent with the FTIR spectrum that the epoxy peak declines sharply in SGQDs. Taken together, the oxygen functionalities in SGQDs are mainly phenolic OH, COOH/C=O, and SO₃H. Similar to GQDs, SGQDs show a peak of C=C (~284.7 eV), suggesting that the graphitic structure is still preserved after sulfonation. GQDs and SGQDs share similar O1s spectrum whereas SGQDs display a new peak at 169.8 eV in S2p spectrum caused by SO₃H groups. Elemental analysis and cation exchange experiment are used to confirm the composition of SGQDs, and it is determined to be CH_{0.465}O_{0.573}S_{0.079}. The amount of SO₃H, COOH, and phenolic OH groups are calculated to be 3.1, 1.5, and 3.5 mmol·g⁻¹ respectively.

The acidity of GQDs and SGQDs is determined by pyridine adsorption FTIR (Figure 4-1d). After pyridine desorption at 150 °C, a small peak at 1456 cm⁻¹ (indicative of Lewis acidity) and a prominent peak at 1531 cm⁻¹ (indicative of Brønsted acidity) are observed in SGQDs. The Lewis acidity is probably originated from the dehydration of Brønsted acid sites or electron inductive effect of the S=O bonds as demonstrated by Pravin et al.,²⁵⁴ while Brønsted acidity is originated from -SO₃H and -COOH groups. When desorption temperature is increased to 300 °C, Lewis acidity peak remains unchanged while Brønsted acidity peak decreases

obviously due to the loss of weak Brønsted acidity. In comparison, original GQDs show weaker Brønsted acidity and no obvious Lewis acidity. Taken together, after sulfonation, not only Brønsted acidity is significantly enhanced by addition of SO₃H groups, but also a small amount of Lewis acidity is induced onto SGQDs. The ratio of Brønsted acidity to Lewis acidity was determined to be 3.73 (Figure 4-1d).

The acid strength and amount are evaluated by temperature programmed desorption of ammonia (NH₃-TPD). 1.05 mmol·g⁻¹ of weak acid sites (<270 °C), 2.31 mmol·g⁻¹ of medium acid sites (270~400 °C) and 0.22 mmol·g⁻¹ of strong acid sites (>400 °C) are found in SGQDs while 1.23 mmol·g⁻¹ of weak acid sites and 0.35 mmol·g⁻¹ of medium acid sites are observed in GQDs. Evidently, medium acid sites dominate in SGQDs, which is favorable to dehydration of hexoses to HMF or HMF-derivatives. The acidity distribution of SGQDs is in accordance with the co-existence of weak and strong Brønsted acidity as revealed by pyridine adsorption FTIR experiments. The observations that GQDs have no strong acidic sites and a much less amount of medium acidic sites is also in line with the notion that GQDs only have weak Brønsted acidity.

Figure 4-3. (a) TEM image of SGQDs with corresponding EDS mapping for S element. (b) TEM-EDS line scanning with a spectrum for C, O, S element distribution. (c) AFM image of SGQDs. Inset shows the height profile along the indicated line. (d) Diameter distribution of SGQDs ($n = 110$). (e) height distribution of SGQDs ($n = 152$).

Figure 4-4. (a) TEM image and (b) AFM image of GQDs.

As uncovered by transmission electron microscopy (TEM), SGQDs have a diameter about 10.4 nm (± 3.1 nm, $n = 110$) with a lattice spacing of 0.245 nm corresponding to (1120) plane of graphene (Figure 4-3a and d). GQDs have similar morphology (Figure 4-4), indicating that sulfonation doesn't cause structural changes. Energy-dispersive X-ray (EDX) spectroscopy mapping reveals that, rather than only residing at the edge sites, S element is uniformly distributed on the basal plane (presumably on both sides) of SGQD (Figure 4-3a). This is further confirmed by the TEM-EDS line scanning spectrum (Figure 4-3b). Such homogeneous conjugation of SO_3H groups is desirable for full utilization of active catalytic sites. Furthermore, atomic force microscopy (AFM) reveals that SGQDs have an average thickness of 1.06 nm (± 0.34 nm, $n = 152$), i.e., they are mostly single or double layered (Figure 4-3c and e).

Figure 4-5. Photograph of suspended GQDs (left) and SGQDs (right) in the aqueous system.

Both original GQDs and SGQDs can disperse well in aqueous solution to serve as quasi-homogenous acidic catalysts (Figure 4-5). We examined SGQD's ability to dehydrate fructose into 5-HMF in different solvent systems. As shown in Figure 4-6a, the production yield of 5-HMF is very low (17.1%) in pure water

accompanied with a considerable amount of condensation compounds (43.5%) because water is a non-selective solvent for Brønsted acid-catalysed conversion of carbohydrates because many reaction pathways are possible.²⁶³ Adding organic solvent can extract the produced 5-HMF and consequently avoid its further reactions in aqueous phase (e.g., condensation and rehydration).²⁶⁴ Using MIBK: butanol (v/v of 7:3) as the extracting solvent (solvent: water at w/w of 2:1),²⁶⁵ conversion of fructose and yield of 5-HMF are increased to 46.1% and 22.3% respectively. Meanwhile, produced 5-HMF is extracted from aqueous phase into organic phase with high purity. Such in-situ extraction not only improves the yield but also is desirable for convenient and high purity collection of 5-HMF. However, a large amount of condensation compounds (42.1%) is still observed. Previous work has shown that DMSO can effectively inhibit the formation of condensations such as insoluble humins.²⁵⁵ As shown in Figure 4-6a, with addition of DMSO in water (DMSO: water of v/v of 7:3), conversion of fructose and yield of 5-HMF are significantly enhanced to 89.5% and 41.7% while the undesired condensation compounds are obviously decreased to 38.1%. However, it is difficult to separate 5-HMF from DMSO by distillation because DMSO has a high boiling point (189 °C). Therefore, it is conceivable that combining both extraction solvent and inhibitory solvent shall be desirable. Indeed, in the biphasic system (aqueous phase containing DMSO and water with v/v of 7:3; organic phase containing MIBK and butanol with v/v of 7:3; total aqueous to organic w/w ratio of 1:2), conversion of fructose and the yield of 5-HMF are increased to 91.8% and 51.7%, while condensation is decreased

to 36.5% (Figure 4-6a). Noteworthy, this system allows collection of 5-HMF with high purity simply by evaporation while SGQDs remain in the aqueous phase.

Figure 4-6. Effects of solvent composition (a) and initial fructose concentration (b) on product yields (left y axis) and fructose conversion rate (right y axis).

Also note that in the above experiments, we used a very high fructose concentration (20 wt%). Generally, a high substrate concentration is preferable to improve the absolute production yield in a chemo-catalytic process. But the higher the initial fructose concentration the lower production yield of 5-HMF due to formation of condensation compounds (Figure 4-6b). Therefore, most of current methods do not use initial fructose concentration >5 wt%.²⁶⁶⁻²⁶⁷ Not surprisingly, when we reduce the initial fructose concentration to 5 wt%, the yield of 5-HMF is further increased to 65.3% (Figure 4-6b). The allowance of high substrate concentration by SGQD is attributable to its abundant medium acid sites which favors the dehydration of fructose to 5-HMF since strong acid sites are favorable for the formation of unwanted coking material (e.g. char, humins).²⁶⁸ Increase of fructose concentration leads to a higher conversion due to the production of more

condensation products through polymerization of fructose.²⁶⁹ Therefore, 20 wt% of fructose is chosen to balance the absolute production yield and selectivity of 5-HMF.

Figure 4-7. Correlation between a) SO₃H density and 5-HMF yield; b) total acidity and fructose conversion.

Table 4-1. The efficiency of different catalysts in the dehydration of fructose

Entry	Catalysts ^a	Total acidity ^b (mmol/g)	SO ₃ H density ^c (mmol/g)	Conversion (%)	Molar yield (%)		
					5-HMF	Condensation Compounds	Rehydration Compounds
1	Blank	—	—	14.7	0.6	3.0	0.15
2	GQDs	2.0	—	54.6	31.2	17.6	0.78
3	SGQDs	4.7	3.1	91.8	51.7	36.5	1.34
4	H ₂ SO ₄	20.4	—	63.7	44.2	17.5	1.29
5	HCl	27.3	—	97.6	60.1	12.8	1.86
6	Brønsted ionic liquid	13.8	—	77.5	48.4	26.5	1.29
7	ZSM-5	0.6	—	27.3	8.5	1.36	2.67
8	Amberlyst-15	4.9	4.5	62.3	36.5	5.35	0.62
9	Nafion	0.7	6.8	49.1	30.2	3.25	0.75
10	SCNT	1.8	1.5	50.2	28.1	10.2	0.32
11	SAC	3.3	2.1	55.1	33.5	8.9	1.25
12	SGQDs-MTS	4.5	3.0	69.8	29.1	7.26	1.33

^a Reaction condition: The initial fructose concentration of 20 wt% with respect to aqueous phase was used in the reaction. The catalyst dosage is 40 mg. The reaction was performed at 170°C for 2 h under a biphasic solvent system (7:3 (v/v) DMSO: water and 7:3 (v/v) MIBK: butanol).

^b Total acidity was determined by titration.

^c SO₃H density was determined by element analysis.

Various acid catalysts at the same dosage are tested for comparison (Table 4-1). Notably, even weakly acidic GQDs can give a 5-HMF yield of 31.2% and a fructose conversion of 54.6%, outperforming other non-SO₃H functionalized graphene oxide sheets with similar total acidity.²⁵⁴ This implies that the quasi-homogeneity of GQD is desirable owing to full exposure of the active sites to the reactants in the same phase and unhindered mass transport. SGQD is much superior not only to original GQD because of its abundant medium Brønsted acidic sites but also to the common heterogeneous catalysts (Amberlyst-15, ZSM-5 and Nafion), sulfonated carbon nanotube (SCNT), and sulfonated activated carbon (SAC) with a considerably higher SO₃H density (entry 7-11, Table 4-1) because of the full utilization of SGQD's active sites. As shown in Figure 4-7a and b, although the SO₃H density and total acidity of SGQD are lower than some solid catalysts, it outperforms them. It suggests that the quasi-homogeneity and other properties of SGQDs also play important roles.

Remarkably, SGQD even exhibits better catalytic activity than the commonly used homogeneous catalysts (Brønsted acidic ionic liquid and H₂SO₄) which have much higher total acidity than SGQD (entry 4 and 6, Table 4-1). It

implies that the physicochemical properties of SGQD also determine in its catalytic performance. Conceivably, the chemical moieties on SGQDs may exert synergistic effects. Although HCl offers slightly higher yield than SGQD, it is corrosive, environmental unfriendly and not recoverable. Interestingly, in contrast to other heterogeneous or homogeneous catalysts, SGQD gives almost 100% carbon mass balance without apparent carbon loss to rehydration reaction and production of CO₂. It means that fructose dehydration and condensation are the two dominating reactions catalyzed in parallel by SGQD. We speculate that it may be possible to further functionalize SGQD in order to inhibit the condensation pathway whereby to improve the yield and selectivity of 5-HMF production.

Table 4-2. Production of 5-HMF from various carbohydrates catalyzed by SGQDs ^a.

Entry	Substrate	Conversion (%)	Molar yield (%)		
			5-HMF	Condensation compounds	Rehydration compounds
1	Inulin	90.7	52.3	—	0.87
2	Xylose	41.9	18.3	14.9	7.85
3	Sucrose	79.5	39.2	—	1.68
4	Glucose	45.1	19.5	4.68	1.35
5	Cellobiose	91.2	13.2	19.4	0.11
7	Ball-milled cellulose ^b	78.9	22.2	40.7	10.2

^a Reaction condition: The initial concentration of substrate is 10 wt%. The catalyst concentration is 60 mg. The reaction was performed at 170°C for 2 h under a biphasic solvent system (7:3 (v/v) DMSO: water and 7:3 (v/v) MIBK: butanol).

^b Reaction is conducted in a 15 mL autoclave in presence of 25mg cellulose and 100mg SGQDs under hydrothermal for 2 h at 170°C. The yield of all the products in the reaction refers to weight percentage (wt%).

SGQD was further evaluated for biomass transformation to 5-HMF using different feedstocks. As shown in Table 4-2, dehydrations of inulin and xylose catalyzed by SGQD give 52.3% and 18.3% of 5-HMF yield respectively. Xylose is the major compound in hemi-cellulose while inulin is a fructose polymer obtainable from chicory, the successful degradation of these compounds suggests the potential of SGQD in biomass transformation. Sucrose is the most abundant disaccharide containing a glucose unit and a fructose unit. 39.2% yield of 5-HMF is obtained from sucrose. When glucose is subjected to this reaction, 19.5% yield and 45.1% conversion rate are obtained (entry 4, Table 4-2). In contrast to fructose dehydration via cyclic furanose intermediate pathway, glucose dehydration undertakes acyclic intermediate pathway mediated by Brønsted acidic sites on SGQDs.²⁷⁰ Due to the stable acyclic structure of the sugar intermediates, the energy barrier for 5-HMF production is much higher from glucose than from fructose. Interestingly, the yield of 5-HMF from glucose catalyzed by SGQD is considerably higher than that from commonly used SO₃H-functionalized catalysts (typically <5%).²⁷¹ Therefore, it is conceivable that the Lewis acid sites on SGQD catalyze the isomerization of glucose into fructose with a low energy barrier and subsequently Brønsted acidic sites converts fructose into 5-HMF (Scheme 4-1). As compared to glucose, cellobiose shows a slight decrease of 5-HMF yield (13.2%) but much higher conversion (91.2%). Surprisingly, a good 5-HMF yield of 22.2 wt% and conversion rate of 78.9% is produced from cellulose under atmospheric pressure, which is the most abundant biomass resources and whose decomposition involves a cascade of complicated reactions.²⁷² Likely, SGQD is able to readily catalyze cellobiose and cellulose into

glucose because of abundant medium Brønsted acid sites on SGQD (Figure 4-1d). These results demonstrate the unique potential of SGQD for transformation of nonedible lignocellulosic biomass.

Figure 4-8. The geometries between fructose and a) -OH, b) -COOH, and c) -SO₃H of SGQDs. The geometry with lowest EZPE* in the three cases refers to geometry I, geometry II and geometry III respectively.

Figure 4-9. Hydrogen bonding between fructose (F) and functional groups of -OH, -COOH, and -SO₃H in SGQDs.

The enhanced catalytic performance of SGQD cannot be explained only by the good dispersibility and the strong Brønsted acidity since H₂SO₄ is inferior to SGQD in fructose dehydration (Table 4-1). In a study using a sulfonated amorphous carbon material, Suganuma et al. guessed that -OH groups can adsorb cellulose whereby facilitating the proton attack on cellulose from -SO₃H groups.²⁵³ Pravin et al. also suggested that the synergistic effect of -SO₃H with other functional groups such as -OH and -COOH is responsible for the high catalytic performance in decomposition of glucose.²⁵⁷ Nonetheless, they just provide a hypothesis rather than any mechanistic insights into this synergistic effect. Since SGQDs predominately

carry -COOH, -OH, and -SO₃H groups, the synergic cooperation between the groups and the reactant can be similarly speculated.

A DFT calculation is performed to investigate the hydrogen bonding interactions between fructose and the -OH group, -COOH group, and -SO₃H group on SGQD. Different geometries with possible interaction modes between fructose and the three groups of SGQDs are systematically optimized (Figure 4-8). The most three stable geometries with lowest relative zero-point energy (ΔE_{ZPE}^*) in the three respective groups are obtained and as indicated as geometry I, geometry II and geometry III respectively (as shown in Figure 4-9). The HB distribution is identified in these geometries. As seen, two inter-HBs ($\text{O}_1\text{-H}_1\cdots\text{O}_2$ and $\text{O}_3\text{-H}_5\cdots\text{O}_4$) and three intra-HBs ($\text{O}_4\text{-H}_3\cdots\text{O}_1$, $\text{O}_2\text{-H}_4\cdots\text{O}_5$ and $\text{O}_5\text{-H}_2\cdots\text{O}_3$) are observed in the geometry I. These HBs form a loop which presumably resulting in strong affinity of SGQDs for the fructose molecule. Because a small SGQD has abundant and uniformly distributed -SO₃H groups, which shall be available in the close vicinity of the interacting fructose. The proton attack from the -SO₃H group of SGQDs on the O₅-H₂ group at the anomeric carbon atom in fructose will become more efficient due to their proximity. Since the protonation of O₅-H₂ is the most thermodynamically favored step that induces the subsequent dehydration steps to produce 5-HMF, the efficient protonation of it will result in enhanced reaction efficiency. Although similar HB distribution is also observed in geometry II and geometry III, the HB strength and interaction energy (E) of the three geometries are different. As seen in Table 4-3, the parameters of charge density (ρ), the Laplacians of the charge density ($\nabla^2\rho$), and the energy density (H), which are considered as the descriptors of the

hydrogen bonding strength, show that the intra-molecular HB of $O_4-H_3\cdots O_1$ in geometry I presents the largest charge ρ , $\nabla^2\rho$ and H among all the HBs, implying the strongest interaction between the two neighboring -OH groups in SGQDs. This HB is even higher than the inter-molecular HB of $O_1-H_1\cdots O_2$ in geometry III which is well-known to be a strong HB. The significantly stronger HB strength of $O_4-H_3\cdots O_1$ is probably due to the σ -type orbital overlap between the lone pairs of O_1 as HB acceptor and the bonding orbital of O_4-H_3 as HB donator. The participation of $O_3-H_4\cdots O_1$ in the loop is believed to facilitate the stabilization of geometry I, resulting in a much lower E than that of geometry II and geometry III. Accordingly, the presence of HB resulted from the neighboring -OH groups is predominantly responsible for the strong affinity of SGQDs with fructose via the HB loop while the -COOH groups and the -SO₃H groups execute Brønsted acid function as catalytic active sites. But eSO₃H is more catalytically active than -COOH. In sum, SGQDs absorb fructose via the strong HB resulting from the neighboring -OH groups on SGQD (the blue shift in the Raman spectra of SGQD indicates the presence of adjacent -OH groups) while the -COOH groups and -SO₃H groups, rather than form the HBs with fructose, release the proton to activate the fructose. Such synergy greatly enhances the catalytic efficiency.

Table 4-3. Charge density (ρ), Laplacian of charge density($\nabla^2\rho$), and Energy density (H) at the bond critical point of HBs by AIM study and interaction energies at B3LYP/6-311++G(d) level of theory.

	Geometry I				
	Inter-molecular HB		Intra-molecular HB		
	O ₁ -H ₁ ...O ₂	O ₃ -H ₅ ...O ₄	O ₄ -H ₃ ...O ₁	O ₂ -H ₄ ...O ₅	O ₅ -H ₂ ...O ₃
$\rho (\times 10^{-2})$	5.174	2.853	6.774	4.144	2.883
$\nabla^2\rho (\times 10^{-1})$	1.489	0.818	2.038	1.337	9.587
$H (\times 10^{-4} \text{ a.u.})$	-36.65	-17.63	-75.15	-19.04	-9.886
E ^a (kJ/mol)	14.64				
	Geometry II				
	Inter-molecular HB		Intra-molecular HB		
	O ₁ -H ₁ ...O ₂	O ₃ -H ₂ ...O ₄	O ₆ -H ₃ ...O ₁	O ₅ -H ₄ ...O ₆	
$\rho (\times 10^{-2})$	3.351	5.020	3.171	2.534	
$\nabla^2\rho (\times 10^{-1})$	1.089	1.546	1.032	0.985	
$H (\times 10^{-4} \text{ a.u.})$	-5.349	-22.97	-13.04	-6.275	
E ^a (kJ/mol)	33.68				
	Geometry III				
	Inter-molecular HB		Intra-molecular HB		
	O ₁ -H ₁ ...O ₂	O ₄ -H ₂ ...O ₃	O ₂ -H ₃ ...O ₅	O ₅ -H ₄ ...O ₄	
$\rho (\times 10^{-2})$	6.032	2.991	4.340	3.168	
$\nabla^2\rho (\times 10^{-1})$	1.687	0.943	1.404	1.036	
$H (\times 10^{-4} \text{ a.u.})$	-54.10	-9.917	-19.71	-12.82	
E ^a (kJ/mol)	36.89				

^a. E is the interaction energy between the pairs and the corresponding isolated compound. All of the energies include BSSE and ZPVE corrections based on the results at the B3LYP/6-311++G(d) level of theory.

To experimentally illustrate their critical roles, -OH groups on SGQD are blocked by methoxytrimethylsilane (MTS), which is confirmed by the decrease of the hydrophilicity index (HI) of SGQD-MTS from 2.86 to 2.61. As the consequence, 5-HMF yield and conversion rate obtained from SGQD-MTS is drastically reduced (yield: 29.1% vs. 51.7%; conversion: 69.8% vs. 91.8%) as compared with SGQD (Table 4-1). This experiment unambiguously corroborates the critical importance of -OH groups on SGQD. When -OH groups are not present, the degradation in catalytic performance is attributable to i) weakened interaction between SGQD and fructose and ii) weakened Brønsted acidity from -SO₃H groups because they can form HBs with fructose.

Figure 4-10. (a) Recycling scheme. (b) The performance of recycled SGQDs in dehydration of fructose to 5-HMF. The reaction conditions are the same as that in Table 4-1.

After reaction, the biphasic reaction system undertakes phase separation without stirring. 5-HMF molecules were extracted into the organic phase while SGQDs are still homogeneously dispersed in the aqueous phase. Subsequently 5-HMF molecules can be simply collected from the organic phase by evaporation while SGQDs are separated from the aqueous phase by dialysis for reuse (Figure 4-

10a). As shown in Figure 4-10b, even after 7 times of reuse, 36.8% of 5-HMF yield and 81.3% of fructose conversion still can be achieved. This is likely due to ~0.85 mol% S loss as revealed by element analyses. On the other hand, FTIR characterization shows that -SO₃H groups, Brønsted acidity, and Lewis acidity are still well-preserved in SGQDs after reuses (Figure 4-11). Similar to SGQD, after 5 times of reuse of GQD, its 5-HMF yield and fructose conversion rate only slightly decreased from 31.2% to 28.7% and 54.6% to 50.3% respectively. Furthermore, TEM and TEM-EDS characterizations of reused GQDs and SGQDs indicate that the morphology, size and element contents of both GQD and SGQD are well preserved (Figure 4-12). Unavoidably, a small amount of insoluble humins is produced from conversion of carbohydrates to 5-HMF. Deactivation of heterogeneous catalysts is largely caused by humins. In contrast, well-dispersed SGQDs are immune from this. Even after reuses, SGQD is still highly and stably dissolvable. Taken together, SGQDs can serve as quasi-homogeneous carbocatalysts with both good efficiency and recyclability.

Figure 4-11. (a) FTIR spectra and (b) pyridine-adsorption FTIR spectra for the reused SGQDs.

Figure 4-12. (a) TEM image of reused SGQDs after 5 times recycling; (b) EDS line scanning with spectrum for C, O, S element distribution; (c) TEM image of reused GQDs after 5 times recycling; (d) EDS line scanning with spectrum for C, O element distribution.

4.3 Conclusions

A novel quasi-homogeneous catalyst, namely sulfonated GQDs (SGQDs), is developed for one-pot biomass transformation to 5-HMF. SGQDs unify the advantages of both homogeneous and heterogeneous catalysts. Specifically, it can achieve high efficiency as homogeneous catalysts because its excellent dispersibility and molecular size ensure full accessibility by the reactants and unhindered mass transport. On the other hand, unlike the corrosive and unrecoverable homogeneous catalysts (e.g., H_2SO_4 , HCl), SGQD is environmentally friendly, and can be recycled just like heterogeneous catalysts. Although sulfurizing GQDs requires strong acid, the amount needed is several orders lower than the acid needed as the homogeneous

catalyst. Furthermore, the superior catalytic ability of SGQD is also benefited from the synergistic cooperation between the Brønsted acidic sites ($\text{-SO}_3\text{H}$ groups) and hydroxyl (-OH) groups on SGQDs. Lastly, the large amount of medium acid sites on a SGQD enhances its catalytic performance. This study suggests the potential of SGQD as an efficient and green carbocatalyst for one-pot transformation of biomass or biomass-derivatives and more generally the unique potential of functionalized GQDs as novel quasi-homogeneous catalysts for various reactions. In principle, GQDs could be equipped with multiple catalytic properties (e.g., by doping heteroatoms, grafting of different chemical moieties, or decoration with functional nanoparticles), so that, to gain the ability of one-pot catalysis of multi-step reaction to produce complex molecules in molecular proximity.

Chapter 5 Systematic Bandgap Engineering of Graphene Quantum Dots and Applications for Photocatalytic Water Splitting and CO₂ Reduction

In this chapter, we demonstrate two distinct strategies to systematically narrow the bandgap of GQDs to produce a series of GQDs with varying bandgaps. Because the bandgap of pristine GQD (separation between π and π^* orbitals) is inversely proportional to the size of sp^2 domain,^{19, 77, 80} narrowing bandgap can be achieved by conjugating GQDs with poly aromatic rings to enlarge the π -conjugated sp^2 -carbon network. Alternatively, bandgap narrowing can be realized by introducing an intermediate n-orbital between π and π^* orbitals *via* functionalization with electron-donating chemical groups. Many types of GQDs contain electron-withdrawing oxygenated functional groups (e.g., $-COOH$ and $-CHO$), conferring the GQD with p-type conductivity.^{158, 160, 273} Hence upon conjugation with electron-donating chemical groups, intramolecular Z-schemes structure²⁷⁴ forms on GQD, which consists of p-type oxygenated groups, n-type conjugates,^{158, 160, 275-276} and sp^2 ohmic contact (mediator) in between.

Both narrow bandgap and Z-scheme structure are desirable for photocatalysis because the former ensures stronger and wider light adsorption, while the latter promotes separation of photoexcited electron-hole pairs. In this work, we demonstrate gradual bandgap narrowing of GQDs from 2.4 to 1.88 eV (green to red) and apply the narrow bandgap GQDs for photocatalytic water splitting and CO₂ reduction with high performance.

5.1 Materials and methods

5.1.1 Synthesis of coal GQDs and functionalization.

Coal GQDs were obtained from Dotz Nano (Israel). As previously reported,²⁰ GQDs were prepared from anthracite coal through refluxing at 120 °C for 24 h with concentrated nitric acid and sulfuric acid, followed by cross-flow ultrafiltration (cutoff molecular weight 5 kDa). To functionalize GQDs, toluene (10 mL) containing 10 mg of coal GQDs was added with o-phenylenediamine (OPD, 50 mg), 2,3-diaminonaphthalene (DNPT23, 50 mg), 1,8-diaminonaphthalene (DNPT18, 50 mg), 1,1'-bi(2-naphthylamine) (BNPTL, 50 mg), panisidine (Anln-OCH₃, 50 mg), 4-(trifluoromethoxy)aniline (Anln-OCF₃, 50 mg), or 4-(trichloromethoxy)aniline (Anln-OCCL₃, 50 mg), followed by solvothermal reaction at 180 °C for 12 h in a sealed Teflon-lined autoclave. Subsequently, the resulting solutions were dialyzed with cellulose ester dialysis membrane (MWCO 500–1000 Da) to remove excessive organic molecules and toluene. Finally, the solutions were concentrated by a rotatory evaporator and freeze-dried.

5.1.2 Characterization

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were conducted with JEOL JEM 2010 and Bruker ICON AFM, respectively. X-ray photoelectron spectroscopy (XPS) measurement was performed on VG Multilab 2000 spectrometer (Thermo) with an Al K α 1846.6 eV anode. C 1s peak at 284.6 eV was employed as reference to calibrate the binding energy. The Fourier-transform infrared spectroscopy (FTIR) and UV–vis absorption spectroscopy were obtained from PerkinElmer FTIR spectrometer (Spectrum One) and Shimadzu UV-

2450, respectively. Photoluminescence spectroscopy and lifetime measurement were carried out by a Fluorolog® TCSPC fluorescence spectrometer (HORIBA). The mass spectrometry (MS) has employed the Agilent LCMS 6130. The linear sweep voltammetry (Chenhua Electrochemical Station) was conducted at scan rate of 5 mV/s in 0.5 M Na₂SO₄ solution. The type of conductivity was determined by Mott–Schottky analysis¹⁵⁸ using an impedance spectrometer (Zahner IM6e, Germany) equipped with Thales software.

5.1.3 Density functional theory calculation

The Gaussian 09 program package was used to conduct DFT calculation. To simplify calculation without losing generality, the original GQD is represented by a 7-benzene ring, while the functionalized GQD only contains one conjugated moiety.

5.1.4 Photocatalytic performance

The photocatalytic water-splitting was conducted in a gas-enclosed irradiation system equipped with an evacuation setup and 300 W Xe lamp (Newport) with a 420 nm cutoff filter. 0.1 g of GQD catalysts was dispersed in 100 mL of water containing 10 vol % TEOA, with Pt as the co-catalyst (3 wt % Pt relative to GQDs). The amounts of generated H₂ or O₂ were examined by an online gas chromatography (Agilent, GC Model 6890N, TCD, carrier gas argon, 0.5 nm molecular sieve column). Before irradiation, the reaction vessel was evacuated and refilled with argon for five times to fill with pure argon gas (removing air), reaching about 30 Torr, kept at 20 °C by cooling water. Monochromatic illumination at 420, 460, 500, and 550 nm were used to determine the apparent quantum yield (AQY),¹⁶⁷ with illumination intensity of 0.74, 1.2, 1.2, and 1.1 mW·cm⁻², respectively. The irradiated area is 12.56 cm².

The CO₂ photoreduction reactions were conducted in a gas enclosed circulation system using Pyrex cell reactor. In each reaction, 0.1 g GQDs was uniformly spread on a glass reactor with the area of 4.2 cm². A xenon lamp (300 W) armed with a 420 nm cutoff filter (Newport) was used to irradiate the reactions. This reaction system was evacuated for several times, before purging high-purity CO₂ into the reaction system until ambient pressure. Then ultrapure water (1.0 mL) was injected into the system for humidity and electron donor. The Xe lamp was turned on after several hours when adsorption and desorption equilibrium of the gas and the photocatalyst was attained. The gaseous products from CO₂ photoreduction were analyzed by gas chromatography (Agilent GC 7890A, FID, carrier gas argon, Hayesep Q 80–100 column). Photoreduction of isotopically labeled ¹³CO₂ was analyzed by GC-MS (Agilent, GC 6890N, MS 5973 inert).

5.2 Results and discussion

As previously reported, GQDs were first synthesized through a one-step strong acid cutting using anthracite coal as the precursor.²⁰ This was followed by ultrafiltration and dialysis to obtain GQDs with an average diameter of 5.86 nm (± 1.13 nm; $n = 127$) and thickness of 1.19 nm (± 0.31 nm, 115 samples), as shown in Figure 5-1. The high-resolution TEM identifies the lattice spacing (0.21 nm) corresponding to graphene (100) facet.^{10, 277-278}

Figure 5-1. (a) TEM image of coal GQDs. (b) high-resolution TEM image of coal GQD. The inset shows the size distribution of GQDs (n=127). (c) AFM image of coal GQD. (d) Height distribution of coal GQD (n=115).

GQDs can disperse very well in water because of its extremely small size and many charged functional groups (e.g., $-\text{COOH}$). To enlarge the π -conjugated system (essentially, the size of GQD), we conjugated GQDs with four polyaromatic compounds, specifically, o-phenylenediamine (OPD), 2,3-diaminonaphthalene (DNPT23), 1,8-diaminonaphthalene (DNPT18), and 1,1'-bi(2-naphthalene) (BNPTL), through the condensation reaction between $\text{C}=\text{O}$ and $-\text{NH}_2$ to form $\text{C}=\text{N}$

bond under solvothermal condition (Figure 5-2). Conjugated GQDs can still disperse well in water, although the abundance of the charged functional groups is reduced.

Figure 5-2. Illustration of bandgap narrowing by enlarging π -conjugated system via conjugating GQD with poly aromatic rings or by introducing intermediate n-orbital via conjugating with electron-donating groups. For clarity, GQDs (contains ~ 60 carbon rings and various chemical groups) are oversimplified to a seven-ring structure. And for the same reason, only one conjugated moiety is illustrated for modified GQDs.

In Fourier transform infrared spectroscopy (FTIR), all GQDs exhibit the bands at 3500 cm^{-1} due to O–H stretching vibration from hydroxyl groups and at 1600 cm^{-1} due to C=C stretching from sp^2 carbon network (Figure 5-3a). Coal GQD shows a prominent C–O band at 1385 cm^{-1} and a widened C=C band at 1600 cm^{-1} due to overlapping from C=O stretching at 1631 cm^{-1} . The four modified GQDs all display a C–H band at 2900 cm^{-1} from the conjugates, a 1460 cm^{-1} band due to C=N between the conjugates and GQD, and a shifted C–O band at 1380 cm^{-1} . The large reduction of C=O vibration signal at 1631 cm^{-1} indicates the consumption of C=O sites on coal GQD by the conjugation reaction.

Figure 5-3. FTIR (a) and full-range XPS (b) of coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL.

Full range X-ray photoelectron spectroscopy (XPS) demonstrates C 1s, O 1s, and N 1s peaks at 284, 532, and 398 eV, respectively (Figure 5-3b).^{167, 279-280} Because of its high oxygen content, original GQD can also be regarded as graphene oxide quantum dot. The (O 1s)/ (C 1s) ratios are largely reduced after conjugating original GQD with OPD, DNPT23, DNPT18, and BNPTL because of C=N bond formation (Table 5-1). As expected, the (N 1s)/ (C 1s) ratios increase from 0 to ~5% after conjugating nitrogen-containing poly aromatic compounds. Both FTIR and XPS

characterizations unambiguously confirm the success of conjugation through the condensation reaction.

Table 5-1. Atomic ratios of (O 1s)/ (C 1s) and (N 1s)/ (C 1s) determined by XPS (Figure 5-3) of coal GQDs, GQDOPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL.

S/N	Name	Atomic ratio O 1s/C 1s	Atomic ratio N 1s/C 1s
1	Coal GQD	51%	NA
2	GQD-OPD	40%	5.8%
3	GQD-DNPT23	38%	5.4%
4	GQD-DNPT18	37%	5.5%
5	GQD-BNPTL	35%	4.3%

High-resolution C 1s spectra further confirm that the conjugation with OPD, DNPT23, DNPT18, and BNPTL apparently increases π -conjugated C=C bonds and consumes C=O bonds to generate C=N bonds (Figure 5-4a). The N 1s XPS peaks (Figure 5-4b) can be deconvolved into pyrazine N, pyrimidine N, amino N, and amide N peaks resulting from the three reaction modes between GQDs and aromatic amines (Figure 5-5). But note that pyrazine N is the dominating N form when a 1,4-diazine (pyrazine) ring is formed by condensation between two C=O and two ortho-amino groups (Figure 5-2). This observation also suggests that the other two reaction modes and physical adsorption of aromatic amines (which contributes to amino N peak) are negligible. The obtained conjugated GQDs are stable because the bonding energy of C=N is ~ 615 kJ/mol, decomposition of which only occur above 1200 K.

Figure 5-4. High-resolution C 1s XPS (a), and high-resolution N 1s XPS spectra (b) of coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL. In (b), the peak values for pyrazine N1s, pyrimidine N1s, amino N1s and amide N1s are 398.1 eV, 399.8 eV, 399.0 eV and 400.9 eV, respectively.

Figure 5-5. Solvothermal reaction pathways. Note that GQD is over-simplified as a coronene derivative.

According to the increase of molecular weight after conjugation as determined by mass spectrometry (Figures 5-6), it is estimated that on average 4.05 OPD, 4.16 DNPT23, 4.29 DNPT18, or 3.99 BNPTL molecules are conjugated onto one GQD. This is in a good agreement with the (N 1s)/ (C 1s) ratio characterized by XPS. In a control experiment, a small aromatic molecule 1,2-benzoquinone was conjugated with OPD. As evidenced by the FTIR characterization (as shown in Figure 5-7), phenazine is formed as expected without apparent other byproducts. This experiment proves that the used conjugation strategy works not only for GQDs (in a way they can be regarded as a giant aromatic molecule) but also small aromatic molecules.

Figure 5-6. The mass spectrometry (MS) of (a) coal GQD, (b) GQD-OPD, (c) GQD-DNPT23, (d) GQD-DNPT18, and (e) GQD-BNPTL.

Figure 5-7. Reaction equation (a) and FTIR spectra (b) of 1,2-benzoquinone, ophenylenediamine (OPD) and their reaction product phenazine.

Figure 5-8a presents the photographs of the aqueous dispersions of original GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL under UV mercury lamp. As seen, their fluorescence varies from green to red indicating the progressive bandgap narrowing (red shifting), while the size of the conjugated poly aromatic ring increases. Consistently, the photoluminescence (PL) emission peaks of original GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL also red-shift in order (Figure 5-8b). As revealed by the UV-vis absorption spectra (Figure 5-9a), the light adsorbing abilities are ranked as follows: GQD-BNPTL > GQD-DNPT18 > GQD-DNPT23 > GQD-OPD > GQD. As compared to the original wide bandgap green GQD, the light absorption of red GQD-BNPTL, which has the narrowest bandgap among all, is much stronger and extends much further into the

visible range. The strong absorption between 200–300 nm for all GQDs is due to $\pi-\pi^*$ transition in sp^2 basal plane, which is common for all graphene materials.⁷ The absorption shoulder at ~ 480 nm for original GQDs results from the electron transition from n-orbital (induced by the weak electron-donating $-\text{OH}$ group on GQD) to π^* orbital.⁶⁹ The absorption shoulders (550–600 nm) for the conjugated GQDs are caused by the electron transition from n-orbital (introduced by the electron-donating pyrazine N on the conjugated moieties) to π^* orbital.³² There is an obvious redshift of the absorption shoulder peak as the bandgap is narrowed further by conjugating GQD with a larger poly aromatic molecule.

Figure 5-8. Photographs taken under UV mercury lamp (a) and PL spectra (b) of the aqueous solutions of coal GQD, GQD-OPD, GQDDNPT23, GQD-DNPT18, GQD-BNPTL (from left to right, with emission peaks located at 520, 610, 637, 652, and 663 nm, respectively). Photographs taken under UV mercury lamp (c) and PL spectra (d) of the aqueous solutions of coal GQD, GQD-Anln-OCH₃, GQD-AnlnOCF₃, and GQD-Anln-OCCl₃ (from left to right, with emission peaks located at 598, 621, and 643 nm, respectively).

Figure 5-9. UV–vis absorbance spectra (a) and accordingly obtained plots (b) of $(\alpha E)^2$ versus photon energy (E) (where α denotes the absorbance coefficient) of coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL. The horizontal intercept of tangent line in (b) indicates the bandgap of each GQD type. (c) Cathodic linear sweep voltammetry (c) and anodic linear sweep voltammetry (d) of coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL. The horizontal intercept of tangent line in (c) or (d) determines the CBM or VBM of each GQD type, respectively.

In the $(\alpha E)^2$ versus (E) plot derived from UV–vis spectrum, where E is photon energy and α is the normalized adsorption coefficient, the GQD bandgap can be determined by the horizontal intercept of the extrapolation from the linear region (Figure 5-9b).^{160, 167, 281} The bandgaps of original GQD, GQDOPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL are 2.40, 2.05, 1.95, 1.91, and 1.88 eV, respectively, which are consistent with their fluorescence colors. Alternatively, we utilize the linear sweep voltammetry to determine the conduction band minimum (CBM), valence band maximum (VBM), and thus bandgap (CBM-VBM) (Figure 5-

9c, d and Table 5-2).¹⁶⁰ The bandgaps determined by both methods are in good accordance. The CBMs of GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL are -1.40, -1.10, -1.04, -1.01, and -0.99 eV (vs Ag/AgCl), respectively, while the corresponding VBMs are 1.00, 0.95, 0.91, 0.90, and 0.89 eV (vs Ag/AgCl), respectively. As seen from the energy diagram in Figure 5-10a, conjugation of poly aromatic rings lowers CBM (π^*) in a ring-size-dependent manner, while VBM remains relatively stable, whereby leading to band gap reduction. These observations are further supported by density functional theory (DFT) calculations (Table 5-3).

Table 5-2. CBM, VBM and bandgap values determined from Figure 5-9c and d. The Fermi levels of n- type (E_{Fn}) and p-type (E_{Fp}) are determined by Mott-Schottky method.

S/N	Name	CBM (eV vs Ag/AgCl)	CBM (eV vs Vacuum)	VBM (eV vs Ag/AgCl)	VBM (eV vs Vacuum)	E_{Fn} (eV vs Ag/AgCl)	E_{Fp} (eV vs Ag/AgCl)	Band gap (eV)
1	Coal-GQD	-1.40	-3.3	1.00	-5.70	NA	0.97	2.40
2	GQD-OPD	-1.10	-3.6	0.95	-5.65	-0.94	0.83	2.05
3	GQD-DNPT23	-1.04	-3.66	0.91	-5.61	-0.90	0.80	1.95
4	GQD-DNPT18	-1.01	-3.69	0.90	-5.60	-0.87	0.76	1.91
5	GQD-BNPTL	-0.99	-3.71	0.89	-5.59	-0.85	0.75	1.88

Figure 5-10. Illustration of energy level diagram and simplified structure of (a) coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18, and GQD-BNPTL and (b) coal GQD, GQD-Anln-OCH₃, GQD-Anln-OCF₃, and GQD-Anln-OCCL₃. The Fermi levels for p-type conductivity (E_{Fp}) and n-type conductivity (E_{Fn}) are indicated in the energy diagram.

Table 5-3. DFT calculation results of CBM, VBM and band gap of the simplified coal GQD, GQD-OPD, GQD-DNPT23, GQD-DNPT18 and GQD-BNPTL to unravel the influence by π -system enlargement.

S/N	Name	Structure	CBM (a.u.) ^a	VBM (a.u.)	Band gap (a.u.)	Band gap (eV)
1	GQD		-0.065	-0.212	0.147	4.00
2	GQD-OPD		-0.101	-0.21	0.109	2.97

3	GQD-DNPT23		-0.11	-0.206	0.096	2.61
4	GQD-DNPT18		-0.115	-0.194	0.079	2.15
5	GQD-BNPTL		-0.116	-0.193	0.077	2.09

^a 1 a.u. = 27.2 eV

The Mott–Schottky analysis is applied to identify the types of conductivity for each kind of GQDs.^{160, 282} Linear region(s) of $1/C^2$ (C is the capacitance) versus the applied potential can be fitted with Mott–Schottky equation (Figures 5-10, Table 5-2). Negative linearity suggests the existence of p-type conductivity, while positive linearity suggests n-type. Original GQD only manifests p-type conductivity caused by the strong electron-withdrawing oxygenated groups (e.g., $-\text{COOH}$ and $-\text{CHO}$) despite the coexistence of weak electron-donating $-\text{OH}$ groups. In contrast, GQD-OPD, GQD-DNPT23, GQDDNPT18, and GQD-BNPTL exhibit both p- and n-type of conductivity where n-type is endowed by the electron-donating pyrazine N atoms (Figure 5-10). The Fermi levels of n-type conductivity (E_{Fn}) and p-type conductivity (E_{Fp}) are determined by the horizontal intercepts of the positive or negative linear extrapolations of $1/C^2$, respectively (Figure 5-11, Table 5-2 and Figure 5-10a). Evidently, conjugated GQDs, but not the original GQD, possess both p-type and n-type domains. The coexistence of p- and n-type conductivities has also been

previously observed in other GQDs^{158, 160} and nanoparticles.²⁸³⁻²⁸⁴ Unlike a conventional heterojunction where p-type and n-type semiconductors are in direct physical contact or interface, the p-type and n-type domains on a GQD molecule are coupled through the sp^2 carbon network of the GQD basal plane, forming intramolecular Z-scheme structure.^{274, 285} Such structure favors charge separation and thus coupling between photo-excited anodic and cathodic redox reactions.

Figure 5-11. Capacitance (C) vs. potential (E) for (a) coal GQD, (b) GQD-OPD, (c) GQD-DNPT23, (d) GQD-DNPT18, and (e) GQD-BNPTL. The Fermi levels of n-type (E_{Fn}) and p-type (E_{Fp}) conductivity determined by horizontal intercept of the linear extrapolation are summarized in Table 5-2.

Alternatively, GQD bandgap can be narrowed by introducing n-orbital between π and π^* orbitals. For this, we graft GQDs with electron-donating

functionalities, specifically, p-anisidine (AnIn-OCH₃), 4-(trifluoromethoxy) aniline (AnIn-OCF₃), and 4-(trichloromethoxy) aniline (AnIn-OCCl₃) through the condensation reaction between -COOH and -NH₂ to form N-C=O amide bond under solvothermal conditions (Figure 5-2). The three modified GQDs all display a C-H peak (2900 cm⁻¹) from the conjugates and a C=O peak (1650 cm⁻¹) and a C-N peak (1456 cm⁻¹) from the formed O=C-N amide bonds between the conjugates and GQD (Figure 5-12a).²⁸⁶ The stretching vibrations of C-F²⁸⁷⁻²⁸⁸ from GQD-AnIn-OCF₃ and C-Cl²⁸⁹ from GQD-AnIn-OCCl₃ are located at 1300 and 750 cm⁻¹, respectively. All these observations confirm the successful functionalization.

Figure 5-12. (a) FTIR, and (b) full-range XPS of coal GQD, GQD-AnIn-OCH₃, GQD-AnIn-OCF₃, and GQD-AnIn-OCCl₃.

The overall XPS spectra in Figure 5-12b present F 1s (686 eV)²⁹⁰ for GQD-Anln-OCF₃, Cl 2p (200 eV)²⁹¹ for GQD-Anln-OCCL₃, and N 1s (401 eV) for all conjugated GQDs in addition to the common C 1s (284 eV) and O 1s (532 eV) peaks. The (O 1s)/ (C 1s) ratio is reduced as expected after functionalization through condensation between -COOH and -NH₂. The consequent formation of O=C-N amide bonds is evidenced by C=O and C-N peaks in high-resolution C 1s XPS spectra (Figure 5-13a). In addition, the N 1s peak at 401 eV is characteristic to amide N (Figure 5-13b). A control experiment of conjugation between benzoic acid and aniline to form benzanilide (yield 95.2%, Figure 5-14) has been conducted to prove that the used conjugation strategy universally works for not only for GQDs but also for small aromatic molecules. According to the increase of molecular weight after functionalization determined by mass spectrometry (Figure 5-15), it is estimated that ~8.57Anln-OCH₃, ~8.60 Anln-OCF₃, and ~8.41 Anln-OCCL₃ are functionalized onto one GQD. This is in good agreement with the (N 1s)/ (C 1s) ratios determined by XPS.

Figure 5-13. High-resolution (a) C 1s XPS and high-resolution (b) N 1s XPS spectra of coal GQD, GQD-AnIn-OCH₃, GQD-AnIn-OCF₃, and GQD-AnIn-OCCL₃.

Figure 5-14. (a) Reaction equation and (b) FTIR spectra of benzoic acid, aniline and their reaction product benzanilide.

Figure 5-15. The mass spectrometry of (a) GQD-AnIn-OCH₃, (b) GQD-AnIn-OCF₃, and (c) GQD-AnIn-OCCL₃.

As shown in Figure 5-8c, the fluorescence of original GQD, GQD-AnIn-OCH₃, GQD-AnIn-OCF₃, and GQD-AnIn-OCCL₃ progressively redshifts, indicating gradual bandgap narrowing while the electron donating ability increases (AnIn-OCH₃ < AnIn-OCF₃ < AnIn-OCCL₃) (Figure 5-8d). The light adsorbing abilities are ranked as GQD-AnIn-OCCL₃ > GQD-AnIn-OCF₃ > GQD-AnIn-OCH₃ > GQD (Figure 5-16a). Specifically, compared to the original green GQD, the light adsorption of red GQDAnIn-OCCL₃ is much stronger and extends much further into the visible range due to bandgap narrowing. The prominent absorption peaks between 250 and 300 nm from GQD-AnInOCF₃ and GQD-AnIn-OCCL₃ (Figure 5-

16a) could be the electron transition from n to σ^* orbital (Figure 5-10b). The absorption shoulders (between 530 and 600 nm) for the functionalized GQDs are due to the electron transition from the n -orbital (induced by lone pair electrons from N, F, or Cl) to π^* orbital.²⁹² There is an apparent redshift of this absorption shoulder when the bandgap is narrowed further by the stronger electron-donating groups.

Figure 5-16. UV-vis absorbance spectra (a) and accordingly obtained plots (b) of $(\alpha E)^2$ versus photon energy (E) (where α denotes the absorbance coefficient) of coal GQD, GQD-Anln-OCH₃, GQD-Anln-OCF₃, and GQD-Anln-OCCL₃. The horizontal intercept of tangent line in (b) indicates the bandgap of each GQD type. (c) Cathodic linear sweep voltammetry (c) and anodic linear sweep voltammetry (d) of coal GQD, GQD-Anln-OCH₃, GQD-Anln-OCF₃, and GQD-Anln-OCCL₃. The horizontal intercept of tangent line in (c) or (d) determines the CBM or VBM of each GQD type, respectively.

Based on the $(\alpha E)^2$ versus E plot (Figure 5-16b), the bandgaps of GQD-Anln-OCH₃, GQD-Anln-OCF₃ and GQD-AnlnOCCL₃ are determined as 2.08, 2.02, and

1.94 eV, respectively, which are narrowed from the original GQD (2.40 eV). These bandgaps are in line with their fluorescence colors. Linear sweep voltammetry (Figure 5-16c,d) is used to identify CBM (π^*) and VBM (n orbital), which are illustrated in the energy diagram shown in Figure 5-10b (also see Table 5-4).¹⁶⁰ The obtained bandgaps (CBM-VBM) are consistent with the values determined by Figure 5-16b. Mott–Schottky analysis (Table 5-4 and Figure 5-17) reveals that GQD-Anln-OCH₃, GQDAnln-OCF₃, and GQD-Anln-OCCl₃ possess Z-scheme structure with both p-type and n-type conductivity (their Fermi levels are indicated in Figure 5-10b).

Table 5-4. CBM, VBM and band gap values based on Figure 5-16c and d. The Fermi levels of n-type (E_{Fn}) and p-type (E_{Fp}) are determined by Mott-Schottky method.

S/N	Name	CBM (eV vs Ag/AgCl)	CBM (eV vs Vacuum)	VBM (eV vs Ag/AgCl)	VBM (eV vs Vacuum)	E_{Fn} (eV vs Ag/AgCl)	E_{Fp} (eV vs Ag/AgCl)	Band gap (eV)
1	Coal-GQD	-1.40	-3.3	1.00	-5.70	NA	0.97	2.40
2	GQD-Anln-OCH ₃	-1.38	-3.32	0.70	-5.40	-1.29	0.63	2.08
3	GQD-Anln-OCF ₃	-1.36	-3.34	0.66	-5.36	-1.24	0.59	2.02
4	GQD-Anln-OCCl ₃	-1.31	-3.39	0.63	-5.33	-1.19	0.55	1.94

Figure 5-17. Capacitance (C) vs. potential (E) for (a) GQD-AnIn-OCH₃, (b) GQD-AnInOCF₃, (c) GQD-AnIn-OCCl₃. The Fermi levels of n-type (E_{Fn}) and p-type (E_{Fp}) conductivity determined by horizontal intercept of the linear extrapolation are summarized in Table 5-4.

The intramolecular Z-scheme structure (i.e., p-type, n-type domains with sp^2 ohmic contact in between) on a functionalized GQD favors charge separation to promote coupled photocatalytic redox reactions on the same GQD molecule.²⁷⁴ And because the standard redox potentials of water splitting (H^+/H_2 at -0.41 V, H_2O/O_2 at 0.82 V vs NHE, pH = 7)²⁹³ and CO_2 reduction (CO_2/CH_3OH at -0.38 V vs NHE,

$\text{H}_2\text{O}/\text{O}_2$)²⁹⁴⁻²⁹⁵ are enclosed within the CBM and VBM of the GQDs, they are able to photo-catalyze these reactions (Figure 5-18a).

Figure 5-18. (a) Illustration of standard redox potentials, CBM and VBM of GQD, and CO_2 reduction process. (b and c) Time courses of H_2 evolution (b) and CO_2 reduction (c) of all GQD types under visible light (420–800 nm). (d) Schematic illustration of GQD Z-scheme-based photocatalysis of CO_2 reduction.

Figure 5-18b presents the time course (over 72 h with the system evacuated every 12 h) of H_2 evolution for each GQD type under visible light (420–800 nm). GQD-BNPTL with the narrowest bandgap (thus strongest light absorption ability and widest absorption range) gives the highest H_2 yield ($130 \mu\text{mol}\cdot\text{h}^{-1}$), which is about 9-fold higher than the original GQD. This is also higher than the previously reported GQDs,^{157-158, 160} GQDbased²⁹⁶ and graphene-based composites.²⁹⁷ Apparent

quantum yields (AQYs) of GQD-BNPTL are 11%, 5.6%, 3.0% and 2.7% under 420, 460, 500, and 550 nm illuminations, respectively. The decrease of AQYs with increasing illumination wavelength is due to decreased adsorption. As seen from Table 5-5, the photocatalytic performance in H₂ generation of our GQDBNPTL offers top performance among all the carbon photocatalysts. In addition, its performance could be further improved by hybridization with nanoparticles of noble metals, transition-metal oxides/sulfides/phosphides, or metal alloys.

Table 5-5. Comparison among carbon materials as the photocatalysts for H₂ generation.

Catalyst	Light source	Sacrificial reagent	Co-catalyst	Performance	Ref.
GO	400 W Hg lamp	20 vol% Methanol	5 wt% Pt	H ₂ : 5.6 mmol·g _{cat} ⁻¹ h ⁻¹	298
N-doped Graphene	367 mW laser (355 nm)	30 vol% Methanol	Nil	H ₂ : 82.8 mmol·g _{cat} ⁻¹ h ⁻¹	299
Ammonia-modified GO, NGO	450 W Hg lamp	20 vol% Methanol	Nil	H ₂ : 2.0 mmol·g _{cat} ⁻¹ h ⁻¹	300
N-doped GQD	300 W Xe lamp	10 vol% TEOA	3 wt% Pt	H ₂ : 20.5 mmol·g _{cat} ⁻¹ h ⁻¹	158
N-doped GOQD	300 W Xe lamp	Nil	Nil	H ₂ : 0.5 mmol·g _{cat} ⁻¹ h ⁻¹	160
P-doped graphene	1.3 Wm ⁻² Xe lamp	30 vol% Methanol	2 wt% Pt	H ₂ : 0.25 mmol·g _{cat} ⁻¹ h ⁻¹	301
Carbon nanodots	300 W Hg lamp	20 vol% Methanol	Nil	H ₂ : 12.0 mmol·g _{cat} ⁻¹ h ⁻¹	302
g-C ₃ N ₄	300 W Xe lamp	15 vol% TEOA	3 wt% Pt	H ₂ : 424 mmol·g _{cat} ⁻¹ h ⁻¹	303
GQD-BNPTL	300 W Xe lamp (with 420 nm cutoff filter)	10 vol% TEOA	3 wt% Pt	H ₂ : 1.28 mmol·g _{cat} ⁻¹ h ⁻¹	This work

Figure 5-18c presents the time courses of CO₂ reduction to form methanol under visible light. GQD-BNPTL also offers the best performance (yield rate of 0.695 μmol·h⁻¹·g_{cat}⁻¹), which is about three times higher than that of original GQD,

and the performance is superior to previously reported graphene oxide microsheets³⁰⁴ and TiO₂ (P-25).³⁰⁵ Pure carbon photocatalysts have been rarely explored for CO₂ reduction (Table 5-6). GQD-BNPTL as a quasi-homogeneous photocatalyst offers advantages, and its performance could be further improved by hybridization with other functional nanoparticles and using sacrificial reagents.

Table 5-6. Comparison among carbon materials as the photocatalysts for CO₂ reduction.

Catalyst	Light source	Sacrificial reagent	Co-catalyst	Performance	Ref.
GO	300 W Halogen lamp	Nil	Nil	Methanol: 0.172 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$	304
GO	20 W LED	Nil	Ru Complex	Methanol: 20 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$	306
g-C ₃ N ₄	300 W Xe lamp	OH ⁻ ions	Nil	Methanol: 6.28 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$ Methanol: 4.51 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$	307
GQD-BNPTL	300 W Xe lamp (with 420 nm cutoff filter)	Nil	Nil	Methanol: 0.7 $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\text{h}^{-1}$	This work

Photoreduction reaction using isotopically labeled ¹³CO₂ proves that CO₂ is the only carbon source (but not GQD) for methanol production (Figure 5-19a and b). The mechanism of CO₂ reduction to methanol in a six-electron-transfer process is elucidated in Figure 5-18a. Only a small amount of CO is generated as the byproduct (Figure 5-19c), because the standard reduction potential for CO₂/CO (−0.53 V vs NHE)³⁰⁸ is more negative than that of CO₂/CH₃OH. O₂ has been generated as the photoanodic counterpart (Figure 5-19d) for the photocathodic CO₂ reduction. As seen from Figure 5-18b and c, all GQD catalysts are rather stable against photo corrosion.

Figure 5-19. Mass spectrum of methanol produced from (a) natural CO_2 ($^{12}\text{CO}_2$) and (b) $^{13}\text{CO}_2$. (c) Time course of CO production rate from CO_2 reduction using different GQDs as the photocatalysts. (d) Time course of O_2 evolution rate during the CO_2 photo-reduction using different GQDs as the photocatalysts.

The good performance of GQD-BNPTL is attributable to the chemical inertness of GQD, good light absorption ability, and the existence of intramolecular Z-scheme structure.^{274, 309-310} As illustrated in Figure 5-18d, the electrons are photoexcited from valence band (VB) to conduction band (CB) on both p-type subdomains with electron-withdrawing oxygenated groups and n-type subdomains with electron-donating nitrogen. The excited electrons on the CB of p-type subdomains are used for photocathodic CO_2 reduction, while the holes on the VB of n-type subdomains are consumed by photoanodic O_2 generation. As the CBs of n-type subdomains are lower than that of p-type subdomains, the photoexcited electrons there combine with the holes from the VB of p-type subdomains through

the ohmic contact (sp^2 carbon network on GQD with low resistance) between the two different types of subdomains, instead of being used for CO_2 reduction. Such charge combination in the ohmic contact promotes the photoinduced electron–hole separation in both p-type and n-type subdomains, whereby facilitates photocathodic reduction on p-type subdomains and photoanodic oxidation on n-type subdomains. A similar mechanism was previously proposed by Teng et al. for H_2 evolution.¹⁶⁰ The intramolecular Z-scheme mechanism proposed here is consistent with the conventional Z-scheme mechanism recognized in hybridized systems.^{274, 309} According to the time-resolved decay profiles (Figure 5-20), the lifetime of GQD-BNTPL (6.4 ns) is much longer than that of original GQD (3.1 ns), confirming that GQD-BNTPL permits much improved charge separation (i.e., prevention of recombination of photoexcited electron and hole pairs) due to Z-scheme structure.

Figure 5-20. Time-resolved decay profiles of coal GQDs and GQD-BNPTL.

5.3 Conclusions

In summary, this study demonstrates two different strategies to systematically narrow the bandgap of GQD. Specifically, conjugating GQDs with poly aromatic moieties to enlarge π conjugated sp^2 -carbon systems narrows the GQD bandgap (consequently increasing PL wavelength) mainly due to lowering of π^* orbital. Alternatively, bandgap lowering can be achieved via introducing the intermediate n orbital between π and π^* orbitals after conjugation with electron-donating functional groups. In our functionalized GQDs, intramolecular Z-scheme structure exists, which consists of p-type and n-type domains separated by sp^2 -carbon ohmic contact.

We have only selected several chemicals to demonstrate the strategies. In principle, GQD bandgap can be continuously tuned simply by changing the number and the properties of the conjugates. The former may be controlled by the reaction time or the abundance of carboxyl groups (chemical handles) on the original GQDs. Such precise bandgap engineering can make GQDs snugly suitable for particular applications. For example, a series of GQDs emitting different fluorescence wavelengths can be produced to extend the application scope of GQDs for bioimaging or fluorescence-based sensing.

The narrow bandgap of a GQD promotes light absorption fraction and range. Intramolecular Z-scheme structure assists to couple redox reactions on the same molecule by preventing the recombination of photoexcited electron-hole pairs. Taking advantage of these two features, our functionalized GQDs are utilized for water splitting and CO_2 reduction under visible light. Comparing to other

photocatalysts, GQDs offer several advantages. They are synthesized from earth-abundant, cheap, and environmentally friendly carbon materials. And owing to the molecular size, GQDs disperse well in aqueous solution and their active sites are fully exposed. Compared with their micro-sized counterparts (graphene oxide sheets) or bulk materials, GQDs possess a larger fraction of the active sites (mostly edges). On one hand, GQDs act as quasi-homogeneous catalysts to achieve high efficiency, and on the other hand, they can be recycled for reuse.

Chapter 6 Conclusions and Future Perspectives

6.1 General conclusions

Owing to their intrinsic properties, GQD, as a new derivative of graphene, holds tremendous promise for numerous applications in multi-disciplinary areas. In this thesis, we have optimized synthetic routes, developed post-synthesis modifications for GQDs in order to obtain higher brightness and/or functional groups on the GQD molecules and further explored their uses in biomedical and catalytic applications. The primary experimental results, findings and discussion which contribute in this area are summarized in this chapter.

First, inspired by a reported synthesis method using pyrene as precursors, we developed a new synthesis strategy and prepared GQDs with a much higher quantum yield (up to 31 %). Most interestingly, the GQDs bear sufficient -COOH groups which are easy to be covalently conjugated with biomolecules with exposed amine groups. Here for the first time, we successfully grafted sugar moieties (specifically, galactose and mannose) onto GQDs. Such sweet GQD conjugates are instrumental to specifically label carbohydrate receptors on the cancer cells and track their dynamics in real-time. This study opens a new perspective in the application of GQDs for bioimaging.

GQDs have a large surface area and functional groups which endow them with abundant active sites for catalytic applications. In this respect, we have demonstrated a novel quasi-homogeneous catalyst based on sulfonated GQD (SGQD) for one-pot biomass transformation to 5-HMF. SGQDs are prepared from a facile

synthesis method using carbon black as starting materials and subsequently treated with chlorosulfonic acid. The catalysts unify the advantages of both homogeneous and heterogeneous catalysts. Specifically, it can achieve high efficiency as homogeneous catalysts because its excellent dispersibility and molecular size ensure full accessibility by the reactants and unhindered mass transport. On the other hand, unlike the corrosive and unrecoverable homogeneous catalysts (e.g., H_2SO_4 , HCl), SGQD is much more environmentally friendly, and can be recycled like heterogeneous catalysts. Furthermore, the superior catalytic ability of SGQD is also benefited from the synergistic cooperation between $-\text{SO}_3\text{H}$ groups and hydroxyl ($-\text{OH}$) groups on SGQDs. This study suggests the potential of SGQD as an efficient and green carbon-based catalyst for one-pot transformation of biomass or biomass-derivatives and more generally the unique potential of functionalized GQDs as novel quasi-homogeneous catalysts for various reactions.

One of the most intriguing property of GQDs is their tunable band gap, thus emission colors. In the third work, we have devised two different strategies to systematically narrow the band gap of GQD. Specifically, conjugating GQDs with poly aromatic moieties to enlarge π conjugated sp^2 -carbon systems narrows the GQD band gap mainly by lowering the π^* orbital. Alternatively, bandgap lowering can be achieved via introducing the intermediate n orbital between π and π^* orbitals after conjugation with electron-donating functional groups. The narrow band gap of a GQD promotes light absorption range. Intramolecular Z-scheme structure assists to couple redox reactions on the same molecule by preventing the recombination of photoexcited electron-hole pairs. Taking advantage of these two features, our

functionalized GQDs are utilized as catalysts for water splitting and CO₂ reduction under illumination of visible light. Comparing to other photocatalysts, GQDs offer several advantages. They are synthesized from earth-abundant, cheap, and environmentally friendly carbon materials. Besides, their excellent dispersity in aqueous solution allow full exposure of active sites on their surface and edges. On one hand, GQDs act as quasi-homogeneous catalysts to achieve high efficiency, and on the other hand, they can be recycled for reuse.

6.2 Future directions

As a newly emerging zero-dimensional nanocarbon material, GQD has shown many advantages in several aspects over conventional fluorescent materials, or metal/non-metal catalysts. However, the research and exploration of GQDs are still expanding. There are several challenges or problems which require to be overcome. Here we propose some research topics or future directions that remain open in the GQD research.

Firstly, the systematical study of underlying PL mechanism is in high demand. Though many studies have summarized and discussed their possible PL origins based on control experiments or theoretical calculations, the precise control of GQD size, thickness, chemical composition and morphology during synthesis process is still necessary for validation of these hypothesis. Meanwhile, through systematic design, the well-defined GQDs exhibiting desired properties and characteristics will be beneficial for specific applications.

Secondly, fluorophores with high quantum yield are always favorable for imaging, luminescent sensing or displays. Now one of the drawbacks of GQDs is their relatively low emission brightness (QY) as comparison to carbon dots, inorganic QDs or organic dyes. An improved QY of GQDs would allow more applications in the field of *in vivo* imaging and other bio-photonic applications, as well as LEDs et al.

Thirdly, as a high-performance quasi-homogeneous catalyst, currently the use of GQD in catalysis is still limited in laboratory scale. Though many GQDs are using earth-abundant materials as precursors, such as coal, carbon black et al., while the reagent needed for the synthetic process is strong acid or oxidant, e.g., H_2SO_4 , HNO_3 , potassium permanganate, which are corrosive and environmentally unfriendly. Alternatively, bottom-up synthesis usually has a high production yield, yet the precursors are generally expensive, and the large-scale purification and filtration are not easy to be realized. Currently, in our efforts, we are trying to use some low-cost aromatic materials as starting materials and through hydrothermal treatment and crossflow filtration, the large-scale preparation of GQDs could be achieved.

In sum, GQD is still a new and promising material, and its scope of applications has already covered a wide range of directions and is expanding rapidly. There are several challenges remaining to be tackled though while it is believed that GQDs will start a new era in the history of nanomaterial utilization.

Appendix: List of Publications

1. **J. Chen**, A. Than, N. Li, A. Ananthanarayanan, X. Zheng, F. Xi, J. Liu, J. Tian, and P. Chen, Sweet Graphene Quantum Dots for Imaging Carbohydrate Receptors in Live Cells, *FlatChem*, 5 (2017) 25-32.
2. K. Li[#], **J. Chen**[#], Y. Yan, Y. Min, H. Li, F. Xi, J. Liu, P. Chen, Quasi-homogeneous carbocatalysis for one-pot selective conversion of carbohydrates to 5-hydroxymethylfurfural using sulfonated graphene quantum dots, *Carbon* 136 (2018) 224-233. ([#]Co-first author)
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5. J. Tian, **J. Chen**, J. Liu, Q. Tian, P. Chen, Graphene quantum dot engineered nickel-cobalt phosphide as highly efficient bifunctional catalyst for overall water splitting, *Nano Energy* 48 (2018) 284-291.
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12. N. Li, A. Than, C. Sun, J. Tian, **J. Chen**, K. Pu, X. Dong, P. Chen, Monitoring Dynamic Cellular Redox Homeostasis Using Fluorescence-Switchable Graphene Quantum Dots, *ACS Nano* 10(12) (2016) 11475-11482.
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