

Carbon Quantum Dots and Applications in Photocatalytic Energy Conversion

K. A. Shiral Fernando,^{†,‡} Sushant Sahu,^{†,§} Yamin Liu,[§] William K. Lewis,[‡] Elena A. Guliyants,[‡] Amirhossein Jafariyan,[§] Ping Wang,[§] Christopher E. Bunker,^{*,‡} and Ya-Ping Sun^{*,‡}

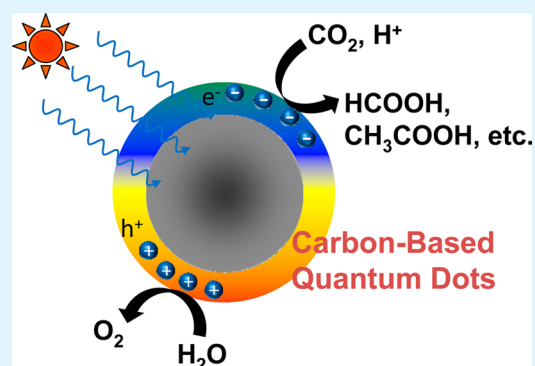
[‡]Energy Technology and Materials Division, University of Dayton Research Institute, Dayton, Ohio 45469, United States,

[§]Department of Chemistry and Laboratory for Emerging Materials and Technology, Clemson University, Clemson, South Carolina 29634, United States, and

[‡]Aerospace Systems Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States

ABSTRACT: Quantum dots (QDs) generally refer to nanoscale particles of conventional semiconductors that are subject to the quantum-confinement effect, though other nanomaterials of similar optical and redox properties are also named as QDs even in the absence of strictly defined quantum confinement. Among such nanomaterials that have attracted tremendous recent interest are carbon dots, which are small carbon nanoparticles with some form of surface passivation, and graphene quantum dots in various configurations. In this article, we highlight these carbon-based QDs by focusing on their syntheses, on their photoexcited state properties and redox processes, and on their applications as photocatalysts in visible-light carbon dioxide reduction and in water-splitting, as well as on their mechanistic similarities and differences.

KEYWORDS: quantum dots, carbon dots, graphene quantum dots, photocatalysts, CO₂ photoreduction, water-splitting



INTRODUCTION

Quantum dots (QDs) generally refer to nanoscale particles that are subject to the quantum-confinement effect.^{1,2} Among extensively investigated QDs are semiconductor nanocrystals of physical dimensions smaller than the exciton Bohr radius.² For the now more established cadmium selenide (CdSe) QDs, as a representative example, the characteristic dependencies of their electronic and optical properties on the nanocrystal sizes are reflected in the famous display of beautiful fluorescence colors by the QDs of different diameters.^{3,4} Therefore, the term “quantum dot” in the literature is mostly associated with nanoscale entities exhibiting size-dependent multicolor fluorescence emissions, despite the fact that the quantum-confinement has many consequences, especially with respect to photoinduced redox processes.⁵ These processes drive many widely pursued energy conversions, from photons to electrons and vice versa. In fact, there have been extensive investigations on using semiconductor QDs or nanorods in energy conversion devices and systems. For example, there have been recent reports on CdS/CdSe core-shell QDs as “dyes” in dye-sensitized solar cells (DSSCs) to attain a higher power conversion efficiency (PCE) than that of traditional DSSCs.^{6,7} On the other hand, CdSe/CdS core-shell QDs of high fluorescence quantum yields have been used as electroluminescent materials in high-performance light emitting diodes (LEDs).⁸ Semiconductor QDs have also been popular in the pursuit of other solar energy conversion pathways, especially as photocatalysts in the water-splitting for hydrogen

molecules^{5,9–11} and the reduction of carbon dioxide (CO₂) into small organic molecules.^{12–14} Again using CdSe/CdS core-shell materials for harvesting visible photons (around 450 nm), Amirav et al. made nanorods of the semiconductors with platinum metal as cocatalyst for the water-splitting, achieving high quantum yields.⁹ Han et al. used dihydrolipoic acid (DHLLA) to cap CdSe nanocrystals for QD-sensitized semiconductor photocatalysts for improved photochemical quantum yields in the hydrogen production with visible light (around 520 nm).¹¹ However, the performance of semiconductor QDs in the widely pursued visible-light photocatalytic CO₂ reduction has not been so inspiring, with generally low to very low quantum yields. For example, Chaudhary et al. used enzyme-modified CdS nanocrystals as visible-light photocatalysts for the conversion of CO₂ to carbon monoxide (CO), but the observed quantum yields were rather low.¹³ Interestingly, more recent improvements in performance have been due to the modification of semiconductor QDs with carbon nanomaterials for hybrid photocatalysts.^{14,15} As reported by Yu et al.,¹⁵ the composite of CdS nanorods and reduced graphene oxides (CdS-RGO) could be used as photocatalyst for the conversion of CO₂ into methane and a trace amount of methanol under visible light (around 420 nm) illumination, with the apparent quantum yields significantly

Received: January 15, 2015

Accepted: April 6, 2015

Published: April 6, 2015

higher than those achieved with the semiconductor QDs alone.¹⁵ This and other similar examples argue for the valuable role of carbon nanomaterials, carbon-based QDs in particular, in the presently extensively studied energy conversion systems.

Carbon “quantum” dots or carbon dots (Figure 1)^{16–19} have been leading the recent emergence of various carbon-based

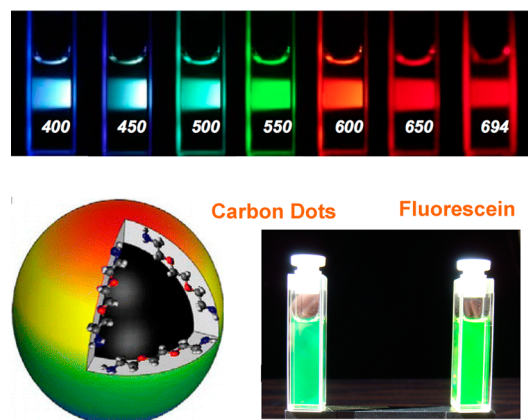


Figure 1. Top: Photographs for an aqueous solution of the PEG_{1500N}-functionalized carbon dots excited at the indicated wavelengths.¹⁶ Bottom left: Cartoon illustration on an EDA-functionalized carbon dot, which is essentially a special “core–shell” nanostructure with a small carbon nanoparticle as the core and a soft shell of tethered EDA molecules.¹¹⁵ Bottom right: Photographs comparing an aqueous solution of PEG_{1500N}-functionalized carbon dots and an ethanol solution of fluorescein under sunlight.²⁶ Reprinted in part with permission from ref 26. Copyright 2010 John Wiley and Sons.

QDs, including the popular graphene quantum dots (GQDs).^{20–25} These carbon-based QDs share some major features, including broad optical absorptions due primarily to π -plasmon and photoluminescence emissions associated with structural and surface or edge defects.^{18,19,25} In particular their photoinduced redox properties and processes are rather significant and in some cases unique, amenable to applications in technologies for energy efficiency and renewable energies.^{20–25} In this article, we highlight carbon dots and other carbon-based QDs including especially various variations of GQDs, focusing on their syntheses, optical and photoexcited state properties and redox processes, and applications as photocatalysts in visible-light CO₂ conversion and H₂ generation from water.

CARBON DOTS

Carbon dots (Figure 1, also referred to in some literature as carbon quantum dots or C-Dots) were found originally for their fluorescence emissions (Figure 1) appearing similar to those in conventional semiconductor QDs.^{16–19} As in the original study,¹⁶ carbon dots are generally defined as small carbon nanoparticles with various forms of surface passivation,^{18,19,25} among which the chemical modification or functionalization with organic molecules or polymeric species have been more effective for bright fluorescence emissions.^{25,26} While fluorescence from “naked” carbon nanoparticles in various suspensions has been observed, the intensities are relatively weak, thus making the surface passivation necessary for much enhanced fluorescence quantum yields.²⁷ This is to a certain extent analogous to the surface-capping of CdSe nanocrystal with ZnS in the development history of semiconductor QDs.

The surface passivation likely protects the emissive excited states, and/or the transient species leading to the emissive excited states, from possible “quenching”, which should have similar effects on the energy and charge transfer processes associated with the same excited states and/or transient species, thus also relevant to the use of carbon dots in energy conversion systems.

Optical Properties. Unlike in conventional semiconductor QDs with band gap absorptions that are subject to the quantum confinement effect, the photoexcitation of carbon dots is due to π -plasmon absorption in the core carbon nanoparticles. The absorption covers a broad UV/vis spectral range, extending into the near-IR, thus overlapping with a significant portion of the solar spectrum (Figure 2). In terms of absorptivity values per

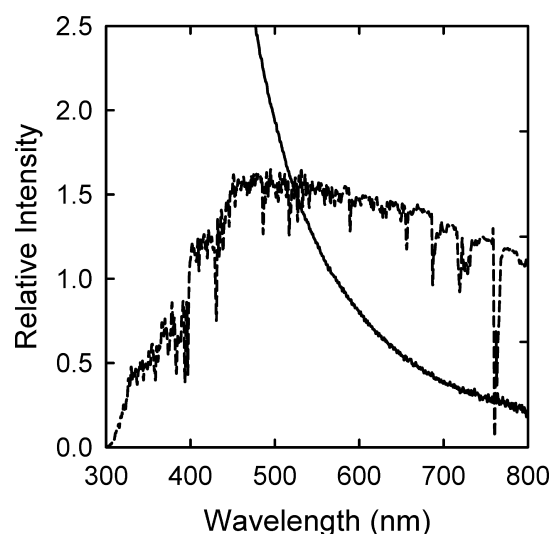


Figure 2. Observed absorption spectrum of broadly distributed carbon dots in aqueous solution (solid line) compared with the solar spectrum at the sea level (dashed line).

molar concentration of carbon atoms in the core carbon nanoparticles, the absorption of carbon dots is relatively strong, especially in the UV to blue/green spectral region. For example, results from experiments on carbon nanoparticles of 5–10 nm in diameter suggested absorptivity values of 50–100 $M_{C\text{ atom}}^{-1}\text{cm}^{-1}$ around 450 nm, where $M_{C\text{ atom}}$ denotes molar concentration in terms of carbon atoms in the core carbon nanoparticles, compared with 16 $M_{C\text{ atom}}^{-1}\text{cm}^{-1}$ for C₆₀ at the first absorption band maximum.²⁸ These absorptivity values are roughly the equivalent of up to 750 000 and 6×10^6 $M_{C\text{ particle}}^{-1}\text{cm}^{-1}$ for the carbon nanoparticles of 5 and 10 nm in diameter, respectively.

Carbon dots with effective surface passivation are brightly fluorescent.^{18,19} Among the best performing carbon dots are those from the functionalization of small carbon nanoparticles (around 4 nm in average diameter) with diamine-terminated oligomeric poly(ethylene glycol) (average molecular weight 1500, denoted as PEG_{1500N}). As reported by Wang et al.,²⁶ the as-synthesized sample of PEG_{1500N}-carbon dots exhibited fluorescence quantum yields around 20% in the green. Similar fluorescence quantum yields in the blue-green could be achieved in carbon dots of carbon nanoparticles (from the carbonization of polyvinylpyrrolidone) surface-passivated with 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) molecules, as reported recently by Ding et al.²⁹ However, upon gel column

separation of the PEG_{1500N}-carbon dots, the most fluorescent fraction was much brighter, with observed emission quantum yields close to 60%.²⁶ The performance is competitive to that of the commercially supplied green CdSe/ZnS QDs in aqueous solution and on a substrate at the individual dot level (Figure 3).²⁶ The effect of improved surface passivation on brighter

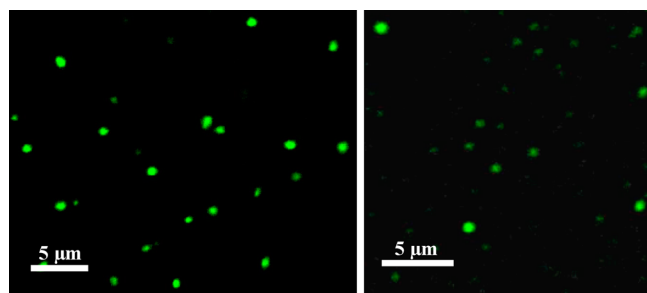


Figure 3. Fluorescence microscopy images (458 nm excitation) comparing individual PEG_{1500N}-functionalized carbon dots (left) with Invitrogen “QD525PEG” QDs (right) on glass substrate.²⁶ Reprinted with permission from ref 26. Copyright 2010 John Wiley and Sons.

fluorescence emissions was also demonstrated in the doping of the carbon nanoparticle surface with a conventional semiconductor (ZnO, ZnS, or TiO₂), combined with the functionalization by the same PEG_{1500N} molecules.^{30,31} The fluorescence quantum yields of these doped carbon dots were 40–50% in the as-synthesized sample and 75–80% for the most fluorescent fraction from the gel column separation.³¹

Carbon dots are strongly multiphoton fluorescent, with the pulsed laser excitation in the near-IR (800–900 nm) and emissions detected in the visible.^{18,19,32,33} The observed two-photon absorption cross sections are very large, on the order of 40,000 GM (Goepfert-Mayer unit, 1 GM = 1 × 10⁻⁵⁰ cm⁴ s/photon) at 800 nm,³² again competitive to those of the best-performing semiconductor QDs and considerably better than benchmark organic dyes. More recently, Liu et al. found higher two-photon absorption cross sections in the dots doped with nitrogen.³⁴

Syntheses. The original preparation of carbon dots was based on the surface functionalization of carbon nanoparticles with organic and polymeric molecules using established chemical reactions.^{16,32} Such an approach is now classified as being a synthesis with deliberate functionalization.^{18,19} Since then, a large number of methods for the preparation or formation of carbon dots have been reported, though most of them share a common feature that is the carbonization of

organic or other carbon-rich/containing precursors often in “one-pot” processing.^{18–20} These syntheses are generally different from the deliberate functionalization approach, though in some cases there may be an overlap, such as the use of carbon nanoparticles from the carbonization processing as precursors for deliberate surface chemical functionalization to obtain brightly fluorescent carbon dots. For example, Peng and Travas-Sejdic prepared carbon dots by the dehydration of carbohydrates with strong acids and the passivation with 4,7,10-trioxa-1,13-tridecanediamine (TTDDA).³⁵ There have been many choices of surface passivation agent for the chemical functionalization approach, such as various oligomeric PEG diamines in addition to PEG_{1500N} discussed above, amino-polymers, and other amine-terminated molecules.

The one-pot processing is convenient and versatile, but less controllable, yielding carbon dots of widely varying optical performances.^{18–20} Among some representative examples, Dong et al. used a mixture of citric acid and branched polyethylenimine as precursor for the one-step carbonization synthesis of carbon dots.³⁶ Zhu et al. made carbon dots by heating a solution of saccharide and PEG in a microwave oven;³⁷ and Yang et al. obtained carbon dots from the hydrothermal carbonization of chitosan.³⁸ The list goes on for the carbonization synthesis of carbon dots, with the selection of precursors as diverse as one could imagine, including various fruit juices, watermelon or pomelo peels, many food items, grass and plant leaves, and so on.^{18–20} Although there is nothing unique about the carbon dots prepared with many of these selected precursors, the diversity of sources does suggest that carbon dots are not so “picky” with respect to the purity or exact composition of the underlying dot materials beyond the predominating carbon content. This is probably due to the fact that the excited-state properties of carbon dots are dictated by defects.²⁵

Mechanistic Issues. The presently adopted mechanistic framework is such that the photoexcitation of core carbon nanoparticles in carbon dots results in efficient charge separation, with the electrons and holes (or radical anions and cations in a different description) trapped at various surface sites of the nanoparticles, with the radiative recombinations of the electrons and holes being responsible for the observed fluorescence emissions (Figure 4).^{25,39} This is in some respects similar to the photoexcited state mechanism in conventional semiconductor QDs. Although the classical quantum confinement found in semiconductor QDs is not applicable in carbon dots, as the emission colors in the latter are associated with different trapping sites and/or recombination paths of the

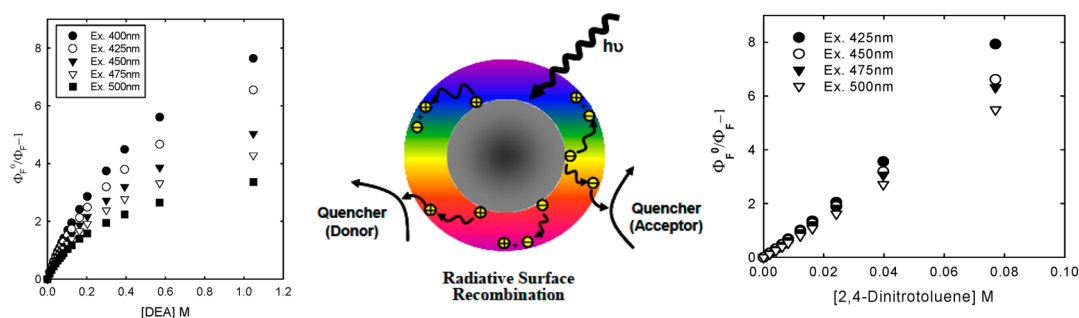


Figure 4. Middle: Cartoon illustration of the mechanistic framework on photoexcited state processes in carbon dots (with the rainbow color showing fluorescence from radiative recombinations of the electrons and holes). Left and right: Stern–Volmer plots for the fluorescence quenching by (left) electron donor *N,N*-diethylaniline (DEA) and (right) by acceptor 2,4-dinitrotoluene at different excitation wavelengths.^{25,39}

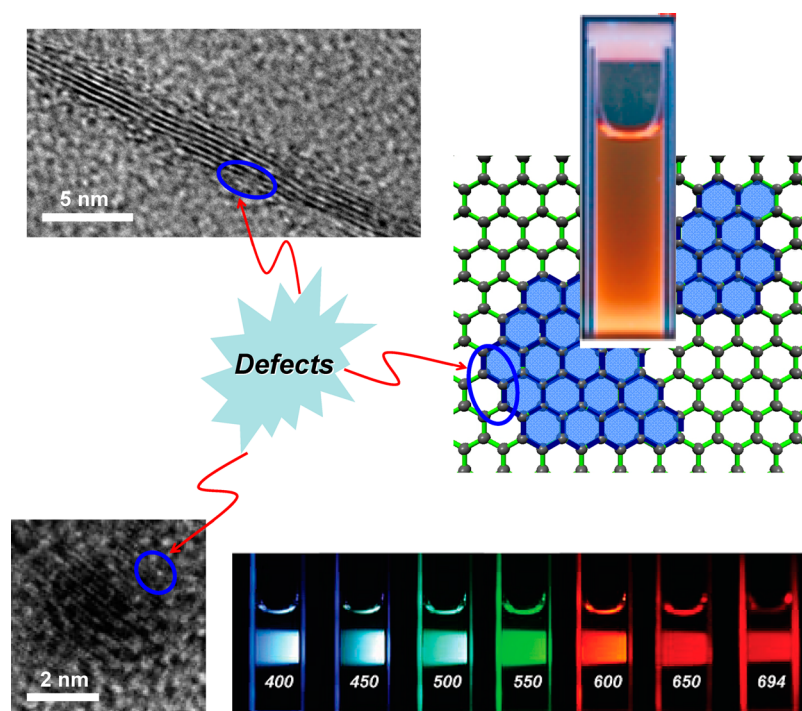


Figure 5. Top: Isolated sp^2 islands in a graphene sheet and a photo showing bandgap fluorescence in solution (right), and a multiple-layer graphene piece (left). Bottom: Carbon nanoparticle with surface defects (left), and fluorescence emission color variations in carbon dots (right).²⁵

electrons and holes, the small size for the core carbon nanoparticles is required for an extremely large surface-to-volume ratio to ensure a large population of diverse surface defect sites. Therefore, the “quantum-sized” for core carbon nanoparticles in carbon dots has different meanings and consequences in the associated optical and electronic properties from those with semiconductor nanocrystals. Similarly, the size dependence in carbon dots, for which well-controlled experimental investigations are still needed, also has different characteristics. In principle, a change in the particle size alters the surface-to-volume ratio for the particle, which may change the surface defect sites and the radiative recombination paths, among other possible structural and energetic effects.

The diverse nature in structures and energetics of defect-derived surface sites is likely responsible for a large population of emissive excited states accessible with a selection of different excitation energies. This is manifested experimentally by the progressive excitation wavelength dependent multicolor fluorescence emissions, which collectively cover the entire UV/vis spectral region, extending into the near-IR.^{16,18–20} The inhomogeneity in the emissive excited states of carbon dots is also reflected in the results of fluorescence decays, which are generally mixtures of multiple components.^{26,33,40} Despite the obvious complexity, the experimental decay curves have allowed an estimate of the fluorescence lifetimes, which are mostly on the order of nanoseconds.^{26,33,40}

A direct probing of the photoinduced charge separation and/or the associated electrons and holes in carbon dots has yet to be accomplished. However, there is indirect experimental evidence on the excited state redox species and processes.^{39,41,42} Among more compelling are the results suggesting that photoexcited carbon dots are both excellent electron donors and acceptors, with fluorescence emissions quenched efficiently by electron acceptor and donor molecules statically and dynamically in a diffusion-controlled fashion

(Figure 4).³⁹ Mechanistically, the fluorescence quenching results are readily explained in terms of the electron acceptor or donor quenchers scavenging the electrons and holes in carbon dots, respectively, thus disrupting the redox species’ radiative recombinations (Figure 4). The photoinduced electron transfer properties were confirmed by Kang et al. in fluorescence decay studies of carbon dots with the same electron acceptor and donor quenchers as those in ref 39 (Figure 4), 2,4-dinitrotoluene and *N,N*-diethylaniline, respectively.⁴¹ The redox active nature of photoexcited carbon dots was also demonstrated in the reduction of metal ions in an aqueous solution.^{42,43} Specifically, the photoirradiation of carbon dots solution with a noble metal (silver, gold, or platinum) salt resulted in the formation and deposition of the noble metal on the dot surface. Because the noble metal is electron affinitive, it takes electrons from the attached carbon dots, again disrupting the radiative recombinations, to result in the observed extremely efficient static quenching of fluorescence emissions.⁴² The photoreductive deposition of metals on carbon dots has valuable applications, such as the use of carbon dots as photocatalysts with the deposited metal as a cocatalyst (discussed in more detail below). Choi et al. also exploited the same processing to decorate the surface of carbon dots with plasmonic silver nanoparticles for hybrid nanodots of enhanced light harvesting capability in optoelectronic devices.⁴³

Carbon dots are obviously capable of harvesting photons over the solar spectrum, with their photoexcited states and the associated transient species responsible for bright fluorescence emissions as well as redox processes amenable to productive uses in energy conversion systems. Because of their optical and photoinduced redox properties, which derive exclusively from defects in the core carbon nanoparticles and are enhanced dramatically by effective passivation of the defects, carbon dots may play a dominating role among carbon-based nanostruc-

tures in which the same properties can be attributed mostly to the presence of structural and/or surface-edge defects.

OTHER CARBON-BASED QDS

Again, the term “QDs” in the literature has often been associated with the observation of multicolor fluorescence emissions corresponding to different excitation wavelengths. In this regard, the finding of carbon dots could be traced back to the study of defect-derived photoluminescence emissions in functionalized carbon nanotubes.⁴⁴ Indeed, those emissions and their excitation wavelength dependence were rather similar to what were subsequently found in carbon dots, though no naming of QDs for those photoluminescent carbon nanomaterials has been used.

From carbon nanotubes to nanosheets, now commonly referred to as few-layer graphene sheets (denoted as GNs), similar structural and/or edge defects are abundant.²⁵ Therefore, it is no surprise that largely the same excitation wavelength dependent multicolor fluorescence emissions as those in carbon nanotubes were found in GNs, more so in chemically functionalized GNs.^{45,46} These fluorescent carbon nanomaterials, along with single-layer graphene oxides (GOs) or other single-layer graphene sheets with defects, are now generally and apparently rather loosely referred to as “graphene quantum dots” (GQDs).^{21–25} As to be discussed in more detail below, a common characteristics shared by these fluorescent carbon nanomaterials is their surface and edge defects (Figure 5), as well as the often dramatic effect associated with the passivation of the defects.²⁵

Single-Layer Reduced GOs as GQDs. When strictly defined, a GQD should be a conjugated “ π -island” in a single-layer graphene sheet (thus without any interlayer quenching effect, which could be substantial), as clearly presented in some literature reports, such as the one due to Chhowalla and co-workers (Figure 6).⁴⁷ There have only been a few studies in which the π -islands (also called “ sp^2 -islands”) were created from single-layer graphene sheets.^{48–50} As an example, Gokus

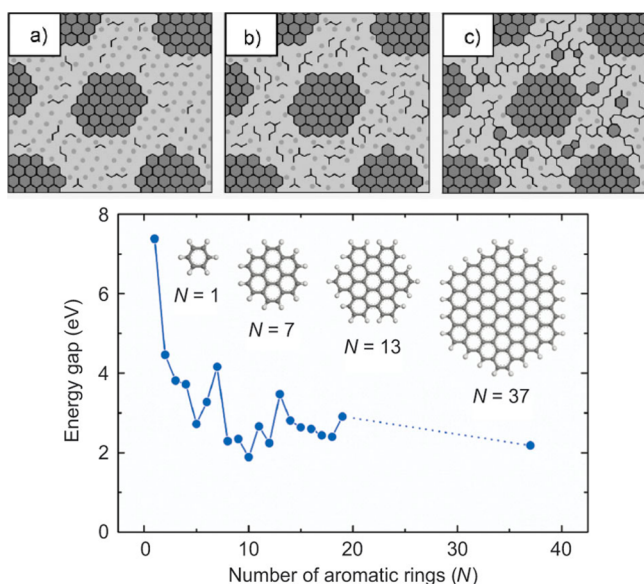


Figure 6. Top: (a–c) Illustration on π -islands on a graphene sheet. Bottom: The energy gap of π – π^* transitions calculated based on DFT as a function of the number of fused aromatic rings.⁴⁷ Reprinted with permission from ref 47. Copyright 2009 John Wiley and Sons.

et al. used single-layer graphene from mechanical exfoliation for oxygen plasma etching, from which the resulting sample exhibited significant photoluminescence, whereas the same processing of multilayer graphene flakes yielded samples of no photoluminescence emissions, a manifestation of the expected significant interlayer quenching effect.⁴⁸

Single-layer graphene sheets represent a precious commodity, so that their use as precursor in oxidative processing for GQDs has understandably been scarce. The reverse has been applied to the preparation of GQDs in most studies, namely that single-layer graphene oxides (GOs) from the exhaustive oxidation of graphite and then exfoliation have been used as precursor for partial reduction into GQDs.^{23,24} Therefore, these GQDs are essentially reduced (partially or somewhat controlled in the reduction processing) single-layer GOs (or single-layer rGOs). To avoid any interlayer quenching, the photoluminescent rGOs must be protected from restacking or the like.⁴⁸ Widely cited among such preparations was again the study by Chhowalla and co-workers.⁴⁷ The single-layer rGOs thus prepared were targeted to contain conjugated sp^2 carbon clusters of various dimensions, corresponding to different band-gaps and their associated optical transitions (Figure 6),⁴⁷ which are conceptually and practically similar to those found in conventional semiconductor QDs.^{3,4}

Lu et al. reported on the direct synthesis of mostly single-layer graphene sheets by using C_{60} precursor on Ru (0001) surface under different annealing conditions.⁴⁹ These sheet-like GQDs were of different shapes (triangular, parallelogram, and hexagonal) and varying lateral dimensions, which enabled a correlation on the size dependence of the electronic band gap.⁴⁹ Unfortunately, no evaluation on the photoluminescence properties in these small pieces of single-layer graphene was reported, as one might wonder how substantial would be the effect due to the relatively large number of surface defects (with respect to the sizes of these pieces). Conceptually similar was the work done by Chen et al.,⁵⁰ in which one-step microwave-assisted hydrothermal processing of GOs in strong acid media was used for primarily single-layer graphene pieces as GQDs. The average diameter of the GQDs was estimated as being around 3 nm in TEM analyses, and topographic heights less than 0.7 nm based on AFM imaging. The GQDs at 260 nm excitation emitted blue luminescence (centered around 420 nm). Although the optical transitions were assigned as being π – π^* in nature associated with the aromatic sp^2 domains,⁵⁰ the extremely large apparent Stokes shift would suggest that the observed luminescence might contain significant contributions from defect-derived emissions.²⁵

It should be recognized that for the strictly defined GQDs (essentially the same as conventional semiconductor QDs in two-dimension) the desired observation of semiconductor QD-like optical properties is problematic because of the intrinsic association of GQDs with defects. In fact, the creation of the π -islands in a graphene sheet (Figures 5 and 6) or a standalone small piece of single-layer graphene relies on the introduction of defects in the sheet structure or at the sheet edges, respectively, so that effects of the defects on the photoexcited state and redox properties in GQDs are unavoidable. The available experimental results have suggested that photoluminescence emissions from defect-derived contributions are generally strong and often overwhelming in comparison with those due to the mechanism of the strictly defined GQDs.²⁵ Many of the reported studies specifically targeting single-layer graphene sheets were subject to “contaminations” due to

defects and also multilayer pieces in which the defect contributions might mask the presence of substantial interlayer quenching.^{25,51,52} The same level of defect-derived effects should also be expected in the photoexcited state redox processes relevant to the energy conversion.

Other GQDs. Most of the reported GQDs have been small pieces of rGOs, as highlighted above for some of those closer to single-layer graphene pieces, and also pieces from few-layer graphene sheets (GNs). In fact, the multilayer GQDs are essentially naked (without deliberate passivation or functionalization) graphitic nanoparticles, namely carbon nanostructures containing ordered graphitic layers, though their being naked has not always been the case because of some of the methods used for their syntheses.

Pan et al. applied a hydrothermal method to cutting partially reduced GOs into small pieces as GQDs (1–2 nm in thickness and about 10 nm in average diameter).⁵³ With UV excitation, these GQDs exhibited blue emissions of quantum yields about 7%, comparable to those found in luminescent carbon nanoparticles. Interestingly, the same group reported that the similarly prepared GQDs of somewhat different physical dimensions were capable of emitting in the green, with quantum yield about 7.5% at 420 nm excitation.⁵⁴ On the other hand, Sun et al. recently did similar cutting of the GOs from modified Hummers' method into small pieces as GQDs (average thickness around 1.3 nm) but found only rather weak photoluminescence emissions in the blue to green spectral region (quantum yields around 1%, improved to 3% upon hydrothermal treatment of the sample).⁵⁵ Li et al. used microwave irradiation of GOs under acidic conditions to obtain GQDs of greenish-yellow emissions at 360 nm excitation, with quantum yields close to 12%.⁵⁶ There have been other similar studies with somewhat altered experimental strategies, thought a common attribute of the various GQDs is the photoluminescence emissions being nonband-gap in nature, primarily due to structural and/or edge defects in the graphitic nanomaterials, as discussed in the report by Galande et al.⁵⁷ The term "quasi-molecular fluorescence" was used to describe the defect-derived emissions, which were mechanistically rationalized as being from "carboxylic acid groups electronically coupled with nearby atoms in polycyclic aromatic compound like moieties" in these partially reduced GO pieces.⁵⁷

As discussed above, the available experimental results have suggested that even in single-layer graphene sheets the defect-derived photoluminescence emissions are much brighter than the fluorescence due to band gap transitions. The passivation of the defects through chemical functionalization or other modifications, including even the passivation effect by solvent molecules,²⁷ would result in the emissions being enhanced substantially. However, these passivated GQDs are conceptually and structurally little different from carbon dots, sharing essentially the same mechanistic framework. Highlighted below are representative recent examples for GQDs with deliberate defect passivation through chemical functionalization or other strategies.

Shen et al. used the PEG diamine (PEG_{1500N}) to passivate GQDs (small pieces of rGOs) to significantly increase the photoluminescence quantum yields, more than doubling those at corresponding excitation wavelengths in GQDs without the surface passivation.⁵⁸ Xue et al. introduced polyethylenimine into the hydrothermal cutting of GOs, coupled with ultrafiltration to isolate the targeted GQDs exhibiting enhanced photoluminescence emissions.⁵⁹ Tetsuka et al. synthesized

amino-functionalized GQDs in ammonia-mediated reactions of GOs, achieving photoluminescence quantum yields in the 19–29% range at 365 nm excitation (Figure 7).⁶⁰ Similar amino-functionalized GQDs were prepared by Chattopadhyay and co-workers from GOs in a more recent study.⁶¹

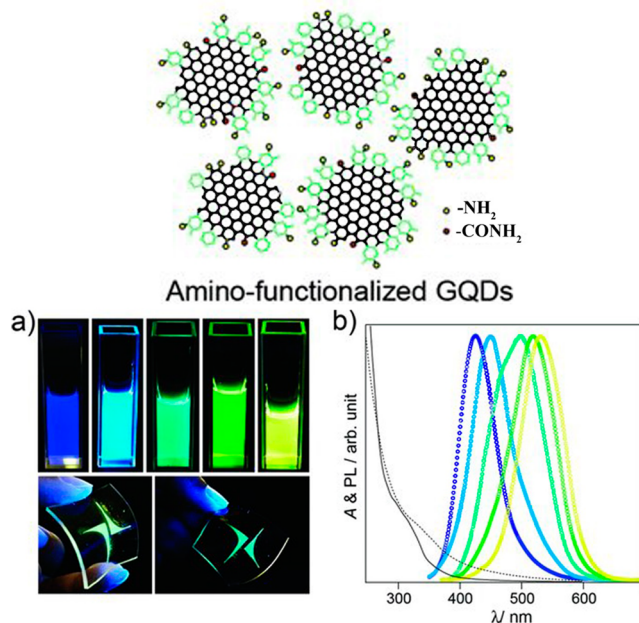


Figure 7. Top: Cartoon illustration on amine-functionalized GQDs (af-GQDs). Bottom: (a) Emission images of af-GQDs dispersed in water (upper) and af-GQD@polymer hybrids (lower) under irradiation from a 365 nm UV lamp. (b) Photoluminescence and selected UV/vis absorption spectra of af-GQDs.⁶⁰ Reprinted with permission from ref 60. Copyright 2012 John Wiley and Sons.

The photoluminescence emissions in GQDs of the different kinds, from the predominantly π -islands to small pieces cut from GOs, are generally in the blue and to a limited extent green spectral regions under UV excitation. The observed emission spectra are mostly broad, and mechanistically they are dominated by defect-derived contributions even in the GQDs with isolated π -domains for band gap transitions, because the emissions due to defects and especially passivated defects are much brighter. Therefore, like in carbon dots, defects in GQDs play a critical role in dictating the photoexcited state properties and their associated redox processes, and it is in this regard that GQDs share essentially the same mechanistic framework with carbon dots.

Nitrogen-Doped GQDs. The optical properties associated with defects in carbon nanostructures are apparently not negatively affected by the presence of other elements such as nitrogen in the structure or on the surface, and in some cases the doping with nitrogen actually enhances photoluminescence emissions significantly.⁶² For example, GQDs structurally doped with nitrogen, or "N-GQDs", were prepared in hydrothermal processing with citric acid and ethylene diamine as the carbon and nitrogen sources, respectively, and bright blue photoluminescence emissions were observed.⁶² Similar N-GQDs exhibiting bright green emissions at 390 nm excitation were obtained from one-pot solvothermal synthesis with DMF as both solvent and nitrogen source.³⁴ More recently, Wang et al. reported on the synthesis of crystalline GQDs by the

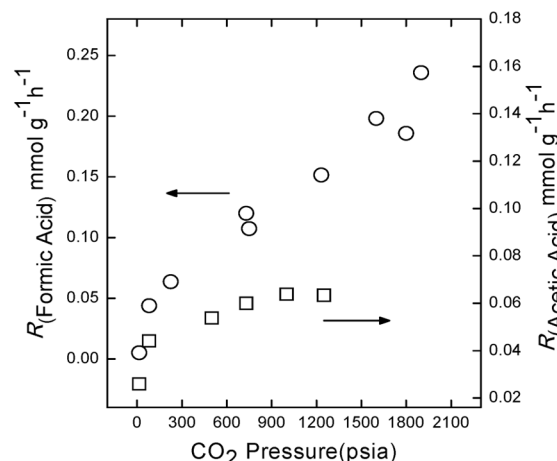
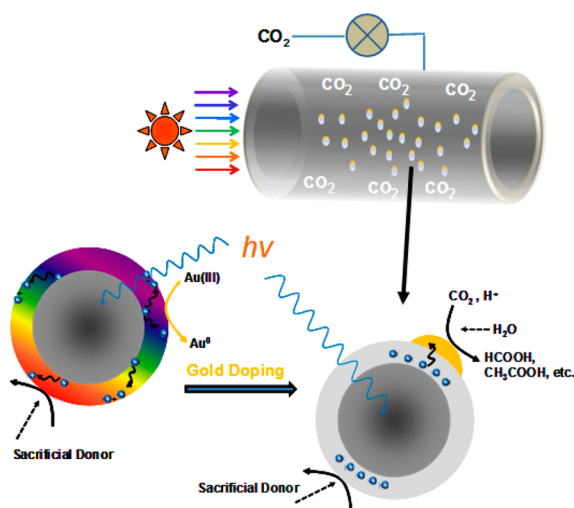


Figure 8. Left: Cartoon illustrations on the high-pressure optical reactor (upper); the photoreductive doping of the carbon dot with gold, completely quenching the dot surface-based fluorescence (illustrated as the change of the dot surface from rainbow to gray, lower-left); and the gold-doped carbon dot as photocatalyst for CO₂ conversion (lower-right). Right: The increase in the photoproducts formic acid (o) and acetic acid (□) with the increasing CO₂ pressure in reactions under otherwise the same experimental conditions.⁶⁹

nitration of pyrenes, followed by hydrothermal treatment in alkaline solutions with hydrazine hydrate and ammonia, and the GQDs were found to be strongly absorptive and emissive in the visible spectral region.⁶³

Yeh et al. doped GO-like nanostructures with nitrogen to affect the photoexcited state properties for the use of these materials as photocatalysts.⁶⁴ Conceptually somewhat similar has been the preparation of carbon-based composite or hybrid nanostructures for the purpose of improved excited state redox characteristics.⁶⁵ These nanomaterials, many of which are photocatalysts, have been designed for potential applications in various energy conversion systems.

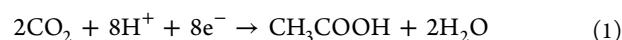
■ PHOTOCATALYTIC ENERGY CONVERSION

Solar-driven conversion of CO₂ into small molecular fuels is considered as not only an alternative to photovoltaics in the harvesting of solar energy but also an ultimate solution to the growing environmental challenge on carbon sequestration. Semiconductor nanomaterials like colloidal TiO₂ and CdS as representative examples have traditionally been employed as photocatalysts in the relevant reactions. However, many of these nanoscale semiconductors used for this purpose are absorptive only or mostly in UV, so that dye sensitization has been a popular approach to extend the photon harvesting into the visible.⁶⁶ Conceptually similar has been the use of semiconductor-carbon nanocomposites as photocatalysts to take advantage of the optical absorption by nanoscale carbon in the visible spectrum. As shown in Figure 2, the core carbon nanoparticles in carbon dots are strongly absorptive over the UV/vis, extending into the near-IR. The photoexcitation in carbon dots drives the excited state redox processes, which are not only responsible for the observed fluorescence emissions but also make the associated electrons and holes available for the catalytic energy conversion reactions.^{67–69} The same mechanistic framework and photocatalytic activities are apparently shared by those GQDs and other carbon-based QD-like nanomaterials in which the photoinduced redox processes are dominated by defects (Figure 5).²⁵ Highlighted here are some representative studies in which carbon dots and

other carbon-based QDs were used as photocatalysts in CO₂ reduction and for the generation of H₂ from water-splitting.

Photocatalytic CO₂ Reduction with Carbon Dots or the Like. Again conceptually similar to the photoinduced redox processes in conventional nanoscale semiconductors, in carbon dots the photoexcitation results in rapid charge separation for the formation of electrons and holes, which are likely “trapped” at various surface sites stabilized (protected from quenching effects) by the surface passivation (Figure 4). The photogeneration of these redox species and their associated properties make carbon dots “nanoscale semiconductor-like” in terms of driving photocatalytic processes. Indeed, it has been demonstrated that carbon dots with surface passivation by amino or other molecules are capable of serving as visible-light photocatalysts for CO₂ reduction in aqueous solution (Figure 8).^{67–70} More specifically, the carbon dots with the surface functionalization by the PEG diamine (PEG_{1500N}) or 2,2'-(ethylenedioxy)bis(ethylamine) (EDA) molecules were irradiated with visible light in an aqueous solution saturated with CO₂ (or NaHCO₃ as the CO₂ source) and the presence of a sacrificial electron donor like isopropanol, and the reactions were monitored by the detection and quantification of formic acid as the primary product (Figure 8).⁷⁰ There was significant production of formic acid from the reactions, around 40 μmol g⁻¹ h⁻¹, better than the performance with the use of colloidal TiO₂ (Degussa P25) and UV irradiation.⁷⁰ Since carbon dots are carbon-containing photocatalysts, potential involvement of the carbon associated with the core carbon nanoparticles was a concern, and elaborate control experiments with the use of ¹³C-labeled CO₂ source as well as deuterium-labeled water were performed to confirm the role of carbon dots in the reactions as photocatalysts, not reactants.^{69,70} The photocatalytic reduction results have also contributed to the further understanding of the presently adopted mechanistic framework for carbon dots, providing valuable experimental evidence for the presence of photoinduced charge separation to form harvestable electrons and holes in carbon dots, as suggested separately by the fluorescence quenching results (Figure 4).^{39,42,43}

In colloidal TiO₂ and other nanoscale semiconductors for the photocatalytic conversion, it has been well-established that the doping or coating of the catalysts with a noble metal, which concentrates the photogenerated electrons against their wasteful recombination with the holes, could improve the photocatalytic conversion substantially.⁶⁶ The same strategy was applied to carbon dots, with their doping by gold or platinum achieved in photoreductive deposition in aqueous solution of the corresponding metal salt, which was in fact itself a photocatalytic reaction based on carbon dots as photocatalysts.^{67–69} For the gold- or platinum-doped carbon dots as photocatalysts (Figure 8), the CO₂ photoconversion was found to be considerably more efficient.⁶⁷ Beyond formic acid, other photoproducts have been identified, in which the characterization and quantification of acetic acid are particularly significant,⁶⁹ as the photoreduction of CO₂ to acetic acid requires overall eight electrons, regardless of any detailed mechanisms.⁷¹



where the electrons are typically from sacrificial electron donors. All of the proposed mechanisms in the literature on the conversion to acetic acid invoked the involvement of other small organic molecules as intermediate products,^{66,69,72} not only suggesting complexity in the photoreduction reactions but also supporting the notion that carbon dots are uniquely capable visible-light photocatalysts for the CO₂ conversion.

The same photodeposition reaction could be used for the doping of carbon dots with silver, though the resulting photocatalysts appeared somewhat less effective in comparison with their gold- or platinum-doped counterparts. In a related recent study by Choi et al.,⁴³ the photodeposition method was used to prepare carbon dots with the dot surface decorated by silver nanoparticles. In the preparation, PEG-passivated carbon dots obtained from the decomposition of cyclodextrin were photoirradiated with UV light in the presence of AgNO₃. The resulting silver nanoparticle-decorated carbon dots were found to be sub-10 nm in sizes in TEM imaging.⁴³ The same method was further applied to making the silver nanoparticles more significant, with the resulting nanostructures characterized as “heterodimeric silver–carbon dot nanoparticles”, and the effective quenching of fluorescence in carbon dots by the presence of neighboring silver nanoparticles was observed.⁷³ Similarly, Mazzier et al. exploited the electron-donating character of photoexcited carbon dots to grow silver nanoparticles on the surface of carbon dots.⁷⁴ The results again served as experimental evidence for the availability of photogenerated electrons in carbon dots that could be harvested for productive purposes.

An interesting observation in the use of carbon dots as photocatalysts for CO₂ reduction was the apparent CO₂ concentration dependence of the product yields, higher at a higher CO₂ concentration.⁶⁹ Experimentally, the CO₂ concentration variations were achieved with varying CO₂ pressures over an aqueous solution in a high-pressure optical cell, with again the gold-doped carbon dots as photocatalysts for visible-light excitation (Figure 8) and isopropanol as sacrificial electron donor. The formic acid production obviously increased more significantly with the increasing CO₂ pressure (Figure 8) and thus correspondingly increasing CO₂ concentration in the aqueous solution. At 1,900 psia (about 1.37 M CO₂ in the solution), the amount of formic acid was more than an order of magnitude higher than that produced under ambient CO₂

pressure. Because all other experimental conditions of the photoreduction reaction were kept the same except for the CO₂ pressure (thus correspondingly concentration), the number of photons harvested by the carbon dots as photocatalysts should be constant. Therefore, the observed increase in formic acid production at the high CO₂ pressure should be a reflection of the same magnitude of increase in the reaction quantum yield for this photoproduct.⁶⁹ This is unique, as no reports are found on similar results with the use of conventional semiconductor photocatalysts. Nevertheless, the substantially enhanced photoconversion in aqueous solution under higher CO₂ pressures is not only important mechanistically, suggesting the role of the CO₂ concentration in the harvesting of photogenerated electrons in carbon dots, but also valuable technologically, with pressurized CO₂ as a more favorable reaction condition to yield larger quantities of the photoproducts.

The photocatalytic characteristics of carbon dots were also exploited in the fabrication of rGO nanocomposites with gold nanoparticles.⁷⁵

GQDs for Photocatalytic CO₂ Conversion. In contrast to their popularity in studies of photoluminescence emissions, GQDs without surface passivation (thus “naked” when suspended in a solvent) have apparently generated only limited interest in terms of their serving as photocatalysts for CO₂ conversion. Among scarce reports in the literature was the one due to Chen and co-workers on the GOs as photocatalysts for CO₂ conversion to methanol with simulated solar-light irradiation.⁷⁶ The conversion rate was relatively low, 0.172 μmol g⁻¹ h⁻¹, but still approximately 6-fold better than that of the reference with the use of TiO₂ in the same study.⁷⁶ Similarly, the photocatalytic functions of GOs were exploited for the photoreduction of noble metal ions into corresponding metals, which were deposited on the surface of GOs.^{77,78} The conception and results of the photocatalytic reduction and deposition of noble metals were the same as those used in the preparation of the metal-doped carbon dots as photocatalysts for CO₂ conversion reactions,^{67–69} but no such applications were explored with the metal-doped GOs.

One possible explanation on a general lack of popularity with naked GQDs in photocatalytic conversion of CO₂ is with their less robust photoexcited state redox properties, as the CO₂ conversion represents one of the most challenging photocatalytic reactions. Supporting such an explanation are the results from the evaluation on using naked carbon nanoparticles as photocatalysts.⁷⁰ Without any deliberate surface functionalization by organic or other molecules, small carbon nanoparticles, especially those processed by the oxidative acid treatment, could be dispersed to form relatively stable aqueous suspensions.²⁸ The suspended carbon nanoparticles could also harvest visible photons for the photoreductive deposition of a noble metal like gold or platinum to yield metal-doped carbon nanoparticles.²⁸ The carbon nanoparticles without metal doping were found to be generally poor in photocatalytic performance in the CO₂ reduction, whereas those with gold doping exhibited significant improvements, though still not competitive to their surface-passivated counterparts.⁷⁰ Mechanistically, the photocatalytic performance might be associated with the relative stability of the photogenerated redox species in carbon nanoparticles, which is likely enhanced substantially by the surface passivation in carbon dots for protection against quenching effects. The same stability of redox species may be correlated with the brightness in photoluminescence emissions, as carbon nanoparticles are only weakly photoluminescent in

the visible, but upon their effective surface passivation via chemical functionalization to become carbon dots, the emissions are dramatically enhanced.

Other Carbon-Based QD-Like Photocatalysts for CO₂ Conversion. The photon-harvesting capabilities of carbon-based QDs or nanoscale carbon entities in general have been explored for nanocomposite or other hybrid photocatalysts, especially those for visible-light excitation.^{65,79,80} These are both conceptually and practically similar to photocatalysts of dye-sensitized semiconductor nanostructures,⁶⁶ except that here the nanoscale carbon domains are also themselves involved directly in the photoinduced redox processes.

In graphene composites, for example, the graphene acts either as a functional component or as a substrate for immobilizing other components. Its large specific surface area coupled with high conductivity facilitates charge transfer, transport and subsequent redox reactions, as well as provides mechanical strength for the composite structure.^{65,79,80} Li et al. investigated the use of rGO-ZnO nanocomposites for CO₂ photoreduction to methanol, obtaining a production rate of 4.58 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under simulated sunlight.⁸¹ Tan et al. prepared rGO-TiO₂ nanocomposites for the CO₂ conversion to methane under visible light, with a formation rate of 0.135 $\mu\text{mol g}^{-1} \text{h}^{-1}$ (Figure 9).⁸² An et al. synthesized rGO-Cu₂O nanocomposites for the CO₂ conversion to CO with 400 nm light, achieving approximately 0.34% in quantum yield.⁸³ Hersam and co-workers reported that graphene-TiO₂ nano-

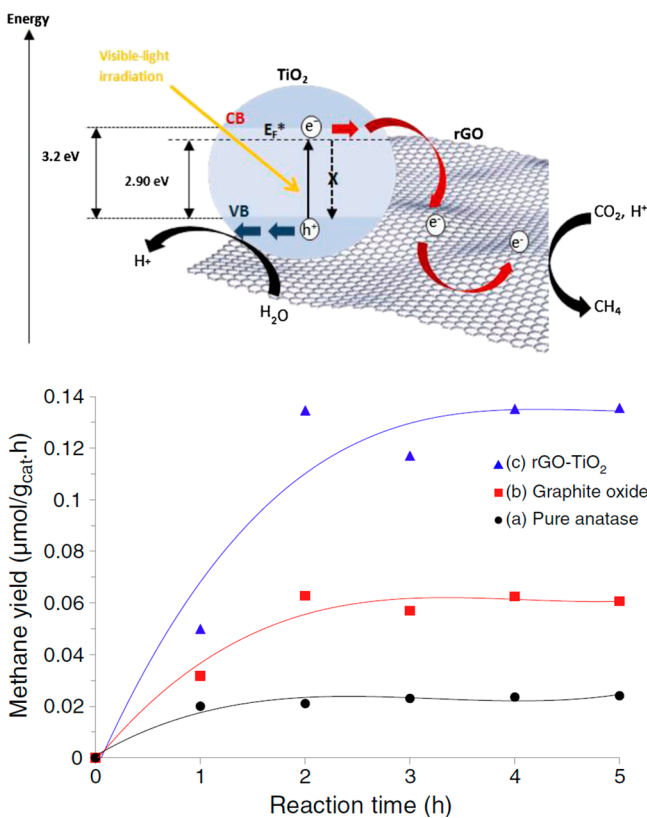


Figure 9. Top: Schematic illustration on the charge transfer and separation in the rGO-TiO₂ composite for the photoreduction of CO₂ under visible-light irradiation. Bottom: Time-dependent photocatalytic formation of methane over pure anatase TiO₂, graphite oxide, and rGO-TiO₂ under visible-light irradiation.⁸² Reprinted with permission from ref 82. Copyright 2013 Springer.

composites with low defect densities in the graphene were significantly better than bare TiO₂ in the visible-light photoreduction of CO₂ into methane.⁸⁴ They also found that the dimension of the carbon nanomaterial played a role in determining the spectral response of the composite photocatalysts, and thus the reaction specificity in CO₂ photoreduction.⁸⁵ Wang et al. used graphene-WO₃ composites from hydrothermal processing for the photoreduction of CO₂ to methane under visible light irradiation (production rate $\sim 0.11 \mu\text{mol/h}$).⁸⁶ Lv et al. also applied hydrothermal processing to the preparation of a composite containing Ni/NiO, rGOs, and Ta₂O₅ for the photocatalytic reduction of CO₂ (or CO₂/NaHCO₃) and H₂O to methanol and H₂ under UV light.⁸⁷

Tu et al. fabricated hollow spheres with alternating Ti_{0.91}O₂ nanosheets and graphene nanosheets for the photocatalytic CO₂ conversion to CO and CH₄, with observed production rates of 8.91 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and 1.14 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively.⁸⁸ In a related study, 2D sandwich-like graphene-TiO₂ hybrid nanosheets were prepared by using an in situ simultaneous reduction-hydrolysis technique and used as photocatalysts for CO₂ conversion to hydrocarbons (CH₄ and C₂H₆) in the presence of water vapor, with the highest production rates of 8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for CH₄ and 16.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for C₂H₆.⁸⁹

The composite or hybrid nanostructures have also included those containing nitrogen atoms for their serving as photocatalysts in the CO₂ conversion,^{90–92} especially the stacked 2D graphite-like structures called graphitic carbon nitride (g-C₃N₄, Figure 10). For example, Dong et al. synthesized g-C₃N₄ by

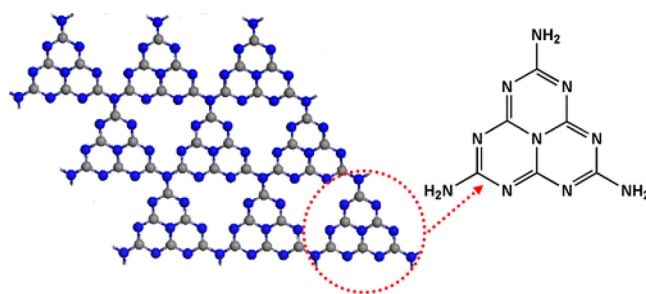


Figure 10. Representative chemical structure of g-C₃N₄, with carbon atoms in gray and nitrogen atoms in blue.⁹¹

heating melamine for the visible-light (wavelength longer than 420 nm) photoreduction of CO₂ into CO in the presence of water vapor ($\sim 1.9 \text{ mM/h}$ production rate).⁹³ Mao et al. prepared g-C₃N₄ from the pyrolysis of urea for the visible-light photocatalytic conversion of CO₂ into methanol (6.28 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and ethanol (4.51 $\mu\text{mol g}^{-1} \text{h}^{-1}$), with an overall quantum efficiency of 0.18%.⁹⁴ Niu et al. reported on the product selectivity in CO₂ photoconversion depending on the band structure of g-C₃N₄, with the bulk g-C₃N₄ of 2.77 eV in bandgap corresponding to CH₃CHO as the major product and the g-C₃N₄ nanosheets of 2.97 eV in bandgap to CH₄ as the major product.⁹⁵ Zheng et al. recently synthesized helical g-C₃N₄ rods on a chiral mesoporous silica template for their serving as photocatalysts in the CO₂ conversion, yielding CO (8.9 $\mu\text{mol h}^{-1}$) and H₂ (0.3 $\mu\text{mol h}^{-1}$) as major gaseous products with Co(bpy)₃Cl₂ as a redox mediator and triethanolamine as an electron donor in acetonitrile under visible-light (wavelength longer than 420 nm) irradiation.⁹⁶

There have also been various modifications to g-C₃N₄ targeting improved photocatalytic performance.^{91,92} For example, Yu et al. prepared Pt-doped g-C₃N₄ as photocatalysts for the CO₂ reduction into CH₄, CH₃OH, and HCHO under simulated solar irradiation.⁹⁷ Similarly, Au or Ag nanoparticles were photochemically deposited onto g-C₃N₄, with the resulting photocatalysts exhibiting improved performance in the CO₂ conversion to CH₃OH, HCOOH, and CH₄ under visible light irradiation.⁹⁸ In another approach, Wang et al. prepared graphitic carbon nanocomposites with mesostructured TiO₂ as photocatalysts for the conversion of CO₂ to CH₄ (1.53 μmol g⁻¹ h⁻¹) and CO (10.05 μmol g⁻¹ h⁻¹) under simulated solar irradiation.⁹⁹ Recently, Maeda et al. developed hybrid photocatalysts consisting of carbon nitride (C₃N₄) and a small amount of ruthenium complex for the visible-light photo-reduction of CO₂ into formic acid (~431 μmol g⁻¹ h⁻¹), with an apparent quantum efficiency of up to 1.5% for 400 nm light irradiation.¹⁰⁰ In further investigation they found that the photoactivity was sensitive to specific surface area and crystallinity of the C₃N₄, but largely insensitive to the pore size and the volume.¹⁰¹ Similarly, the cobalt complex Co(bpy)₃Cl₂ was combined with g-C₃N₄ for being used as photocatalysts in the conversion of CO₂ to CO (1.85 μmol h⁻¹), with triethanolamine as the electron donor and hydrogen source.¹⁰²

For the study of carbon-based QD-like photocatalysts for CO₂ reduction in general, a reviewer of this article made some valuable points, which should be considered in further investigations. One is on the need to look at and specify the source of the electrons, as correctly stated by the reviewer that the “CO₂ reduction does not occur without oxidation of something else”, namely the electrons needed for the photocatalyzed CO₂ reduction have to come from somewhere. This has not been a critical issue so far probably because the conversion yields have generally been very low, thus only a small number of electrons are needed, which might come from organic residues in the reaction even without a purposely added sacrificial electron donor. The other is on the popular use of photoproduct formation rates for the evaluation of photocatalyzed CO₂ reduction. Again correctly pointed by the reviewer: “While the rates are indeed important, they are meaningless unless one knows the light source (wavelength and intensity).” Experimentally, measurements for the rates are apparently easier than those for the quantum yields, as for the latter an accurate determination on the number of photons absorbed by the photocatalysts is more difficult (especially in more turbulent reaction mixtures with substantial light scattering). Therefore, more effort is required for the measurement of quantum yields and for their correlations with the rates, including those already available in the literature.

Photocatalytic Generation of H₂ from Water-Splitting.

In the photocatalytic water-splitting reaction, the photo-generated electrons and holes act as reducing and oxidizing agents, producing H₂ and O₂, respectively. The efficient separation of the gases thus produced is generally a challenge, so a popular strategy has been the reduction for H₂, coupled with the use of a sacrificial electron donor to scavenge the holes.^{5,65,91,103} Thermodynamically, the minimal photon energy required to drive the reactions is in theory about 1.23 eV (~1,000 nm), but in practice somewhat higher, close to 1.35 eV (~920 nm) to account for various energy losses.¹⁰³ Therefore, photons over the entire visible spectrum are capable of driving the reactions, so that there has been extensive effort on the

search and development of potent visible-light photocatalysts for ultimately solar H₂ production.^{65,91,103} Again with the absorption of core carbon nanoparticles overlapping with the solar spectrum for much of the visible (Figure 2), carbon dots have been explored as photocatalysts for H₂ generation from water-splitting.^{67,104–107}

Cao et al. demonstrated the use of PEG_{1500N}-functionalized carbon dots, with the doping of gold or platinum metal, for the visible-light photocatalytic H₂ generation from water.⁶⁷ There have also been some limited explorations on the use of GQDs without any surface modification or other neat carbon nanostructures as photocatalysts for water-splitting.^{65,91,108} More popular and effective have been the photocatalysts based on nanocomposites containing GQDs or the like, or the hybrid nanostructures in which the nanoscale carbon serves essentially the role of visible-light photosensitizer.⁸⁰ The materials development for these photocatalysts and their applications have been largely similar to those in the CO₂ conversion discussed above.

Among representative examples, Yu et al. prepared carbon nanocomposites with TiO₂ for water-splitting under either UV- or visible-light illumination.¹⁰⁴ The observed highest hydrogen production rate was about 9.1 μmol/h, several times higher than the rate obtained with neat TiO₂ photocatalysts.¹⁰⁴ Wang et al. applied hydrothermal processing to vitamin C as the carbon source to obtain carbon-TiO₂ composite photocatalysts for H₂ generation, with the highest production rate up to 739 μmol h⁻¹ g⁻¹.¹⁰⁷ Further performance improvements were achieved with TiO₂ nanowires in the composite photocatalysts.¹⁰⁷ Similarly, composite nanostructures of carbon with various combinations of ZnS, CdSe, TiO₂, Ag, and/or Ag₃PW₁₂O₄₀ were developed for the purpose of photocatalytic H₂ generation from water.^{109–111}

The carbon-based nanoscale entities in composite photocatalysts could be graphene, GOs, and/or g-C₃N₄. In the early work by Yeh et al.,¹⁰⁸ the H₂ production was achieved by photoirradiating a solution of GOs in water–methanol, where the role of methanol was to serve as a sacrificial electron donor. In their recent study, the GOs were nitrogen-doped in order to move the light absorption by the photocatalysts to the visible.⁶⁴ Li et al. used GOs as support for CdS nanoclusters in the solvothermal synthesis, followed by the deposition of Pt nanoparticles as cocatalysts.¹¹² With the resulting photocatalysts, an H₂ production rate of 1.12 mmol/h was achieved under visible-light irradiation.¹¹² Xiang et al. coupled graphene with g-C₃N₄ for use as photocatalysts, with Pt as a cocatalyst, achieving a H₂ evolution rate ~451 μmol h⁻¹ g⁻¹ under visible-light irradiation, better performance than that with only g-C₃N₄.¹¹³ The approach for composite photocatalysts apparently has few limits, with a number of more complex nanostructures and configurations already explored.⁶⁵

Some of the photocatalysts have also been used in the photoelectrochemical water-splitting for H₂ generation.^{105,106,110,114} For example, Zhang et al. used TiO₂ nanotube array loaded with carbon quantum dots as photoanode in photoelectrochemical cell.¹⁰⁵ Meng and co-workers combined GQDs with TiO₂ nanotube array and also the array modified by CdS for their evaluation in photoelectrochemical hydrogen production under simulated sunlight.¹¹⁴

The studies highlighted above have shown clearly that nanoscale carbon particles, graphitic pieces (graphene or rGO sheets), or domains in composite nanostructures not only serve the function of dyes in dye-sensitized semiconductor photo-

Table 1. Summary of Relatively High-Yield Photocatalytic Reactions with Carbon-Based Quantum Dots

carbon-based quantum dots	CO ₂ photoreduction				H ₂ generation			
	photocatalyst	product yield	quantum yield (%)	ref.	photocatalyst	H ₂ generation	quantum yield (%)	ref.
carbon dots	carbon dots	formic acid 40 μmol g ⁻¹ h ⁻¹	0.1–0.2	70	carbon dots	424 μmol g ⁻¹ h ⁻¹		116
	Au-doped carbon dots	formic acid 1.2 mmol g ⁻¹ h ⁻¹ acetic acid 0.06 mmol g ⁻¹ h ⁻¹	up to 1–3	69				
other carbon-based QD-Like nanomaterials	GO	methanol 20 μmol g ⁻¹ h ⁻¹	0.044	117	GO	2.8 mmol h ⁻¹	2.17	108
	rGO-ZnO	methanol 4.58 μmol g ⁻¹ h ⁻¹		81	carbon-TiO ₂	739 μmol g ⁻¹ h ⁻¹		107
	graphene-TiO ₂	methane 8 μmol g ⁻¹ h ⁻¹		89	Pt/CdS-GOs	1.12 mmol h ⁻¹	22.5	112
		ethane 16.8 μmol g ⁻¹ h ⁻¹						
	g-C ₃ N ₄	methanol 6.28 μmol g ⁻¹ h ⁻¹	0.18	94	Pt/graphene/ g-C ₃ N ₄	451 μmol g ⁻¹ h ⁻¹	2.6	113
		ethanol 4.51 μmol g ⁻¹ h ⁻¹						
C ₃ N ₄ - ruthenium complex		formic acid 431 μmol g ⁻¹ h ⁻¹	1.5	100				

catalysts but also participate directly in the photoreduction reactions for CO₂ conversion and water-splitting (Table 1). Particularly interesting and promising for further development are carbon-based nanocomposite or hybrid photocatalysts, providing competitive alternatives to the presently dominating conventional semiconductor-based systems and unique opportunities.

CONCLUSION

Carbon-based QDs and related nanomaterials have obviously emerged to become an important research field that is still experiencing rapid advances, as reflected by the large number of recent publications. While most of the research and development effort has been on their photoluminescence properties, which are often considered as being characteristic of QDs, the photoinduced redox processes in these nanomaterials relevant to various energy conversion schemes are clearly attracting growing attention. Among the superior and/or unique features of carbon-based QDs are their broad and strong absorption across a major portion of the solar spectrum, efficient charge separation upon photoexcitation, and subsequent formation of electrons and holes that can drive productive chemical reactions (CO₂ reduction and H₂ generation from water-splitting in particular). The fact that carbon at the nanoscale (specifically small carbon nanoparticles with only a limited content of randomly mixed graphitic structures) could function similarly to conventional nanoscale semiconductors challenges the presently established theoretical frameworks on electronic structures and transitions, in which a clear distinction between a molecule and a size-wise comparable nanoscale solid (a C₆₀ molecule vs a carbon nanoparticle of 1 nm in diameter, for example) is still needed or to be improved. What makes the nanoparticle distinct is the presence of structural and/or surface-edge defects, which apparently play a dominating role in carbon dots, GQDs, and their various “derivatives” in terms of photoexcited state properties and redox processes. Investigations for further mechanistic understanding of carbon-based

QDs are certainly in demand. For photocatalytic energy conversion applications, composite, or hybrid nanostructures derived from the carbon-based QDs may represent a more promising platform, and significant advances in high-yield CO₂ photoconversion and water-splitting may be expected.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: christopher.bunker@us.af.mil

*E-mail: syaping@clemson.edu

Author Contributions

†K.A.S.F. and S.S. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge funding from the Air Force Office of Scientific Research through the support of Dr. Michael Berman (C.E.B.), the Air Force Research Laboratory (C.E.B.), and the National Science Foundation (Y.-P.S.).

REFERENCES

- Brus, L. E. Electron-Electron and Electron-Hole Interactions in Small Semiconductor Crystallites-the Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80*, 4403–4409.
- Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. The Quantum Mechanics of Larger Semiconductor Clusters (“quantum dots”). *Annu. Rev. Phys. Chem.* **1990**, *41*, 477–496.
- Smith, A. M.; Nie, S. Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering. *Acc. Chem. Res.* **2010**, *43*, 190–200.
- Kairdolf, B. A.; Smith, A. M.; Stokes, T. H.; Wang, M. D.; Young, A. N.; Nie, N. Semiconductor Quantum Dots for Bioimaging and Biodiagnostic Applications. *Annu. Rev. Anal. Chem.* **2013**, *6*, 143–162.
- Wilker, M. B.; Schnitzenbaumer, K. J.; Dukovic, G. Recent Progress in Photocatalysis Mediated by Colloidal II-VI Nanocrystals. *Isr. J. Chem.* **2012**, *52*, 1002–1015.

- (6) Santra, P. K.; Kamat, P. V. Mn-Doped Quantum Dot Sensitized Solar Cells: A Strategy to Boost Efficiency over 5%. *J. Am. Chem. Soc.* **2012**, *134*, 2508–2511.
- (7) Pan, Z.; Zhang, H.; Cheng, K.; Hou, Y.; Hua, J.; Zhong, X. Highly Efficient Inverted Type-I CdS/CdSe Core/Shell Structure QD-Sensitized Solar Cells Highly Efficient Inverted Type-I CdS/CdSe Core/Shell Structure QD-Sensitized Solar Cells. *ACS Nano* **2012**, *6*, 3982–3991.
- (8) Saha, A.; Chellappan, K. V.; Narayan, K. S.; Ghatak, J.; Datta, R.; Viswanatha, R. Near-Unity Quantum Yield in Semiconducting Nanostructures: Structural Understanding Leading to Energy Efficient Applications. *J. Phys. Chem. Lett.* **2013**, *4*, 3544–3549.
- (9) Amirav, L.; Alivisatos, A. P. Photocatalytic Hydrogen Production with Tunable Nanorod Heterostructures. *J. Phys. Chem. Lett.* **2010**, *1*, 1051–1054.
- (10) Zhu, H.; Song, N.; Lv, H.; Hill, C. L.; Lian, T. Near Unity Quantum Yield of Light-Driven Redox Mediator Reduction and Efficient H₂ Generation Using Colloidal Nanorod Heterostructures. *J. Am. Chem. Soc.* **2012**, *134*, 11701–11708.
- (11) Han, Z.; Qiu, F.; Eisenberg, R.; Holland, P. L.; Krauss, T. D. Robust Photogeneration of H₂ in Water Using Semiconductor Nanocrystals and a Nickel Catalyst. *Science* **2012**, *338*, 1321–1324.
- (12) Wang, C.; Thompson, R. L.; Baltrus, J.; Matranga, C. Visible Light Photoreduction of CO₂ Using CdSe/Pt/TiO₂ Heterostructured Catalysts. *J. Phys. Chem. Lett.* **2010**, *1*, 48–53.
- (13) Chaudhary, Y. S.; Woolerton, T. W.; Allen, C. S.; Warner, J. H.; Pierce, E.; Ragsdale, S. W.; Armstrong, F. A. Visible Light-Driven CO₂ Reduction by Enzyme Coupled CdS Nanocrystals. *Chem. Commun.* **2012**, *48*, 58–60.
- (14) Fan, W.; Zhang, Q.; Wang, Y. Semiconductor-Based Nanocomposites for Photocatalytic H₂ Production and CO₂ Conversion. *Phys. Chem. Chem. Phys.* **2013**, *15*, 2632–2649.
- (15) Yu, J.; Jin, J.; Cheng, B.; Jaroniec, M. A Noble Metal-Free Reduced Graphene Oxide-CdS Nanorod Composite for the Enhanced Visible-Light Photocatalytic Reduction of CO₂ to Solar Fuel. *J. Mater. Chem. A* **2014**, *2*, 3407–3416.
- (16) Sun, Y.-P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K. A. S.; Pathak, P.; Mezziani, M. J.; Harruff, B. A.; Wang, X.; Wang, H.; Luo, P. G.; Yang, H.; Kose, M. E.; Chen, B.; Veca, L. M.; Xie, S.-Y. Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *J. Am. Chem. Soc.* **2006**, *128*, 7756–7757.
- (17) Sun, Y.-P. Fluorescent Carbon Nanoparticles, U.S. Patent 7,829,772. Oct. 27, 2006.
- (18) Luo, P. G.; Sahu, S.; Yang, S.-T.; Sonkar, S. K.; Wang, J.; Wang, H.; LeCroy, G. E.; Cao, L.; Sun, Y.-P. Carbon “Quantum” Dots for Optical Bioimaging. *J. Mater. Chem. B* **2013**, *1*, 2116–2127.
- (19) Luo, P. G.; Sonkar, S. K.; Yang, S.-T.; Yang, F.; Yang, L.; Broglie, J. J.; Sun, Y.-P. Carbon-Based Quantum Dots for Fluorescence Imaging of Cells and Tissues. *RSC Adv.* **2014**, *4*, 10791–10807.
- (20) Wang, Y.; Hu, A. Carbon Quantum Dots: Synthesis, Properties and Applications. *J. Mater. Chem. C* **2014**, *2*, 6921–6939.
- (21) Shen, J.; Zhu, Y.; Yang, X.; Li, C. Graphene Quantum Dots: Emergent Nanolights for Bioimaging, Sensors, Catalysis and Photovoltaic Devices. *Chem. Commun.* **2012**, *48*, 3686–3699.
- (22) Zhang, Z.; Zhang, J.; Chena, N.; Qu, L. Graphene Quantum Dots: an Emerging Material for Energy-Related Applications and Beyond. *Energy Environ. Sci.* **2012**, *5*, 8869–8890.
- (23) Li, L.; Wu, G.; Yang, G.; Peng, J.; Zhao, J.; Zhu, J.-J. Focusing on Luminescent Graphene Quantum Dots: Current Status and Future Perspectives. *Nanoscale* **2013**, *5*, 4015–4039.
- (24) Bacon, M.; Bradley, S. J.; Nann, T. Graphene Quantum Dots. *Part. Part. Syst. Charact.* **2014**, *31*, 415–428.
- (25) Cao, L.; Mezziani, M. J.; Sahu, S.; Sun, Y.-P. Photoluminescence Properties of Graphene versus Other Carbon Nanomaterials. *Acc. Chem. Res.* **2012**, *46*, 171–180.
- (26) Wang, X.; Cao, L.; Yang, S.-T.; Lu, F.; Mezziani, M. J.; Tian, L.; Sun, K. W.; Bloodgood, M. A.; Sun, Y.-P. Bandgap-Like Strong Fluorescence in Functionalized Carbon Nanoparticles. *Angew. Chem., Int. Ed.* **2010**, *49*, 5310–5314.
- (27) Cao, L.; Anilkumar, P.; Wang, X.; Liu, J.-H.; Sahu, S.; Mezziani, M. J.; Myers, E.; Sun, Y.-P. Reverse Stern-Volmer Behavior for Luminescence Quenching in Carbon Nanoparticles. *Can. J. Chem.* **2010**, *89*, 104–109.
- (28) Xu, J.; Sahu, S.; Cao, L.; Anilkumar, P.; Tackett, K. N., II; Qian, H.; Bunker, C. E.; Gulians, E. A.; Parenzan, A.; Sun, Y.-P. Carbon Nanoparticles as Chromophores for Photon Harvesting and Photoconversion. *ChemPhysChem.* **2011**, *12*, 3604–3608.
- (29) Ding, H.; Zhang, P.; Wang, T.-Y.; Kong, J.-L.; Xiong, H. M. Nitrogen-Doped Carbon Dots Derived from Polyvinyl Pyrrolidone and Their Multicolor Cell Imaging. *Nanotechnology* **2014**, *25*, 205604 (9pp).
- (30) Sun, Y.-P.; Wang, X.; Lu, F.; Cao, L.; Mezziani, M. J.; Luo, P. G.; Gu, L.; Veca, L. M. Doped Carbon Nanoparticles as a New Platform for Highly Photoluminescent Dots. *J. Phys. Chem. C* **2008**, *112*, 18295–18298.
- (31) Anilkumar, P.; Wang, X.; Cao, L.; Sahu, S.; Liu, J.-H.; Wang, P.; Korch, K.; Tackett, K. N., II; Parenzan, A.; Sun, Y.-P. Toward Quantitatively Fluorescent Carbon-Based “Quantum” Dots. *Nanoscale* **2011**, *3*, 2023–2027.
- (32) Cao, L.; Wang, X.; Mezziani, M. J.; Lu, F.; Wang, H.; Luo, P. G.; Lin, Y.; Harruff, B. A.; Veca, L. M.; Murray, D.; Xie, S.-Y.; Sun, Y.-P. Carbon Dots for Multiphoton Bioimaging. *J. Am. Chem. Soc.* **2007**, *129*, 11318–11319.
- (33) Li, H.; Kang, Z.; Liu, Y.; Lee, S.-T. Carbon Nanodots: Synthesis, Properties and Applications. *J. Mater. Chem.* **2012**, *22*, 24230–24253.
- (34) Liu, Q.; Guo, B.; Rao, Z.; Zhang, B.; Gong, J. R. Strong Two-Photon-Induced Fluorescence from Photostable, Biocompatible Nitrogen-Doped Graphene Quantum Dots for Cellular and Deep-Tissue Imaging. *Nano Lett.* **2013**, *13*, 2436–2441.
- (35) Peng, H.; Sejdic, J. T. Simple Aqueous Solution Route to Luminescent Carbogenic Dots from Carbohydrates. *Chem. Mater.* **2009**, *21*, 5563–5565.
- (36) Dong, Y.; Wang, R.; Li, H.; Shao, J.; Chi, Y.; Lin, X.; Chen, G. Polyamine-Functionalized Carbon Quantum Dots for Chemical Sensing. *Carbon* **2012**, *50*, 2810–2815.
- (37) Zhu, H.; Wang, X.; Li, Y.; Wang, Z.; Yang, Z.; Yang, X. Microwave Synthesis of Fluorescent Carbon Nanoparticles with Electrochemiluminescence Properties. *Chem. Commun.* **2009**, 5118–5120.
- (38) Yang, Y.; Cui, J.; Zheng, M.; Hu, C.; Tan, S.; Xiao, Y.; Yang, Q.; Liu, Y. One-Step Synthesis of Amino-Functionalized Fluorescent Carbon Nanoparticles by Hydrothermal Carbonization of Chitosan. *Chem. Commun.* **2012**, *48*, 380–382.
- (39) Wang, X.; Cao, L.; Lu, F. S.; Mezziani, M. J.; Li, H.; Qi, G.; Zhou, B.; Harruff, B. A.; Kermarrec, F.; Sun, Y.-P. Photoinduced Electron Transfers with Carbon Dots. *Chem. Commun.* **2009**, 3774–3776.
- (40) Barman, M. K.; Bhattacharyya, S.; Patra, A. Steady State and Time Resolved Spectroscopic Study of C-Dots-MEH-PPV Polymer Nanoparticles Composites. *Phys. Chem. Chem. Phys.* **2013**, *15*, 16834–16840.
- (41) Zhang, H.; Huang, H.; Ming, H.; Li, H.; Zhang, L.; Liu, Y.; Kang, Z. Carbon Quantum Dots/Ag₃PO₄ Complex Photocatalysts with Enhanced Photocatalytic Activity and Stability under Visible Light. *J. Mater. Chem.* **2012**, *22*, 10501–10506.
- (42) Xu, J.; Sahu, S.; Cao, L.; Bunker, C. E.; Peng, G.; Liu, Y.; Fernando, K. A. S.; Wang, P.; Gulians, E. A.; Mezziani, M. J.; Qian, H.; Sun, Y.-P. Efficient Fluorescence Quenching in Carbon Dots by Surface-Doped Metals-Disruption of Excited State Redox Processes and Mechanistic Implications. *Langmuir* **2012**, *28*, 16141–16147.
- (43) Choi, H.; Ko, S.-J.; Choi, Y.; Joo, P.; Kim, T.; Lee, B. R.; Jung, J.-W.; Choi, H. J.; Cha, M.; Jeong, J.-R.; Hwang, I.-W.; Song, M. H.; Kim, B.-S.; Kim, J. Y. Versatile Surface Plasmon Resonance of Carbon-Dot-Supported Silver Nanoparticles in Polymer Optoelectronic Devices. *Nat. Photonics* **2013**, *7*, 732–738.
- (44) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. Strong Luminescence of Solubilized Carbon Nanotubes. *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.

- (45) Veca, L. M.; Lu, F.; Mezzani, M. J.; Cao, L.; Zhang, P.; Shrestha, M.; Sun, Y.-P. Polymer Functionalization and Solubilization of Carbon Nanosheets. *Chem. Commun.* **2009**, 2565–2567.
- (46) Loh, K. P.; Bao, Q.; Eda, G.; Chhowalla, M. Graphene Oxide as a Chemically Tunable Platform for Optical Applications. *Nat. Chem.* **2010**, *2*, 1015–1024.
- (47) Eda, G.; Lin, Y.-Y.; Mattevi, C.; Yamaguchi, H.; Chen, H.-A.; Chen, I.-S.; Chen, C.-W.; Chhowalla, M. Blue Photoluminescence from Chemically Derived Graphene Oxide. *Adv. Mater.* **2010**, *22*, 505–509.
- (48) Gokus, T.; Nair, R. R.; Bonetti, A.; Böhmeler, M.; Lombardo, A.; Novoselov, K. S.; Geim, A. K.; Ferrari, A. C.; Hartschuh, A. Making Graphene Luminescent by Oxygen Plasma Treatment. *ACS Nano* **2009**, *3*, 3963–3968.
- (49) Lu, J.; Yeo, P. S. E.; Gan, C. K.; Wu, P.; Loh, K. P. Transforming C₆₀ Molecules into Graphene Quantum Dots. *Nat. Nanotechnol.* **2011**, *6*, 247–252.
- (50) Chen, S.; Liu, J.-W.; Chen, M.-L.; Chen, X.-W.; Wang, J.-H. Unusual Emission Transformation of Graphene Quantum Dots Induced by Self-Assembled Aggregation. *Chem. Commun.* **2012**, *48*, 7637–7639.
- (51) Jin, S. H.; Kim, D. H.; Jun, G. H.; Hong, S. H.; Jeon, S. Tuning the Photoluminescence of Graphene Quantum Dots through the Charge Transfer Effect of Functional Groups. *ACS Nano* **2013**, *7*, 1239–1245.
- (52) Stengl, V.; Bakardjieva, S.; Henych, J.; Lang, K.; Kormunda, M. Blue and Green Luminescence of Reduced Graphene Oxide Quantum Dots. *Carbon* **2013**, *63*, 537–546.
- (53) Pan, D.; Zhang, J.; Li, Z.; Wu, M. Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots. *Adv. Mater.* **2010**, *22*, 734–738.
- (54) Pan, D.; Guo, L.; Zhang, J.; Xi, C.; Xue, Q.; Huang, H.; Li, J.; Zhang, Z.; Yu, W.; Chen, Z.; Li, Z.; Wu, M. Cutting sp² Clusters in Graphene Sheets into Colloidal Graphene Quantum Dots with Strong Green Fluorescence. *J. Mater. Chem.* **2012**, *22*, 3314–3318.
- (55) Sun, Y.; Wang, S.; Li, C.; Luo, P.; Tao, L.; Wei, Y.; Shi, G. Large Scale Preparation of Graphene Quantum Dots from Graphite with Tunable Fluorescence Properties. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9907–9913.
- (56) Li, L.-L.; Ji, J.; Fei, R.; Wang, C.-Z.; Lu, Q.; Zhang, J.-R.; Jiang, L.-P.; Zhu, J.-J. A Facile Microwave Avenue to Electrochemiluminescent Two-Color Graphene Quantum Dots. *Adv. Funct. Mater.* **2012**, *22*, 2971–2979.
- (57) Galande, C.; Mohite, A. D.; Naumov, A. V.; Gao, W.; Ci, L.; Ajayan, A.; Gao, H.; Srivastava, A.; Weisman, R. B.; Ajayan, P. M. Quasi-Molecular Fluorescence from Graphene Oxide. *Sci. Rep.* **2011**, *1*, 3–18.
- (58) Shen, J.; Zhu, Y.; Yang, X.; Zong, J.; Zhang, J.; Li, C. One-Pot Hydrothermal Synthesis of Graphene Quantum Dots Surface-Passivated by Polyethylene Glycol and Their Photoelectric Conversion under Near-Infrared Light. *New J. Chem.* **2012**, *36*, 97–101.
- (59) Xue, Q.; Huang, H.; Wang, Z.; Chen, Z.; Wu, M.; Li, Z.; Pan, D. Nearly Monodisperse Graphene Quantum Dots Fabricated by Amine-Assisted Cutting and Ultrafiltration. *Nanoscale* **2013**, *5*, 12098–12103.
- (60) Tetsuka, H.; Asahi, R.; Nagoya, A.; Okamoto, K.; Tajima, I.; Ohta, R.; Okamoto, A. Optically Tunable Amino-Functionalized Graphene Quantum Dots. *Adv. Mater.* **2012**, *24*, 5333–5338.
- (61) Kumar, S. G.; Roy, R.; Sen, D.; Ghorai, U. K.; Thapa, R.; Mazumder, N.; Saha, S.; Chattopadhyay, K. K. Amino-Functionalized Graphene Quantum Dots: Origin of Tunable Heterogeneous Photoluminescence. *Nanoscale* **2014**, *6*, 3384–3391.
- (62) Qu, D.; Zheng, M.; Zhang, L.; Zhao, H.; Xie, Z.; Jing, X.; Haddad, R. E.; Fan, H.; Sun, Z. Formation Mechanism and Optimization of Highly Luminescent N-Doped Graphene Quantum Dots. *Sci. Rep.* **2014**, *4*, 5294.
- (63) Wang, L.; Wang, Y.; Xu, T.; Liao, H.; Yao, C.; Liu, Y.; Li, Z.; Chen, Z.; Pan, D.; Sun, L.; Wu, M. Gram-Scale Synthesis of Single-Crystalline Graphene Quantum Dots with Superior Optical Properties. *Nat. Commun.* **2014**, *5*, 5357.
- (64) Yeh, T.-F.; Teng, C.-Y.; Chen, S.-J.; Teng, H. Nitrogen-Doped Graphene Oxide Quantum Dots as Photocatalysts for Overall Water-Splitting under Visible Light Illumination. *Adv. Mater.* **2014**, *26*, 3297–3303.
- (65) Xie, G.; Zhang, K.; Guo, B.; Liu, Q.; Fang, L.; Gong, J. R. Graphene-Based Materials for Hydrogen Generation from Light-Driven Water Splitting. *Adv. Mater.* **2013**, *25*, 3820–3839.
- (66) Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. Photocatalytic Reduction of CO₂ on TiO₂ and Other Semiconductors. *Angew. Chem., Int. Ed.* **2013**, *52*, 7372–7408.
- (67) Cao, L.; Sahu, S.; Anilkumar, P.; Bunker, C. E.; Xu, J.; Fernando, K. A. S.; Wang, P.; Gulians, E. A.; Tackett, K. N., II; Sun, Y.-P. Carbon nanoparticles as visible-light photocatalysts for efficient CO₂ conversion and beyond. *J. Am. Chem. Soc.* **2011**, *133*, 4754–4757.
- (68) Wang, J.; Sahu, S.; Sonkar, S. K.; Tackett, K. N., II; Sun, K. W.; Liu, Y.; Maimaiti, H.; Anilkumar, P.; Sun, Y.-P. Versatility with Carbon Dots-from Overcooked BBQ to Brightly Fluorescent Agents and Photocatalysts. *RSC Adv.* **2013**, *3*, 15604–15607.
- (69) Sahu, S.; Liu, Y.; Wang, P.; Bunker, C. E.; Fernando, K. A. S.; Lewis, W. K.; Gulians, E. A.; Yang, F.; Wang, J.; Sun, Y.-P. Visible-Light Photoconversion of Carbon Dioxide into Organic Acids in an Aqueous Solution of Carbon Dots. *Langmuir* **2014**, *30*, 8631–8636.
- (70) Sahu, S. Development and Evaluation of Carbon-based Quantum Dots for Carbon Dioxide Photoconversion. *Ph.D. Thesis*, Clemson University, Clemson, SC, December 2014.
- (71) Hong, J.; Zhang, W.; Ren, J.; Xu, R. Photocatalytic Reduction of CO₂: A Brief Review on Product Analysis and Systematic Methods. *Anal. Methods* **2013**, *5*, 1086–1097.
- (72) Shkrob, I. A.; Marin, T. W.; He, H.; Zapol, P. Photoredox Reactions and the Catalytic Cycle for Carbon Dioxide Fixation and Methanogenesis on Metal Oxides. *J. Phys. Chem. C* **2012**, *116*, 9450–9460.
- (73) Choi, Y.; Ryu, G. H.; Min, S. H.; Lee, B. R.; Song, M. H.; Lee, Z.; Kim, B.-S. Interface-Controlled Synthesis of Heterodimeric Silver-Carbon Nanoparticles Derived from Polysaccharides. *ACS Nano* **2014**, *8*, 11377–11385.
- (74) Mazzier, D.; Favaro, M.; Agnoli, S.; Silvestrini, S.; Granozzi, G.; Maggini, M.; Moretto, A. Synthesis of Luminescent 3D Microstructures Formed by Carbon Quantum Dots and Their Self-Assembly Properties. *Chem. Commun.* **2014**, *50*, 6592–6595.
- (75) Qin, X.; Lu, W.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. Green, Low-Cost Synthesis of Photoluminescent Carbon Dots by Hydrothermal Treatment of Willow Bark and Their Application as an Effective Photocatalyst for Fabricating Au Nanoparticles-Reduced Graphene Oxide Nanocomposites for Glucose Detection. *Catal. Sci. Technol.* **2013**, *3*, 1027–1035.
- (76) Hsu, H. C.; Shown, I.; Wei, H. Y.; Chang, Y. C.; Du, H. Y.; Lin, Y. G.; Tseng, C. A.; Wang, C. H.; Chen, L. C.; Lin, Y. C.; Chen, K. H. Graphene Oxide as a Promising Photocatalyst for CO₂ to Methanol Conversion. *Nanoscale* **2013**, *5*, 262–268.
- (77) Tjoa, V.; Chua, J.; Pramana, S. S.; Wei, J.; Mhaisalkar, S. G.; Mathews, N. Facile Photochemical Synthesis of Graphene-Pt Nanoparticle Composite for Counter Electrode in Dye Sensitized Solar Cell. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3447–3452.
- (78) Moon, G.-H.; Kim, H.; Shin, Y.; Choi, W. Chemical-Free Growth of Metal Nanoparticles on Graphene Oxide Sheets under Visible Light Irradiation. *RSC Adv.* **2012**, *2*, 2205–2207.
- (79) Sun, H.; Wang, S. Research Advances in the Synthesis of Nanocarbon-Based Photocatalysts and Their Applications for Photocatalytic Conversion of Carbon Dioxide to Hydrocarbon Fuels. *Energy Fuels* **2014**, *28*, 22–36.
- (80) Chen, D.; Zhang, H.; Liu, Y.; Li, J. Graphene and its Derivatives for the Development of Solar Cells Photoelectrochemical, and Photocatalytic Applications. *Energy Environ. Sci.* **2013**, *6*, 1362–1387.
- (81) Li, X.; Wang, Q.; Zhao, Y.; Wu, W.; Chen, J.; Meng, H. Green Synthesis and Photo-Catalytic Performances for ZnO-Reduced Graphene Oxide Nanocomposites. *J. Colloid Interface Sci.* **2013**, *411*, 69–75.

- (82) Tan, L.-L.; Ong, W.-J.; Chai, S.-P.; Mohamed, A. R. Reduced Graphene Oxide-TiO₂ Nanocomposite as a Promising Visible-Light-Active Photocatalyst for the Conversion of Carbon Dioxide. *Nanoscale Res. Lett.* **2013**, *8*, 465(pp 9).
- (83) An, X.; Li, K.; Tang, J. Cu₂O/Reduced Graphene Oxide Composites for the Photocatalytic Conversion of CO₂. *ChemSusChem* **2014**, *7*, 1086–1093.
- (84) Liang, Y. T.; Vijayan, B. K.; Gray, K. A.; Hersam, M. C. Minimizing Graphene Defects Enhances Titania Nanocomposite-Based Photocatalytic Reduction of CO₂ for Improved Solar Fuel Production. *Nano Lett.* **2011**, *11*, 2865–2870.
- (85) Liang, Y. T.; Vijayan, B. K.; Lyandres, O.; Gray, K. A.; Hersam, M. C. Effect of Dimensionality on the Photocatalytic Behavior of Carbon-Titania Nanosheet Composites: Charge Transfer at Nanomaterial Interfaces. *J. Phys. Chem. Lett.* **2012**, *3*, 1760–1765.
- (86) Wang, P. Q.; Bai, Y.; Luo, P. Y.; Liu, J. Y. Graphene-WO₃ Nanobelt Composite: Elevated Conduction Band Toward Photocatalytic Reduction of CO₂ into Hydrocarbon Fuels. *Catal. Commun.* **2013**, *38*, 82–85.
- (87) Lv, X. J.; Fu, W. F.; Hu, C. Y.; Chen, Y.; Zhou, W. B. Photocatalytic Reduction of CO₂ with H₂O over a Graphene-Modified NiOx-Ta₂O₅ Composite Photocatalyst: Coupling yields of Methanol and Hydrogen. *RSC Adv.* **2013**, *3*, 1753–1757.
- (88) Tu, W. G.; Zhou, Y.; Liu, Q.; Tian, Z. P.; Gao, J.; Chen, X. Y.; Zhang, H. T.; Liu, J. G.; Zou, Z. G. Robust Hollow Spheres Consisting of Alternating Titania Nanosheets and Graphene Nanosheets with High Photocatalytic Activity for CO₂ Conversion into Renewable Fuels. *Adv. Funct. Mater.* **2012**, *22*, 1215–1221.
- (89) Tu, W. G.; Zhou, Y.; Liu, Q.; Yan, S. C.; Bao, S. S.; Wang, X. Y.; Xiao, M.; Zou, Z. G. An in Situ Simultaneous Reduction–Hydrolysis Technique for Fabrication of TiO₂-Graphene 2D Sandwich-Like Hybrid Nanosheets: Graphene-Promoted Selectivity of Photocatalytic-Driven Hydrogenation and Coupling of CO₂ into Methane and Ethane. *Adv. Funct. Mater.* **2013**, *23*, 1743–1749.
- (90) Wang, X.; Maeda, K.; Thomas, A.; Takanebe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light. *Nat. Mater.* **2009**, *8*, 76–80.
- (91) Cao, S.; Yu, J. g-C₃N₄-Based Photocatalysts for Hydrogen Generation. *J. Phys. Chem. Lett.* **2014**, *5*, 2101–2107.
- (92) Zhao, Z.; Sun, Y.; Dong, F. Graphitic Carbon Nitride Based Nanocomposites: A Review. *Nanoscale* **2014**, *7*, 15–37.
- (93) Dong, G.; Zhang, L. Porous Structure Dependent Photo-reactivity of Graphitic Carbon Nitride under Visible Light. *J. Mater. Chem.* **2012**, *22*, 1160–1166.
- (94) Mao, J.; Peng, T.; Zhang, X.; Li, K.; Ye, L.; Zan, L. Effect of Graphitic Carbon Nitride Microstructures on the Activity and Selectivity of Photocatalytic CO₂ Reduction under Visible Light. *Catal. Sci. Technol.* **2013**, *3*, 1253–1260.
- (95) Niu, P.; Yang, Y.; Yu, J. C.; Liu, G.; Cheng, H.-M. Switching the Selectivity of the Photoreduction Reaction of Carbon Dioxide by Controlling the Band Structure of a g-C₃N₄ Photocatalyst. *Chem. Commun.* **2014**, *50*, 10837–10840.
- (96) Zheng, Y.; Lin, L.; Ye, X.; Guo, F.; Wang, X. Helical Graphitic Carbon Nitrides with Photocatalytic and Optical Activities. *Angew. Chem., Int. Ed.* **2014**, *53*, 11926–11930.
- (97) Yu, J.; Wang, K.; Xiao, W.; Cheng, B. Photocatalytic Reduction of CO₂ into Hydrocarbon Solar Fuels over g-C₃N₄-Pt Nanocomposite Photocatalysts. *Phys. Chem. Chem. Phys.* **2014**, *16*, 11492–11501.
- (98) Ohno, T.; Murakami, N.; Koyanagi, T.; Yang, Y. Photocatalytic Reduction of CO₂ over a Hybrid Photocatalyst Composed of WO₃ and Graphitic Carbon Nitride (g-C₃N₄) under visible Light. *J. CO₂ Util.* **2014**, *6*, 17–25.
- (99) Wang, Y.; Chen, Y.; Zuo, Y.; Wang, F.; Yao, J.; Li, B.; Kang, S.; Li, X.; Cui, L. Hierarchically Mesoporous TiO₂/Graphitic Carbon Composite as a New Efficient Photocatalyst for the Reduction of CO₂ under Simulated Solar Irradiation. *Catal. Sci. Technol.* **2013**, *3*, 3286–3291.
- (100) Maeda, K.; Sekizawa, K.; Ishitani, O. A Polymeric-Semiconductor-Metal Complex Hybrid Photocatalyst for Visible-Light CO₂ Reduction. *Chem. Commun.* **2013**, *49*, 10127–10129.
- (101) Maeda, K.; Kuriki, R.; Zhang, M.; Wang, X.; Ishitani, O. The Effect of the Pore-Wall Structure of Carbon Nitride on Photocatalytic CO₂ Reduction under Visible Light. *J. Mater. Chem. A* **2014**, *2*, 15146–15151.
- (102) Lin, J.; Pan, Z.; Wang, X. Photochemical Reduction of CO₂ by Graphitic Carbon Nitride Polymers. *ACS Sustainable Chem. Eng.* **2014**, *2*, 353–358.
- (103) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-Based Photocatalytic Hydrogen Generation. *Chem. Rev.* **2010**, *110*, 6503.
- (104) Yu, H.; Zhao, Y.; Zhou, C.; Shang, L.; Peng, Y.; Cao, Y.; Wu, L.-Z.; Tung, C.-H.; Zhang, T. Carbon Quantum Dots/TiO₂ Composites for Efficient Photocatalytic Hydrogen Evolution. *J. Mater. Chem. A* **2014**, *2*, 3344–3351.
- (105) Zhang, X.; Wang, F.; Huang, H.; Li, H.; Han, X.; Liu, Y.; Kang, Z. Carbon Quantum Dot Sensitized TiO₂ Nanotube Arrays for Photoelectrochemical Hydrogen Generation under Visible Light. *Nanoscale* **2013**, *5*, 2274–2278.
- (106) Yu, X.; Liu, R.; Zhang, G.; Cao, H. Carbon Quantum Dots as Novel Sensitizers for Photoelectrochemical Solar Hydrogen Generation and Their Size-Dependent Effect. *Nanotechnology* **2013**, *24*, 335401.
- (107) Wang, J.; Gao, M.; Ho, G. W. Bidentate-Complexes-Derived TiO₂/Carbon Dots Photocatalysts: in Situ Synthesis, Versatile Heterostructures, and Enhanced H₂ Evolution. *J. Mater. Chem. A* **2014**, *2*, 5703–5709.
- (108) Yeh, T. F.; Syu, J. M.; Cheng, C.; Chang, T. H.; Teng, H. Graphite Oxide as a Photocatalyst for Hydrogen Production from Water. *Adv. Funct. Mater.* **2010**, *20*, 2255–2262.
- (109) Wang, J.; Lim, Y.-F.; Ho, G. W. Carbon-Ensemble-Manipulated ZnS Heterostructures for Enhanced Photocatalytic H₂ Evolution. *Nanoscale* **2014**, *6*, 9673–9680.
- (110) Zhang, X.; Huang, H.; Liu, J.; Liu, Y.; Kang, K. Carbon Quantum Dots Serving as Spectral Converters through Broadband Upconversion of Near-Infrared Photons for Photoelectrochemical Hydrogen Generation. *J. Mater. Chem. A* **2013**, *1*, 11529–11533.
- (111) Liu, J.; Zhang, H.; Tang, D.; Zhang, X.; Yan, L.; Han, Y.; Huang, H.; Liu, Y.; Kang, Z. Carbon Quantum Dot/Silver Nanoparticle/Polyoxometalate Composites as Photocatalysts for Overall Water Splitting in Visible Light. *ChemCatChem* **2014**, *6*, 2634–2641.
- (112) Li, Q.; Guo, B.; Yu, J.; Ran, J.; Zhang, B.; Yan, H.; Gong, J. R. Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production of CdS-Cluster-Decorated Graphene Nanosheets. *J. Am. Chem. Soc.* **2011**, *133*, 10878–10884.
- (113) Xiang, Q.; Yu, J.; Jaroniec, M. Preparation and Enhanced Visible-Light Photocatalytic H₂-Production Activity of Graphene/C₃N₄ Composites. *J. Phys. Chem. C* **2011**, *115*, 7355–7363.
- (114) Yu, Y.; Ren, J.; Meng, M. Photocatalytic Hydrogen Evolution on Graphene Quantum Dots Anchored TiO₂ Nanotubes-Array. *Int. J. Hydrogen Energy* **2013**, *38*, 12266–12272.
- (115) LeCroy, G. E.; Sonkar, S. K.; Yang, F.; Veca, L. M.; Wang, P.; Tackett, K. N., II; Yu, J.-J.; Vasile, E.; Qian, H.; Liu, Y.; Luo, P. G.; Sun, Y.-P. Toward Structurally Defined Carbon Dots as Ultra-Compact Fluorescent Probes. *ACS Nano* **2014**, *8*, 4522–4529.
- (116) Yang, P.; Zhao, J.; Wang, J.; Cui, H.; Li, L.; Zhu, Z. Pure Carbon Nanodots for Excellent Photocatalytic Hydrogen Generation. *RSC Adv.* **2015**, *5*, 21332–21335.
- (117) Kumar, P.; Bansiwala, A.; Labhsetwar, N.; Jain, S. L. Visible Light Assisted Photocatalytic Reduction of CO₂ Using a Graphene Oxide Supported Heteroleptic Ruthenium Complex. *Green Chem.* **2015**, *17*, 1605–1609.