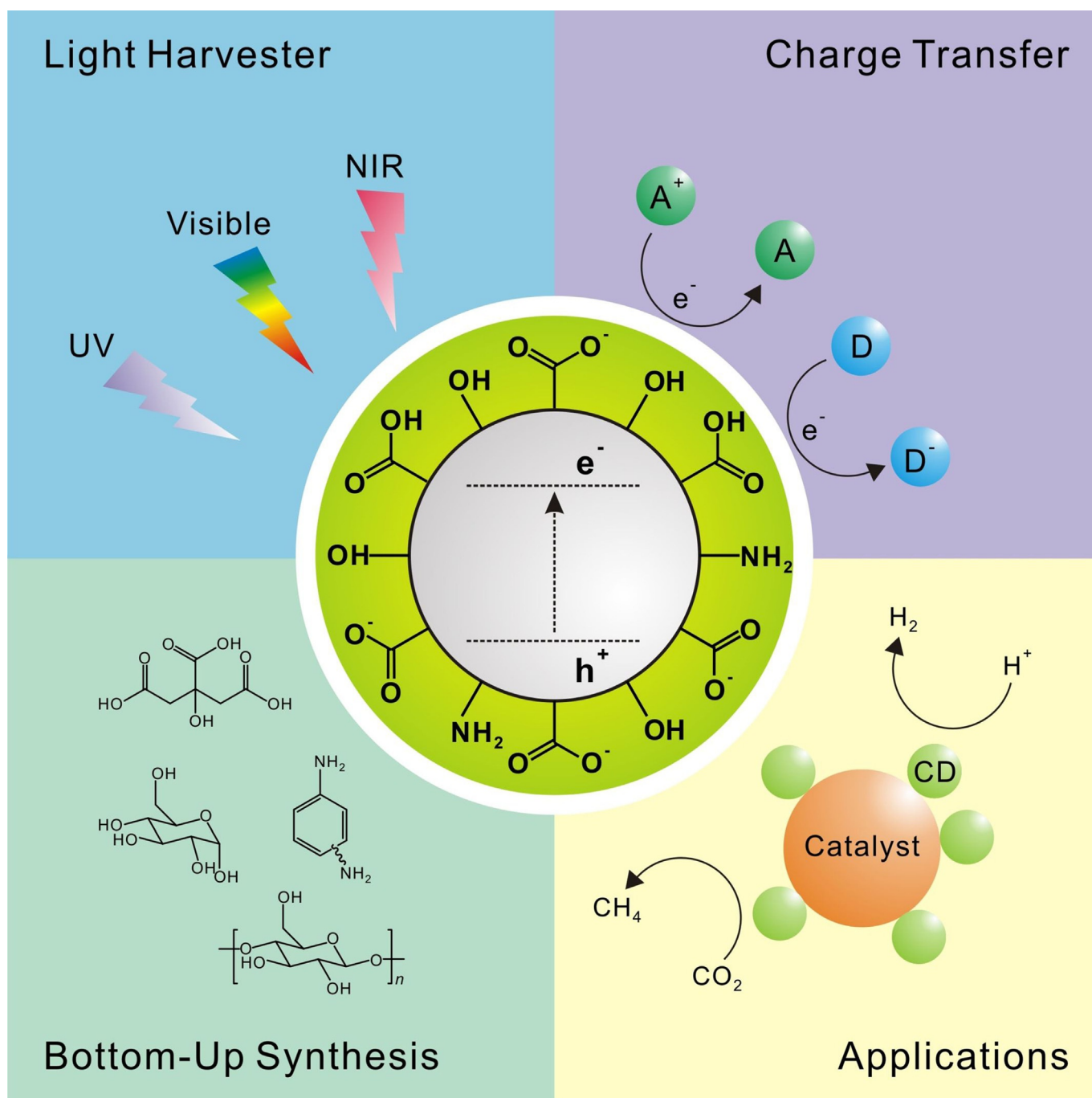


Nanostructures

Carbon Dots: Bottom-Up Syntheses, Properties, and Light-Harvesting Applications

Yuri Choi^{+, [a]} Yeongkyu Choi^{+, [a]} Oh-Hoon Kwon^{+, [a, c]} and Byeong-Su Kim^{*, [a, b]}



Abstract: The development of cost-effective and environmentally friendly photocatalysts and photosensitizers has received tremendous attention because of their potential utilization in solar-light-harvesting applications. In this respect, carbon dots (CDs) prepared by bottom-up methods have been considered to be promising light-harvesting materials. Through their preparation from various molecular precursors and synthetic methods, CDs exhibit excellent optical and charge-transfer properties. Furthermore, their photophysical

properties can be readily optimized and enhanced by means of doping, functionalization, and post-synthetic treatment. In this review, we summarize the recent progress in CDs synthesized using bottom-up approaches. These CDs exhibit strong light absorption and unique electron donor/acceptor capabilities for light-harvesting applications. We anticipate that this review will provide new insights into novel types of photosensitizers and photocatalysts for a wide range of applications.

1. Introduction

Carbon nanomaterials including graphene,^[1] carbon nanotubes,^[2] and carbon black^[3] have received widespread attention in the scientific community owing to their excellent mechanical, chemical, and physical properties for promising potential applications.^[4] Among these nanomaterials, carbon dots (CDs) are interesting because they possess many advantages such as high biocompatibility, low toxicity, good aqueous solubility, and abundant functional groups.^[5] CDs, which are typically quasi-spherical carbon nanoparticles of less than 10 nm, were initially isolated during the purification of single-walled carbon nanotubes in 2004.^[6] Since then, the development of synthetic methods for CDs has followed two synthetic routes: top-down and bottom-up approaches. Top-down methods include laser ablation, discharge, and electrochemical oxidation, which generally require expensive equipment and harsh conditions for the exfoliation or oxidation of carbon powder or graphitic rods.^[7] In contrast, CDs can be readily synthesized using facile bottom-up methods, including hydrothermal or solvothermal carbonization, acid hydrolysis, and microwave pyrolysis, starting from abundant and low-cost organic precursors.^[8]

In particular, CDs display excellent light absorption and carrier generation properties, which result in high photoluminescence (PL) as well as efficient charge transfer to/from the materials hybridized.^[9] Thus, CDs can act as photosensitizers and photocatalysts in light-harvesting applications such as solar

cells, hydrogen evolution, water splitting, and carbon dioxide conversion.^[10] In particular, hybrid composites of CDs with photocatalysts such as semiconductors or molecular catalysts have primarily been developed, and these materials demonstrate better efficiency in a variety of applications.^[11] CDs prepared by top-down methods have been reported to demonstrate excellent photophysical properties in hybrid structures.^[12] However, the mass production of CDs for commercial applications often requires mild reaction conditions. In this regard, bottom-up approaches for the preparation of CDs have been proposed to increase feasibility to achieve not only low cost, eco-friendliness, and multi-gram-scale production but also comparable properties and functionalities to those prepared by top-down approaches.^[13]

Although there are several excellent reviews concerning the synthesis and application of CDs in the field of energy conversion,^[14] recent studies on the use of CDs in light-harvesting applications are still limited. Thus, in this review, we will outline the recent progress in the preparation of CDs by using bottom-up methods for light-harvesting applications, along with a focus on the contribution of our studies. First, the choice of synthetic methods and organic molecules for the bottom-up methods is covered. Next, we present the optical properties of CDs and introduce several methods for improving these properties by means of doping and surface passivation. Finally, the role of CDs as light harvesters and electron donor/acceptors is discussed with regard to energy applications. We anticipate this review will provide not only an overview of the synthesis of CDs from organic compounds but also insight into the development of advanced types of nanomaterials for photocatalysts, photovoltaic devices, and a wide range of applications.

2. Preparation of CDs

2.1. Synthetic Methods


The synthesis of CDs can be classified into two approaches: top-down and bottom-up methods. The top-down approaches include laser ablation, discharge, and electrochemical oxidation. After the exfoliation and cutting of graphene oxide, carbon nanotubes, and activated carbon, single or a few graphitic layers of CDs are obtained.^[15] The drawback of these approaches, however, is that they require harsh reaction condi-

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tions, long processing times, and expensive materials and equipment.

In contrast, CDs can be readily synthesized through thermal carbonization such as hydrothermal and solvothermal reactions, microwave pyrolysis, and ultrasonication.^[16] Hydrothermal synthesis is one of the most facile methods for the preparation of water-soluble CDs. In this method, the precursors are carbonized in aqueous solution at high temperatures (typically, 150–200 °C) under high vapor pressures. This method has also inspired the development of solvothermal synthesis using various solvents such as ethanol and *N,N*-dimethylformamide (DMF). In parallel, microwave-assisted pyrolysis can be used to carbonize a precursor in a solution at high temperature using microwave irradiation, which can mass-produce CDs within ten minutes. Ultrasonic synthesis can also produce CDs in a short time by generating instantaneous heat, which causes carbonization. After thermal treatment, CDs comprise amorphous or partial graphitic structures depending on the synthetic methods used.

Interestingly, the properties and structures of CDs prepared using these methods are different from those obtained from top-down methods. For example, CDs prepared using bottom-up methods show high PL intensity and high production yields. Therefore, one can readily tune the properties of CDs through the careful choice of the synthetic approaches and the type of molecular precursors.

2.2. Precursors

The properties of CDs largely depend on the type of precursors as well as synthetic methods. In particular, the cost-effectiveness and the availability of organic compounds as precursors for the synthesis of CDs must be considered. In this section, we categorize the representative precursors for the synthesis of CDs into small molecules, aromatic molecules, and polymers.

2.2.1. Small Molecules

Small molecules have been traditionally used as precursors in the bottom-up synthesis of CDs because of their commercial availability and facile carbonization, along with their rich functional groups such as hydroxyl, carboxylic acids, and amine groups (Figure 1a). After carbonization, the functional groups are condensed and graphitic and/or amorphous cores are formed, while functional groups remain on the surface of the CDs.

Citric acid is one of the most representative small molecules for the synthesis of CDs that easily carbonize into CDs through microwave or hydrothermal reactions.^[17] For example, when citric acid was thermally treated during a hydrothermal reaction in the presence of NaOH, graphitic structures of CD with a quantum yield (QY) of 22% were formed.^[18] As another popular small-molecule precursor of CDs, glucose is a biomass-derived molecule that is advantageous for mass production at low cost.^[19] CD can be produced from glucose through the microwave-assisted method, and the resultant CDs have a QY of

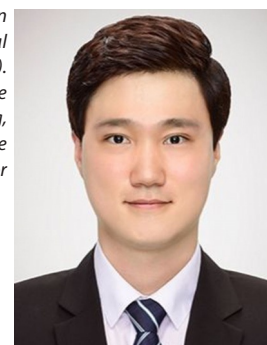
7% with oxygen functional groups on the surface that originate from glucose (Figure 1b).^[20]

In fact, the carbonization of small molecules results in low production yields and low QY, usually below 25%. Thus, there have been many attempts to improve the optical properties of CDs. For example, when CDs were thermally treated with amine molecules, the CDs usually exhibited high PL QY. Zhai

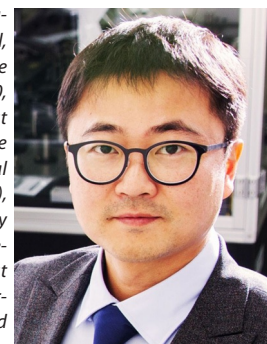
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Following postdoctoral training under the supervision of the late Dr. Ahmed H. Zewail, Nobel Laureate of Chemistry in 1999, at the California Institute of Technology until 2010, Dr. Oh-Hoon Kwon served as Senior Scientist in the same institute. In 2013, he joined the Department of Chemistry at Ulsan National Institute of Science and Technology (UNIST), Ulsan, Korea as an Assistant Professor. By combining the two parallel methods of time-resolved optical spectroscopy and ultrafast electron microscopy, one of his recent interests is the dynamic phenomena of hard and soft matter in real space and time.



Dr. Byeong-Su Kim has been an Associate Professor in the Department of Chemistry at UNIST, Korea, since 2009. His research and education programs cover a broad span of macromolecular chemistry in the study of novel polymer and hybrid nanomaterials, including the molecular design and synthesis of self-assembled polymers, layer-by-layer assembly for functional thin films, and complex macromolecular systems such as carbon nanomaterials.



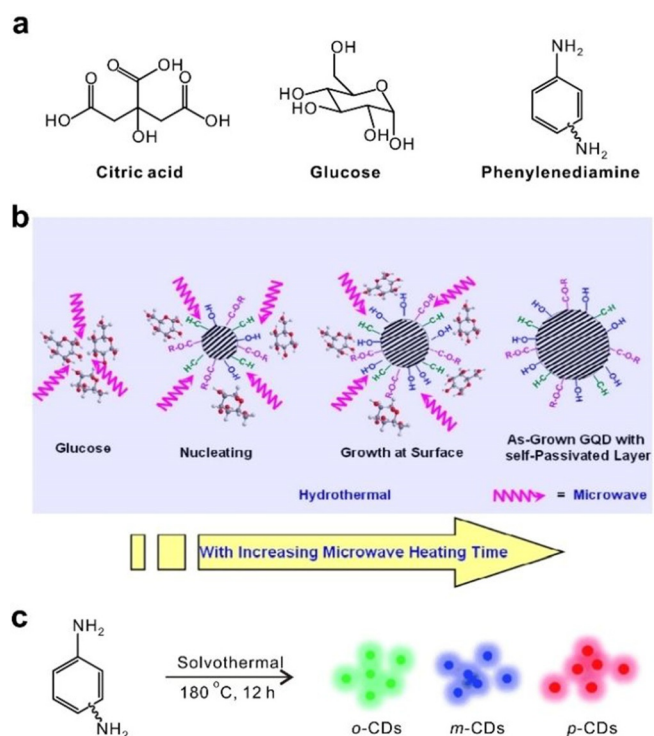


Figure 1. a) Carbon sources widely used in bottom-up synthesis (citric acid, glucose, and phenylenediamine). b) Synthetic scheme for glucose-derived CDs by microwave irradiation. Reprinted with permission from Ref. [20]. Copyright 2012 American Chemical Society. c) Preparation scheme for the green, blue, and red PL of CDs from different *ortho*-, *meta*-, and *para*-phenylenediamine isomers to yield *o*-CDs, *m*-CDs, and *p*-CDs, respectively. Reprinted with permission from Ref. [25]. Copyright 2015 John Wiley and Sons.

et al. reported CDs that were carbonized by the microwave-assisted pyrolysis of citric acid in the presence of ethylenediamine, which acted as both a doping precursor and passivating agent for improving the QY up to 40%.^[21] Urea has also been suggested as a doping source for enhancing the QY of CDs that possess a pyrrolic-N configuration that originates from amide bonds and dehydration reactions.^[22] The improvement of the PL properties by means of heteroatom doping will be discussed in more detail in the following section. Moreover, to synthesize CDs with high QY from small molecules, the hydrothermal reaction is performed at high temperature (e.g., 180 °C).^[23] As pyrolysis proceeds, carbogenic cores and molecular fluorophores are formed together.^[24] Further carbonization at high temperatures above 230 °C resulted in the formation of graphitic carbon structures at the expense of fluorophores, thus yielding relatively low QY.

2.2.2. Aromatic Molecules

In recent years, aromatic molecules have attracted a great deal of attention as alternative precursors because of the interesting multicolor PL from the resulting CDs, unlike that of conventional CDs prepared from small molecules. Phenylenediamine is the most commonly used aromatic molecule as a precursor for the preparation of CDs. As a representative example, Jiang et al. reported CDs prepared from isomers of *ortho*-,

meta-, and *para*-phenylenediamine by means of the solvothermal method in the presence of ethanol that showed full-color PL (Figure 1c).^[25] Using transmission electron microscopy, atomic force microscopy, and elemental analysis, they confirmed that the various emission wavelengths of these CDs originated from the differences in particle sizes and nitrogen (N) content. They also successfully fabricated full-color emissive poly(vinyl alcohol) (PVA) films by controlling the composition of CDs of different sizes. Furthermore, when *para*-phenylenediamine was heated with formamide and phosphorus acid, the prepared CDs produced orange and red emission, respectively, because of N-defect states.^[26] Similarly, Yuan et al. reported the synthesis of CDs that showed blue, green, and orange emission prepared using structural isomers of naphthalene as a precursor.^[27] In addition, pyrene-based CDs have also been developed that exhibited green emission under visible-light irradiation.^[28] These aromatic-molecule-based CDs are highly soluble in organic solvents, unlike other small-molecule-derived CDs. Furthermore, the purification of these CDs from unreacted molecules after carbonization can be readily carried out through column chromatography.

2.2.3. Polymers

Polymers used as precursors for CDs can be classified into biomass-based natural polymers and synthetic polymers. First, biopolymers such as chitosan and alginate are abundant in nature and environmentally friendly.^[8b] Our group has developed alginate- and chitosan-derived CDs through microwave reactions, and these showed a 10% QY.^[29] Similar to those derived from small molecules, these CDs have good emission properties with carbon cores surrounded by surface functional groups. Moreover, synthetic polymers often have advantages, such as introducing hybrid structures depending on the design of precursor polymers. Ge et al. synthesized three types of CDs that showed blue, green, and red PL color by using conjugated polymers as precursors and applied these CDs in ultra-stable full-color fluorescence patterning.^[30] Wang and co-workers developed CDs from polythiophene derivatives, which displayed red emission, wide absorption, and generation of singlet oxygen under visible-/NIR-light irradiation.^[31] These CDs were applied not only to photothermal and photodynamic therapy for cancer diagnosis and treatment but also to successful dye degradation under visible-light irradiation. Furthermore, they reported tunable multicolor CDs that could be controlled through the change in the ratio of different polythiophene derivatives.^[32]

3. Optical Properties

As demonstrated in the preceding examples, CDs consist of graphitic and amorphous carbon structures and functional groups formed by the carbonization of organic molecules. These CDs display unique optical properties, which largely depend on their structures, such as the sp^2 -carbon cores and surface states. The optical properties of CDs are generally analyzed by means of UV/Vis and PL spectroscopic measurements.

In UV/Vis spectra, CDs typically exhibit two characteristic absorption peaks at approximately 240 nm (sp^2 -carbon network) and approximately 350 nm ($n-\pi^*$ transition of surface carbonyl groups). Because of the carboxylic acid groups of CDs, a few examples show a shoulder peak at approximately 450 nm related to the lower-energy states.^[33] Recently, absorbance above 450 nm has also been reported, which results from the different surface states corresponding to a small bandgap.^[25,27] These broad spectra were affected by the efficiency of photocatalytic systems under UV and visible light.

Furthermore, upon irradiation, charge separation occurs within CDs, followed by rapid charge recombination, which leads to the characteristic PL properties. Most CDs generally emit blue PL under UV- and visible-light illumination.^[34] Some CDs also show excitation-dependent PL properties, whereas the independence of excitation wavelength has also been reported for some CDs depending on the nature of the surface states.^[17a,35]

The origins of the PL properties of CDs have been proposed to be the quantum confinement effects, surface defects, functional groups, and the degree of passivation on the surface.^[36] Although a deeper understanding is still needed, many researchers have suggested that surface defects by heteroatom doping and functional groups are closely related to the unique optical properties of CDs. Our group has studied the mechanism of PL using citric acid based CDs.^[33b] We confirmed that the graphitic structure and well-distributed surface states are responsible for the enhanced PL and excitation-independent properties through various analyses such as FTIR, X-ray photoelectron spectroscopy, time-correlated single-photon counting (TCSPC), and density functional theory calculations.

For the further use of CDs in a wide range of applications, the development of CDs with emission at longer wavelengths has been pursued in recent years. According to the types of precursors, green, yellow, and red emission of CDs have been reported. For example, Qu et al. observed orange emission with a QY of 46% from CDs derived from citric acid and urea prepared by means of solvothermal reactions in the presence of DMF.^[37] Miao et al. developed CDs of tunable emission derived from citric acid and urea by tuning the ratio of precursors and the carbonization temperature.^[38] Furthermore, Li et al. improved the QY to 53% for the red emission of CDs by using 1,3-dihydroxynaphthalene and KIO_4 in a solution of ethanol, thereby resulting in large-sized conjugated sp^2 clusters with well-distributed hydroxyl groups on the surface.^[39]

Apart from these studies, various efforts have been made to control the optical properties of CDs by means of heteroatom doping, surface passivation, separation, and solvatochromism to extend their potential applications. These investigations have successfully enhanced the PL properties as well as tuned the emission wavelength from blue to red.

3.1. Doping

Heteroatom doping is one of the most convenient and effective tailoring methods to control the intrinsic optical and electronic properties of CDs, thereby resulting in enhanced PL in-

tensity. N is a widely used element for this purpose.^[34] In general, organic molecules as carbon sources are carbonized in the presence of N- or sulfur (S)-containing molecules, which results in heteroatom-doped CDs. For example, Dan et al. developed N-doped CDs from citric acid as a carbon source and ethylenediamine and urea as sources for N.^[18] During the carbonization process, pyrrolic-N was formed from the amide bond between citric acid and the amines and was subsequently transformed into graphitic N with further hydrolysis. The QY was significantly increased from 22% for undoped CDs to 94% for the N-doped CDs. Furthermore, our group has confirmed that the additives can improve the carbonization degree during the N-doping process.^[40] The addition of HCl as additives, for example, enhanced the efficiency of hydrolysis of xylitol and ethylenediamine, thereby resulting in high PL of N-doped CDs. For S-doped CDs, Zhou and co-workers synthesized CDs using sodium citrate and sodium thiosulfate as precursors during the hydrothermal reaction, and the QY of the obtained CDs was 67%.^[41] A few papers have also discussed the doping of CDs with phosphorous and boron (B).^[42]

To enhance the PL intensity of CDs even further, the co-doping of multiple heteroatoms has been suggested; this allows the formation of well-distributed surface states as well as a reduction in non-radiative recombination, which increases the QY of the CDs. For example, our group has demonstrated the co-doping effect of B and N co-doped CDs (BN-CD) with an 80% QY in clear comparison to N-doped CDs (N-CD) with a 40% QY (Figure 2).^[33b] With thorough structural analyses, BN-CD was found to consist of graphitic N and well-distributed surface states including hydroxyl and carbonyl groups, unlike N-CD. This unique structure of BN-CD influenced the dynamics of charge recombination, thus leading to high QY in both the solution state (80%) and the solid state (67.7%). In addition, Yu and co-workers reported N and S co-doped CDs by using L-cysteine and citric acid.^[9b] The synthesized CDs showed a high QY of 73% and excitation-independent emission that arose from the enhancement of the N defect states by means of S co-doping.

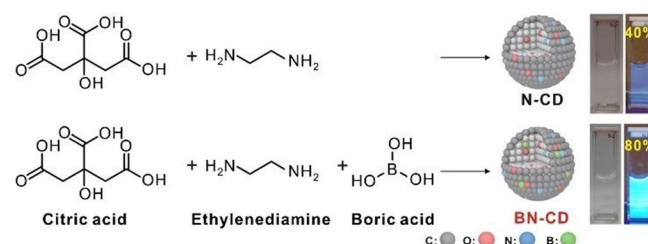


Figure 2. Synthetic scheme for the N-doped CD (N-CD) and B- and N-co-doped CDs (BN-CD). Optical images show respective CD suspensions (left) under ambient light and (right) UV illumination at 365 nm. Reprinted with permission from Ref. [33b]. Copyright 2016 American Chemical Society.

3.2. Surface Passivation

Surface passivation with other functional molecules has also been suggested as a method for tailoring the optical properties of CDs. Through functionalization using the surface func-

tional groups of the CDs and organic materials, surface-passivated CDs exhibit enhanced optical properties. For example, we improved the optical properties of α -cyclodextrin-derived CDs by passivation with poly(ethylene glycol) (PEG) (Figure 3a).^[43] After PEG passivation, the QY was enhanced from

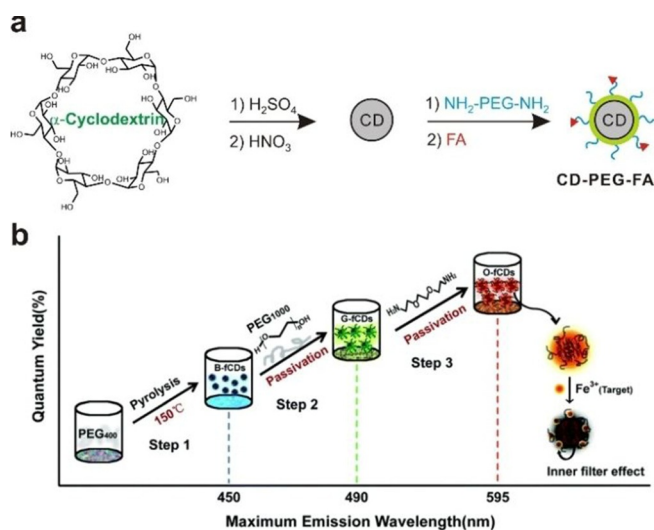


Figure 3. Schematic illustration of the preparation of CDs from a) α -cyclodextrin and passivation with poly(ethylene glycol) (PEG) for folic acid functionalization and b) PEG and additional passivation with PEG1000 and with 2,2'-(ethylenedioxy)-bis(ethylamine) for different emission colors. Reprinted with permission from Ref. [43]. Copyright 2014 John Wiley and Sons. Reprinted with permission from Ref. [44]. Copyright 2016 Royal Society of Chemistry.

2.1 to 7.8%, and excitation-independent PL behavior was observed because of the formation of uniform surface states. In addition, the optical properties were changed following the passivation. Zhang et al. reported the synthesis of the green, blue, and orange emission of CDs through the sequential passivation with PEG1000 and 2,2'-(ethylenedioxy)bis(ethylamine), which resulted from the different oxygen states and N configurations (Figure 3b).^[44] As shown in the above examples, surface passivation plays an important role in controlling the surface state of CDs without altering the core states of the CDs.

3.3. Separation

CDs prepared by means of bottom-up methods often possess heterogeneous surface states and structures, which can result in various optical properties, even within the same batch.^[35a,45] With this intrinsic limitation, a number of different separation processes have been suggested recently, including column chromatography and ultrafiltration, to obtain optically pure CDs with controlled emission (Figure 4). In a notable example, Hui et al. synthesized CDs using urea and *para*-phenylenediamine by means of a hydrothermal reaction and sorted the CDs through column chromatography.^[46] Despite the similar sizes of the separated CDs, they showed different PL characteristics, yielding blue, green, yellow, and even red because of the changes in the bandgap of the CDs according to the degree of

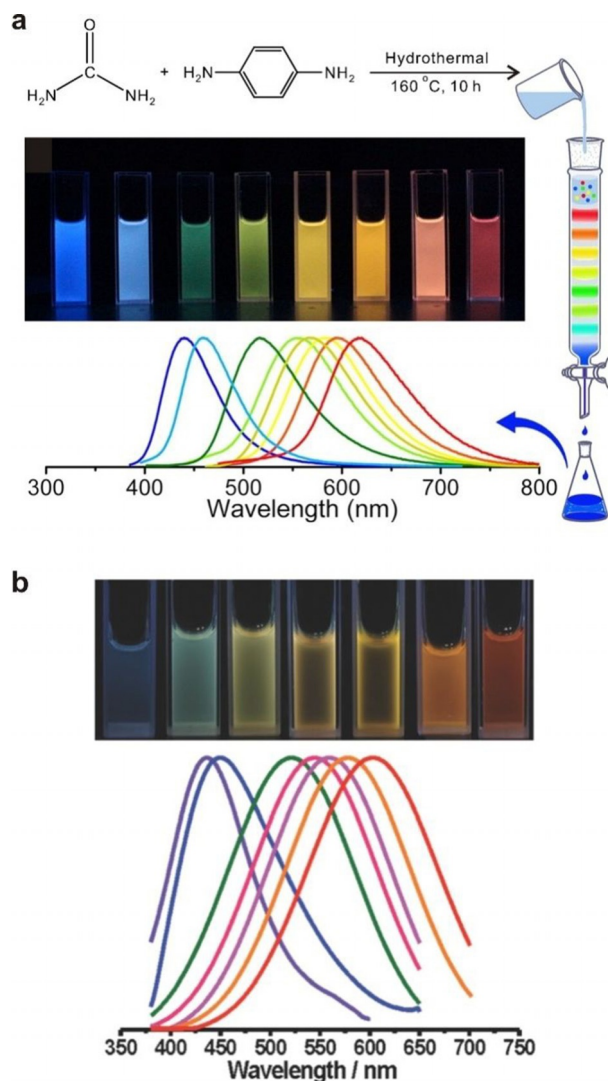


Figure 4. Separation of CDs with distinct fluorescence characteristics by means of a) gel chromatography and b) ultrafiltration. Each photograph and PL graph shows the PL of CDs under UV light and the corresponding emission light. Reprinted with permission from Ref. [46]. Copyright 2016 American Chemical Society. Reprinted with permission from Ref. [47]. Copyright 2015 John Wiley and Sons.

surface oxidation. As the degree of oxidation on the surface increased, the bandgap of the CDs became smaller, which, in turn, redshifted the PL emission. This result indicates that the control of surface states is closely associated with the optical properties of CDs. In addition, Bao et al. introduced CDs of different sizes and degrees of surface oxidation-dependent PL through effective separation by ultrafiltration.^[47] They separated CDs according to their molecular-weight equivalent to below 3, 3–10, and 10–30 kDa, which had diameters of 2.7, 3.3, and 4.1 nm, respectively. As the size of the CDs increased, the emission color redshifted from blue to orange.

3.4. Solvatochromism

Interestingly, the PL property of some CDs is highly sensitive to environmental conditions such as solvent polarity and hy-

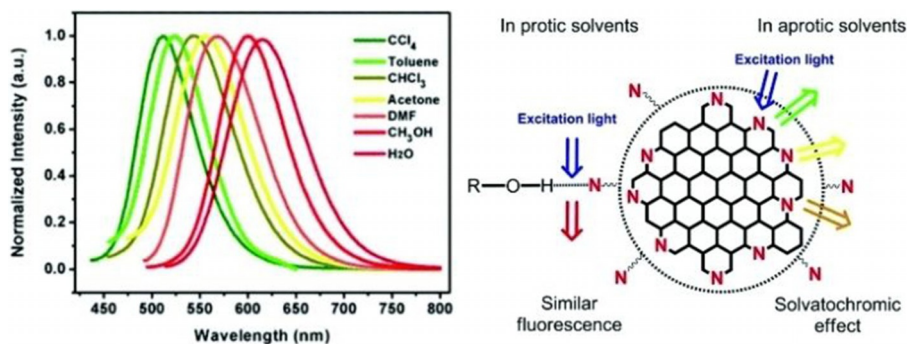


Figure 5. The PL spectra of one type of CD in seven different solvents excited at 420 nm with an illustration of the possible emission processes of the CDs in solvents of different polarity. Reprinted with permission from Ref. [49]. Copyright 2017 Royal Society of Chemistry.

drogen-bonding ability.^[48] In different solvents, not only the orientation of the solvent dipole but also the hydrogen-bonding interactions between the solute and solvent are different, thereby resulting in tunable PL, known as solvatochromism. When the CDs were dissolved in solvents of different polarity, from toluene to water, the emission was redshifted with increasing solvent polarity (Figure 5).^[49] In polar protic solvents, the hydrogen-bonding interaction between the functional groups of CD and the solvent was strong. Thus, non-radiative recombination was enhanced, producing a red emission. However, the PL intensity still remained low in highly polar solvents like water because of non-radiative recombination. For example, yellow-emissive CDs synthesized from 1,2,4-triaminobenzene showed a 32% of QY in ethanol but a 10.8% of QY in water.^[50] Therefore, the development of stable surface states for red or yellow emission of CD with high QY is still desirable in a wide range of solvents. In addition to hydrogen-bonding interactions, the aggregation of CDs in solvents of different polarity also influences the emission of CDs. Chen et al. reported that PVA-derived CDs showed polarity-induced dissolution of the aggregate, thereby resulting in yellow-green, white, and blue emission as solvent polarity increased.^[48a]

4. Light-Harvesting Applications

CDs synthesized using bottom-up methods have a high absorptivity in the UV/Vis range, which can induce charge separation and photoinduced charge-carrier transfer under irradiation. These unique properties can enhance the chemical and physical characteristics of CD-based composites. In this section, we discuss the light-harvesting and electron-donating/-accepting behavior of CDs for efficient H₂ evolution, CO₂ conversion, and solar cells.

4.1. Light Harvesters

Semiconductors, quantum dots, and organic dyes usually exhibit photocatalytic properties; however, they have several disadvantages such as a large bandgap, which limits light absorption to the UV range only.^[51] The formation of hybrid materials with CDs has therefore attracted significant attention because CDs can help to absorb a broad range of wavelength, from UV

to visible light. Recently, Geogina et al. reported light-harvesting CDs prepared from citric acid for use in a light-driven photocatalyst with enzymes such as [NiFeSe]-H₂ase and fumarate reductase for H₂ generation and alkene hydrogenation under visible-light irradiation (Figure 6a).^[52] In this study, amine-modified CDs showed enhanced efficiency compared to unmodified CDs, not only because of visible-light absorption but also because of interfacial interactions and direct electron transfer. This work demonstrated that CDs are promising photosensitizers for solar-driven photocatalysis.

Interestingly, CDs can act as a spectral converter as well as a harvester for efficient photocatalytic activity over a broad spectral range, from visible to NIR irradiation. For example, CDs syn-

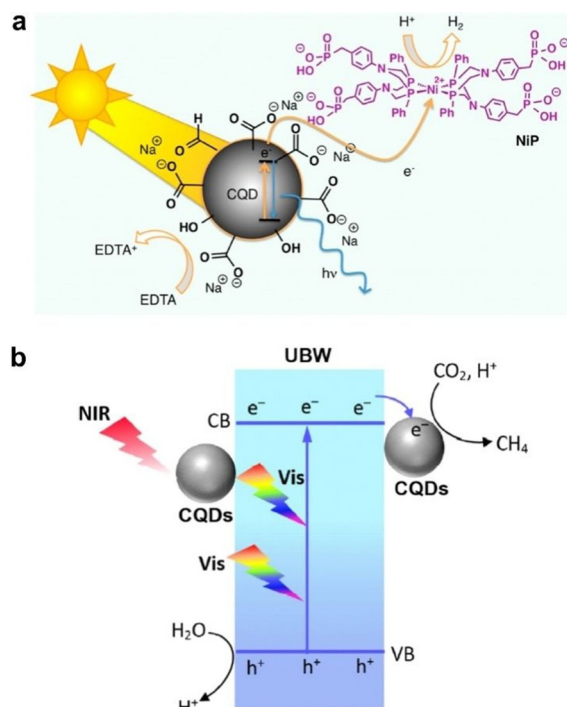


Figure 6. a) Representation of solar H₂ production using the hybrid CD-NiP system. Reprinted with permission from Ref. [52]. Copyright 2015 American Chemical Society. b) Schematic illustration of photocatalytic CO₂ reduction over CD/Bi₂WO₆ hybrid nanocomposites under visible- and NIR-light irradiation. Reprinted with permission from Ref. [53]. Copyright 2017 Springer.

thesized from citric acid/ Bi_2WO_6 nanosheets have been developed for CO_2 photoreduction under visible/NIR light (Figure 6b).^[53] This composite exhibited excellent catalytic properties under visible (> 400 nm) and even NIR (> 700 nm) light because of the enhanced light absorption with the redshifting of the band edge.

4.2. Electron Donors and Acceptors

CDs can absorb visible light and induce charge separation. Thus, the photoexcited charge carriers in CDs can transfer to organic molecules, quantum dots, and semiconductors under visible-light irradiation. This charge-transfer behavior has been confirmed by simple experiments that involved the addition of electron acceptors (i.e., 2,4-dinitrotoluene and *N,N'*-methylviologen) or electron donors (i.e., *N,N*-diethylaniline and triethanolamine) to CD solutions, which exhibited quenched emission or reduced lifetime in the PL spectra or TCSPC measurements, respectively (Figure 7).^[54]

On the basis of their unique photoinduced charge-carrier transfer properties, CDs play an important role in affording active photocatalytic nanomaterials in combination with other semiconducting materials or organic dyes.^[54a] Haitao et al. reported CDs prepared from glucose decorated on Cu_2O composites for CO_2 conversion to methanol under visible-light irradiation. The as-prepared CDs showed excellent charge separation and electron transfer to the $\text{Cu}_2\text{O}/\text{CD}$ photocatalyst, thus leading to enhanced stability and CO_2 conversion yield ($55.7 \mu\text{mol g}^{-1} \text{h}^{-1}$).

Taking advantage of this interesting property, metal nanoparticles can also be synthesized by using CDs as a reducing agent under irradiation with light and without the use of an additional reductant.^[55] Because the metal ions act as electron scavengers, the photoexcited electrons are transferred to the metal ions, thus producing metal nanoparticles under irradiation with light.^[55,56] For example, our group has developed different morphologies of heterodimeric Ag/CD nanomaterials formed under UV irradiation (Figure 8a,b).^[29] The polysaccharide-based CDs were synthesized with the addition of an additive, HCl, through microwave-assisted pyrolysis. Under UV-light irradiation, the free electrons from the photoexcited CDs reduce the Ag^+ ions on the surface, and the interfacial junction allows more electrons to pass through to the conductive Ag nucleation sites and to recruit more Ag^+ ions, eventually leading to heterodimeric Ag/CD nanoparticles (NPs). Furthermore, the interface between the Ag and CD nanoparticles can be precisely controlled by the amount of additive and the type of CD precursors.

These metal/CD composites have been used as light-harvesting materials with the surface plasmon resonance effect, which enhances the power conversion efficiency of photovoltaic devices. In another example, our group synthesized Ag nanoparticles hybridized with PEG-passivated CDs (Ag/CD-PEG) prepared from α -cyclodextrin through photochemical reduction under UV irradiation (Figure 8c).^[56] In this composite, CD-PEG served as a reducing agent, supporting materials, and an assistant for efficient electron transfer. The Ag/CD-PEG was incorporated within the active layer, which helped to enhance the current efficiency of 27.16 cd A^{-1} and a luminous efficiency of

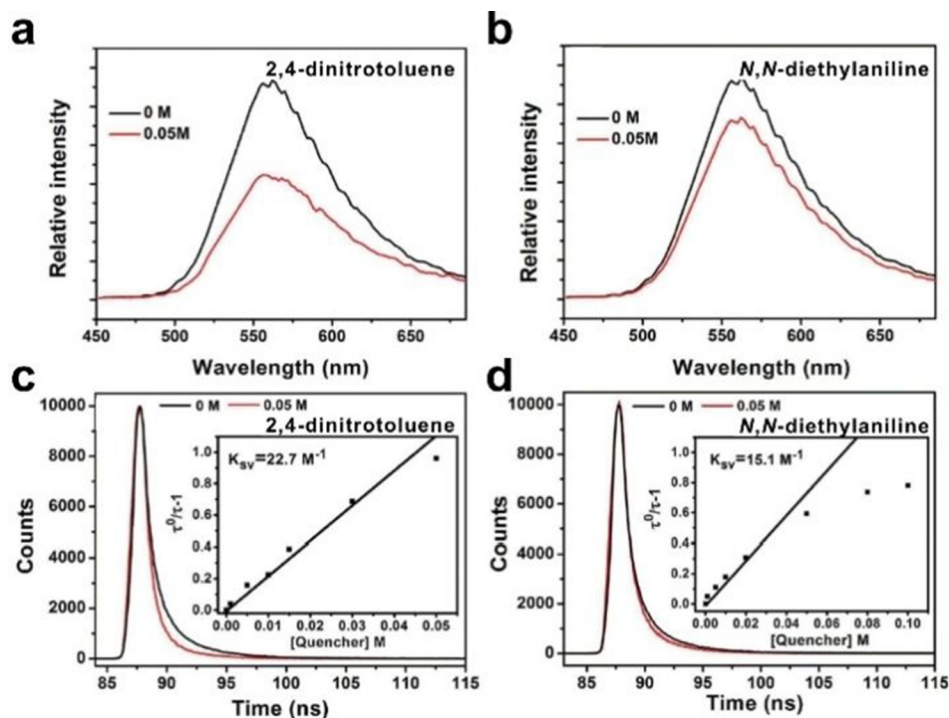


Figure 7. a, b) PL spectra (450 nm excitation) of CDs in toluene in the absence and presence of the quenchers (2,4-dinitrotoluene and *N,N*-diethyl aniline, both 0.05 m). c, d) Photoinduced electron-transfer properties of CDs: PL decays (450 nm excitation, monitored at 560 nm using a narrow bandpass filter) of the CDs with c) 2,4-dinitrotoluene and d) *N,N*-diethylaniline. Inset: Stern–Volmer plots for the quenching of the luminescence quantum yields (450 nm excitation) of the CDs by c) 2,4-dinitrotoluene and d) *N,N*-diethylaniline. Reprinted with permission from Ref. [54a]. Copyright 2015 John Wiley and Sons.

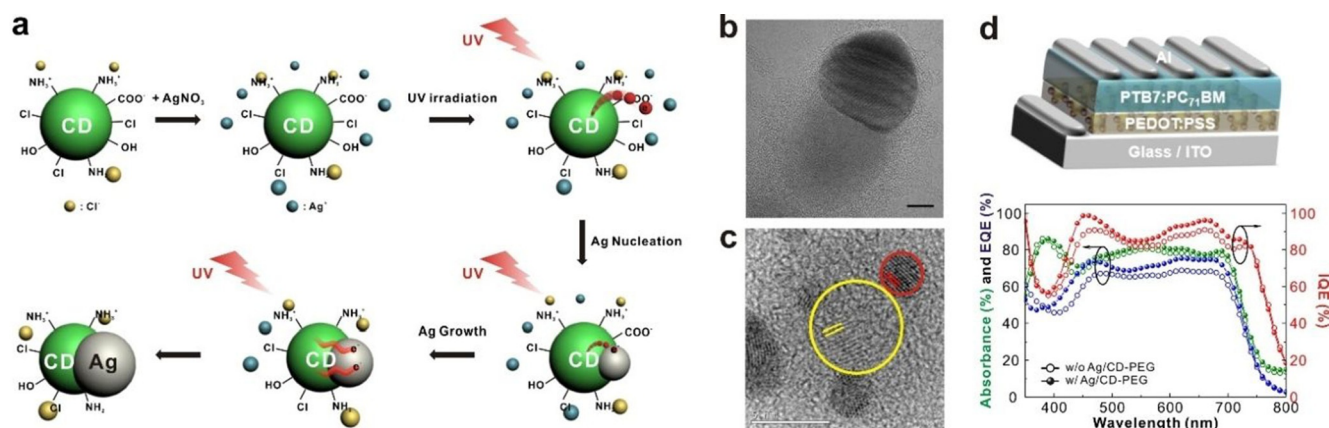


Figure 8. a) Proposed formation mechanism of heterodimeric Ag/CD nanoparticles. b) High-resolution TEM image of heterodimeric Ag/CD nanoparticles. Reprinted with permission from Ref. [29]. Copyright 2014 American Chemical Society. c) High-resolution TEM image of Ag/CD-PEG nanoparticles. d) The device structure of polymer solar cell. e) The internal quantum efficiency of polymer solar cells with Ag/CD-PEG nanoparticles. Reprinted with permission from Ref. [56]. Copyright 2013 Nature Publishing Group.

18.54 lmW⁻¹ in polymer-based light-emitting diodes. Surprisingly, a high power conversion efficiency of 8.31% and an internal quantum efficiency of 99% were exhibited in the polymer solar cells (Figure 8d,e). Thus, when these CDs were modified with metal nanoparticles, the composites could demonstrate synergetic effects, such as light-harvesting and charge-transfer enhancement, thereby increasing the overall efficiency of the photoelectronic devices.

5. Applications

With their interesting photophysical properties, as described above, CDs are promising electron acceptor/donors and photosensitizers in applications such as H₂ evolution, CO₂ reduction, and solar cells. Although the use of CDs as the sole photocatalyst has rarely been reported to date, CD-based composites with semiconductors and organic molecules have been developed to enhance the catalytic efficiency because of the increased charge transfer and light absorption assisted by CDs. In this section, we introduce examples of the excellent efficien-

cy of CD hybrids in photovoltaic devices and water splitting, as summarized in Table 1.

5.1. H₂ Evolution

H₂ evolution is considered an attractive goal in the field of solar energy conversion and would alleviate fossil fuel shortages and solve environmental issues.^[57] The basic principle of H₂ evolution is that the photoexcited electron reduce H⁺ ions to H₂ gas in water upon irradiation with solar light.^[58]

To enhance the catalytic efficiency of H₂ evolution, CDs play a critical role as electron acceptor/donors and photosensitizers.^[59] For example, Bhattacharyya et al. developed N-doped CDs to confirm the N effect in photocatalytic efficiency. They prepared the different N contents and configuration of CDs (from citric acid) by controlling the amounts of polyethyleneimine (PEI).^[60] At a high PEI content, N atoms were distributed at the edge sites of the aromatic domains, thus enabling efficient charge separation and production of H₂ at a rate of 18.7 μmol g⁻¹ h⁻¹. Xu et al. synthesized a Pt/CD (from citric

Table 1. Summary of applications with CD-based hybrid materials for various applications.

| Precursor | Component | Applications | Efficiency | Reference |
|-----------------------------|-------------------------------------|----------------------------|---|-----------|
| glucose | Ag, g-C ₃ N ₄ | H ₂ evolution | 626.93 μmol h ⁻¹ g ⁻¹ | [63] |
| | g-C ₃ N ₄ | CO ₂ reduction | CH ₄ (37.06 μmol g ⁻¹) CO (68.80 μmol g ⁻¹) | [70] |
| citric acid | Cu ₂ O | CO ₂ conversion | CH ₃ OH (55.7 μmol g ⁻¹) | [54a] |
| | g-C ₃ N ₄ | H ₂ evolution | 2.18 mmol h ⁻¹ g ⁻¹ | [59a] |
| | TiO ₂ , Pt | H ₂ evolution | 4.3 mol h ⁻¹ (50 mg) | [59b] |
| | - | H ₂ evolution | 18.7 μmol h ⁻¹ g ⁻¹ | [60] |
| | Pt | H ₂ evolution | 681 μmol h ⁻¹ g ⁻¹ | [61] |
| | Cu nanoparticles | H ₂ evolution | 64 mmol h ⁻¹ g ⁻¹ | [59] |
| 1,3,6-trinitropyrene | redox enzyme | H ₂ evolution | 298 μmol h ⁻¹ g ⁻¹ | [65] |
| | Bi ₂ WO ₆ | CO ₂ reduction | CH ₄ (7.19 μmol g _{cat} ⁻¹) | [53] |
| | TiO ₂ | H ₂ evolution | 2.2 μmol h ⁻¹ (20 mg) | [59c] |
| | CdS | H ₂ evolution | 95.4 μmol h ⁻¹ | [59d] |
| EDTA-2 Na·2H ₂ O | g-C ₃ N ₄ | H ₂ evolution | 50.5 μmol h ⁻¹ g ⁻¹ | [59e] |
| L-ascorbic acid | Pt, g-C ₃ N ₄ | H ₂ evolution | 183.0 μmol h ⁻¹ | [62] |
| aspartic acid | NiP | H ₂ evolution | 7950 μmol h ⁻¹ g ⁻¹ | [66] |

acid) composite with excellent activity in H₂ evolution.^[61] The functional groups of CDs were reduced from the carboxylic and carbonyl groups to hydroxyl groups to enhance the electron transfer and electrostatic adsorption of Pt anionic species. The surface-reduced CDs absorbed solar light and generated electrons, which transferred to Pt clusters, thus yielding 681 μmol g⁻¹ h⁻¹ of H₂ evolution. Ong et al. prepared a g-C₃N₄/CD (from L-ascorbic acid) composite by means of in situ carbonization on the surface of g-C₃N₄, as shown in Figure 9a.^[62]

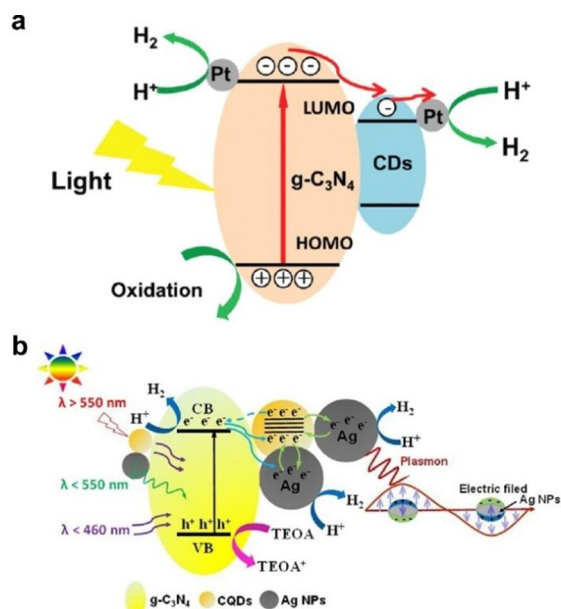


Figure 9. a) Schematic of the photocatalytic H₂-evolution mechanisms for Pt-CD/g-C₃N₄. Reprinted with permission from Ref. [62]. Copyright 2017 Royal Society of Chemistry. b) Schematic presentation illustrating the charge generation and transfer procedure over the Ag/CD/g-C₃N₄ composite combined with a proposed photocatalytic H₂-evolution mechanism. Reprinted with permission from Ref. [63]. Copyright 2017 Elsevier.

After the successful modification of g-C₃N₄ with CDs, the absorption edge was redshifted and an additional shoulder peak above 450 nm was observed, thus leading to the efficient absorption of visible light. This composite demonstrated H₂ evolution because of the rapid photoexcited electron transfer from g-C₃N₄ to the CDs and the increased number of active sites offered by the CDs. Furthermore, Pt nanoparticles were integrated into the composite to enhance the catalytic efficiency even further, thereby resulting in 183.0 μmol h⁻¹ of H₂ production under visible-light irradiation.

When the surface plasmon resonance effect was adjusted in the CD-based composite, the efficiency was enhanced because of the prevention of recombination of photogenerated carriers and the enhancement of visible-light absorption. Qin et al. reported a Ag/CD (from glucose)/g-C₃N₄ composite (Figure 9b).^[63] In this composite, the Ag nanoparticles acted as the light harvester above 500 nm, whereas the CDs worked as the electron donor/acceptors to g-C₃N₄ and Ag nanoparticles. In addition, the Ag nanoparticles and CDs served as electron scavengers, which prevented the recombination of photoexcited electrons

in g-C₃N₄, thereby resulting in the generation of 626.93 μmol g⁻¹ h⁻¹ of H₂ in the presence of triethanolamine, a hole sacrificial agent. Zang et al. developed a Cu/CD (from citric acid) composite by means of photoreduction.^[64] In this system, Cu nanoparticles absorbed light and the CDs acted as an electron reservoir to trap electron and prevent charge recombination, which resulted in efficient charge separation for H₂ evolution.

Recently, CDs have been used as photosensitizers to increase the efficiency of enzymes and a water-soluble molecular Ni(bis(diphosphine) (NiP)-based catalyst. Reisner's group used CDs as a visible-light photosensitizer for active redox enzymes.^[65] In addition, to increase the catalytic efficiency, they developed graphitic-N-doped CDs prepared from aspartic acid to improve the light absorption because of the increased number of delocalized optical transitions from the sp² graphitic core structure.^[66] Interestingly, this study demonstrated the mechanism of charge transfer from CDs to NiP using transient absorption spectroscopy. When a hole scavenger, ethylenediaminetetraacetic acid (EDTA), was added to the CDs, the lifetime at 500 nm was increased, which was associated with the extraction of holes and the inhibition of charge recombination, thereby resulting in the production of 7950 μmol⁻¹ h⁻¹ of H₂ under visible-light irradiation.

5.2. CO₂ Reduction

The rapidly increasing concentration of CO₂, a greenhouse gas, in the atmosphere has a profound impact on global climate change.^[67] The photocatalytic conversion of CO₂ to hydrocarbon fuels has progressed significantly over the last few decades, driven by environmental and economic issues.^[68] Because of the UV absorption, low stability, and low conversion rates of the photocatalysts developed thus far, it is still highly desirable to develop efficient catalysts and photosensitizers for CO₂ reduction.^[69]

In this regard, CDs can be used as electron donor/acceptors and photosensitizers to increase the CO₂ reduction yield. For example, a g-C₃N₄/CD composite was prepared from glucose and formed through electrostatic attractions (Figure 10a).^[70] This composite contained 4 nm of CD in the g-C₃N₄ sheets. Because of high electron scavenger ability of CDs, the photogenerated electron from g-C₃N₄ can be rapidly transferred to the CDs, thereby resulting in the efficient conversion of CO₂ to CH₄ (29.23 μmol g_{catalyst}⁻¹) and CO (58.82 μmol g_{catalyst}⁻¹) under visible-light irradiation. In another example, MacFarlane's group has developed a Cu₂O/CD for CO₂ conversion to methanol (Figure 10b).^[54a] In this composite, CDs acted as the photogenerated electron donors and hole acceptors, thereby inhibiting the recombination of charge carriers; thus, the photoexcited electron was consumed on the surface of Cu₂O, reducing CO₂ to methanol.

5.3. Solar Cells

CDs are used as sensitizers in optoelectronic devices because of their excellent light absorption ability and their eco-friendly

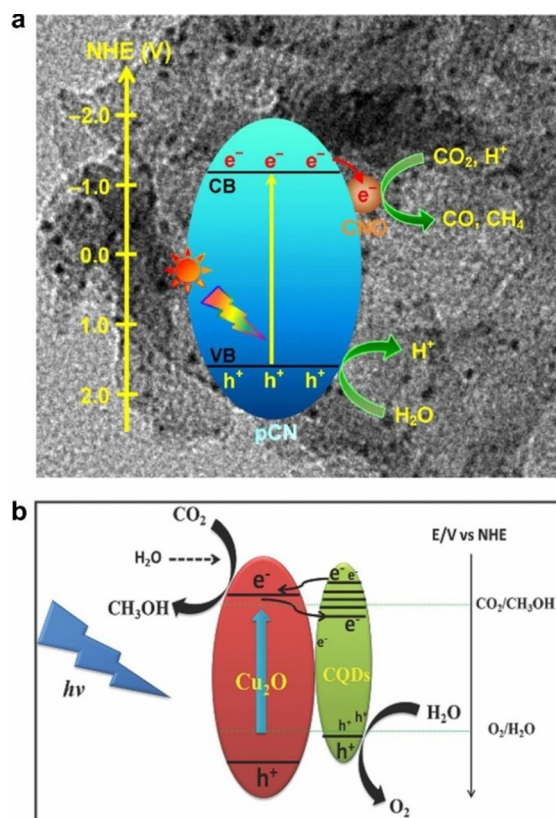


Figure 10. a) Charge transfer and separation in the enhanced photoreduction of CO_2 to CO and CH_4 using CD/ $\text{g-C}_3\text{N}_4$ samples under visible-light or simulated solar irradiation. Reprinted with permission from Ref. [70]. Copyright 2017 Springer. b) A schematic of the proposed photocatalytic mechanism of CO_2 reduction catalyzed by CD/ Cu_2O . Reprinted with permission from Ref. [54a]. Copyright 2015 John Wiley and Sons.

nature. Biomass-derived CDs, such as those derived from glucose, chitin, and chitosan, have been prepared by means of hydrothermal reactions, and these CDs have been used as sensitizers in ZnO-nanorod-based solid-state nanostructured solar cells (Figure 11a).^[71] With varying types of biomass, the functional groups and N doping can be controlled, which has been found to be associated with the efficiency of the solar cell (Figure 11b,c). The chitin- and chitosan-based CDs doped with N displayed a high efficiency of 0.077%. Guo et al. developed CDs from bee pollen, citric acid, and glucose through hydrothermal reactions.^[72] Because of hole transfer and the small size of the pollen-based CDs, the efficiency of the sensitized solar cell reached 0.11%. In addition, Mirtchev et al. reported the charge transport and injection properties of CDs (from γ -butyrolactone) in TiO_2 solar cells, which showed 0.13% power conversion efficiency.^[5a] In solar cell systems, CDs limit charge recombination and enhance charge transport, thereby enhancing these properties, especially after heteroatom doping.

6. Conclusion and Outlook

In this paper, we have reviewed the recent progress in bottom-up-synthesized CDs. This review has focused on synthetic strategies and common precursors for the bottom-up synthesis along with their intrinsic optical and photochemical properties with a view toward the light-harvesting applications of CDs. Many groups have investigated the control over the types of precursors and synthetic methods, separation, heteroatom doping, and surface passivation to tune the photophysical properties of CDs. Furthermore, the activity of the synthesized CDs as light harvesters and electron donor/acceptors in photocatalysts, photosensitizers, and photovoltaic devices has been investigated intensively.

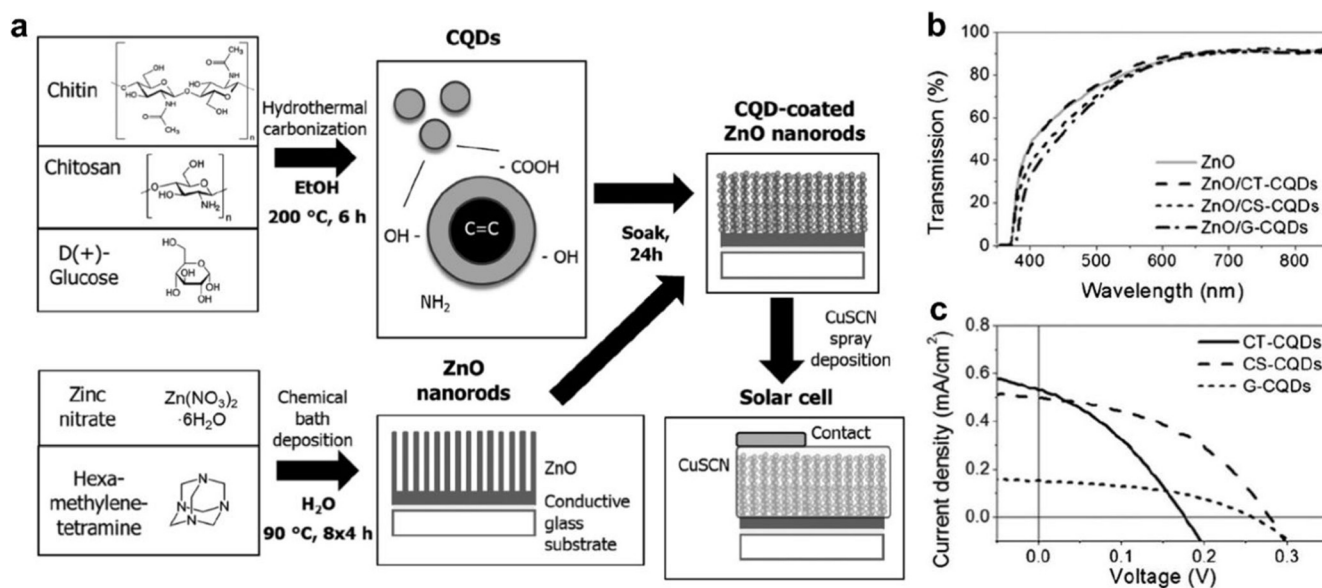


Figure 11. a) Preparation of a CD-sensitized solar cell by means of the hydrothermal carbonization of biomass precursors and their combination with chemically grown ZnO nanorods. b) UV/Vis transmission for ZnO nanorods coated with CD and c) illuminated current–voltage plot of ZnO/CD/CuSCN solar cells. Reprinted with permission from Ref. [71]. Copyright 2015 John Wiley and Sons.

Despite the significant progress in the field of CDs to date, there are still challenges to address. First, the surface state of the CDs is reported to influence the optical properties of CDs significantly. However, the available evidence is still insufficient to correlate the synthetic protocol and type of precursor with the targeted surface state with the desired optical properties.

In addition, the mechanism of charge transfer of CDs, regardless of its origin, should be further established for the desired energy application to bridge the gap between the excellent optical properties of CDs and their integration in real high-efficiency devices. Next, the matter of stability, which is related to the photo-oxidation of CDs and arises from the imbalance in emitted and incoming electrons, should be further improved.

Finally, given their facile synthetic nature combined with their unique chemical and optical properties, CDs have great potential as a viable candidate to replace expensive metal-based nanomaterials in photosystems. We anticipate that this review will aid researchers in the construction of effective photocatalytic and photovoltaic systems based on CDs.

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Keywords: carbon • charge transfer • nanotechnology • photochemistry • synthetic methods

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