Chem Soc Rev

TUTORIAL REVIEW

Carbon dots as photosensitisers for solar-driven catalysis

Georgina A. M. Hutton,† Benjamin C. M. Martindale† and Erwin Reisner*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Artificial photosynthesis is the mimicry of the natural process of solar energy conversion into chemical energy carriers. Photocatalytic systems that combine light-harvesting materials and catalysts in solution or suspension provide a promising route towards this goal. A key requirement for a sustainable photocatalytic fuel production system is a low-cost, stable and non-toxic light harvester. Photoluminescent carbon nanoparticles, carbon dots (CDs), are promising emerging light-harvesters for photocatalytic fuel production systems. CDs possess many desirable properties for this purpose, such as low-cost, scalable synthetic routes, low-toxicity and tuneable surface chemistry. In this tutorial review, the integration of CDs in photocatalytic fuel generation systems with metallic, molecular and enzymatic catalysts is discussed. An overview of CD types, synthesis and properties is given along with a discussion of tuneable CD properties that can be optimised for photocatalysis applications. Current understanding of the photophysical electron transfer processes present in CD photocatalytic systems is outlined and various avenues for the further development of improved CD photocatalytic systems are highlighted.

Key Learning Points

1) Understanding CD synthesis, characterisation, structure and properties;
2) Application of CDs in photocatalytic solar fuel and chemical synthesis;
3) Performance limitations of CDs in photocatalysis;
4) Mechanism and kinetics of electron transfer in CD photocatalytic systems;
5) Future avenues for development of CD materials for photocatalysis applications.

Introduction

Sunlight holds great promise as a renewable, sustainable and globally available energy supply. One approach to capture and store solar energy is to harvest that energy to drive the synthesis of fuels (“solar fuels”) and chemicals (“solar chemicals”), *via* artificial photosynthesis. This approach derives inspiration from natural photosynthesis by which plants convert sunlight, CO_2 and water into carbohydrates. Key goals of solar fuel synthesis *via* artificial photosynthesis are the photocatalytic reduction of aqueous protons to produce H_2 and the photocatalytic reduction of CO_2 to form CO, and hydrocarbons and alcohols such as HCO_2H and CH_3OH.

Artificial photosynthesis can be achieved by combining the essential components of natural photosynthesis, a light harvester and catalyst(s), in solution or suspension with electron donor and acceptor substrates (Figure 1).[1,2] The photosensitiser absorbs light creating a photoexcited electron-hole pair. Electron transfer to a reduction catalyst drives the reduction of substrates such as protons or CO_2. Photoexcited holes are used to carry out an oxidation reaction, such as water oxidation, or a useful chemical substrate oxidation to form a value-added product. Photocatalytic systems with sustainable oxidation processes are still an emerging technology. As such, a sacrifical electron donor (ED) is often employed to study fuel-making reductive half reactions, a first step towards the goal of developing closed-redox cycle photocatalytic systems.

A key requirement for achieving a sustainable photocatalytic system for artificial photosynthesis is the development of efficient, low-cost light harvesters. Commonly used photosensitisers include organic and inorganic synthetic dyes,[1,2] and semiconductor nanoparticles.[3] Synthetic dyes have high visible light absorption coefficients, but they often suffer

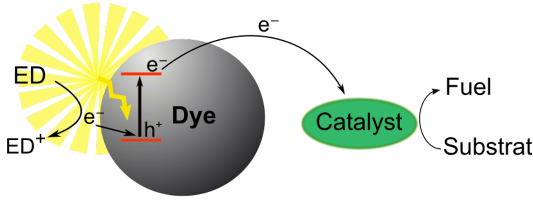


Figure 1. Schematic representation of a photocatalytic system for solar fuel synthesis. The dye absorbs light creating a photoexcited electron-hole pair. The hole is quenched by oxidation of an electron donor (ED) and the photoexcited electron is transferred to a reduction catalyst for the conversion of a substrate into a fuel or value-added chemical.

Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK
Email: reisner@ch.cam.ac.uk. Web: http://www-reisner.ch.cam.ac.uk/

† These authors contributed equally.

from limited photostability in water, can be synthetically demanding to prepare and modify, and often contain precious metals (*e.g.* Ru(2-2'-bipyridine)$_3^{2+}$ derivatives).

Semiconductor materials utilised as photosensitisers in photocatalytic systems include TiO_2 nanoparticles,[2] chalcogenide quantum dots[4] and graphitic carbon nitrides (ideal structure C_3N_4).[5,6] These semiconductor materials are often more photostable than molecular dyes[3] and are capable of accumulating long-lived, multiple excited state charges.[7] However, common disadvantages include poor visible light absorption (TiO_2, g-C_3N_4), poor interfacial interaction between the light harvester and catalyst (g-C_3N_4),[5] limited aqueous dispersibility (TiO_2, g-C_3N_4) and low elemental abundance (Cd, Te, and In) or toxicity (CdS, CdSe). Non-toxicity and aqueous solubility are desirable characteristics for biological applications, for example *in vivo* photocatalysis with enzymes.

In this tutorial review, carbon dots (CDs), an emerging light-absorbing nanomaterial, are discussed for applications in photocatalytic fuel production. First, an overview of CD classes, synthesis, characterisation and properties are presented. The application of CDs in photocatalytic schemes for solar fuel production with heterogeneous, molecular and enzymatic catalysts is then discussed including a discussion of the kinetics of CD charge transfer reactions. Finally, CDs are compared to established state-of-the-art photosensitisers for solar H_2 production.

Classification of Carbon Dots

Photoluminescent carbon nanoparticles are a relatively new class of low-cost carbon nanomaterial, which has drawn increasing attention over the last decade with a rapidly growing number of publications appearing each year.[8] Carbon nanoparticles (ranging from 1–10 nm diameter) consist of a nanoscale carbon core stabilised by oxidised surface groups such as carboxylic acids and alcohols. A long list of desirable general properties have ensured a burgeoning interest in this new form of carbon as a rival to conventional semiconductor nanoparticles.[9]

Carbon nanoparticles consist entirely of abundant and significantly, readily accessible elements. As a result of their surface chemistry, which is typically rich in carboxylic acid and amine functionalities, carbon nanoparticles are hydrophilic, making them highly compatible with aqueous chemistry. They are generally considered to be environmentally benign and exhibit low toxicity and hence are widely investigated for *in vivo* applications.[9,10] The common feature among all types of carbon nanoparticles, which led to their initial identification and subsequent interest is that, unlike the majority of black carbon varieties, they are fluorescent and have a strong UV-visible absorption band. However, the structure and composition of the carbon nanoparticle can vary enormously based on the preparation procedure and this has a large impact on their photophysical properties. It is therefore necessary to categorise the different types of carbon nanoparticle based on key structural and physical characteristics and importantly, to be clear on the topic of nomenclature.

Types and nomenclature

In the early stages of photoluminescent carbon nanoparticle development, the term carbon quantum dot (CQD) was widely used to describe all fluorescent carbon nanoparticles, creating a historical precedent. This represented a departure in some cases from the traditional term *quantum dot* (QD), which referred specifically to semiconductor nanoparticles with dimensions sufficiently small to cause quantum confinement effects. Over the past decade a variety of additional terms have emerged in the literature describing different categories of carbon nanoparticle, such as graphene quantum dot (GQD), carbon nanodot (CND), carbon nanocluster, C-dot and carbon dot (CD). These names, however, have regularly been used loosely and interchangeably without consideration for the structure of the particle in question and without resolving the controversy over the use of the 'quantum' moniker.

This issue and 'the need for consistency' has recently been addressed by defining three distinct categories of carbon nanoparticle: CND, CQD and GQD.[8] GQDs, produced by exfoliation of graphitic structures, consist of small fragments of single or few-layer graphene sheets and hence are two-dimensional disc-shaped nanoparticles. CQDs, on the other hand, are quasi-spherical nanoparticles with a multi-layered crystalline graphitic core structure.[11] Under this framework, the use of the word *quantum* is strictly limited to particles that have predominantly delocalised band structure, akin to conventional semiconductor QDs though perhaps with a contribution from molecular-like surface states. CNDs are defined as amorphous, quasi-spherical nanoparticles that have exclusively molecular-like excited states and therefore do not display any quantum confinement effects.

Nevertheless, it remains challenging to classify the various carbon nanoparticles which may fall somewhere between these limiting cases. Quasi-spherical nanoparticles with partial or highly graphitic structure may exhibit neither fully delocalised nor fully molecular electronic structure, and it is difficult to conclusively determine the presence or absence of quantum confinement effects since precise synthetic size control or separation is challenging to achieve. Hence, to date, a "true CQD" has not been unequivocally demonstrated and we refrain from using this nomenclature.

In this review, the term carbon dot (CD) is used to describe all quasi-spherical carbon nanoparticles, including those with significant delocalisation, those with predominantly localised chromophores and the scope of structures in between, as previously suggested.[12] Each CD is then classified according to the structural elements, which can be spectroscopically characterised, *e.g.* amorphous (*a*-CD) or graphitic (*g*-CD).

Synthesis

Unlike many other carbon nanomaterials, CDs can be easily and inexpensively synthesised on a multi-gram scale by a number of simple methods. Two distinct approaches can be employed for this purpose: top-down and bottom-up synthesis (Figure 2).

Top-down synthesis

Top-down methods involve the breakdown of carbon structures, such as by partial oxidation of candle or natural gas soot[13] and electrochemical oxidation of graphite rods.[10,14]

Exfoliation and oxidation of existing ordered carbon structures including graphene (oxide) and graphite (oxide)[15] produces nanoparticles with significant graphitic structure retained from the precursor material.[15] These particles often fall into the category of GQDs, which as described above, consist of small fragments of single or few-layer graphene sheets and hence have lateral dimensions that are substantially larger than their height.[11] In contrast, CDs are quasi-spherical nanoparticles, which may consist of graphitic carbon and/or amorphous carbon. CDs synthesised by top-down procedures usually contain high degrees of graphitisation and often require surface functionalisation, such as with polyethylene glycol diamine species, to impart photoluminescence (see below, *surface functionalisation*).[16]

Top-down synthetic procedures for synthesising CDs and GQDs have been comprehensively addressed in recent reviews (for further details see references 9 and 10 and citations therein). Top down procedures are comparatively more expensive and less scalable than bottom-up procedures for CD synthesis.

Bottom-up synthesis

Bottom-up methods predominantly involve the thermal decomposition of cheap organic molecular precursors or polymers. Carboxylic acid and hydroxyl containing molecules, such as citric acid[17] or glucose[18] can be pyrolysed or hydrothermally treated resulting in the loss of small molecules (CO_2, H_2O) and the build-up of a carbon core. A variety of exotic precursors and waste products from organic landfill to watermelon peel have been used in bottom-up CD synthesis.[9] CDs produced by bottom-up syntheses typically have diameters between 2–10 nm with different compositions of their carbon core, ranging from amorphous (*a*-CD) to graphitic (*g*-CD) depending on the temperature of decomposition employed.[8,19] Generally temperatures above 300 °C lead to significant graphitisation whilst those below 300 °C result in amorphous particles.[8,19] CDs can also be built-up electrochemically by passing a large voltage through alcohols.[20]

Bottom-up CD syntheses from molecular precursor compounds can be further divided into two categories: those utilising a single molecular precursor, “single source precursor” (SSP) approach, and those involving multiple precursor compounds, “multi-component” (MC) approach (Figure 2). The synthetic procedure employed results in CDs with different structure and properties, which will be detailed in the following sections.

Single source precursor (SSP). For CDs synthesised via the SSP approach, a suitable molecular precursor compound susceptible to pyrolytic decomposition should be chosen, typically a compound containing a carbon backbone with alcohol or carboxylic acid functionalities.[18,21] Citric acid is a common CD precursor compound used in both SSP and MC syntheses, since it is readily susceptible to CD formation through dehydration, decarboxylation and condensation reactions.[18,19,22]

The CD synthesis temperature should be chosen above the decomposition temperature for the precursor. Higher temperature will result in faster decomposition, but care must be taken not to exceed the boiling/sublimation temperature of the precursor.

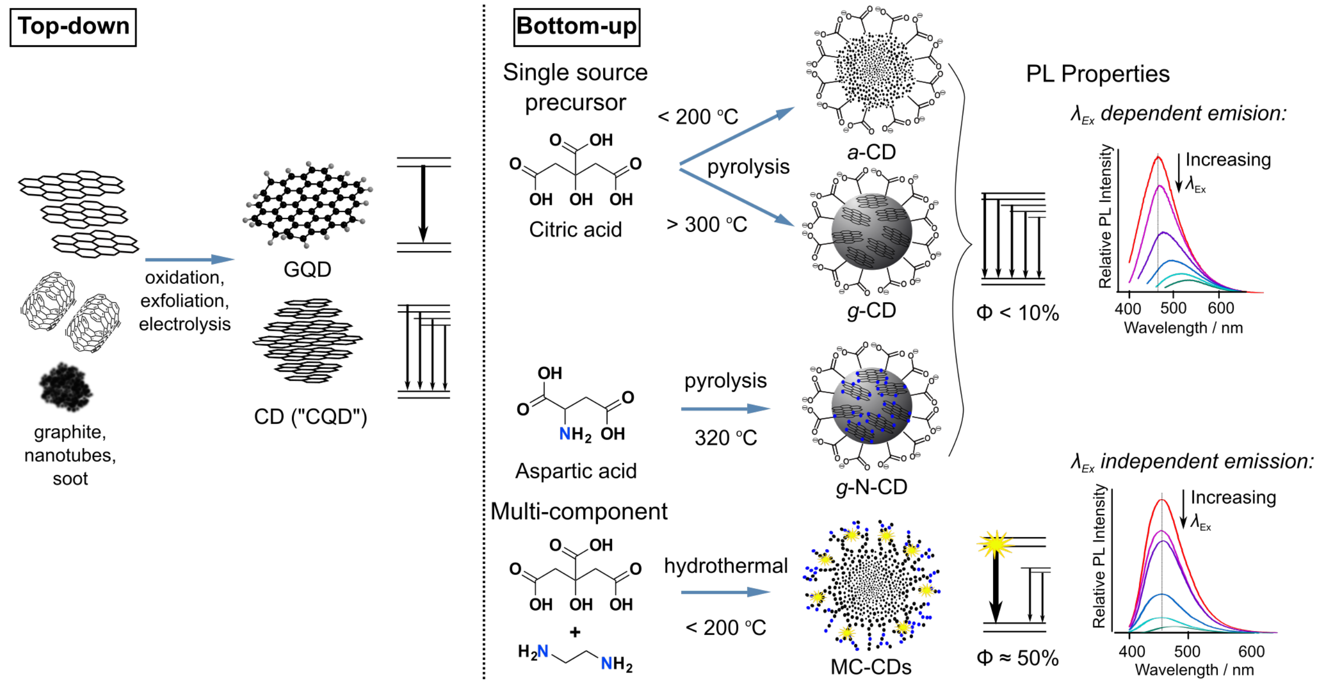


Figure 2. Top-down and bottom-up approaches to CD synthesis along with classes of CDs and their photoluminescent properties. *Left:* Top-down synthetic approaches typically lead to CDs with significant graphitic structure.[8] *Right:* Bottom-up approaches to CD synthesis are divided into two categories: single source precursor (SSP) and multi-component (MC) synthetic procedures. SSP synthetic procedures lead to CDs of graphitic or amorphous composition depending on the synthesis temperature, and both cases give rise to CDs with low PL QY (Φ) and excitation-dependent fluorescence properties, due to many mid-band energy states.[8,19] Selecting a precursor with a heteroatom e.g. aspartic acid can direct doping into the bulk of the CD (*g*-N-CD).[23] MC synthetic procedures result in amorphous CDs with nitrogen capping groups (blue colour), which result in molecular-like fluorophores (yellow stars) with high PL QY and excitation-independent emission properties.[24]

A temperature where the precursor can decompose as a melt (*e.g.*, citric acid, 180 °C) is optimal to maximise yield and reproducibility. Generally, temperatures above 300 °C lead to significant graphitisation (*g*-CD, Figure 2), whereas those below 300 °C produce entirely amorphous particles (*a*-CD, Figure 2),[8,19,21] unless sp^2- or sp- hybridised carbon is already present in the precursor molecule.[18] CDs produced by bottom-up methods are significantly more disordered than particles prepared by top-down methods, such as GQDs. The synthesis time should be optimised to ensure full decomposition of the precursor to facilitate/minimise subsequent purification procedures such as dialysis or gel chromatography.

Heteroatom doping can be achieved by selecting a precursor in which all desired dopant elements are present in the SSP and covalently bound to the carbon chain. In doing so, heteroatom incorporation is directed into the core of the forming carbon nanoparticle. For example, nitrogen-doped graphitic carbon dots have been synthesised by the SPP approach using aspartic acid as the precursor compound (*g*-N-CD, Figure 2).[23]

CDs synthesised from precursors rich in carboxylic acid functionality, such as citric acid or aspartic acid as shown in Figure 2, display carboxylic acid functionalities at the surface. Following heat treatment of the precursor compound, neutralisation of the resulting CDs by addition of NaOH may be required to deprotonate the surface carboxylic acid groups and aid dissolution of the CDs in water. *a*-CDs are soluble in water without neutralisation as well as in polar organic solvents such as methanol and acetone. Avoiding neutralisation can be beneficial when using CDs for subsequent synthetic procedures, such as surface functionalisation reactions (see *CD Surface Functionalisation* Section below) to allow solubility in organic solvents and avoid excess salt build-up in the procedure.[25] *g*-CDs on the other hand, generally have limited solubility in organic solvents and are insoluble in water without neutralisation with NaOH.

Multi-component. In the MC approach, a carbonaceous CD precursor, such as citric acid, is decomposed in the presence of additional species containing heteroatoms, for example ethylenediamine or urea for nitrogen, as well as H_3PO_4 and H_3BO_3 for phosphorus and boron, respectively.[22,24,26,27] In CDs synthesised by the MC approach, the heteroatom incorporation is thought to be localised largely at the CD surface, with surface functionalities largely consisting of amide and/or amine functionalities, as well possibly carboxylic acids (Figure 2).[21,24,27] These CDs are often referred to as “doped” or “surface passivated”, with the heteroatom capping the CD formed from the carbonaceous precursor.[19,21,27] MC synthetic procedures are often used as an approach to synthesising amine-terminated CDs, for use in further functionalisation reactions (*vide infra*).

MC syntheses typically take place in an autoclave either in aqueous solution or with a liquid capping agent, such as ethylenediamine, as the solvent. Since pressure limitations within the autoclave generally limit the synthesis temperatures to < 200 °C, CDs synthesised by the MC approach are amorphous. In contrast, higher synthesis temperatures can be achieved using the SSP approach, and accordingly, greater degrees of graphitisation. The low temperature and closed system of the autoclave typically leads to incomplete reaction of the precursor compounds,[21] so CDs synthesised by the MC synthetic procedure generally require further post-synthetic purification, usually *via* dialysis (see below). MC synthetic procedures conducted in an open atmosphere have shown significantly different optical properties to those synthesised under pressure.[22,28]

MC synthetic procedures can lead to profound changes in the optical properties of the CD compared to CDs synthesised by the SSP approach, which will be discussed in the *Optical Properties* section below.

Purification and isolation of CDs. Freeze-drying aqueous solutions of CDs allows CDs to be isolated as a powder. Purification of CD materials is challenging as the small size and low density of CDs render them difficult to isolate by regular centrifugation (rpm < 14,000). The most commonly utilised purification procedure is dialysis.[22,26] The smallest possible dialysis membrane (< 1000 Da) should be used to avoid significant loss of material through the dialysis membrane.[29] CDs have also been purified by Sephadex gel chromatography,[30] which has also been reported to separate CDs into size-resolved fractions.[27,30] Silica gel chromatography has been used to separate CDs, which has lead to the identification of fluorescent molecular species in the CD sample.[28,29] Isolating and distinguishing CDs and molecular species remains a significant and important challenge.[28,29]

Surface Functionalisation. One attraction of using CDs as light-harvesters in photocatalytic schemes is their solubility and the versatility of their surface chemistry. CD surfaces are typically rich in carboxylic acid or amine residues, providing ample opportunities for surface functionalisation.

Various approaches to the functionalisation of CD surfaces have been employed, although examples are largely limited to imparting additional functionality for applications in sensing and bio-imaging rather than catalysis.[31] A common strategy is using carbodiimide chemistry for the coupling of carboxylic acid containing functionalities with amine-terminated CDs.[27] An alternative approach is treating carboxylic acid terminated CDs with thionyl chloride to create acyl chloride groups on the CD surface, as shown schematically in Figure 3. Functionalisation with thionyl chloride is commonly used for CDs synthesised by top-down procedures, where surface functionalisation with polyethylene glycol diamines (PEG_{1500N}) is often required to impart photoluminescence properties.[16]

There are several advantages of the acyl-chloride route to CD surface functionalisation.[25] First, the by-products of the reaction with thionyl chloride are volatile, which avoids difficult purification procedures. The acyl-chloride functionalised CD can be isolated and stored for subsequent use in various functionalisation reactions. Secondly, thionyl chloride can be used as the solvent in large excess enabling full coverage of the surface without the need to estimate reaction stoichiometry. Finally, monitoring the shift in the IR absorption of the CD carbonyl (C=O) stretch provides a spectroscopic handle with which to monitor reaction progress and completion.

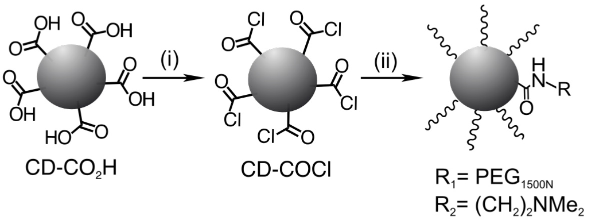


Figure 3. Functionalisation of CD carboxylic acid groups via an acyl chloride intermediate CD-COCl. (i) $SOCl_2$, reflux 80 °C; (ii) addition of alcohol or amine reagent such as polyethylene glycol diamine (PEG$_{1500N}$)[16] or dimethylethylenediamine (DMEN)[25] for R_1 and R_2, respectively.

The versatility of CD surface chemistry offers significant advantages for applications in photocatalysis. Modification of the CD surface allows for tuning the interaction between CDs and catalytic species *via* electrostatic interactions or by the covalent immobilisation of catalytic species. For the application of surface-functionalised CDs in photocatalysis, see the sections *CDs with metallic catalysts* and *CDs with redox enzymes*, below.

Properties and characterisation

Physical characterisation techniques

Physical characterisation techniques useful for characterising CD structures are: ^{13}C NMR and FT-IR spectroscopies for information about surface functionalities; and ^{13}C NMR, Raman, and XPS spectroscopies as well as TEM and AFM for characterising the phase and type of carbon environments present, such as the extent of sp^2/sp^3 hybridisation.

FT-IR is a particularly useful technique for monitoring surface-functionalisation reactions, by monitoring the characteristic shift of C=O environments on the surface of the CDs.[25] Zeta potential measurements are useful for the determination of CD charge.[22,25] Dynamic light scattering experiments to determine CD hydrodynamic size can be challenging due to the small size, low density and fluorescence of the CDs.

TEM sample preparation can be difficult as CDs are prone to aggregation on the grid,[21,27] or may have too-low contrast.[22] AFM provides another useful technique by which to determine CD size (height),[21,27] generally using a silicon wafer as the substrate.[22,23] Combined AFM and TEM characterisation can provide a more complete picture of the CD morphology than either technique alone. To date there has been no imaging analysis that captures both the height and lateral diameter of a single CD in the same measurement.

For ^{13}C NMR spectroscopy experiments that rely on the natural abundance of ^{13}C, a large number of scans and high CD concentrations (200 mg mL^{-1}) are required to achieve sufficient signal to noise ratio for accurate analysis. In addition to characterising sp^2/sp^3 C content, ^{13}C NMR spectroscopy is useful for monitoring reaction progress and ensuring complete decomposition of the precursor compound.[23] In the case of heteroatom doped CDs, other NMR-active nuclei, such as ^{15}N and ^{31}P (should P-doped CDs be synthesised),[19,23] provide further opportunities for structural characterisation. NMR spectroscopy can be a particularly powerful technique when utilised in 2D correlation experiments.[23,27]

UV-visible absorption and fluorescence spectroscopy are important techniques for characterising the optical properties of CDs, which will be detailed in the following section.

Optical properties

The origin of absorption in CDs stems from a variety of π–π* (C=C) and n–π* (C=O) transitions in the core and on the surface of the particles.[32] Carboxylic acid-terminated CDs, such as those synthesised by the SSP approach, typically have a broad UV-visible absorption profile, lacking clearly resolved features, whereas CDs synthesised by MC procedures (*a*-CD-NH_2), show an additional characteristic peak at approximately 355 nm for the n–π* (amide) transition (Figure 4).[24] CDs with higher levels of graphitisation display much higher absorption than amorphous CDs, due to the greater number of π–π* (C=C) present (Figure 4). Due to the complex nature of the absorption and the range of CD structures, little progress has been made so far in determining the position of their ground or excited state energy levels.

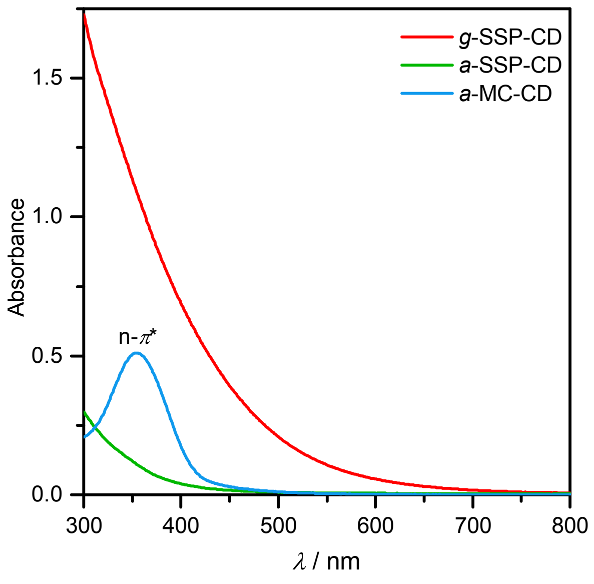


Figure 4. Representative UV-visible absorption spectra for amorphous and graphitic CDs synthesised by the SSP approach (*a*-SSP-CD and *g*-SSP-CD, respectively) and by the MC-approach (*a*-MC-CD).[23,26]

The intriguing photoluminescent emission properties of CDs have attracted significant research attention, in particular for applications in biological imaging and sensing.[21] CDs synthesised by the SSP approach typically display excitation wavelength-dependent emission properties,[21,32] *i.e.* the emission wavelength is red-shifted with increasing excitation wavelengths (Figure 2), distinguishing them from traditional semiconductor QDs which display a nanocrystal size-dependent emission due to their well defined band gap. Typically quantum yields of fluorescence (Φ) for SSP CDs are low (< 10 %),[21] indicating that there exists a number of non-radiative recombination pathways.

Despite extensive research efforts, the origin of photoluminescence in CDs still is not fully understood.[22] The prevailing view is that that there are three main possible sources of emission in CDs depending on their structure:[8] (1) emission from polyaromatic units in the carbon core;[33] (2) emission from surface confined defects states at the edge of sp^2 carbon domains (surface trap states);[32] and/or (3) emission from molecular-like fluorophores.[8,19,24,32] Whether or not these highly-emissive molecular-like fluorophores are attached to the CD surface or are isolated species in solution remains controversial.[24,28,29]

The contribution from core sp^2 carbon domains generally requires CDs with a significant fraction of sp^2 aromatic units, e.g. those synthesised at high temperatures (> 200 °C).[8,19,21,24,32] The photoluminescence properties of amorphous CDs synthesised by multi-component procedures are increasingly thought to result from highly emissive amide-containing molecular-like fluorophores (Figure 2), corresponding to the well-defined absorption observed in the UV-visible spectrum (Figure 4).[19,21,24,29] The presence of these fluorophores generally results in excitation wavelength independent emission and enhanced quantum yields (Φ approx. 50%) compared to CDs synthesised by the SSP approach (Φ < 10%).[19,21,24,29] Exceptions to this include MC syntheses utilising a tertiary amine, such as triethanolamine,[24] or high temperatures (300 °C)[19,21] where the highly emissive fluorophores do not form or are carbonised, resulting in CDs with no resolved absorption peak, excitation-wavelength dependent emission and Φ < 10 %. CDs synthesised by MC approaches open to atmosphere (rather than in a microwave or a closed autoclave reactor) have also shown non-uniform photoluminescence properties.[22,28]

For all CD types, PL lifetimes are typically < 20 ns.[22,24,26] These PL lifetimes are orders of magnitude shorter than the timescales typically required for electron transfer in photocatalytic systems, for example, μs–s timescales in dye-sensitised semiconductor photocatalysis.[2] Further discussion of the photophysics of electron transfer kinetics relevant to CD photocatalysis is given in the *Kinetics of Electron Transfer* section below.

Photocatalysis

CDs are an emerging low-cost photosensitiser material for applications in photocatalysis and a promising alternative to semiconductor QDs and molecular dyes.[11,34] In addition to low-cost and low-toxicity, CDs possess both excellent photostability, and high solubility in aqueous solution. Despite these properties, CDs have been under-explored in photocatalytic applications and have predominantly been used in conjunction with another photosensitiser (*e.g.*, $BiVO_4$, Ag_3PO_4, Cu_2O, ZnO, Fe_2O_3) for the photodegradation of organic dyes and toxic gases, a topic which has recently been reviewed elsewhere.[11] The electron reservoir properties of CDs have been reported to enhance photocatalytic H_2 evolution by acting as an electron relay between an organic photosensitiser and Pt nanoparticles (rather than a light-absorber).[35]

Distinct from the CDs synthesised by the bottom-up approach described above, several GQD based systems have been reported to photocatalyse full water splitting[15,36] (for a recent review including GQD-based materials see references 11 and 34 and references cited therein). In contrast, reports of photocatalytic fuel production involving CDs as the light harvester are limited and typically involve composite materials, for example CD-sensitised TiO_2.[11] CD-based fuel production systems which utilise CDs as the sole photosenstiser almost exclusively[37] require the addition of a catalyst to drive the reductive transformation.

This *tutorial review* will focus on the use of CDs, as distinct from graphite-derived materials, in photocatalytic systems for solar fuels production where CDs have been utilised as the primary light-harvester in conjunction with a catalyst (and sacrificial ED). Figure 5 summarises the various catalysts and EDs that have been used in photocatalytic systems utilising only CDs as the light harvester.

Practical considerations for the set-up and experimental design of photocatalytic experiments, for example choice of light source and product detection, have been described in detail in a previous *tutorial review,*[2] and most of the experimental design is applicable to photocatalysis with CDs. An additional factor to consider when preparing CD solutions for photocatalysis experiments is the CD-catalyst loading per experiment. The CD loading should be normalised for the absorbance of the CDs. Dark CD solutions can block light penetration into the vial and thereby lower the efficiency of the system. Lower CD loadings can result in a higher specific activity efficiency, various pH and ED combinations should be screened and the optimised system will depend on the chosen catalyst, as will the appropriate catalyst loading.

CDs with metallic catalysts

The first example of CDs being used as the sole photosensitiser for solar fuel production was for the photo-reduction of carbon dioxide to formic acid with PEG-passivated CDs modified with deposits of the noble metals Au or Pt.[38] CDs were synthesised by oxidation of carbon powers in nitric acid, followed by surface functionalisation with a poly(ethyleneglycol) diamine and coating with the noble metals by photoreduction of the corresponding metal salt precursor in aqueous solution. The Au and Pt-coated CDs photo-generated formic acid from a CO_2-purged aqueous solution with isopropanol (^{i}PrOH) as the sacrificial ED. The quantum yield of formic acid production was estimated to be relatively low at 0.3 % and the catalyst loading was not reported, preventing calculating the turnover number (TON). The same system under high pressure CO_2 (130 bar) produced a mixture of small acids, though with an order of magnitude rate enhancement (1200 and 60 $\mu molH_2\ g^{-1}\ h^{-1}$ towards formic and acetic acid, respectively).[39] More recently, CDs derived from yeast in ammonia solution were synthesized and, after platinization, they evolved some H_2 (31 $\mu molH_2\ g^{-1}\ h^{-1}$) in TEOA solution under UV irradiation.[40]

Chem Soc Rev

TUTORIAL REVIEW

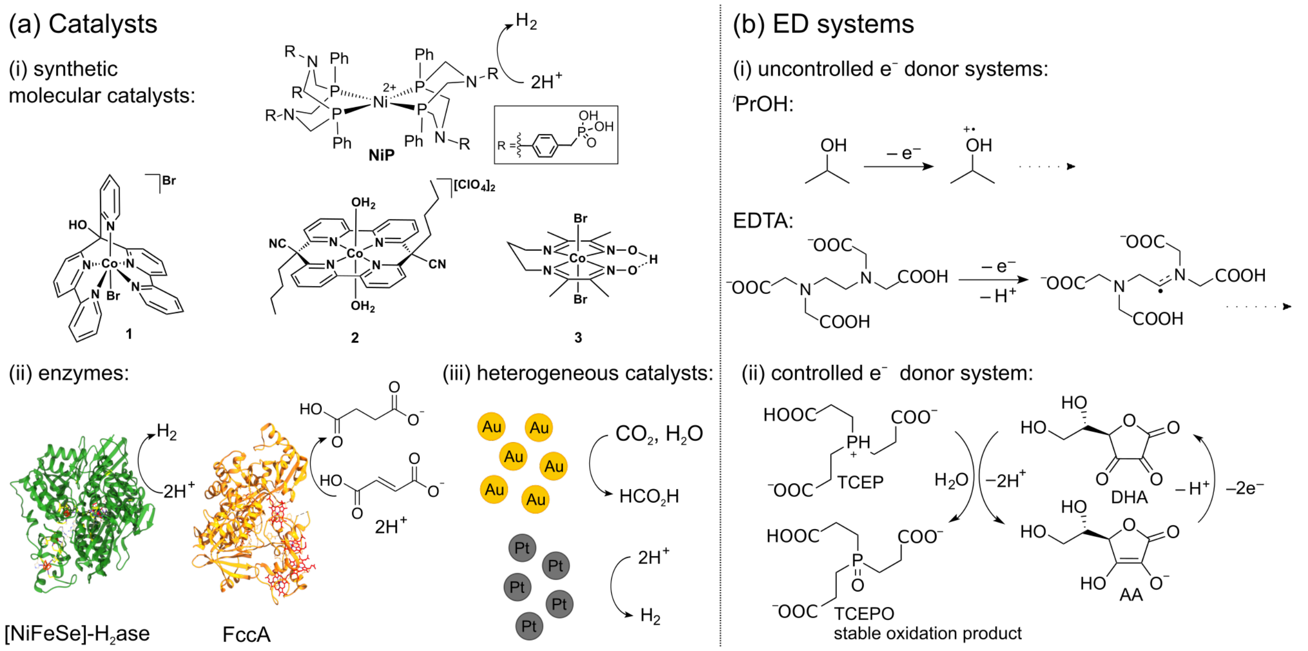


Figure 5. (a) Catalysts used in conjunction with CDs: (i) synthetic molecular catalysts **NiP** and cobalt catalysts **1–3**;[41] enzymatic catalysts [NiFeSe]-hydrogenase (H$_2$ase) for the reduction of protons to H$_2$and fumarate reductase (FccA) for the dehydrogenation of fumarate to succinate;[25] (iii) heterogeneous catalysts Au and Pt nanoparticles, used in conjunction with PEG-functionalised CDs for conversion of CO$_2$ to organic acids.[39] (b) Electron donor systems used in CD photocatalytic systems: (i) ^{i}PrOH[39] and EDTA electron donor system;[25,41] (ii) controlled TCEP/AA donor system.[42]

CDs with synthetic molecular catalysts

CDs have recently been integrated into hybrid systems for solar fuel generation using synthetic molecular 3d transition metal proton reduction catalysts (Figure 5). These catalysts are of interest as low-cost alternatives to precious metals and can be selected for product selectivity and tolerance to inhibitors such as CO and O$_2$.[2]

The first report of CDs in conjunction with a molecular catalyst used CDs synthesised *via* the SSP approach from thermolysis of citric acid at 180 °C in a one-pot, multi-gram, scalable synthesis.[41] The resulting CDs were largely amorphous (*a*-CDs) with some regions of sp^2-hybridised carbon and had an average size of 6.8 nm. The CDs were used in a photocatalytic system which evolved H$_2$ under simulated solar irradiation in conjunction with a molecular $[Ni(P_2N_2)_2]^{2+}$ catalyst (**NiP**) in aqueous solution using ethylenediamine tetraacetic acid (EDTA) as a sacrificial ED (Figure 5).[41] No H$_2$ was observed in the absence of any of the system components, CD, EDTA or **NiP**, indicating that all components of the system are required, and importantly, that these CDs do not act as electron donors or catalysts themselves.

The *a*-CD/**NiP** system achieved an activity of 398 $\mu mol_{H2}\,(g_{CD})^{-1}\,h^{-1}$ and a ‘per Ni catalyst’ turnover frequency of 41 h^{-1}. The CDs displayed activity in the visible region beyond $\lambda > 455$ nm and maintained their full photocatalytic activity for at least one day under full solar spectrum irradiation, with re-addition of the **NiP** catalyst every 6 h. In the absence of catalyst re-addition, however, the system ceased to evolve H$_2$ after a period of hours.

The lifetime of the *a*-CD/**NiP** hybrid photosystem was limited by the stability of the molecular nickel catalyst under the experimental conditions employed (EDTA as sacrificial ED and full solar spectrum irradiation).[41,42] Several decomposition routes of the molecular catalyst were suggested, including UV-light induced ligand displacement and ligand oxidation by photo-generated holes.[42] However, the primary route of catalyst decomposition was found to occur *via* radicals generated upon oxidation of EDTA. Replacement of EDTA in the photosystem with an ascorbate proton-electron relay and a tris(carboxyethyl)phosphine (TCEP) substrate (Figure 5), which undergoes a controlled two-electron oxidation pathway, circumvents radical induced catalyst decomposition, and thereby dramatically increases the lifetime of the photosystem over a period of days (Figure 6).[42] In this way high TONs (> 1000) were achieved for the molecular nickel catalyst, highlighting the photostability of the CDs to sustain photocatalytic H$_2$ production over several days when a robust catalyst is available.

The use of the molecular Ni catalyst was shown to be key to the success of the *a*-CD/**NiP** photosystem, as deposition of heterogeneous catalysts from photoreduction of metallic precursors returned no activity.[41] The applicability of CDs more widely as photosensitisers to molecular species was later demonstrated in the development of hybrid photosystems using a range of cobalt-containing molecular catalysts, **1**–**3** shown in Figure 5.[42] The performance of these systems was compared against the overpotential requirement of the catalyst and the excited state potential of the CDs was estimated using electrochemical methods. A limit on the overpotential of a catalyst suitable for pairing with amorphous CDs of this type in a hybrid photosystem was set at around 500 mV.

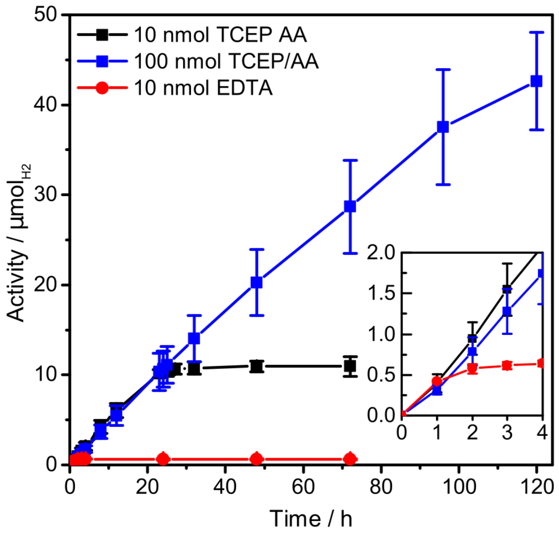


Figure 6. Solar H_2 production using CDs (10 mg) and **NiP** (10 nmol or 100 nmol) with aqueous solutions of the EDs EDTA (0.1 M, pH 6, 3 mL) or TCEP/AA (0.1 M each TCEP and sodium ascorbate, pH 5, 3 mL) under simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}) at 25 °C. The inset shows a magnification of the first 4 h. Data taken from reference 42.

These *a*-CD-molecular catalyst systems were the first demonstration that CDs could be used to sustain long-term H_2 production in a low-cost precious metal-free photocatalytic system. Despite the impressive stability and low-cost properties of the CDs, the overall performance of the aforementioned *a*-CD systems is lower than that achieved with state-of-the-art photosensitisers (see *Comparison to state-of-the-art photosensitisers* section below). The hybrid *a*-CD-molecular catalyst systems are limited by the visible light absorption profile of the CDs. Upon application of a long-pass cut-off filter that limits irradiation to the visible wavelengths (λ > 400 nm), the photocatalytic H_2 production is reduced to 50% to that compared to full-spectrum irradiation.[41] Use of visible-only irradiation does however improve the stability of the molecular catalyst.[42] Strategies to improve the overall absorption of CDs would enhance the overall activity of the CD-molecular catalyst photosystems.

Graphitisation and heteroatom doping

Control over CD structure is a key objective to tune their properties and improve their performance for specific applications. Methods for the synthesis of CDs with varying structure were discussed above and shown in Figure 2. In particular, the carbon core composition (amorphous *vs* graphitic) and heteroatom content can be tuned via the SSP approach for enhanced photocatalytic performance.

Nitrogen-doped graphitic CDs have been synthesised by the SSP approach using aspartic acid as a precursor at 320 °C (Figure 2).[23] Undoped graphitic CDs (*g*-CD) were synthesised by the thermolysis of citric acid at 320 °C for comparison, and the effect of graphitisation and nitrogen doping on photocatalytic performance was investigated.

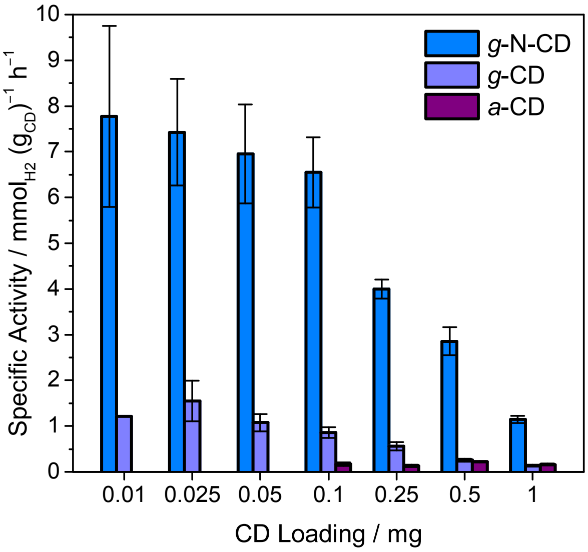


Figure 7. Photo-H_2 generation using various amounts of CDs (0.01 – 1 mg) and 10 nmol **NiP** in aqueous EDTA solution (0.1 M, pH 6, 3 mL) under simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}) at 25 °C. Data taken from reference 23.

The graphitic particles displayed greatly enhanced light absorption due to a higher content of C=C bonds (π–π* transitions), particularly in the visible light range, as shown in Figure 2. This enhanced light absorption resulted in an improved photocatalytic performance in conjunction with **NiP** on a per g of CD basis as compared to *a*-CD (1549 *vs* 226 μmol$_{H2}$ (g$_{CD}$)$^{-1}$ h^{-1} for *g*-CD and *a*-CD, respectively, at equal catalyst loading). *a*-CD have a much lower absorption coefficient and therefore require higher loadings of material (Figure 7). The visible light performance of *g*-N-CD was also significantly improved as compared to *a*-CD.

The nitrogen-doped CDs (*g*-N-CD) outperformed both undoped *g*-CD and *a*-CD (7950 μmol$_{H2}$ (g$_{CD}$)$^{-1}$ h^{-1}), demonstrating that core nitrogen doping correlates with enhanced photocatalytic performance, beyond merely greater visible light absorption caused by graphitisation. Spectroscopic methods indicated that nitrogen doping of the graphitic structure resulted in rapidly quenched holes and a higher concentration of long-lived photogenerated electrons, which led to increased photocatalytic performance (see further discussion in the *Electron transfer kinetics* section below). The performance of *g*-N-CD (the record solar H_2 evolution system using CDs) in comparison to established state-of-the-art light harvesters is discussed below (*Comparison to state-of-the-art photosensitisers* and Table 1).

CDs with redox enzymes

CDs are attractive photosensitisers for use with biological catalysts due to their low-toxicity and aqueous solubility providing potential for use *in vivo*. CDs were recently incorporated into two *in vitro* semi-biological photocatalytic schemes incorporating redox enzymes, taking advantage of the tunability of CD surface chemistry to modulate the CD-enzyme interaction.[25] This was the first demonstration of the use of CDs as light-harvesters for solar-driven enzymatic catalysis for artificial photosynthesis.

Tertiary-amine terminated CDs ($CD-NHMe_2^+$) were synthesised *via* chlorination of the carboxylic acid groups on the surface of CDs synthesised from the thermal decomposition of citric acid. $CD-NHMe_2^+$ were compared to unmodified, negatively charged carboxylate-terminated CDs ($CD-CO_2^-$) for photoelectron transfer to two different redox enzymes: fumarate reductase (FccA) for the solar-driven hydrogenation of fumarate to succinate, and a [NiFeSe]-hydrogenase (H_2ase) for the reduction of protons to H_2. The CD-FccA system for the hydrogenation of fumarate to succinate was the first use of CDs for solar chemical synthesis. $CD-NHMe_2^+$ were capable of transferring photo-excited electrons directly to the negatively charged enzymes with high efficiency, reaching enzyme-based turnover numbers of 6000 mol succinate (mol FccA)$^{-1}$ and 43,000 mol H_2 (mol H_2ase)$^{-1}$ after 24 h. $CD-CO_2^-$ however displayed little or no activity.

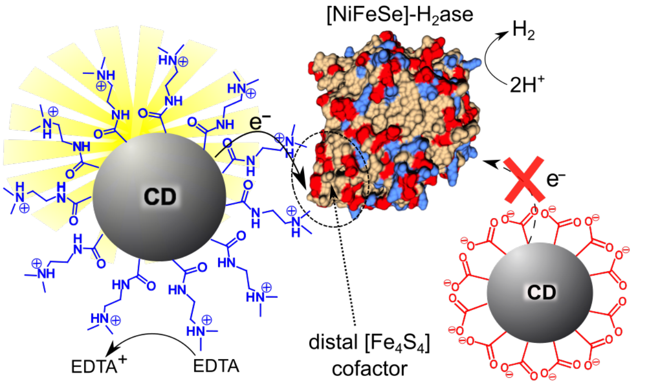


Figure 8. Schematic representation of the favourable electrostatic interaction between positively charged $CD-NHMe_2^+$ and the negatively charged electron entry site ([Fe_4S_4] co-factor) of [NiFeSe]-H_2ase from *Desulfomicrobium baculatum*. The enzyme surface-charge representation of [NiFeSe]-H_2ase shows negatively charged residues highlighted in red and positively charged residues highlighted in blue. Negatively charged carboxylic acid capped CDs display a poor interfacial interaction with [NiFeSe]-H_2ase resulting in negligible electron transfer efficiency.[25]

Productive electrostatic interactions at the CD–enzyme interface were determined to be essential to the high photocatalytic activity observed with $CD-NHMe_2^+$ (Figure 8). FccA and [NiFeSe]-H_2ase both have negatively charged amino acid residues, glutamate and aspartate, surrounding their electron entry site – a surface-exposed co-factor that receives electrons that are then shuttled to the enzyme active site. The orientation of the enzyme with the negatively charged electron-entry pocket close to the positively charged CD is crucial for achieving direct electron transfer to the enzyme.[25]

Electron transfer kinetics

The non-emissive excited state properties and electron transfer kinetics of CD materials have been studied using transient absorption spectroscopy (TAS). TAS is a technique that allows non-emissive transient excited state species to be monitored over femtosectond to second times scales. The sample is excited with a short laser pulse (‘pump’) and a second light source is then used to probe the changes in absorption of the excited state species over time.[2]

There have only been a few studies of CD materials using TAS, and most have been limited to fs–ps timescales. Generally, CD materials that are excited with a UV laser pulse show a broad transient absorption signal, absorbing from 500–750 nm, which decays over a picosecond timescale.[21,22,43] Guldi and co-workers studied photoinduced electron transfer between CDs and electron donors and acceptors, such as triethanolamine and methyl viologen, respectively.[22] They showed that electrostatic interactions between the CD and the electron donor or acceptor were highly important to the electron transfer efficiency. These one-electron electron transfer reactions occurred on ps time scales, which is faster than typically observed for electron transfer to catalysts in photocatalytic systems (microsecond–second timescales).[2]

The electron transfer kinetics and photophysical properties of the CD/**NiP** systems have been investigated using TAS over femtosecond to second timescales, which allowed the electron transfer to catalytic species to be monitored (μs–s time scale).[23] A summary of the charge transfer processes in the CD/**NiP** systems is shown in Figure 9.

All CD types measured (*a*-CD, *g*-CD, *g*-N-CD) gave rise to a transient absorption signal spanning the visible range with features centred near 505 nm and 650 nm, which as mentioned above, is characteristic of CD materials. These signals exhibit relaxation processes on the picosecond timescale, which outcompetes the kinetics of diffusional bimolecular reactions. Since these states with picosecond lifetimes decay faster than the timescale of bimolecular diffusion, there is no possibility of their involvement in charge transfer processes to solution-based species. This picosecond relaxation therefore is a primary restriction on the overall activity achievable for photocatalytic systems limited by bimolecular diffusion kinetics, such as the CD/**NiP** systems.

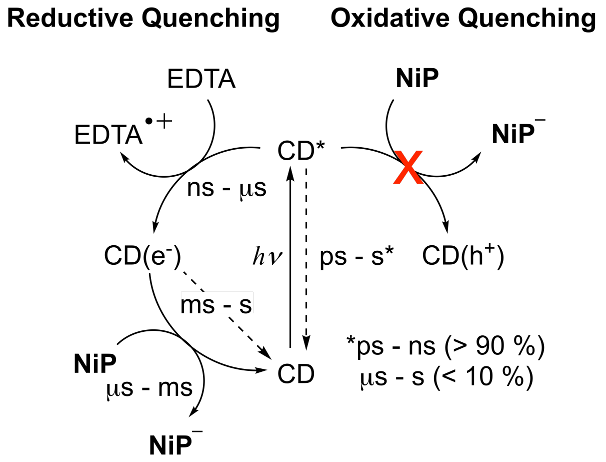


Figure 9. Summary of the timescales of charge transfer processes in CD/**NiP** photosystems.[23]

Up to 10 % of the excited states were observed to have lifetimes reaching the microsecond to second timescales. These long-lived species are photogenerated electrons relevant to charge transfer reactions, in particular the species absorbing at 500 nm. Addition of EDTA resulted in a significant increase in the lifetime of the long-lived species due to extraction of photogenerated holes by EDTA. Upon addition of EDTA, *g*-N-CD showed a greater proportion of the long-lived species as compared to *a*-CD and *g*-CD (Figure 9), which was determined to be the reason for its enhanced efficiency for H_2 production. Accordingly, a greater amount of reduced **NiP** (**NiP**$^{-}$) was observed with *g*-N-CD than for *a*-CD or *g*-CD.

Signals for reduced **NiP**$^{-}$ were only observed when **NiP** was added to a solution of CDs containing EDTA. Thus, electron transfer was determined to proceed *via* a reductive quenching mechanism, whereby electron transfer to **NiP** only proceeds following hole scavenging by EDTA (Figure 9). Electron transfer to **NiP** is therefore the rate limiting charge transfer step and suggests that strategies to enhance electron transfer efficiency to **NiP** would provide a means of optimising the efficiency of the system. For the *g*-N-CD system, however, the reported IQE (5.2 %) was of similar magnitude to the proportion of long-lived species observed (< 10 %), suggesting almost quantitative yields of the charge extraction from the long-lived species to **NiP**. In this case, significant improvement in the photocatalytic performance of the system must come from harnessing the > 90 % of excited states with picosecond decay lifetimes.

TAS investigations showed that i) fast relaxation of the photoexcited CD on the picosecond timescale limits the H_2 photo-production in the CD/**NiP** photocatalytic systems, ii) a reductive quenching mechanism operates and iii) more efficient charge transfer reactions lead to the formation of more reduced **NiP**, and is responsible for the increased photogeneration of H_2 with *g*-N-CD. These findings point to two areas where improvements to the CD photocatalytic systems can be made. First pre-assembly of the CD and catalyst to remove the system from bimolecular diffusion-limited kinetics may provide a means of accessing the fast decaying excited state charges, and may certainly improve the efficiency of the *a*-CD and *g*-CD systems where the overall quantum yield (1.4 %) is significantly less than the proportion of long-lived excited states (< 10 %).

Secondly, the development of CD materials with an enhanced proportion of excited states with long-lived lifetimes available for charge transfer to catalytic species would be highly beneficial. The development of new materials however requires an improved understanding of the photophysical properties of CDs, in particular what the nature of the short-lived and long-lived excited state species are. For example, a recent study using time resolved electron paramagnetic resonance spectroscopy identified the presence of triplet states with observed lifetimes up to 12 µs, which were suggested to be associated with aromatic units in the CD core.[28] Similar studies for photocatalytic systems would be highly informative.

Comparison to state-of-the-art photosensitisers

Table 1 summarises the performance parameters of the CD based H_2 evolution photosystems discussed in this review and compares them to related aqueous sacrificial photosensitiser-catalyst hybrid systems, including both homogeneous (molecular dye) and heterogeneous (chalcogenide QDs and carbon nitrides) photosensitisers. In comparison to similar systems that make use of molecular dyes with catalysts such as Pt, **NiP** or H_2ase, CDs now start to be competitive. In terms of TOF, the engineered CD systems such as *g*-N-CD (with **NiP**) and *a*-CD–$NHMe_2^{+}$ (with H_2ase) perform comparably to systems using analogues using $[Ru(bipy)_3]^{2+}$ and Eosin Y.[44,45] The application of precious-metal based dyes and all-organic dyes are limited by cost and photoinstability, respectively.

Cadmium chalcogenide nanoparticles and QDs are well established photosensitisers in solar fuels production. They benefit from very high absorption coefficients, low recombination rates and fast electron transfer and hence achieve high activity (µmol H_2 g^{-1} h^{-1} basis). A notable system using CdSe QDs and a self-assembling nickel-DHLA catalyst in purely aqueous conditions produced both high rate (TOF_{Ni} 7000 h^{-1}) and long stability.[4] However, the stability of the nickel catalyst and the QDs was the result of repair by the excess of dihydrolipoic acid (DHLA) ligand and hence does not make use of a defined molecular catalyst. A high intensity monochromatic LED at the excitation maximum has also been employed as the light source instead of simulated solar irradiation. Other systems which do not have a repair reagent show more comparable performance parameters to the improved CD materials such as *g*-N-CD.[46,47] Cadmium-based materials, unlike carbon-based ones, also suffer from the intrinsic issue of toxicity as well as elemental abundance in the case of selenides and tellurides.

Graphitic carbon nitrides are low cost and stable carbon-based semiconductors for photocatalytic applications. Notable progress has been made in enhancing the performance of *g*-C_3N_4 materials since it was first reported for use in solar H_2 production.[6] A remarkable activity of 20000 µmolH_2 g^{-1} h^{-1} was recently reported using a urea-derived *g*-C_3N_4, however, this was using a high-intensity Xe arc lamp (with high UV content) as opposed to simulated solar irradiation. With a longpass filter (395 nm), the activity was reduced to 3300 µmol H_2 g^{-1} h^{-1}.[48] Limitations on the activity of carbon nitrides result from their relatively low surface area and hydrophobic interactions in aqueous systems. CDs on the other hand are water-soluble and, like other QDs, have a high surface area. The core nitrogen-doping of *g*-N-CD allows CDs to profit from some of the beneficial properties of carbon nitrides (high photostability, long charge carrier lifetime, precious- and toxic-metal-free), while maintaining the high surface area and dispersibility benefits of QDs. As a result, *g*-N-CD/**NiP** (7950 µmolH_2 g^{-1} h^{-1}) outperforms all reported *g*-C_3N_4 materials on a per gram basis, under simulated solar irradiation (AM1.5G).[5,6]

Thus, CDs perform well in comparison to other water-soluble/dispersible photosensitisers, which suffer from the drawbacks of high cost (Ru dyes), photoinstability (organic dyes) and toxicity (Cd chalcogenide QDs). They also compare favourably to abundant heterogeneous semiconductor photosensitisers such as TiO_2 nanoparticles (poor visible light absorption) and polymeric *g*-C_3N_4 (low surface area, hydrophobic, poor interfacial interactions). This demonstrates that CDs can now compete with other dyes on an activity basis without many of the disadvantages. In comparison to the few reports of CDs in solar H_2 evolution, *g*-N-CD has the highest activity (7950 µmolH_2 g^{-1} h^{-1}) by a combination of its high CD mass absorption coefficient and rapid charge transfer reactions in aqueous solution.

Challenges and Future Direction

CDs present substantial advantages as light-harvesters for photocatalytic solar fuels and chemical synthesis. The combination of low-cost, low-toxicity, scalable synthesis, high photostability and surface area, aqueous solubility and

.

Table 1. Summary of photocatalytic performance parameters of CD proton reduction photocatalytic systems compared to selected aqueous, sacrificial, photosensitiser-catalyst H_2 evolution photosystems.

Photosensitiser	**Catalyst**	**Donor**	**Light Source**	**TOF_{cat} / h^{-1}**	**TON_{cat}**	**Activity / $\mu mol\ g^{-1}\ h^{-1}$**	**QY / %**	**Ref**
CD systems								
a-CD	**NiP**	EDTA	100 mW cm^{-2} (AM1.5G)	41	64	397	1.4[i]	41
a-CD	**NiP**	TCEP/AA[b]	100 mW cm^{-2} (AM1.5G)	53	1094	53[c]	n.d.	42
g-CD	**NiP**	EDTA	100 mW cm^{-2} (AM1.5G)	12	45	1549	n.d.	23
g-N-CD	**NiP**	EDTA	100 mW cm^{-2} (AM1.5G)	143	277	7950	5.2[e]	23
a-CD–$NHMe_2^+$	[NiFeSe]-H_2ase	EDTA	100 mW cm^{-2} (AM1.5G)	5100	44000	80[c]	0.4[e]	25
CD–PEG	Au/Pt	*i*PrOH	unspecified ($\lambda > 425$ nm)	n.d.	n.d.	n.d.	n.d.	38
CD (yeast-derived)	Pt	TEOA[b]	300 W Xe arc	0.1	n.d.	31	n.d.	40
Molecular dye systems								
Porphyrin	Pt	EtOH	150 W Xe arc	6	70	—	n.d.	49
RuP[a]	**NiP**	AA[b]	100 mW cm^{-2} ($\lambda > 420$ nm)	460	723	—	9.7[e]	44
Perylene	$Ni(P_2N_2)_2$	AA[b]	250 mW cm^{-2} ($\lambda > 400$ nm)	19	340	—	n.d.	50
Eosin Y	[NiFeSe]-H_2ase	TEOA[b]	100 mW cm^{-2} ($\lambda > 420$ nm)	50000	500000	—	1.5[e]	45
Chalcogenide QD systems								
CdS QD	Pt	NaS/Na_2SO_3	300 W Xe arc	600[d]	n.d.	1600	51[i]	46
CdTe QD	$Co(N_2S_2)(NO)$	AA[b]	300 W Xe arc ($\lambda > 400$ nm)	850	14400	220[d]	5.3[i]	47
CdSe QD	Ni-DHLA[b]	AA[b]	13 mW cm^{-2} LED (520 nm)	7000	600000	24000[d]	36[i]	4
CdTe QD	[NiFe]-H_2ase	AA[b]	300 mW Nd:YLF laser (527 nm)	8280	92	300000[d]	4[i]	7
Carbon nitride systems								
g-C_3N_4	Pt	TEOA[b]	300 W Xe arc	107	641	20000	26.5[i]	48
g-C_3N_4	**NiP**	EDTA	100 mW cm^{-2} (AM1.5G)	109	166	437	0.4[e]	5
g-C_3N_4	[NiFeSe]-H_2ase	EDTA	100 mW cm^{-2} (AM1.5G)	5532	50000	55[c]	0.07[e]	5

(a) RuP = diphosphonated $[Ru(bipy)_3]^{2+}$. (b) DHLA = dihydrolipoic acid; TCEP = tris(carboxyethyl)phosphine; AA = ascorbic acid; TEOA = triethanolamine. (c) Low catalyst loading. (d) Value estimated from published data. (e) External quantum efficiency. (I) Internal quantum efficiency. n.d. = not determined.

tuneable properties represent significant advantages over well-established state-of-the-art photosensitisers.

Substantial progress has been made recently in the utilisation of CDs in photocatalytic fuel production. CDs have been reported for CO_2 reduction to organic acids as well as in hybrid proton reduction schemes utilising synthetic molecular and enzymatic catalystsThe first CD based solar chemical transformation (double bond hydrogenation) has also been shown. Since the first report of CDs in hybrid photo-H_2 evolution systems, significant improvement in the photocatalytic rate has been achieved through nitrogen-doping, which renders *g*-N-CD competitive with state-of-the-art photosensitisers in terms of per g activity. Furthermore, a variety of molecular and enzymatic catalysts have been shown to be compatible with CDs. In particular, the tuneable surface chemistry of CDs is a particularly attractive feature for optimising interfaces between CDs and biological catalysts.

There is a great scope for the continued development of CD materials with improved properties for photocatalysis. New synthetic procedures for preparation of nitrogen or other heteroatom-doped CDs may allow for further enhancements by tuning the intrinsic photophysical properties of CDs. As foreshadowed by TAS kinetic studies, one of the main limiting factors affecting the quantum yield of H_2 production in the CD photosystems is the rapid decay of the majority of the initial excited states on the picosecond timescale. Thus, preparation of CD materials that have a greatly increased proportion of long-lived excited states would be highly beneficial to improve the yield of charge extraction by catalytic species. However, in the absence of more detailed understanding of the nature of the excited states, and with current synthetic methods, this remains a long-term challenge, though one that could realise significant rewards.

A more immediate route to be considered is the strategy of pre-assembly to overcome the diffusion limitation. Surface modification of CDs could be used to further tune the CD-catalyst interactions and possibly allow for the covalent immobilisation of catalytic species. The immobilisation of catalysts may be achieved by several methods, including electrostatic interactions and the formation of covalent bonds between a photosensitiser and catalyst. Covalent attachment has the benefit of being robust against changes in pH or ion concentration. The carboxylated surface structure of CDs inherently lends itself to this strategy, since stable amide bonds can be formed using organic synthetic or peptide coupling methods. Immobilisation of CDs to electrodes for integration into photoelectrochemical cells presents another avenue for the utilisation of CDs in artificial photosynthetic devices.

There remains uncertainty in the exact structure of CDs produced by bottom-up syntheses and a considerable gap in knowledge regarding structure-property correlations. Thorough identification and understanding of the species present in a CD sample and their corresponding properties should be a priority. Areas which require urgent attention are: distinguishing between molecular fluorophores and CDs;[28] identifying the nature of CD excited state species and what structural features underpin them; developing a thorough understanding of CD synthesis mechanisms. Tackling these challenges will require advanced characterisation techniques, for example, advanced NMR and time-resolved spectroscopies.[23,27,28]

Finally, the identification of new catalysts with improved robustness and which operate at high catalytic rates with suitably low overpotential represents an important strategy to improve the overall performance of CD photosystems. Greater understanding of the CD excited state potentials may allow CDs to be used in a broad range of photocatalytic reactions. The use of CDs in other photobiocatalytic or organic photocatalysis systems beyond fuel-forming reactions is an interesting avenue to pursue. For example, CDs may show great promise for applications for light-driven organic transformations, where precious-metal inorganic dyes are currently used. Furthermore, an understanding of the oxidative potential of CDs should be a key goal to eliminate the sacrificial electron donor from the system and to allow CDs to be used in sustainable full-redox cycle photocatalytic systems.

Acknowledgements

This work was supported by the Christian Doppler Research Association (Austrian Federal Ministry of Science, Research, and Economy and the National Foundation for Research, Technology and Development), the OMV Group, a Poynton PhD scholarship and an Oppenheimer PhD scholarship.

Notes and references

1 T. S. Teets and D. G. Nocera, *Chem. Commun.*, 2011, **47**, 9268–9274.

2 J. Willkomm, K. L. Orchard, A. Reynal, E. Pastor, J. R. Durrant and E. Reisner, *Chem. Soc. Rev.*, 2016, **45**, 9–23.

3 M. Wang, K. Han, S. Zhang and L. Sun, *Coord. Chem. Rev.*, 2014, **287**, 1–14.

4 Z. Han, F. Qui, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321–1325.

5 C. A. Caputo, M. A. Gross, V. W. Lau, C. Cavazza, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.*, 2014, **53**, 11538–11542.

6 X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen and M. Antonietti, *Nat. Mater.*, 2009, **8**, 76–80.

7 B. L. Greene, C. A. Joseph, M. J. Maroney and R. B. Dyer, *J. Am. Chem. Soc.*, 2012, **134**, 11108–11111.

8 A. Cayuela, M. L. Soriano, C. Carrillo-Carrión and M. Valcárcel, *Chem. Commun.*, 2016, **52**, 1311–1326.

9 S. Y. Lim, W. Shen and Z. Gao, *Chem. Soc. Rev.*, 2015, **44**, 362–381.

10 Y. Wang and A. Hu, *J. Mater. Chem. C*, 2014, **2**, 6921–6939.

11 H. Yu, R. Shi, Y. Zhao, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung and T. Zhang, *Adv. Mater.*, 2016, **28**, 9454–9477.

12 V. Georgakilas, J. A. Perman, J. Tucek and R. Zboril, *Chem. Rev.*, 2015, **115**, 4744–4822.

13 L. Tian, D. Ghosh, W. Chen, S. Pradhan, X. Chang and S. Chen, *Chem. Mater.*, 2009, **21**, 2803–2809.

14 H. Ming, Z. Ma, Y. Liu, K. Pan, H. Yu, F. Wang and Z. Kang, *Dalton Trans.*, 2012, **41**, 9526–9531.

15 T.-F. Yeh, J.-M. Syu, C. Cheng, T.-H. Chang and H. Teng, *Adv. Funct. Mater.*, 2010, **20**, 2255–2262.

16 Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S.-Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756–7757.

17 C. X. Guo, D. Zhao, Q. Zhao, P. Wang and X. Lu, *Chem. Commun.*, 2014, **50**, 7318–7321.

18 B. J. Moon, Y. Oh, D. H. Shin, S. J. Kim, S. H. Lee, T.-W. Kim, M. Park and S. Bae, *Chem. Mater.*, 2016, **28**, 1481–1488.

19 M. J. Krysmann, A. Kelarakis, P. Dallas and E. P. Giannelis, *J. Am. Chem. Soc.*, 2012, **134**, 747–750.

20 J. Deng, Q. Lu, N. Mi, H. Li, M. Liu, M. Xu, L. Tan, Q. Xie, Y. Zhang and S. Yao, *Chem. Eur. J.*, 2014, **20**, 4993–4999.

21 S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angew. Chem. Int. Ed.*, 2013, **52**, 3953–3957.

22 V. Strauss, J. T. Margraf, C. Dolle, B. Butz, T. J. Nacken, J. Walter, W. Bauer, W. Peukert, E. Spiecker, T. Clark and D. M. Guldi, *J. Am. Chem. Soc.*, 2014, **136**, 17308–17316.

23 B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo, S. Prantl, R. Godin, J. R. Durrant and E. Reisner, *Angew. Chem. Int. Ed.*, 2017, **56**, 6459 –6463.

24 J. Schneider, C. J. Reckmeier, Y. Xiong, M. Von Seckendorff, A. S. Susha, P. Kasa and A. L. Rogach, *J. Phys. Chem. C*, 2017, **121**, 2014–2022.

25 G. A. M. Hutton, B. Reuillard, B. C. M. Martindale, C. A. Caputo, C. W. J. Lockwood, J. N. Butt and E. Reisner, *J. Am. Chem. Soc.*, 2016, **138**, 16722–16730.

26 M. K. Barman, B. Jana, S. Bhattacharyya and A. Patra, *J. Phys. Chem. C*, 2014, **118**, 20034–20041.

27 F. Arcudi, L. Dordevic and M. Prato, *Angew. Chem. Int. Ed.*, 2016, **55**, 2107–2112.

28 M. Righetto, A. Privitera, I. Fortunati, D. Mosconi, M. Zerbetto, M. L. Curri, M. Corricelli, A. Moretto, S. Agnoli, L. Franco, R. Bozio and C. Ferrante, *J. Phys. Chem. Lett.*, 2017, **8**, 2236–2242.

29 Y. Song, S. Zhu, S. Zhang, Y. Fu, L. Wang, X. Zhao and B. Yang, *J. Mater. Chem. C*, 2015, **3**, 5976–5984.

30 X. Wang, L. Cao, S.-T. Yang, F. Lu, M. J. Meziani, L. Tian, K. W. Sun, M. A. Bloodgood and Y.-P. Sun, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 5310–5314.

31 W. Liu, C. Li, Y. Ren, X. Sun, W. Pan, Y. Li, J. Wang and W. Wang, *J. Mater. Chem. B*, 2016, **4**, 5772–5788.

32 N. Dhenadhayalan, K.-C. Lin, R. Suresh and P. Ramamurthy, *J. Phys. Chem. C*, 2016, **120**, 1252–1261.

33 M. Fu, F. Ehrat, Y. Wang, K. Z. Milowska, C. Reckmeier, A. L. Rogach, J. K. Stolarczyk, A. S. Urban and J. Feldmann, *Nano Lett.*, 2015, **15**, 6030–6035.

34 K. A. S. Fernando, S. Sahu, Y. Liu, W. K. Lewis, E. A. Guliants, A. Jafariyan, P. Wang, C. E. Bunker and Y.-P. Sun, *ACS Appl. Mater. Interfaces*, 2015, **7**, 8363–8376.

35 W. Wu, L. Zhan, K. Ohkubo, Y. Yamada, M. Wu and S. Fukuzumi, *J. Photochem. Photobiol. B*, 2015, **152**, 63–70.

36 P. Yang, J. Zhao, J. Wang, H. Cui, L. Li and Z. Zhu, *RSC Adv.*, 2015, **5**, 21332–21335.

37 X. Xu, Z. Bao, G. Zhou, H. Zeng and J. Hu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 14118–14124.

38 L. Cao, S. Sahu, P. Anilkumar, C. E. Bunker, J. Xu, K. A. S. Fernando, P. Wang, E. A. Guliants, K. N. Tackett and Y.-P. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 4754–4757.

39 S. Sahu, Y. Liu, P. Wang, C. E. Bunker, K. A. S. Fernando, W. K. Lewis, E. A. Guliants, F. Yang, J. Wang and Y.-P. Sun, *Langmuir*, 2014, **30**, 8631–8636.

40 P. Yang, J. Zhao, J. Wang, H. Cui, L. Li and Z. Zhu, *ChemPhysChem*, 2015, **16**, 3058–3063.

41 B. C. M. Martindale, G. A. M. Hutton, C. A. Caputo and E. Reisner, *J. Am. Chem. Soc.*, 2015, **137**, 6018–6025.

42 B. C. M. Martindale, E. Joliat, C. Bachmann, R. Alberto and E. Reisner, *Angew. Chem. Int. Ed.*, 2016, **55**, 9402–9406.

43 L. Wang, S. J. Zhu, H. Y. Wang, S. N. Qu, Y. L. Zhang, J. H. Zhang, Q. D. Chen, H. L. Xu, W. Han, B. Yang and H. B. Sun, *ACS Nano*, 2014, **8**, 2541–2547.

44 M. A. Gross, A. Reynal, J. R. Durrant and E. Reisner, *J. Am. Chem. Soc.*, 2014, **136**, 356–366.

45 T. Sakai, D. Mersch and E. Reisner, *Angew. Chem. Int. Ed.*, 2013, **52**, 12313–12316.

46 H. Yan, J. Yang, G. Ma, G. Wu, X. Zong, Z. Lei, J. Shi and C. Li, *J. Catal.*, 2009, **266**, 165–168.

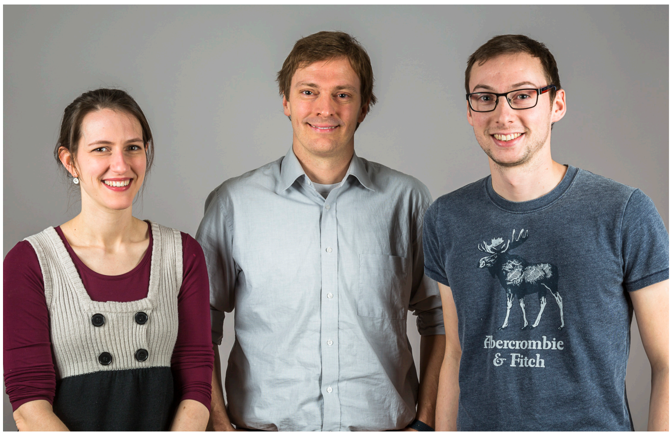
47 K. Han, M. Wang, S. Zhang, S. Wu, Y. Yang and L. Sun, *Chem. Commun.*, 2015, **51**, 7008–7011.

48 D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem. Int. Ed.*, 2014, **53**, 9240–9245.

49 M. Zhu, Y. Du and P. Yang, *Catal. Sci. Technol.*, 2013, **3**, 2295–2302.

50 A. S. Weingarten, R. V Kazantsev, L. C. Palmer, M. McClendon, A. R. Koltonow, A. P. S. Samuel, D. J. Kiebala, M. R. Wasielewski and S. I. Stupp, *Nat. Chem.*, 2014, **6**, 964–970.

Photograph of authors:



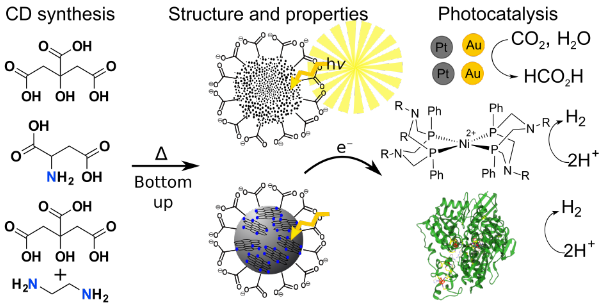
Left to right: Georgina A. M. Hutton, Erwin Reisner and Benjamin C. M. Martindale

Georgina A. M. Hutton obtained her BSc (Hons) degree from the University of Sydney under the supervision of Assoc. Prof. Tony Masters and Prof Thomas Maschmeyer where she worked on iron oxide nanoparticles and chalcogenide quantum dots for nanomedicine applications. She is currently writing-up her PhD in the group of Dr Erwin Reisner. Her research focused on developing carbon dot photocatalytic systems, in particular for application with enzymes.

Erwin Reisner is a University Reader in Energy and Sustainability in the Department of Chemistry at Cambridge University, where he also heads the Christian Doppler Laboratory for Sustainable SynGas Chemistry. He is a co-director of the EPSRC Centre for Doctorial Training in Nanoscience and Nanotechnology and he directs the UK Solar Fuels Network, which coordinates the national activities in artificial photosynthesis.

Benjamin C. M. Martindale recently obtained his PhD at the University of Cambridge as an Oppenheimer fellow under the supervision of Dr. Erwin Reisner. His thesis was about the development of carbon dots for solar H_2 evolution using molecular catalysts. He is currently a postdoctoral research fellow at Harvard University working on sustainable approaches to commodity chemicals synthesis under the supervision of Prof. Daniel Nocera.

Table of Contents figure and text:



‘This Tutorial Review discusses the rational development of structurally distinct carbon dots and their application in photocatalytic fuel synthesis.’