catalysts

Review

The Behavior of Carbon Dots in Catalytic Reactions

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Abstract: Since their discovery in 2004, carbon dots (CDs), with particle sizes < 10 nm, have found use in various applications, mainly based on the material's fluorescent properties. However, other potential uses of CDs remain relatively unexplored when compared to other carbon-based nanomaterials. In particular, the use of CDs as catalysts and as supports for use in catalytic reactions, is still in its infancy. Many studies have indicated the advantages of using CDs in catalysis, but there are difficulties associated with their stability, separation, and aggregation due to their small size. This small size does however allow for studying the interaction of small catalyst particles with small dimensional supports, including the inverse support interaction. However, recent studies have indicated that CDs are not stable under high temperature conditions (especially >250 °C; with and without a catalyst) suggesting that the CDs may agglomerate and transform under some reaction conditions. The agglomeration of the metal in a CD/metal catalyst, especially because of the CDs agglomeration and transformation at high temperature, is not always considered in studies using CDs as catalysts, as post-reaction analysis of a catalyst is not always undertaken. Further, it appears that under modest thermal reaction conditions, CDs can react with some metal ions to change their morphology, a reaction that relates to the metal reducibility. This review has thus been undertaken to indicate the advantages, as well as the limitations, of using CDs in catalytic studies. The various techniques that have been used to evaluate these issues is given, and some examples from the literature that highlight the use of CDs in catalysis are described.

Keywords: carbon dots; thermal stability; metal support; heterogeneous catalysis

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1. Introduction

Carbon allotropes are multifunctional materials, due to their unique physical and chemical properties. Carbon allotropes can be chemically modified by other elements via functionalization or doping, and they can also be used in combination with other materials to form carbon–carbon or metal–carbon composite materials [1]. The modification of carbon allotropes helps to enhance their properties, and also widens their spectrum of applications. Hence, carbon allotropes such as graphite, graphene, fullerene, carbon nanotubes (CNTs), carbon nanofibers (CNFs), carbon black (CB), carbon nano-onions (CNOs), carbon spheres (CSs) and carbon dots (CDs) have been successfully incorporated in fields such as nanomedicine, electronics, sensor fabrication and catalysis [1–4].

Carbon's many allotropes have shown great potential when used as a catalyst support, and the carbon can even act as a catalyst in its own right [1,5]. The enormous interest in carbon-based support materials is due to their surface chemistry, variable surface area and the porosity of the carbon [1,5]. The use of carbon allotropes is also enhanced by their electronic properties, which are influenced by their structure and the carbon atom valence. The electronic effects can promote a high dispersion of the supported (metal) catalyst, and also of surface defects, and this can enhance their capability for gas storage, adsorption and/or separation processes [5,6].

Heterogeneous metal catalysts usually comprise a metallic catalyst that is anchored or supported on the surface of a material that serves to enhance the surface area of the metal while also improving the metal stability during chemical reactions [7]. Support materials are important for immobilizing and anchoring the active metal catalyst, improving its dispersion and durability, and aiding it in avoiding deactivation during a catalytic reaction [8]. Many studies have shown that a catalytic reaction rate is influenced by the catalyst dispersibility [9]. Metal–support interactions (MSI) are an important factor to consider when selecting a catalyst support, as the support directly influences the dispersibility, sintering, reducibility, and overall performance of the catalyst. MSIs are effects measured by the physical and chemical interactions between the metal catalyst and the support [10–12]. The stronger the MSI, the more resistant the catalyst is to deactivation via sintering during a reaction [12,13]. Carbon, in its various allotropes, generally forms a weak MSI with a metal catalyst. However, the MSI can be improved by means of functionalizing or doping of the carbon surfaces with heteroatoms. These effects create defects in the carbon nanostructure, and also alter the electronic properties of the carbon allotrope. Consequently, the dispersibility of the metal catalyst is increased and metal sintering/deactivation is reduced by doping/functionalization [12].

Most carbon allotropes are relatively ‘stable’ under harsh reaction conditions; this makes them less susceptible to structural and/or chemical changes during catalysis [12]. This is important, because the structural disintegration of a catalyst support can lead to deactivation of a catalyst. The properties of carbon supports have been studied under different conditions using varying pH, solvents, temperatures, time, etc. For example, carbon allotropes have successfully been used as supports for titania in photocatalysis [14], platinum in electrocatalysis [15], and cobalt, iron and ruthenium in catalysis for fuel production under a wide range of reaction conditions [12].

Carbon dots (CDs) are a fairly new type of carbon nanomaterial. CDs are defined as zero-dimensional quasi-spherical carbon nanomaterials with particle sizes below 10 nm [16]. Their general structure consists of sp^2- and sp^3-type carbons, with a large number of functional groups or polymer chains attached to their surfaces [17–19]. Numerous reviews have summarized the potential of CDs in many traditional and emerging areas, such as photoluminescence (PL) and photoelectrochemical-driven sensing, catalysis, imaging, and biomedicine applications, where they have been shown to be superior to other carbon allotropes [16,20]. Further, CDs, unlike metal-based quantum dots, have a high water dispersibility, low toxicity, and good biocompatibility [21]. Thousands of papers have been written about CDs in terms of their synthesis, characterization and uses. The aim of this review is not to reproduce the information on the synthesis, applications, and the properties of CDs, which has been summarized in scores of reviews, but to indicate the transformation of CDs into other shaped materials, which is associated with temperature and the presence of catalysts.

CDs, like many carbon allotropes, have been used as both catalysts and catalyst ‘supports,’ and reviews on the use of CDs both as carbocatalysts and as composites with metal and metal oxide supports have been reported [22–24]. As is known, there are many advantages to using CDs and CD/metal complexes in catalysis, but there are also limitations on the use of these carbons. For example, in many of the studies it is not clear if the integrity of the carbon has been retained, and the degree to which metal sintering has taken place during their synthesis or in their catalytic reactions. Indeed, some studies have revealed that CDs and CD/metal materials, lose their shape/size during reaction, especially at high temperatures (>100 °C) and in the presence of easy-to-reduce metals. This has been observed in carbon–carbon coupling reactions [25], hydrogen evolution reactions [26] and hydrogenation reactions, where the CDs either decomposed or were transformed into other carbon structures [27,28].

In this review we have evaluated data on the use of CDs and CD/metal catalysts in catalysis. One of the advantages of using these two types of catalysts, relative to more typical catalyst systems, relates to the easy access to CDs which can be produced at low cost from any carbon source, including waste materials. Since the metal particles are either the same size or larger than the CDs, the terminology CD/metal has been used to describe the catalysts made from CDs and metal particles. We have not comprehensively reviewed all reports where CDs and CD/metal materials have been used in catalysis, but have rather chosen some typical literature reactions to highlight the challenges associated with the use of CDs in catalytic reactions. In particular, we wish to highlight the structural changes or destruction of the CDs that can occur during a reaction that can ultimately lead to metal agglomeration. The techniques that can be used to evaluate the stability of CDs, especially post reaction, are discussed with special reference to metal and carbon agglomeration.

2. The Structure of Carbon Dots (CDs)

2.1. Types of CDs

CDs are usually divided into four distinct subgroups. These are graphene quantum dots (GQDs), carbon quantum dots (CQDs), carbon nanodots (CNDs) and carbonized polymer dots (CPDs) [29–32] (see Figure 1). In the literature, these four types are usually called carbon dots (CDs), and generally they are all regarded as being similar in their catalytic (and many other) properties. However, this may not always be true. To date, this issue has not been explored, and there is evidence to suggest that the different CDs will react differently as a function of temperature and when in the presence of metals that can aid their decomposition [27]. In this review, the term CDs will be used for all carbon dots shown in Figure 1.

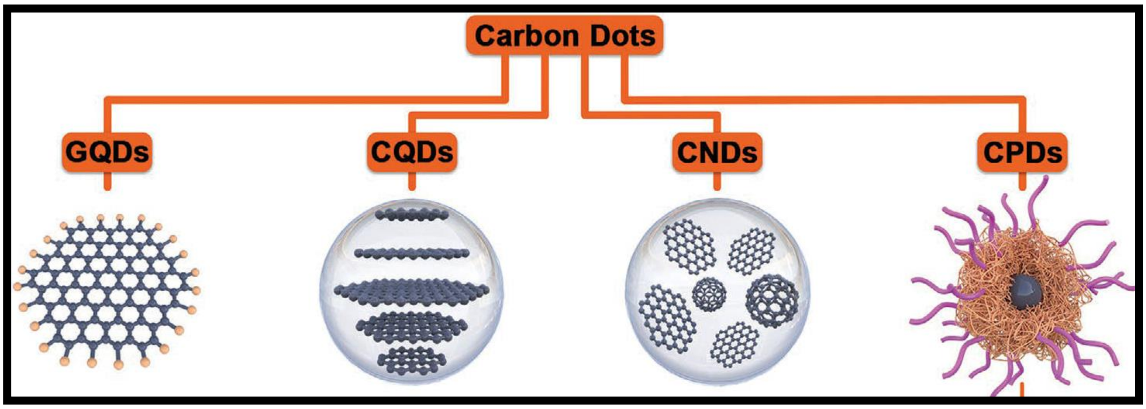

Figure 1. The proposed representative structures of a graphene quantum dot (GQD), carbon quantum dot (CQD), carbon nanodot (CND), and carbonized polymer dot (CPD). Adapted with permission from Wiley-VCH Verlag [33].

CDs must be differentiated from carbon nano-onions (CNOs) and onion-like nanocarbons (OLNCs), which are also in the nanometer range [34]. CNOs and OLNCs have structures with carbon layers similar to those found in a concentric-like onion structure (see Figure 2), while CDs (Figure 1) tend to have the carbon layers arranged as parallel graphene sheets (Figure 1). The CNOs/OLNCs are prepared at high temperatures (>500 °C), while CDs are typically prepared at T < 200 °C. This results in differences in their thermal stabilities that impact on their chemical properties.

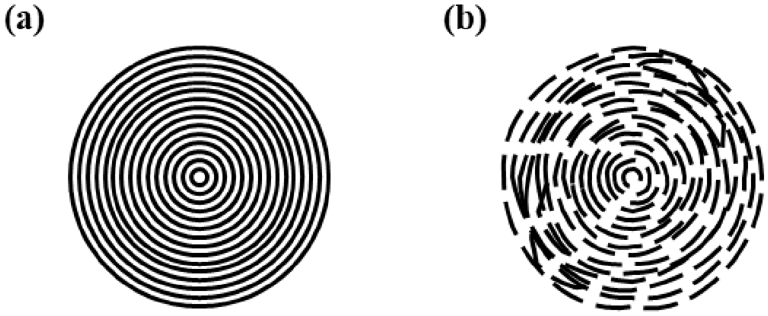

Figure 2. Graphical representation showing the differences between (**a**) a carbon nano-onion (CNOs), and (**b**) an onion-like nanocarbon (OLCN).

There are two methods used to modify the structure/surface of CDs. One method is by functionalization, and this is described in more detail below. The other is by making the CDs with precursors in which reactants provide non-carbon atoms to the CD. This is referred to as doping. The most typical dopant is nitrogen, and the addition thereof in quantities ranging from 1 to 10% can lead to substantial changes in the surface chemistry of a carbon material, including CDs. Many CDs have also been doped with metal ions, and this modification can also impact their chemistry and catalytic reactions [35].

2.2. *Surface Properties of CDs*

CDs have many useful properties associated with their small size and functional groups. While the surface of the CD is important in correlating with their physical and chemical properties, the role of the core is still poorly understood [36]. Thus, most studies on the use of CDs that have been performed have related to their surface chemistry [37]. The surface of a CD contains many functional groups, and these groups are responsible for the catalytic activity of the CD. CDs are typically synthesized with both oxidizing and reducing groups that are used to bring about organic redox transformation reactions. These functional groups are also used to modify their PL spectra. Their surface chemistry can be modified by classical procedures associated with modifying any carbon surface. The surface modification can be achieved by covalent and non-covalent bonding of reactants with the CD surface, as reported in work by Yan et al. [38]. This type of modification is carried out to improve the properties of the CDs for a specific application such as biosensing, or metal and molecule detection [38]. Examples are shown in Figure 3.

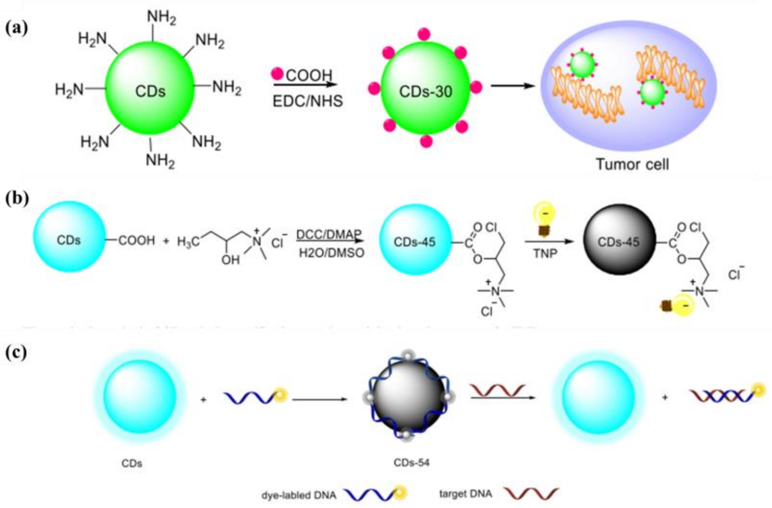

Figure 3. Post-surface functionalization of different CDs via (**a**) amide coupling-type reaction (covalent bonding), (**b**) esterification (covalent bonding) and (**c**) pi–pi interactions (non-covalent bonding). Adapted with permission from [38], Copyright 2018, Springer Nature.

The surface charge on the CD can be modified by changing the functional groups. The starting precursors can be manipulated in order to obtain CDs that are either hydrophilic or hydrophobic [39]. Typically, CDs are synthesized using multifunctional organic chemicals, and this produces hydrophilic CDs. Similarly, hydrophobic CDs can be produced using aliphatic chemicals such as dodecylamine [39,40]. It is further noted that the surface charge on the CD can be modified by changing the functional groups, and this can be done without post modification of the CDs [41]. Thus, CDs with different surface charges [41,42] and polarities [40,43] have been reported. For example, most CDs are made with a negative charge (associated with COO^- groups). An important approach to generate positively charged CDs is by modifying CD surfaces with ionic liquids (ILs) and then annealing the material at *ca.* 240 °C. The IL-covered CDs were then used to detect metal ions in solution [41] or to make inks [42].

CDs can also react with themselves. For example, CD–CD linkages have been achieved from CDs that were made from C_{60} fullerene (by a base reaction). The CDs self-assembled when they were freeze dried [44]. After annealing (600–800 °C), the materials were used in capacitor studies. The self-assembly was proposed to be achieved with ice crystals acting as a template [44]. Studies have also been carried out in which a chemical reaction between two different CDs produced CD assemblies with surface properties associated with the different CDs used. Zhou et al. made three different types of CDs, and under room temperature conditions and with different CD combinations, they were linked together via the functional groups on the CDs. In one instance, the CDs, after reaction with each other, gave nanostructures that were used as drug nanocarriers [45,46]. Many other examples have also been reported [27].

Self-assembly of CDs has been achieved by the use of tannic acid. Modification of the functional groups on the CDs with ionic liquids provided for a good interaction of the CDs, with the negative charges on the tannic acid allowing for formation of assembled species (in some cases, $d_{CD} > 100$ nm), which were readily detected by Tyndall cone measurements and transmission electron microscopy (TEM) measurements [47]. Supramolecular organization of CDs after alkylation of amine-functionalized CDs [39] has led to a series of alkyl-functionalized CDs, which could be separated by chromatography and that formed an organized structure in the solid state. The new assemblies were used in nonlinear optical studies [40]. A recent extension of this work described the self-assembly of CDs made from chiral cholesteryl to make thermotropic liquid crystals with a range of architectures [43]. These self-assembled CDs could provide an entry into novel structures for use as both carbocatalysts and to make CD-metal catalysts.

A key property associated with a CD surface is its hydrophilicity, which has led to the extensive use of CDs in medicinal chemistry [48]. Another important property is their photoluminescence (PL), which has allowed them to be used in sensing devices [49]. Typically, addition of a metal reactant to the CD functional groups results in a decrease in their PL spectrum, and hence these types of experiments are usually conducted to detect metal ions within various media [50]. The changes in the PL spectra of CDs will be influenced, in a catalytic reaction, by the varying concentrations of products and reactants that could bind to the CD surface, thus allowing for the exploration of a reaction mechanism. The addition of polymers to a CD surface has been found to lead to improved PL properties [29].

Due to their small size (<10 nm), the separation and purification of CDs is not simple. Further, yields of the purified CDs are not always reported, and it is thus difficult to assess the usefulness of many synthetic strategies. While CDs have a small size, their surface area tends to vary, and can be lower than expected. The surface area can vary, for example, between 16.4 $m^2 g^{-1}$ [51] and 1690 $m^2 g^{-1}$ [52].Thus, interaction with a metal ion or particle will be limited by this property. However, the many surface groups can be used to reduce metal ions to metal particles and in so doing lead to the formation of small metal particles, by limiting the site of the reduction. As expected, when CD surfaces, as in all carbons, are doped with N atoms, metal particle agglomeration is reduced [53].

The role of carbons as supports is limited by their reactions under oxygen, hydrogen or inert gases. In the presence of oxygen, most carbons will oxidize (to CO, CO_2) below 600 °C [54,55], while under H_2, the carbon can react to form CH_4, typically at temperatures above 500 °C [56]. Under an inert atmosphere, surface groups on the carbon can be removed at temperatures dependent on the carbon-to-element bond. In the absence of a catalyst, and under an inert atmosphere, the carbon core can be stable to temperatures above 600 °C. CDs, because of their size, have a high surface-to-bulk (core) carbon atom ratio [57]. Thus, all the reactions listed above can be expected to be modified when CDs are used, in relation to reactions with larger carbon molecules.

2.3. Synthesis of Carbon Dots and Their Application as Reducing Agents

Many papers and review articles have been written on the synthesis of CDs and this topic will not be discussed in detail here. CDs can be synthesized by "top-down" procedures, by cutting down larger carbon allotropes such as graphene, fullerene and CNTs using strong oxidizing agents like sulphuric and nitric acid [58]. The CDs can also be prepared by the "bottom-up" process, and are generally made from precursors that contain functional groups that are typically retained from their synthesis precursors [29]. For example, CDs can be prepared from highly oxygenated starting materials such as ascorbic acid, sucrose, and citric acid [59,60], using a "bottom-up" synthesis approach (Figure 4). Further functionalization using a variety of methods can be carried out to advance the surface chemistry and other properties of the CDs [29,38]. The CD surface groups affect their overall chemical behavior, such as their electronic properties. These electronic properties have been exploited for oxidizing and reducing metals, and in this way generate CD/metal catalysts [24,61].

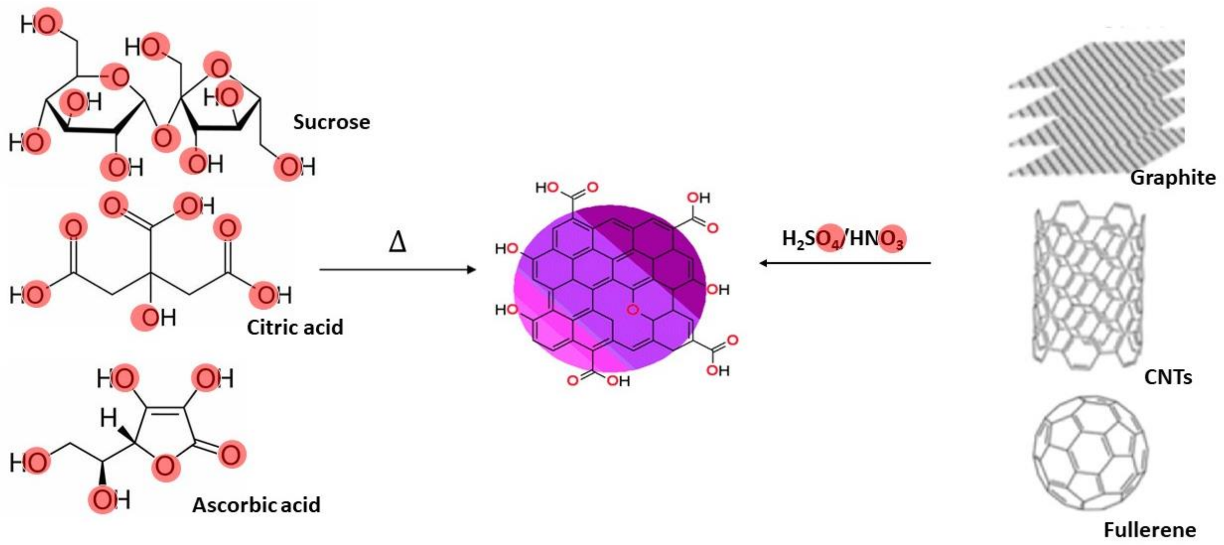

Figure 4. Schematic presentation of the "bottom-up" and "top-down" CDs synthesis procedures from oxygen-rich starting materials (highlighted in red) or by reacting 'large' carbon allotropes with oxidizing acids.

There are numerous studies that have been reported in which CD surface oxygen groups have been modified/reduced after the CDs have been synthesized. These are referred to as reduced CDs (r-CDs). Reducing agents used include $NaBH_4$, ascorbic acid, sodium citrate, and hydrazine hydrate, with $NaBH_4$ being the most effective reducing agent [62]. The r-CDs have been reported to have better luminescence properties than their pristine (more highly oxidized) CD counterparts [37]. These r-CDs have been used to reduce strong oxidizing agents such as $KMnO_4$, KIO_4 and $K_2Cr_2O_7$. These reagents in turn have been used to selectively oxidize the O-H groups in r-CDs to C=O [63]. They have also been used to reduce metal ions, to generate metal catalysts.

3. Carbon Dots in Catalysis

The main role of any carbon in the field of catalysis is that of the carbon acting either as a catalyst (called carbocatalysis) or as a support for a heterogenous catalyst [22]. Because of their small size, CDs add this extra feature of support dimension to their use in catalysis, relative to other carbon supports.

3.1. Applications of Carbon Dots-Based Catalysts

Excellent reviews exist on the use of CDs as carbocatalysts [22–24,64,65] in thermal, photocatalytic and electrocatalytic applications. Many simple and classic chemical transformation have occurred in the presence of CDs (Figure 5) [24].

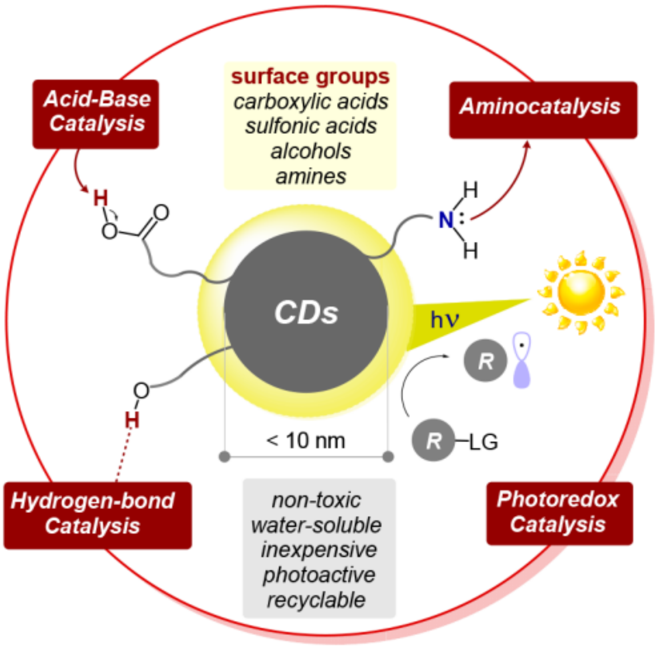

Figure 5. CD application in nano-organocatalysis and photocatalysis. (Adapted with permission from [24] Copyright 2020, American Chemical Society).

As will be seen in these reviews, much focus has been on their surface functionalization and use, rather than on morphology changes of the CDs observed after or during reactions. This is understandable, as in most instances very small amounts of catalyst are used, and re-use studies have indicated that the carbon 'catalyst' is stable after many reaction cycles. However, some studies have shown that the CDs can be converted into other morphologies, typically when reactions occur at high temperatures or in the presence of easily reduced metal ions. The difficulty in using smaller carbon particles (CDs) was hinted at in an early review on the use of nanocarbons in catalysis, viz. "However, it is useful to comment that it is not always proven that functionalized nanocarbons act as real catalysts; e.g., they are not consumed during the reaction" [66]. Some examples where post-reaction studies of CDs have been reported and have revealed CD conversion to other morphologies are given below.

- A limitation of using carbon dots in catalysis

The conversion of CDs into carbons with a different framework was noted in early studies on the synthesis of CNTs when the CDs were decomposed at high temperature in porous anodic aluminas [67]. Later studies showed that CDs, made from acetone, could be easily converted into carbons called porous carbon frameworks (PCFs) at high temperatures of between 400 °C and 800 °C [68]. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR) studies showed that conversion of the CD morphology occurred. A mechanism involving Na ions interacting with the CDs was suggested, in which carbon nanosheets were formed by CD decomposition to carbon atoms which then self-assembled to form sheets; these materials were used in electrochemical studies [68]. The synthesis of P- and N-doped porous materials (NPCNs) was also achieved by adding the above CDs to amino trimethylene phosphonic acid, and heating to 800–1000 °C (Figure 6). The NPCNs and porous carbon frameworks (PCFs) were used in electrochemical studies that gave exceptional behavior as metal-free ORR catalysts [69].

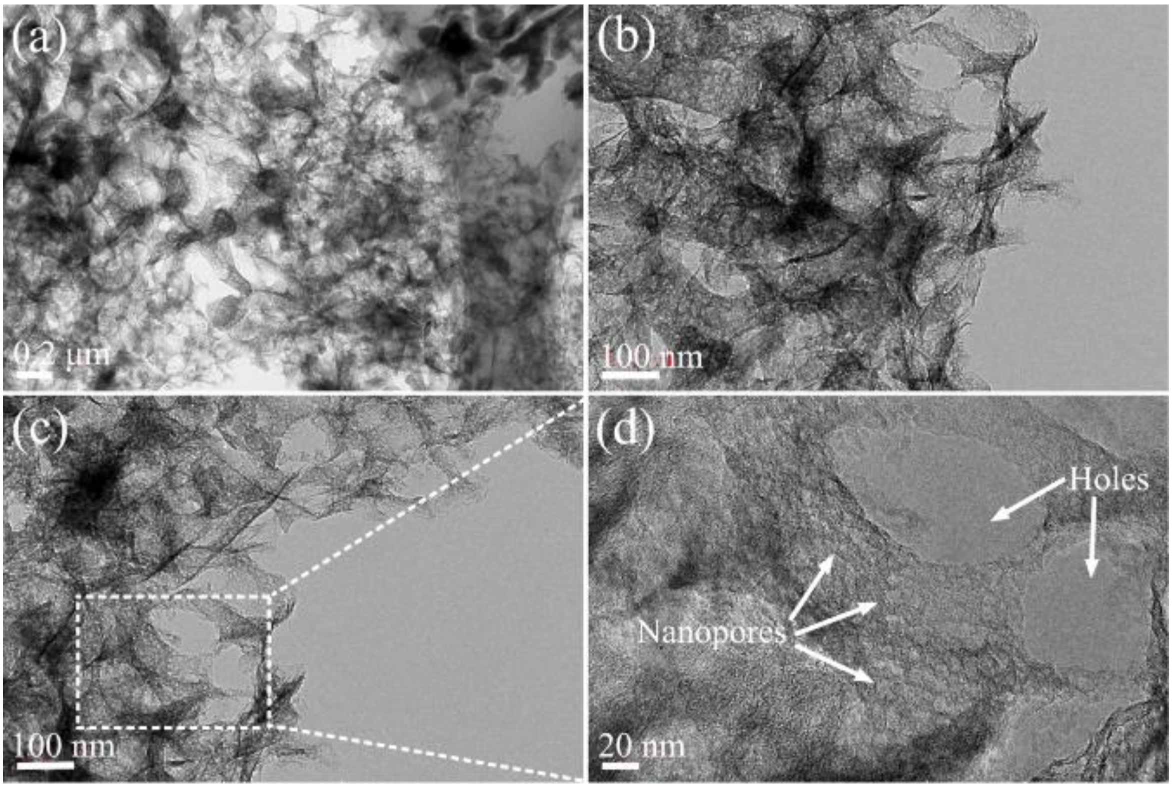

Figure 6. TEM images of NPCN-900 (i.e., carbon heated to 900 °C) at (**a**) 0.2μm scale, (**b**,**c**) 100 nm scale, highlighting the nanoporosity and holes in their structure (**c**), as well as an (**d**) HRTEM (20 nm scale) image of the highlighted nanopores and holes (reproduced with permission from [69], 2017 Elsevier Ltd.).

The reaction of CDs made from acetaldehyde mixed with $NaHPO_4$ at temperatures ranging from 400 °C to 900 °C gave P-doped carbon nanosheets (P-CNSs) [70]. TEM and SEM studies of the CDs (made without the P addition) and the P-CNSs showed that sheet-like materials had been made. These materials were studied for their electrochemical behavior. They showed good sodium ion storage when used as an anode material for sodium-ion batteries [70]. The thermal conversion of CDs made from sucrose or glucose [71,72] has been monitored, and the data clearly indicated a simple morphology change to a layered carbon material with graphene-like structure. These conversion reactions are described in Section 6. In summary, numerous examples have shown that CDs can readily convert to sheet-like materials under thermal conditions.

3.2. *Metals Doped into CDs and Metals Supported on CDs as Catalysts*

Metals salts can be added to CDs in two different ways: (i) during the CD synthesis to give metal-doped CDs [35] and (ii) after reaction, to give metal-supported CD materials. In the literature, the catalysts in which the metal is (i) on/in the surface of a CD, (ii) covered by a carbon layer or, (iii) on a carbon layered material made from a CD, have been given various names. In this review all will be referred to as a CD/metal material, to indicate that the CD is generally smaller than the metal particle.

Different types of CD/metal composites have been studied as catalysts in a variety of organic reactions, including carbon–carbon bond formation, oxidation, reduction, hydrogenation, heterocyclic synthesis, multi-component synthesis, and simple organic conversions under light- or mild-temperature conditions (≤100 °C). This data has been reviewed [22,23]. Furthermore, CDs have also been studied as catalysts in a variety of nano-organocatalytic and nano-photocatalytic reactions [24]. For example, Li et al. have reported on the use of novel nanocomposites made by doping CDs with a variety of metals (Cu, Zn, Co, Fe, etc.) to improve the optical and electronic properties of the CDs for use in photo-/electrocatalysis [35].

When considering data from the literature, it is clear that the mixture of metal ions and CDs at low temperatures leads to a range of possible chemical interactions. Thus, reports have shown that addition of metal ions leads to (i) coordination compounds with the CD surface [73], (ii) metal reduction by the CD surface groups [74], and even (iii) reduction of the metal by the carbon core [25]. These reactions are discussed below.

The ability of the CD core to reduce a metal is determined by the reducibility of the metal. Ellingham diagrams have been used to indicate the role of carbon in reducing bulk metal oxides to a metal, and some date indicating this are shown in Figure 7 [75]. Any metal oxide above the free energy of carbon in the diagram can be reduced by carbon. While it is expected that nano-sized metal oxides will have different phase diagrams and hence different free energy values from those in the Ellingham diagram, the differences will be small, and will allow for similar generalizations to be made. As can be noted, a reduction reaction can occur at T < 100 °C for some metals. Further, the addition of metal ions to carbon, where the metal appears below the carbon free energy line, will not be expected to bring about a reaction with carbon. Post analysis of reactions to support the above, where reported, suggest no reaction with the carbon CD core has occurred and that the CDs have retained their size/shape [35].

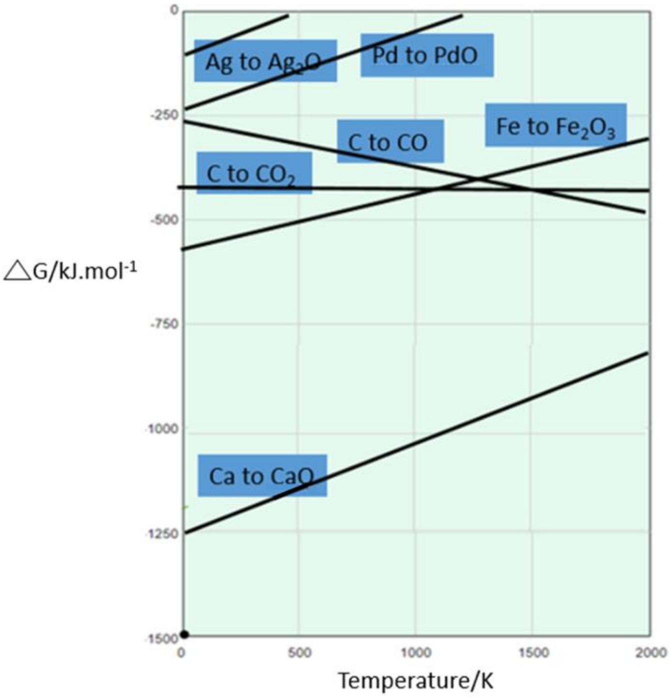

Figure 7. Ellingham diagram showing some metal oxides and carbon.

3.2.1. High-Temperature Reactions of Metals Supported on CDs

Studies have shown that when high-temperature reactions (T > 400 °C) are used to react metal ions with large spherical carbon materials, the carbon itself acts as a reducing agent and in so doing gives a surface with the metal particle 'embedded' in the carbon. For example, the reaction of Co ions with carbon spheres (d = *ca.* 450 nm) under an inert gas, at T *ca.* 450 °C, produced Co/C catalysts with small reduced Co particles for use in the Fischer–Tropsch (FT) reaction (Figure 8). These particle sizes compared with the sizes of Co particles produced under H_2 gas, but with a better ability to prevent Co agglomeration during the FT reaction [76]. The above suggests that the reduction of metal ions on carbon should be possible on smaller carbon spheres, the CDs. However, as the size of the carbon sphere is reduced, there comes a point at which the carbon and the metal particle will have similar sizes, and this could influence the resulting metal–carbon interaction.

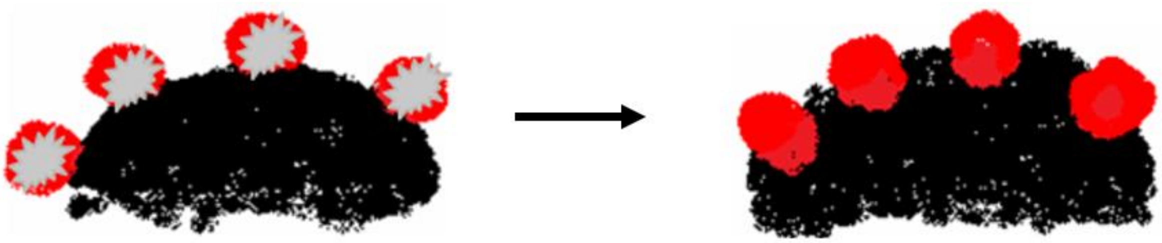

Figure 8. An illustration showing the reaction of CoO_x with a carbon sphere (cobalt oxide = ✹ ; cobalt metal = 🟥).

Indeed, the study of reactions in which the support is comparable in size to the metal is referred to as inverse support catalysis (Figure 9) [77–79]. While this concept is well known when metal oxide supports are used ($SiO_2/TiO_2/Al_2O_3$), this concept has rarely been exploited with carbon as the support.

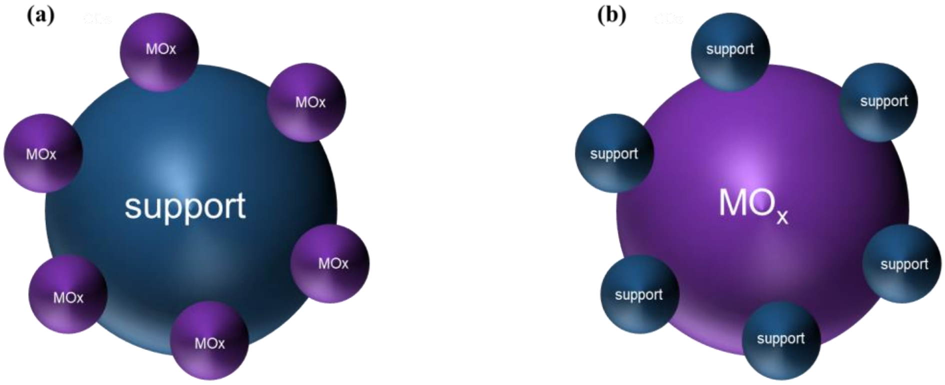

Figure 9. An illustration of (**a**) a conventional support; where small metal catalyst particles are dispersed on a large surface area support, and (**b**) an inverse support; small amounts of a support material are dispersed on the surface of a metal catalyst (forming "nano islands" around the metal).

A previous attempt was made to study catalysts made with Co and CDs (with similar small dimensions) in the Fischer–Tropsch reaction [28]. In the reaction (220 °C/10 bar pressure) the CDs were found to decompose, and this led to Co agglomeration. It is clear that both surface groups and the CD core were altered/removed in the reaction. The residual carbon support showed no CDs, and the CDs were completely transformed into a layered carbon material, as shown in Figure 10. The changes to the CDs were accompanied by the simultaneous reduction of the Co active metal phase. This data clearly illustrated how the support material changed alongside the active metal during the reduction treatment. It is unclear if the Co metal dictates the changes to the CDs, or vice versa.

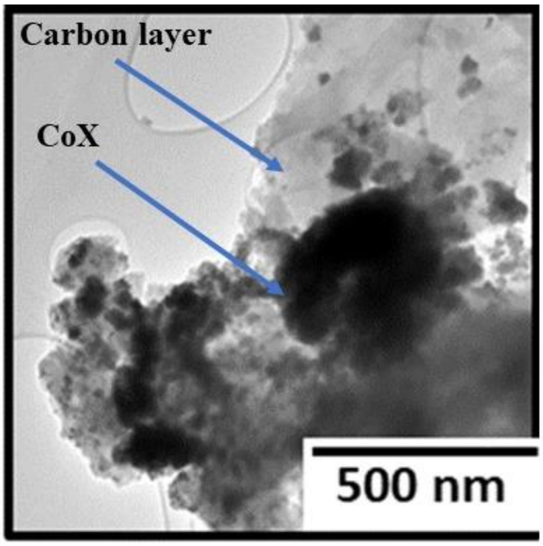

Figure 10. TEM image of CoX/CDs after reaction [28].

The data are consistent with the high-temperature studies of CDs in the absence of a catalyst (see [71]). This could limit the potential use of CDs as metal supports under reducing conditions, but may open up new ways of making metals supported on carbons with unexpected morphologies.

Other studies have also appeared in the literature in which similar observations have been made. CDs were prepared from citric acid and ethylenediamine. To the CDs was added nickel nitrate, and the mixture annealed under a nitrogen atmosphere at 300, 400, 500, and 600 °C for 3 h. The catalysts were used for the nitro-reduction of halogenated nitrobenzenes. The Ni@NCDs (NCD = nitrogen-doped CD) exhibited a nanosheet structure with Ni nanoparticles (6.88 nm) embedded in the NCDs, as observed in high-resolution TEM (HRTEM) images (Figure 11). Ni metal particles could be seen forming from NiO, even at 300 °C (detected by XRD studies) and the NiO had disappeared by 600 °C [80].

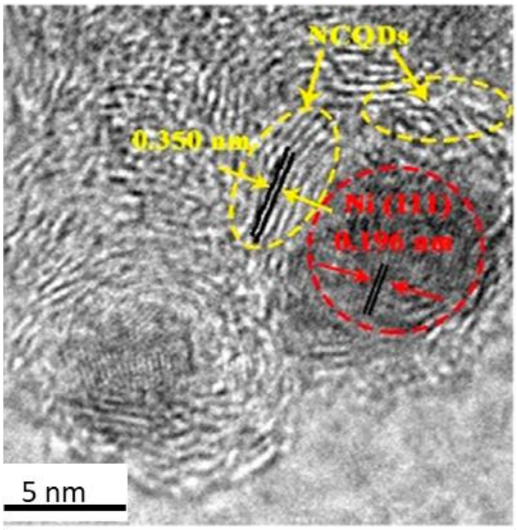

Figure 11. HRTEM image of Ni encompassed by carbon layers made from CDs (adapted with permission from American Chemical Society [80]).

Studies have also shown that CDs can be added to metal complexes to produce carbon covered metal oxide composites. Thus, the addition of CDs (made from acetone) added to $TiCl_3$ (and CTAB) after annealing at 800 °C gave carbon-covered TiO_2 (Figure 12). This provides an excellent method of producing total coverage of the TiO_2 by carbon. The petal-like structures were used to 'store' sodium ions for use in battery studies [81].

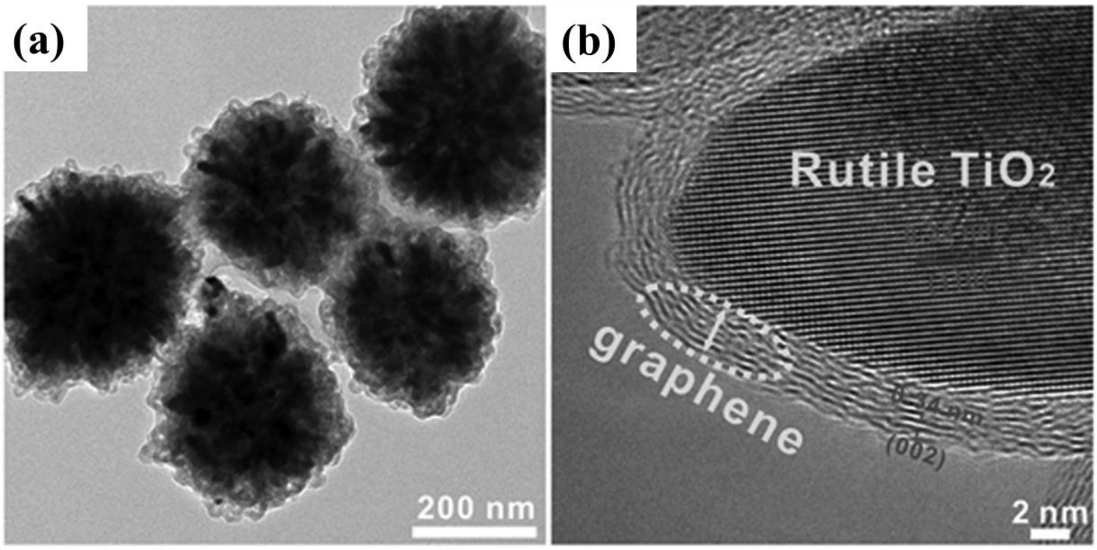

Figure 12. (**a**) TEM and (**b**) HRTEM images of titania covered by carbon layers made from CDs. Adapted with permission from [81], 2016 WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim, Germany).

These results are consistent with the data from Ellingham diagrams discussed above.

3.2.2. Low-Temperature Reactions of Metals Supported on/in CDs

Many reactions have been studied on metal-CD composites in catalysis at temperatures lower than 150 °C. In these studies, the CDs act as a reducing agent for the reduction of a metal salt (and as a capping agent) that is to be used as a catalyst. Any pre-existing O-H groups on the CDs are sufficient to reduce metal salts and metal oxides into a lower oxidation state, and even to the metallic state. It is less likely that the carbon core itself acts as a reducing agent at these low temperatures, but this will be influenced by the metal under study. In general, very few post-reaction studies have been reported to evaluate any changes that may have occurred at the surface or to the carbon after the use of the CD in chemical reactions.

- Examples where the CD structure is retained

Since CDs can reduce metals, it is important to use appropriate reaction conditions and metals (or metal oxides) to make CD/metal composites. Examples where CDs have been loaded onto metals (or metal oxides) and retained their morphology are given below. For example, simple coordination of metal ions onto the CD surface has been shown by studies on single-atom (Fe) catalysts that were added to CDs [82]. The coordination of Fe^{3+} with the carboxyl groups on the CD was studied by the extended X-ray absorption fine structure (EXAFS) technique, and results clearly indicated that the metal had not been reduced and that the Fe was directly linked to the CD [73]. The 'coordination' of CDs with metal oxide particles has also been observed, e.g., with Fe_3O_4 particles [83].

Studies in which the surface groups on CDs have been used to reduce metal ions and then bind metal particles to the CDs are well known. Ferrocene, acetone and hydrogen peroxide were used to make a CDs/Fe_3O_4@CS product in a solvothermal reaction that showed CDs (3.9–9.8 nm) and Fe_3O_4 embedded in a carbon sphere (CS). The average diameter of the nanocomposite, which resembled a pomegranate fruit, was 451.9 nm

(Figure 13). The HRTEM studies clearly showed the co-existence of the CDs and the FeOx particles. The CDs/Fe_3O_4@CS were used in peroxymonosulfate, persulfate and H_2O_2 studies, with and without visible-light illumination, and in ibuprofen degradation studies [84]. Interestingly, when commercial Fe_3O_4 particles and glucose/acetic acid (to make CDs) were heated at 140 °C for various time periods (4 h–18 h), the products formed showed CDs attached to the Fe_3O_4 particles [85]. In contrast, glutaric acid-functionalized Fe_3O_4 particles (14–20 nm) when reacted with CDs (2.5 nm) made from polyacrylamide at 270 °C gave Fe_3O_4 particles encapsulated by carbon layers [86].

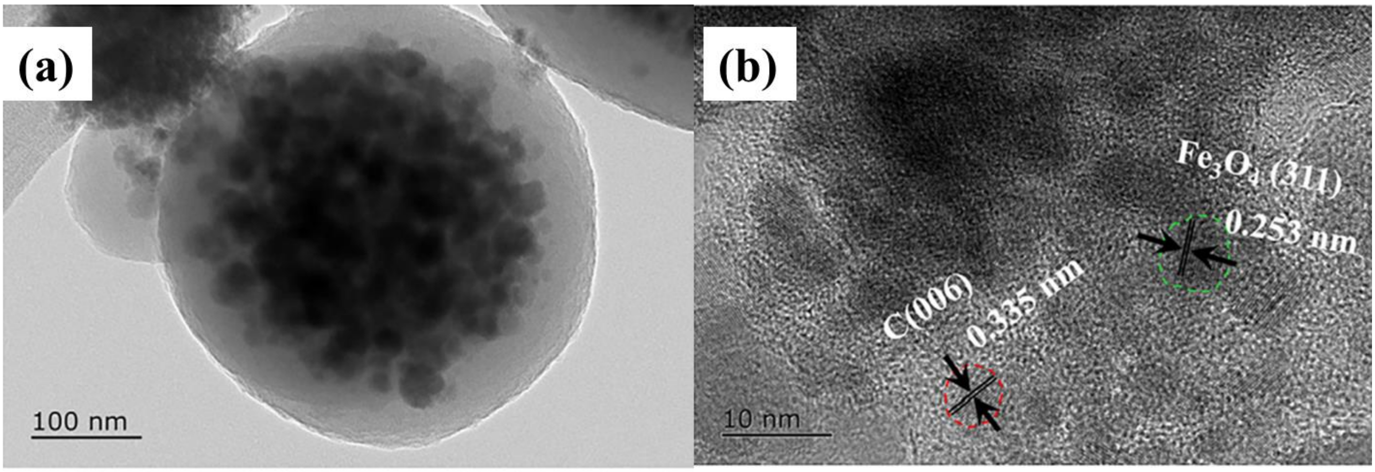

Figure 13. (**a**) TEM and (**b**) HRTEM images of a CDs/Fe_3O_4@CS catalyst at different magnifications. Adapted with permission from [84], Copyright 2020 Elsevier.

CDs were produced from ethylenediamine and citric acid, and these were added to copper acetate solutions in different CD/Cu ratios. The photocatalytic reaction of copper acetate and CDs produced Cu/CDs (4–6 nm), as detected by HRTEM studies (Figure 14). The interaction of the Cu with the CD can be clearly seen in the image. The larger the CD/Cu ratio, the larger the particles that were formed. The Cu/CD catalysts were used for the photocatalytic hydrogen evolution from lactic acid solutions [87].

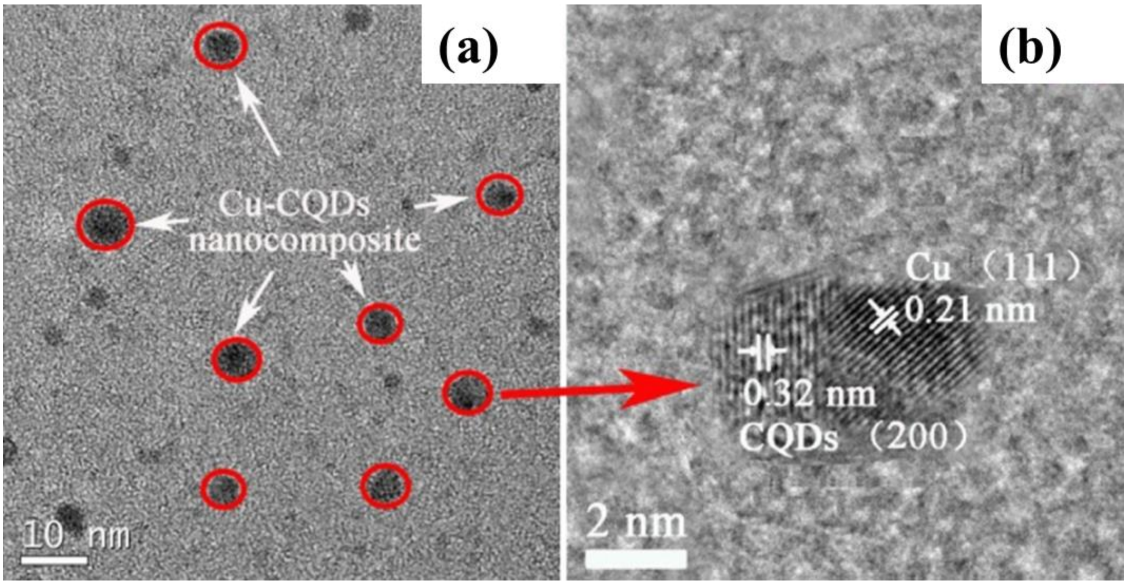

Figure 14. (**a**) TEM and (**b**) HRTEM images of Cu/CDs NPs (reproduced with permission from [87], Copyright 2017 Elsevier.

In another study, the polyoxometalate (POM) clusters, $Na_6[H_2PtW_6O_{24}]$ and $Na_6[H_2PtMo_6O_{24}]$, and carbon dots (CDs) were added together, and were used in the hydrogen oxidation reaction (HOR) in acid [88]. The CDs (*ca.* 5 nm) were made by electrolyzing graphite rods. The CDs improved the catalytic performance of the POM by enhancing the electron acquisition ability of Pt. The HRTEM image (Figure 15) clearly shows well-dispersed CDs on the POM.

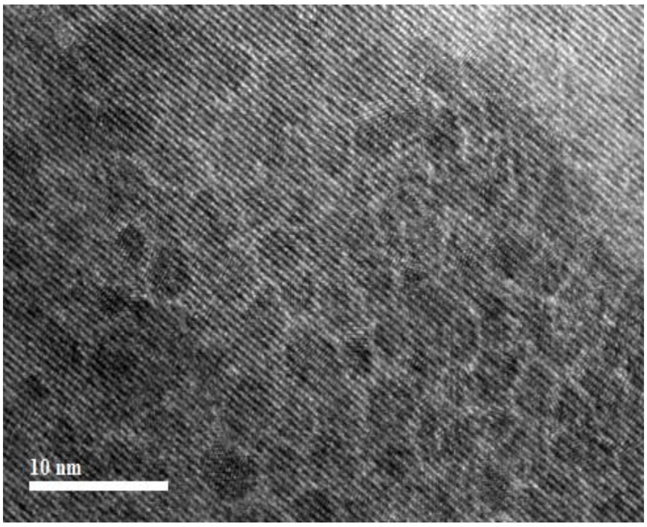

Figure 15. HRTEM image of $Na_6[H_2PtW_6O_{24}]$ with CDs observed on the surface. Adapted with permission from [88], Copyright 2021 Elsevier.

Lu et al. synthesized CDs from ethylene glycol by electrolyzing an electrolyte solution. The as-prepared CDs (particle size range: 2–4 nm) were then used to reduce $HAuCl_4$ and $AgNO_3$ to AuNPs and AgNPs, respectively, using a facile room temperature method [61]. HRTEM images showed the presence of metallic Au particles (12–14 nm). The particle size range for the Ag nanoparticles was 6 to 8 nm. In the study, analysis of the samples using FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS), before and after the reduction reaction, showed that the O-H group concentration on the CDs surface were significantly reduced, while the carbonyl group concentration increased post reduction. Additionally, the as-prepared metal nanoparticles showed good dispersibility, and this was associated with possible hydrogen bonding between the residual CD hydroxyl groups and the metal nanoparticles [61]. The CD-reduced metal catalysts were active in the colorimetric detection of H_2O_2 and glucose. Later, Yang et al. developed a AuPd bimetallic catalyst [89] using CDs prepared from ethylene glycol following the procedure reported by Lu et al. [61]. The reduction of the metals by CDs was also associated with the presence of the hydroxyl functional groups on the surface of the CDs. The prepared AuPd nanoparticles were tested for the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP).

Another interesting study was conducted by Jin et al., who prepared four different types of CDs from sucrose, sucrose and acetylcholine chloride, sucrose and mercaptosuccinic acid, and sucrose and N-acetyl-L-cysteine as precursors to produce pristine CDs (with C and O functionalities only), N-doped CDs, S-doped CDs, and N–S doped CDs. The TEM results showed that doping the CDs, especially with S-functional groups, produced small-sized Ag nanoparticles [90]. The prepared AgNPs showed good antibacterial properties. CDs prepared from polyethyleneimine [91] and chitosan [92] have also been used in the preparation of stable AgNPs from $AgNO_3$. XPS data of the Ag nanoparticles indicated the presence of C, possibly acting as a capping agent.

In another study, Pd nanoparticles (4.7 nm) supported on activated carbon were added to CDs (1.7–3.6 nm) made from citric acid and L-cysteine, to give N−S (nitrogen and sulfur)-doped carbon quantum dots (N,S-CDs). The mixture was dried at 100 °C and the product used for the liquid-phase selective hydrogenation of ρ-chloronitrobenzene. HRTEM data revealed that the Pd interacts with the CDs. (Figure 16) [93], and that coverage does not appear to be complete.

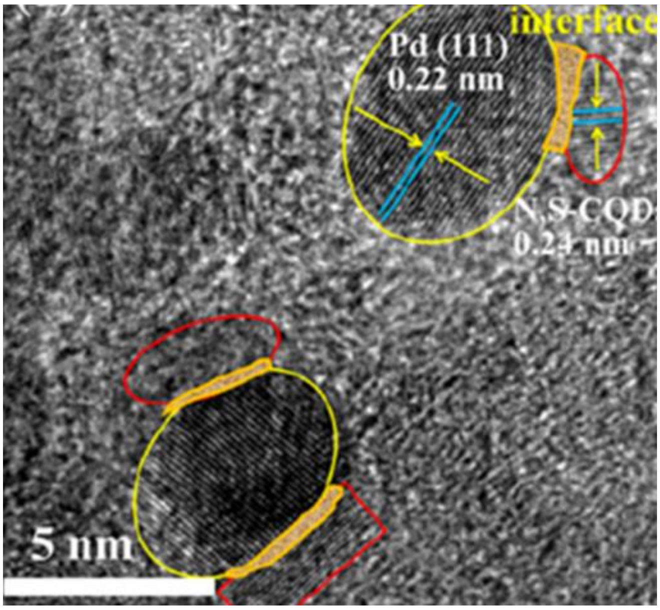

Figure 16. HRTEM image for Pd/N,S-CDs catalysts. Adapted with permission from [93], copyright 2019 American Chemical Society).

Liu et al. produced CDs made by the electrochemical ablation of graphite [94]. To a solution containing the CDs was added a $HAuCl_4$ solution to give an Au nanoparticles/CDs catalyst used in the selective photocatalytic oxidation of cyclohexane. Similar studies were performed on Cu/CD and Ag/CD catalysts made from Ag or Cu ions, and CD mixtures. HRTEM studies showed an interaction between the CDs and the Au (and Cu and Ag) (Figure 17). This was confirmed by X-ray absorption spectroscopy experiments on the Au/CDs composites when the Au/CDs composites were exposed to visible light; EXAFS data indicated Au–C interactions [94].

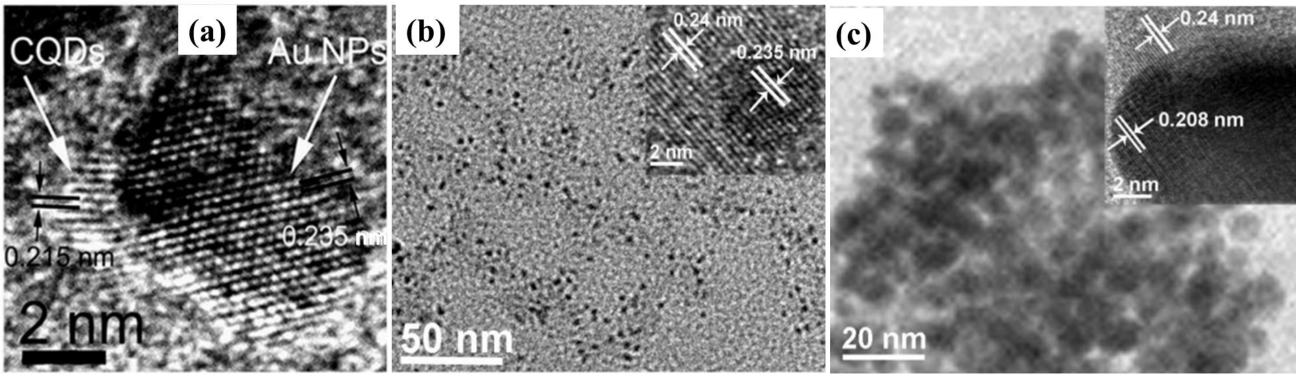

Figure 17. HRTEM images of (**a**) Au/CD, (**b**) Ag/CD and (**c**) Cu/CD catalysts. Adapted with permission from [94], copyright 2014, American Chemical Society.

The above examples show that CDs make good reducing and stabilizing agents for different metals. In summary, it appears that in the examples described above, the CD-metal interaction involves (i) simple coordination chemistry and (ii) reduction of the metal by CD surface functional groups. Additionally, the metal nanoparticles produced usually have uniform size, are well dispersed and have good stability (stable for months, post-synthesis).

- Examples where the CD structure is lost

The examples below show studies in which the CDs have lost their morphology during reaction between a metal salt and the CD. In some studies, the layered carbon takes the shape of the formed metal nanoparticles. These CD-transformed carbons, containing metals, were used in further catalytic studies.

Ag nanoparticles with estimated particle sizes of 40 nm were produced by reducing $AgNO_3$ in a solution containing CDs, at 50 °C for 5 min [95]. The CDs (~2–6 nm sizes), contained $-OH$ and $-NH_2$ surface groups, and it was believed that these groups were responsible for the reduction of the metal salt into metallic Ag. Post analysis of the CDs after reduction was reported. The resulting CDs-Ag nanocomposite had a core-shell structure (called Ag@CD), with the Ag nanoparticles encapsulated inside the CD layers. The thickness of this carbon shell was found to be about 2 nm (see Figure 18a). HRTEM data analysis confirmed the conversion of the Ag salt to metallic Ag. The Ag, surrounded by C, was successfully used for the catalytic oxidation of TMB in the presence of H_2O_2, the plasmon-enhanced-driven photocatalytic reaction of p-nitrothiophenol (PNTP) into 4,4′-dimercaptoazobenzene, and the catalytic-driven reduction of PNTP to PATP in the presence of $NaBH_4$ [95].

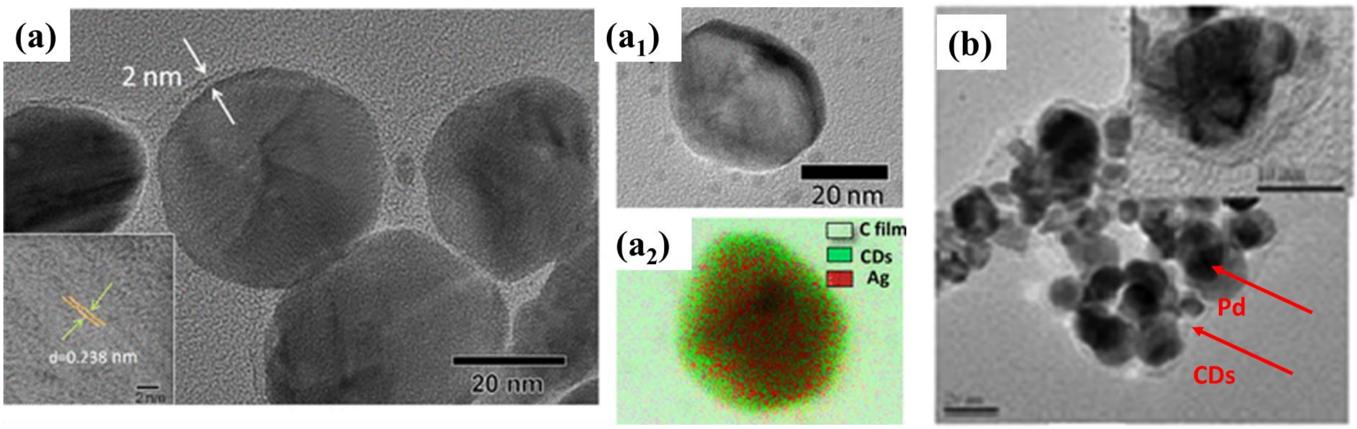

Figure 18. (**a**) TEM images (**a$_1$**) HRTEM image and (**a$_2$**) C and Ag element mapping of Ag@CDs (copyright 2016, American Chemical Society [95]), and (**b**) Pd@CDs nanocomposite (copyright 2013, Royal Society of Chemistry [25]), showing that the CDs are transformed into thin shells that encapsulate the metal catalysts.

Interestingly, Dey at el. produced CDs of estimated particle sizes of 6.6 nm from clotted cream. The CDs were then mixed with H_2PdCl_4 and refluxed at 100 °C for 6 h. From this, a nanocomposite of Pd@CDs was formed, and the HRTEM revealed that the reduced Pd nanoparticles were encapsulated inside a ~3.8 nm carbon layer (Figure 18b). Reduction of the Pd salt to metallic Pd was confirmed by XRD data [25]. The Pd@CDs was tested for activity in the Heck and Suzuki-based coupling reactions, e.g., in the reaction of phenylboronic acid and bromobenzene to give biphenyl. Beyond 4 h reaction time, the catalyst deactivated. PVP was then added to the Pd@CDs to further enhance the dispersibility of the catalyst. This led to an improved conversion of biphenyl from 45% to 95% and a >4 h reaction time, presumably due to a limited agglomeration of the Pd [25].

A study by Zhang et al. showed that CDs produced from chitosan could reduce Rh^{3+} to its active catalytic form, Rh^0 [96]. The CDs were synthesized using a microwave-assisted hydrothermal reaction of chitosan, and the obtained CD particle size was *ca.* 9.6 nm. The prepared CDs were then mixed with $RhCl_3 \cdot 3H_2O$ and allowed to react for 1 h at 120 °C. Post reaction, the sample was analyzed using XRD, and the data showed the presence of metallic Rh^0. TEM results showed that the resulting Rh nanoparticles and CDs formed clustered structures, and their average particle sizes after synthesis at two different CD:Rh salt concentrations (4:1 and 6:1), were 23.4 nm and 27.8 nm, respectively. The TEM images recorded in the study are shown in Figure 19, and were reported to show a close interaction of the Rh particles with the CDs. The prepared catalysts were used to hydrogenate polybutadiene (HTPB) and hydroxy-terminated butadiene-acrylonitrile (HTBN), and showed a high degree of hydrogenation at 80 °C [96]. The CDs also acted as a stabilizing agent during the reactions.

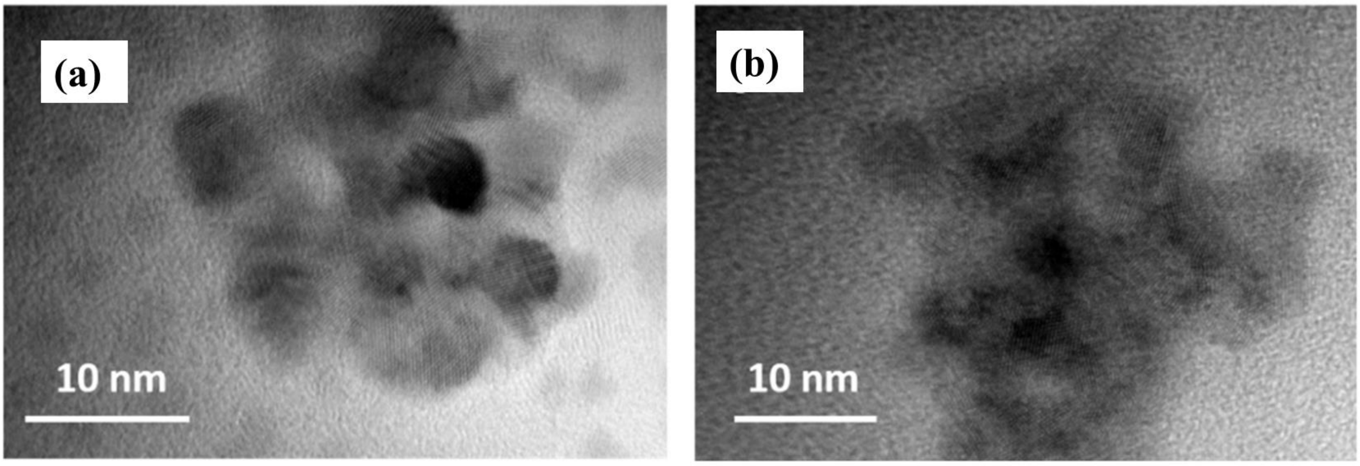

Figure 19. HRTEM images of Rh-CD composites prepared using (**a**) 4:1 and (**b**) 6:1 CDs:Rh salt (reproduced with permission from [96], copyright 2017 Elsevier).

CD precursors, when mixed with $ZnCl_2$, led to the formation of graphitic sheet layered materials in which the Zn is said to link the CDs together. In the absence of Zn, CDs are formed (from citric acid/urea/autoclave at 180 °C). The sheet size was affected by the zinc/carbon ratio, where an increase in Zn produced larger graphene sheets [97].

In summary, it is still not clear as to how the conversion of CDs to the carbon sheets takes place. Loss of the functional groups must lead to a change in the CD morphology, but this in itself would not lead to an obvious stitching of the carbon layers. Also, at high temperatures, a competition will exist between carbon oxidation (by the metal oxide) and carbon stitching.

3.2.3. Post Reduction of CDs as Metal Supports

Post reduction of a CD to give CDs that have been used to support metals have been reported. In the post-reduction process, C=O groups are converted to CH_2OH groups (Figure 20) [62,63,98]. For example, Wang et al. obtained CDs by treating carbon black ("lampblack") in acid under reflux. The obtained CDs were further treated with $NaBH_4$ to produce r-CDs with approximate particle sizes of 3.4 [98]. It was observed that the C=O groups found in the pristine CDs were reduced to C-OH groups. The r-CDs were used for the synthesis of Au metal nanoparticles. When $HAuCl_4$ was mixed with r-CDs and heated at different temperatures (40, 60 and 80 °C) for 24 h [98], the obtained Au nanoparticles had averages sizes of 7 ± 2.1 nm, 16.4 ± 3.8 nm, and 15.9 ± 4.2 nm, respectively. Interestingly, it was observed that the r-CDs were oxidized back to CDs after reaction with the metal salt; the resulting CDs showed an increase in C=O peaks, as detected in the photoluminescence emission spectrum. No post synthesis of the CD-derived Au (e.g., by TEM analysis) was performed. The obtained Au nanoparticles were kept for 6 months without any aggregation. It was believed that the CDs acted as capping agents for the resulting Au nanoparticles, leading to their stability. However, there was no TEM evidence seen for a carbon layer. These nanoparticles were used for the catalytic oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) by H_2O_2, and the CD-reduced Au nanoparticles showed superior performance to Au nanoparticles obtained after treating $HAuCl_4$ with citrate.

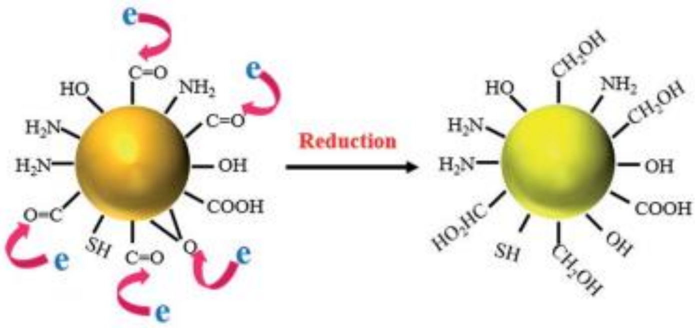

Figure 20. Conversion of CDs to r-CDs by C=O reduction to CH_2OH groups (adapted with permission from [62], copyright 2015 Royal Society of Chemistry).

Zhuo et al. synthesized CDs from cysteine using a microwave-assisted hydrothermal reaction. The CDs were then reduced using sodium borohydride [62]. The average particle sizes of the CDs and r-CDs were 2.0 and 2.3 nm, respectively. The FT-IR spectra of CDs showed a C=O peak at 1639 cm^{-1}, which shifted to 1651 cm^{-1} in the r-CDs, signifying a reduction of the C=O bonds. Additionally, the C=O peak at ~287.9 eV in the XPS was reduced significantly in size for the r-CDs sample, while the O-H peaks increased, further confirming the reduction of the CDs [62]. The reduced CDs (r-CDs) were then used to reduce $AgNO_3$ and $HAuCl_4$ to metallic Ag and Au [62]. The obtained r-CDs-Ag and r-CDs-Au materials had average particle sizes ranging between 6–10 nm and 2–3 nm, respectively.

In summary, the ability to pre-reduce CDs should permit an enhanced ability to reduce metal ions for catalytic reactions.

4. Techniques to Evaluate CD and CD/Metal Transformations

Many different techniques can be used to establish the structure and composition of CDs and CD/metal composites. However, of importance in CD studies is the post analysis of the carbons. As noted in the sections above, the CDs can be modified during reaction. Electron microscopy studies (TEM/SEM) are the most useful techniques to evaluate changes in the CDs, as the CDs typically have dimensions <10 nm. TEM analysis in particular provides a means of establishing if the spherical CDs change into layered materials or core/shell structures. However, it has been noted that CDs may sometimes not be seen in microscope images because of their low contrast, relative to the substrate used [92].

HRTEM has been used extensively to indicate these changes. Various spectroscopic techniques have also been used to determine the bulk and surface structure of CDs and the changes in the CDs with temperature after chemical reactions. These include infrared, photoluminescence, solid state NMR and Raman studies, as well as XPS studies. However, the changes that occur do not necessarily provide definitive data on the difference between CDs and their conversion to layered materials. Careful analysis does show changes in the Raman D and G band intensity ratios, as well as changes in NMR and IR data that relate to C=O/C-O/COOH ratios. XRD studies can follow the changes in the carbon by monitoring the carbon–carbon layers in the structure. The 002 peak in the PXRD data tends to be broad, but does shift as the structure is modified. The use of total X-ray scattering experiments enables the collection of data on the local structural order that exists within the CDs. This means that useful data can be extracted from nano-sized CDs, since a total scattering experiment is insensitive to structural disorder and insensitive to their small size [71,72].

Traditional laboratory-based XRD studies can follow the changes in the carbon by monitoring the carbon–carbon layers in the structure. The 002 peak in the XRD data tends to be broad, but does shift along the x-axis, as the structure is modified. Similarly, total X-ray scattering experiments provide data on the local structural order that exists within the CDs. This type of data contains both Bragg and diffuse X-ray scattering, which allows for a comprehensive analysis of the CD atomic structure. This means that useful information can be extracted via the pair distribution function (PDF) analysis of the data collected on nano-sized CDs, which produce primarily diffuse scattering. This is due to the technique being insensitive to structural disorder and the small size inherent to CDs [71,72]. Accordingly, PDF analysis of high-energy synchrotron X-ray data typically produces information that is more accurate and provides a more representative description of the nanoscale structure of the CDs than what is currently achievable with standard laboratory-based X-ray equipment. Consider the radial functions that were extracted from synchrotron X-ray data that were collected on a set of CDs, each of which was calcined at different temperatures (Figure 21).

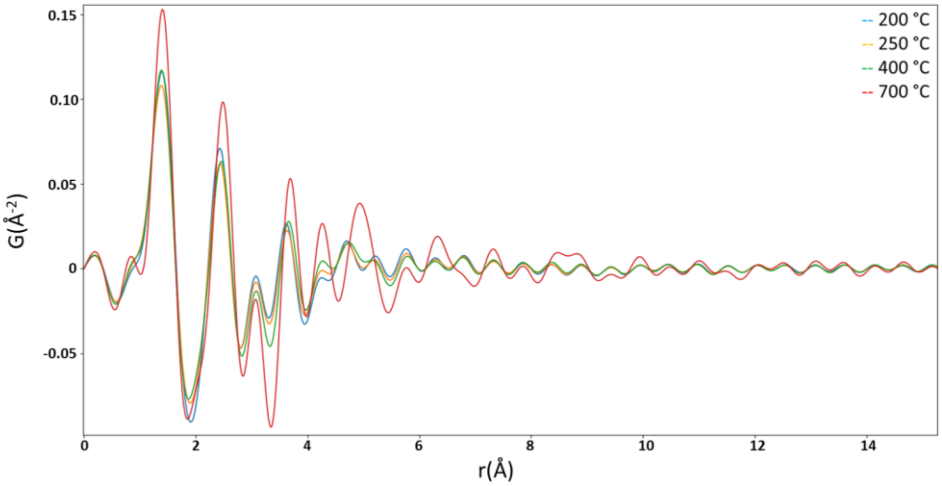

Figure 21. A comparison of the radial distribution function extracted from total scattering data collected on a set of CDs prepared as a function of calcination temperature.

The data in Figure 21 shows the general similarities of the CDs in this sample set up to r = 3Å. The peak at r = 1.38 Å is due to the carbon–carbon double bonds in the structure of the CDs. Beyond this point in the data, departures are seen, as the sample calcined at the highest temperature (700 °C) has better long-range order, with perturbations in the data that extend further afield than when compared to that of the sample calcined at lower temperatures (200, 250 and 400 °C). From this qualitative analysis of the data it is possible to show that an increased calcination temperature produced increasingly more crystalline CDs. By comparison, similar data collected on these samples using ordinary XRD data would typically have shown some evidence of these features with long data acquisitions. However, owing to its brilliance, the sensitivity of the data and speed with which they are generated at a synchrotron are unmatched.

- Summary of CD conversion reactions

A consideration of papers published in the area leads to some generalizations on metal-CD mixtures that can be made, and the role this will have in catalysis.

(i) CDs can react with each other, through physical or chemical bonds, to create CD assemblies. These assemblies could then be used as carbocatalysts.
(ii) CDs can react at temperatures of *ca.* 200 °C to convert to carbon sheet-like structures and the graphicity of the sheets has been shown to increase with temperature.
(iii) CDs can lose many of their surface functional groups at temperatures between 200 and 450 °C, and this will impact on their chemical properties.
(iv) In the presence of easily reducible metal oxide catalysts, CDs can be converted to carbon sheet-like materials at temperatures < 100 °C. The ability to achieve this will be dependent on the metal reducibility, with directions given by Ellingham diagrams.
(v) Ellingham diagrams have been determined for bulk metals, but metal nanoparticles are expected to have similar temperature versus free energy values.
(vi) The chemical process by which a CD is converted to a sheet-like carbon is not known.

5. Future Directions

It is hoped that the review has presented some useful thoughts on the use of CDs as a metal support in catalysis. It is clear from the many reports and reviews in the literature that the area is a fruitful one for further studies.

There are a number of key issues that need to be addressed to provide an understanding of the interaction between CDs and metal, i.e., when the CD-metal is retained and when the CD converts to another morphology in the presence/absence of a metal.

(i) Is the CD conversion dependent on the type of CD?
(ii) Is the conversion dependent on the type of functional group?
(iii) How does the conversion from a CD to other dimensional carbon structures take place?
(iv) The morphology conversion reaction is temperature dependent. What are the temperature ranges in which the CD/metal acts as a catalyst with/without a morphology change?
(v) Is there a carbon layer thickness in which a carbon will only be oxidized by a metal but not undergo a change in morphology? For example, in the presence of Co it is clear that CSs (d = 400 nm) only undergo carbon removal while CDs (d < 10 nm) undergo a morphology change.
(vi) In situ studies could provide valuable information on the CD conversion process.

The review also indicates that post analysis of CD/metal catalysts is needed; the current stability repeat studies do not necessarily give information on the morphology of the active catalyst.

6. Conclusions

The use of CDs and metal-CDs has been extensively reported in the literature. The data suggest that the CDs (as carbocatalysts), when studied at low temperatures (<150 °C) appear to retain their morphology in the reactions. It is possible that morphology changes could occur at the higher temperature, but lack of post-catalysis data has generally not allowed for this to be confirmed. Further, while the surface groups can be modified in the reaction, this does not appear to influence the carbon core. At higher temperatures, the CDs are converted to sheet-like carbons. These new carbons have also been studied as catalysts, e.g., in electrochemical reactions.

Metal-doped CDs also appear to act as classic carbocatalysts/metal catalysts in low-temperature catalytic reactions. High-temperature studies could provide information on CD morphology changes influenced by the metal dopants.

The addition of metals to CDs to make different metal-CD catalysts appears to be dependent on the metal reducibility and the CD reduction ability. If high temperatures are used, the metal/metal salt can react with the carbon core and remove or change the morphology of the carbon.

The use of temperature/pressure/carbon functional groups to produce retention/transformation of the CD structure thus provides exciting possibilities for further studies in this area of catalysis using CDs.

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Conflicts of Interest: The authors declare no conflict of interest.

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