Topical Review

The advanced multi-functional carbon dots in photoelectrochemistry based energy conversion

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Received 30 May 2022, revised 15 June 2022
Accepted for publication 31 August 2022
Published 20 September 2022

Abstract
Carbon dots (CDs), as a unique zero-dimensional member of carbon materials, have attracted numerous attentions for their potential applications in optoelectronic, biological, and energy related fields. Recently, CDs as catalysts for energy conversion reactions under multi-physical conditions such as light and/or electricity have grown into a research frontier due to their advantages of high visible light utilization, fast migration of charge carriers, efficient surface redox reactions and good electrical conductivity. In this review, we summarize the fabrication methods of CDs and corresponding CD nanocomposites, including the strategies of surface modification and heteroatom doping. The properties of CDs that concerned to the photo- and electro-catalysis are highlighted and detailed corresponding applications are listed. More importantly, as new non-contact detection technologies, transient photo-induced voltage/current have been developed to detect and study the charge transfer kinetics, which can sensitively reflect the complex electron separation and transfer behavior in photo-/electro-catalysts. The development and application of the techniques are reviewed. Finally, we discuss and outline the major challenges and opportunities for future CD-based catalysts, and the needs and expectations for the development of novel characterization technologies.

Keywords: carbon dots, photoelectrochemical properties, photocatalysis, electrocatalysis, transient photo-induced voltage, transient photo-induced current

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1. Introduction

Carbon material plays an important role in the development of modern material science and technology, which has shown great application prospects in many research fields. Carbon dots (CDs) are a new type of zero-dimensional carbon material with sizes below 10 nm. In 2004, Xu et al. first used the concept of ‘quantum dot’ to describe this kind of CDs with fluorescence characteristics [1]. The concept of quantum dots, which have different physicochemical properties from the corresponding bulk materials, was proposed in the early 1983 [2]. The classical work related to quantum dots has also become a milestone in the field of functional materials in nanoscience and technology [3, 4]. As a new type of carbon nanomaterial, CDs are quantum sized materials with both molecular and carbon properties. To some extent, CDs further expand the scope and scientific connotation of quantum dot materials. CDs not only have the luminescence and small size characteristics similar to traditional quantum dots, but also have the advantages of good water solubility, low biological toxicity and good electrical conductivity [5–7]. At present, CDs have attracted great attention in the fields of electronics, optics, photochemistry, catalytic chemistry and energy environment [8–10].

After more than 10 years of rapid development, various CDs with different structure and morphology have been prepared, and the developed CDs family includes graphite quantum dots, graphene quantum dots (GQDs), amorphous CDs, polymer dots and so on [11]. However, the structure and surface of CDs are very complex, and the understanding of the CDs’ structure and properties is still in the preliminary stage. Compared with traditional semiconductor quantum dots, CDs are still lagging behind in important basic physical parameters, molecular synthesis mechanism, and spectroscopic study of luminescence mechanism. The structure, synthetic chemistry and photoelectric properties of CDs are quite different from those of traditional quantum dots, which provide new opportunities and challenges for scientists [10, 12].

In-depth research on CDs is conducive to understanding the basic scientific issues of carbon nanostructures and promoting their wide application in energy, catalysis and biomedicine. In this paper, the synthesis, structural characteristics, photoelectric chemical properties and applications of CDs in photoelectric energy catalytic conversion are introduced. In addition, new methods and techniques for characterization of photo-electrocatalytic processes in CDs catalytic systems are discussed. Among them, the working principles and practical applications of characterization techniques named transient photo-induced voltage/current (TPV/TPC) are reviewed. Finally, we analyze the challenges and opportunities in the field of photoelectrocatalysis and advanced characterization techniques of carbon functional materials.

2. Synthesis, structure and properties of CDs

2.1. Synthesis of CDs

The preparation methods of CDs can be divided into two categories: top-down method and bottom-up method. Top-down method is a physical, chemical and electrochemical method, from the large size of carbon materials (such as graphite, etc) etched and exfoliated to obtain small size of carbon particles. The bottom-up method can be concluded as carbonization of small molecules (e.g. carbohydrates, organic acids and amines, etc) or polymer precursors under relatively simple and mild conditions.

The top-down method usually needs harsh conditions such as electrochemical etching [6, 7, 14], arc discharge [15], laser ablation [16, 17] and chemical oxidation [18, 19]. In general, the top-down method is beneficial to the preparation of CDs with high crystallinity and relatively complete structure. Among them, electrochemical etching has been widely used in the preparation of CDs due to its simple operation, environment friendliness and no toxic gas emission. Kang’s group reported a large-scale synthesis of high-quality CDs via an electrochemical approach. The structure of this CDs is shown in figure 1. Two graphite rods were electrolyzed in pure water without the assistance of other chemicals and further purification steps, and the obtained CDs are highly crystalline and water dispersive [13, 20]. In terms of synthesis control, post-treatment such as size separation and surface modification of obtained CDs are usually required due to the difficulty of fine-control in this etching process.

Bottom-up method mainly includes combustion [21, 22], hydrothermal/solvothermal method [18, 19, 23], microwave pyrolysis [24, 25] and so on. CDs produced by these methods tend to have amorphous carbon core with abundant doping sites and functional groups. In the bottom-up method, the key factors affecting the chemical structure and size of CDs are the structure of precursor, reaction time, solvent and temperature, etc, which need to be carefully optimized to control the size and composition of CDs [26–28]. Xiong’s group reported a rapid solid reaction to synthesize red emissive CDs in large scale via a bottom-up method, which needs no solvent, no high pressure reactors and no post-treatment procedures. And the obtained CDs are monodispersed and uniform spherical nanoparticles with abundant functional groups, especially the boron-containing groups [29].

Separation and purification are one of the most important steps in the preparation of CDs, however, the small size and hydrophilic surface of CDs often make the process more challenging [30, 31]. Most obtained CDs are accompanied by incomplete precursors and by-products such as amorphous carbon, oligomers and carbon particles, which require a combined purification process of filtration/centrifugation and dialysis to remove large particles and small molecules or ions [32, 33]. In addition, due to the diversity of functional groups and defect structures on CDs, high-level purification treatments such as dialysis, ultrafiltration and electrophoresis are required for the preliminarily purified CDs [34]. At present, the separation and purification steps mainly focus on regulating the size distribution of CDs, but few studies have focused on phase purity and structure uniformity of CDs. In order to meet the requirements of high quality CDs in application, new separation and purification methods need to be further developed, and factors such as size, morphology, crystallinity and surface specificity need to be considered [35–37].
2.2. Structure of CDs

CDs usually have crystalline or amorphous carbon core with a diameter of less than 10 nm and a thickness of 0.5–6 nm [13]. The recently reported CDs are partially oxidized with amount of surface functional groups connected to the carbon core, so CDs can be considered as a special core–shell structure. The structure of the carbon core in CDs is diverse and complex, which is mainly affected by the synthesis methods and carbon source. Carbon core can be divided into crystalline phase and amorphous phase, including graphene, graphite, amorphous carbon, organic and polymer types. CDs with good crystallites usually have (002), (110), (001) and (100) crystal faces of a graphite lattice [38]. Amorphous CDs are usually obtained by bottom-up polymerization or carbonization of organic precursors. The core of CDs can be simplified into two most typical structural models: graphite (sp²) and diamond (sp³). Therefore, carbon core is generally broadly defined as carbon nanoparticles containing sp²-/sp³- conjugated structure in amorphous carbons. At present, more attention is paid to the size effect of sp² conjugate system [39, 40].

There is a variety of functional groups at the surface of CDs, such as hydroxyl, carboxyl, carbonyl, epoxy/ether, amino groups and so on, which are related to the raw materials and synthesis methods [41, 42]. These functional groups of CDs are covalently bonded to the carbon nucleus by C–C or C–X (X: N, O, S, P, etc) bonds, which greatly expand the further surface modification of CDs. Therefore, CDs can possess the properties of carbon materials and organic molecules at the same time, and the surface functional groups have a significant impact on the physical and chemical properties of CDs [43].

2.3. Basic properties of CDs

CDs are not pure carbon structure, but a coexistence of surface defects, doped atoms, and covalently bonded functional groups. The structure of CDs is diverse and extremely complex, which has the properties of both carbon material and organic molecule, and the surface functional groups have a great influence on the properties of CDs. The properties of CDs are closely related to the raw materials used for preparation and the synthetic pathway. Nevertheless, the structure, surface composition and photochemical properties of highly crystalline CDs have been gradually clarified. In general, CDs have rich optical and photoelectrochemical properties, abundant raw materials, easy to obtain, low biotoxicity and environmental friendliness. It makes up for the limitation of semiconductor quantum dots to some extent, and has broad application prospect in biology, catalysis, devices and other photoelectric applications [44, 45].

In terms of optical properties, CDs usually have strong optical absorption in the UV region, which is attributed to the π→π∗ transition of aromatic C=C bonds and n→π∗ transition caused by some functional groups such as C=O bonds. CDs exhibit different absorption characteristics due
to different size, element composition and structure. The absorption may also extend to visible region after surface modification [46–48]. The fluorescence of CDs can cover deep ultraviolet to near infrared region (NIR), and the emission wavelength can be adjusted. CDs also possess a series of rich optical properties, such as laser emission, upconversion fluorescence, solid phosphorescence, third-order nonlinear optics and aggregation-induced emission [49, 50]. At present, the mechanism of carbon spot fluorescence is still controversial, and there are few in-depth studies on excited state mechanism. Many key exciton dynamical processes at CDs are still controversial or lack of spectral evidence [51, 52].

In addition, CDs are excellent electron or hole acceptor materials because of their high electron mobility, long thermal electron lifetime, fast electron extraction ability, and stable band-gap tunable fluorescence [53, 54]. So far, the quantitative understanding of the chemical or physical properties of CDs remains a great challenge, especially the study of the band structure and electronic properties of CDs. Kang and Lee established a simple theoretical prediction method to determine the valence band/conduction band energy levels of CDs through a simple semi-empirical equation based on the band gap value of CDs. As shown in figure 2(a), the graphitic CDs with various functional groups (–OH, –COOH, –H) on the surface were selected as models to consider the contribution of these functional groups to the work function and energy band. The quantitative linear relationship between $E_{VB}/E_{CB}$ and $E_g$ was established by studying the influence of the intrinsic dipole of functional groups and induced dipole caused by the interface between carbon core and functional groups on the energy band of CDs. Figure 2(b) further shows the three-dimensional relationship between $E_{VB}/E_{CB}$ and $E_g$ and the molar ratio of surface group substances, and the linear relation between $E_{VB}/E_{CB}$ and $E_g$ can be directly obtained without any undetermined coefficients [55].

3. Photoelectrochemical properties of CDs

From the perspective of catalytic chemistry, carbon materials are rich in resources and environmentally friendly, which can overcome the shortcomings of modern catalysts represented by rare precious metals, which are lack of resources and easy poisoning. Traditionally, carbon is considered as a good catalyst carrier for its lack of catalytic activity. The small size effect and surface activity of CDs bring rich photochemical properties. As a bridge between traditional carbon materials and organic molecular materials, CDs are one of the ideal structural models for the study of carbon-based catalysts.

As a photoelectric functional unit with rich properties, CDs also play a variety of roles in the composite catalytic system as shown in figure 3, including improving light absorption, electron storage, promoting charge separation, enhancing adsorption, and surface cocatalysis [56–58]. When used in photocatalysis, the contribution of CDs to the improvement of catalytic activity should be considered mainly due to the enhanced light absorption at the interface, charge transfer, and promotion of photocarrier separation and migration. Furthermore, Liu et al. reported that CDs have the ability to generate a photo-induced potential, which can be combined with hematite to meet the requirement for overall water splitting as shown in figures 4(a) and (b) [59]. Besides, Liu et al. reported that the high optical absorptivity of CDs at visible wavelength enables CDs to be used as a sensitizer in sensitized metal oxide semiconductor based devices, and the regeneration kinetics of CDs were examined by scanning electrochemical microscopy (SECM) (figures 4(c) and (d)) [60]. In electrocatalytic systems, CDs are widely used to reduce the charge transfer resistance of complexes, optimize the adsorption and desorption performance of reactive species such as reactants, reaction products and reaction intermediates, improve the stability and anti-poison of catalysts [61–66]. In addition, the latest researches show that

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E_{va} = 0.55 \times E_g - 4.11 - 4\pi (0.159a - 0.115b - 0.037c)
\]

\[
E_{vb} = -0.45 \times E_g - 4.11 - 4\pi (0.159a - 0.115b - 0.037c)
\]

Figure 2. (a) Surface groups contribute to band gap. Here $a$, $b$ and $c$ are the molar ratio of carboxyl (–COOH), hydroxyl (–OH), and hydrogen (–H) groups on the surface of CDs ($a + b + c = 1$). (b) Three-dimensional map of the relationship based on the theoretical equations for CDs with different ratio of functional groups on the surface [55] (Copyright (2021), with permission from American Chemical Society).
CDs can regulate the charge distribution and the electrocatalytic kinetics [65].

4. Photoelectrocatalysis and energy conversion applications of CDs

CDs become powerful competitor of photoelectrocatalytic materials because of its high stability and photoelectrochemical properties. Herein, the applications of CDs in photocatalytic and electrocatalytic fields are reviewed, including photocatalytic water splitting, photocatalytic CO$_2$ reduction, electrolysis of water, fuel cell cathode reaction and carbon dioxide conversion.

4.1. Applications of CDs in photocatalysis

Photocatalysis is a green way to produce energy and reduce environmental pollutants. CDs play an excellent role in the field of photocatalysis due to its unique photochemical properties. In this section, we briefly introduce the application of CDs-derived photocatalysts in photocatalytic water splitting to generate H$_2$ and O$_2$ and photocatalytic CO$_2$ conversion reaction.
4.1. Photocatalytic water splitting. Photocatalytic water splitting into H₂ and O₂ is a sustainable and promising method for clean energy and fuel production [67]. However, the photocatalytic efficiency is unsatisfactory, due to the unfavorable thermodynamics, sluggish kinetics, and side reaction. Overcoming these obstacles is the key to improve the efficiency of photocatalytic water splitting [68]. CDs perform tunable optical properties due to its adjustable geometric and chemical structure, which allows CDs to play an effective optimization role in photocatalysis, especially in terms of light absorption, charge separation and transfer, band structure and so on [69].

Liu et al reported a metal-free CDs-C₃N₄ nanocomposite with a high overall solar energy conversion efficiency. Instead of the traditional one-step four-electron reaction pathway, CDs-C₃N₄ achieves the overall splitting of water via a stepwise two-electron/two-electron two-step pathway under visible light. During this catalytic reaction, C₃N₄ dominates the photocatalytic process while CDs dominates the chemical catalytic part which involves the splitting of H₂O₂ into O₂ and H₂O. Meanwhile, CDs also increase the value of quantum efficiency and solar-to-hydrogen by increasing the light absorbance [70]. Meng et al introduced CDs and CdS quantum dots into the cages of MIL-101 by double solvent method and heating treatment. The obtained CDs/Cds@ MIL-101 shows a photocatalytic H₂ production rate of 14.66 µmol h⁻¹ under visible light irradiation. This excellent photocatalytic activity can be contributed to the action of CDs, which act as an electron collector thus extending the lifetime of photogenerated charge carriers on CdS@MIL-101 [71]. Shi et al constructed a CdS and octahedral CoO composite material with a H₂ evolution rate of 1.67 µmol h⁻¹ and a O₂ evolution rate of 0.91 µmol h⁻¹. The introduction of CDs increases the photocatalytic activity of pure CoO by six times. On the one hand, CDs enhance the light absorption and the charge separation efficiency, which lead to the increased activity. On the other hand, CDs effectively transfer heat away from the CoO caused by the photo-thermal effect, thus improving the stability [72].

4.1.2. Photocatalytic CO₂ reduction. Photocatalytic reduction of CO₂ is believed to be a promising route to lessen CO₂ emission using solar energy and convert it into energetic molecules such as CO, CH₃, CH₂OH and so on [73, 74]. However, achieving the reduction of CO₂ is difficult due to the high demands on catalysts including a definitive energy band gap and suitable band edge position [75]. It is exciting that CDs have a wide range applications in improving the light absorption range, increasing the electron-vacancy separation efficiency and adjusting the band gap [65, 76, 77].

Liang et al reported a CDs modified Co₃O₄/In₂O₃ photocatalyst that can solar-drive the conversion of CO₂ to CO with a yield of 2.05 µmol h⁻¹ g⁻¹. In this catalytic system, CDs stabilize the electrons and holes and maximize the chance of participating in photo-induced redox reactions by inhibiting the recombination of electrons and holes [78]. Lin et al designed and synthesized an oxygen-deficient ZnO/CD (OD-ZnO/C) material, which shows excellent full spectrum (UV, visible and NIR light)-driven CO₂ photoreduction. And the OD-ZnO/C-N₂-600 exhibited high quantum yields of 0.13% under Vis–NIR and 0.05% under NIR for CO production. It is not only the defects of OD-ZnO that cause the increasing of light utilization efficiency within the UV–Vis to NIR region, but also by CDs. Besides, the formation of heterojunctions between OD-ZnO and CDs promotes the separation of charge carriers, while the defect-rich surface enables the efficient adsorption and activation of CO₂/H₂O into key intermediates [79]. Liu et al found that CDs can not only improve the separation of the photogenerated electron–hole pairs, but also kinetically promote interfacial reaction. In addition, the enhanced adsorption of CO by nitrogenous groups of CDs can also contribute to the further transformation of reaction intermediates. The obtained CDs show the ability of reducing the CO₂ to CH₄ with a selectivity of 74.8% and a generation rate of 983 µmol g⁻¹ h⁻¹ [80].

4.2. Applications of CDs in electrocatalysis

The electrochemical reactions, including hydrogen evolution reaction (HER), oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and carbon dioxide reduction reaction (CO₂RR) are significant for electrochemical energy conversion. However, the limited activity, stability and cost of electrocatalysts hindered the development of renewable energy conversion and utilization devices. Therefore, numerous works have focused on the design and development of such catalyst materials. Recently, CDs show great potential in improving electrocatalytic performance of these electrochemical reactions due to its unique physical and chemical properties, and remarkable research results have been obtained.

4.2.1. HER. Electrocatalyzing HER to produce hydrogen is a facile and clean route to drive the efficient, and sustainable hydrogen economy, which is the core of future renewable energy storage and conversion systems. This reaction requires efficient and stable catalysts to reduce the overpotential and energy consumption. Platinum-based materials have excellent catalytic activity, but they suffer from the high cost and scarcity [81]. Therefore, the study and development of efficient and cheap catalysts to replace platinum has become a hot research topic. The alternative catalysts represented by transition-metal based materials are less capable of adsorbing and desorbing hydrogen intermediates and reactive species than Pt, and their electron transfer efficiency is also suppressed, leading to the fact that their HER activity is hardly comparable with Pt [82, 83].

Bao et al synthesized a CDs/bimetal phosphide (CDs@NiCoP) via a low-temperature annealing method, which shows an initial overpotential of 108 mV for HER higher than that of pure NiCoP (182 mV), due to the reduction of the charge transfer resistance caused by the introduction of CDs [64]. Yang et al prepared a nickel nanoparticle/CD (Ni/CD) hybrid with an onset potential comparable to Pt wire
and a low Tafel slope of 98 mV dec\(^{-1}\), and the enhanced catalytic activity of Ni/CQD can be attributed to the synergetic effects between Ni and CD. CD inhibits the agglomeration and oxidation of Ni particles, enhancing the catalytic stability. The formation of Ni–O–C in Ni/CD will affect the adsorption and desorption of H species, thus enhancing the catalytic activity. Besides, the Ni–O–C can reduce the local work function on the carbon surface by facilitating the electron transfer from Ni to CD [84]. Li et al reported a CDs loaded ruthenium nanoparticle (Ru@CDs), which exhibits an overpotential of 0 mV and a Tafel slope of 47 mV dec\(^{-1}\), superior to Pt/C and most noble metals. In addition to avoiding the agglomeration of Ru nanoparticles, the recombination of CDs and Ru causes the charge density redistribution due to the electron transfer from Ru to CDs, leading the electron-enrichment of CDs and hole-enrichment of Ru, which are the reasons that Ru@CDs has outstanding HER performance [85].

### 4.2.2. OER

OER is also an important reaction for various energy related processes, such as electrochemical water splitting, rechargeable metal–air battery [86]. However, high overpotential is required to promote the splitting of water molecules due to the sluggish reaction kinetics of OER. Ruthenium and iridium-based materials are generally considered to drive OER efficiently, but the commercialization is also limited by their high cost and scarcity [87]. The difficulty of developing other non-noble metal catalysts lies in how to improve the conductivity, intrinsic activity and stability [88]. As a cocatalyst, CDs are used as an effective means to improve the OER activity and stability by inducing charge redistribution and reducing the electrical resistance [62, 89, 90].

Song et al used carboxylated carbon quantum dots CQDs (CQDs–COOH) to induce the generation of two-dimensional metal–organic framework nanosheets (MOF NSs) NiFe-MOF NSs, which show a low overpotential of 261 mV and a small Tafel slope of 56 mV dec\(^{-1}\). Using the electron-withdrawing groups (–COOH), CQDs–COOH induces the formation of NiFe-MOF NSs, and the interlayer spacing of NiFe-MOF NSs is enlarged. Besides, the positive charge on active sites increased by CQDs–COOH promotes the improvement of OER performance [91]. Li et al used graphene CDs (GCDs) to finely tailor the morphology and conductivity of FeNi\(_3\) alloy. Density functional theory (DFT) calculations reveal that GCDs can enhance the adsorption of \(\text{O}^2\) and reduce the energy barrier for the conversion of \(\text{OH}^\bullet\) to \(\text{O}^2\), so as to optimize the free energy of \(\text{O}^2\) at active sites, achieving the improvement of OER performance. The obtained FeNi\(_3\)@GCDs-10 shows the overpotential of 238 mV and a Tafel slope of 48.7 mV dec\(^{-1}\) [92]. Song et al prepared a halogen-doped CDs modifying amorphous cobalt phosphate (X-CDs/CoP), which exhibits both excellent HER/OER activity and stability and only requires 1.48 V in 1 M KOH to achieve a current density of 10 mA cm\(^{-2}\) for overall water splitting. This improved OER performance is related to the coupling interface between F-CDs and CoP, which optimizes the adsorption energy and accelerated the kinetics of water splitting [93].

### 4.2.3. ORR

ORR plays a significant role in fuel cell cathode reaction, and its sluggish kinetic greatly limits the commercial application of clean energy conversion devices, which requires amount of expensive and scarce resources of platinum as electrocatalyst. Carbon materials including graphene, carbon nanotubes and CDs are considered to be one of the potential candidates to replace platinum [94]. Heteroatom (such as B, N, O, S, P, etc) doping and the creation of edge defects are the effective atomic modulation strategies to change the charge/spin state of carbon material, so as to realize the directional adjustment of the surface chemical structure of carbon materials, and thus produce ORR activity [95]. Compared with graphene or carbon nanotubes that limited by disadvantages such as uneven dispersion and low doping amount, CDs can be doped with diverse heteroatom and modified with various functional groups, which are favorable for the oxygen adsorption and reduction [96, 97].

With this inspiration, Wang et al prepared biomass-derived P-doped CDs decorated graphene (P-CD/G) nanocomposites as efficient ORR catalyst, which is comparable to the Pt/C catalyst. When P-CD/G was used as the cathode catalyst for a primary liquid Al–air battery, this device shows a power density of 157.3 mW cm\(^{-2}\), which exceeds that of device assembled by Pt/C (151.5 mW cm\(^{-2}\)) [98]. Niu et al used urea as the nitrogen rich bridge molecule to capture citric acid on the surface of graphene oxide (GO) through amidation reaction, and then carbonized the in-situ formed polymeric intermediates to form N-CDs on GO. This N-CDs/GO hybrid shows excellent electrocatalytic performance with an onset potential of 0.13 V vs. Ag/AgCl and high kinetic current density of 18.4 mA cm\(^{-2}\) at −0.7 V [61]. Pei et al reported B and N co-doped CDs supported by multi-walled carbon nanotubes as high efficiency ORR catalyst synthesized by hydrothermal reaction and calcination. Pyridine N and BC\(_3\) in CDs are regarded as active sites, and the B atom of BC\(_2\)O can promote the adsorption of O intermediates such as OH and H\(_2\)O on the catalyst to improve the catalytic activity [99]. It is well established to derive three-dimensional porous carbon materials by carbonization at high temperature [100]. Zhou et al synthesized CDs-1000 by annealing CDs at 1000 °C, which shows high catalytic activity comparable to the 20% Pt/C catalyst towards the ORR and high durability in alkaline solution. They found that the active sites were derived from C–O–K(Na) groups produced by the removal of carbonate groups on the surface of CDs-1000 under alkaline conditions (KOH or NaOH) [38].

Furthermore, CDs also can be used as excellent carrier of metal elements. Kakaeei used CDs as the support materials of platinum particles, inducing the modulation in the electronic structure of Pt clusters. CDs effectively inhibit the aggregation of Pt particles and promoted the stability of this catalyst [101]. Besides, Kakaeei et al also showed that CDs synthesized by electrochemical corrosion process have high ORR activity and excellent tolerance to methanol, which is typically significantly toxic to Pt-based catalysts [102]. Cheng et al prepared CDs derived N, S co-doped carbon carbon nanosheets (N-S-CNS) with three kinds of dimensional structures by
introducing different templates during the pyrolysis process. The Al-air battery fabricated by 2D N-S-CNS catalyst displays a power density of 144 mW cm\(^{-2}\) in alkaline electrolyte and 21.7 mW cm\(^{-2}\) in neutral electrolyte [103].

4.2.4. CO\(_2\)RR. The electrocatalytic CO\(_2\)RR is an attractive way to convert intermittent green energy sources into chemical energy, reducing the dependence on fossil fuels, while reducing net CO\(_2\) emissions by producing valuable fuels and chemicals from renewable sources [104, 105]. However, as an inert molecule, CO\(_2\) needs highly negative formal potential to drive the reduction process, while the process involves multiple proton-coupled electron transfer, resulting in the low energy conversion efficiency and low selectivity for a specific product [106, 107]. Optimizing the adsorption and activation processes of CO\(_2\) molecules and various intermediates are effective strategies to improve the catalytic activity and selectivity of CO\(_2\)RR, and CDs show unique advantages in this aspect [108, 109].

Lv et al prepared a N-doped MoS\(_2\) nanosheets and N-doped CDs composite (N-MoS\(_2@\)NCDs-180) by solvothermal method, and the composites display a low onset overpotential requirement of 130 mV for CO formation and a high Faradaic efficiency up to 90.2%. NCDs play the role in accelerating the electron transport to promote the electroreduction of CO\(_2\) to CO [110]. Furthermore, Zhou et al combined –NH\(_2\) modified CDs (NCDs) with CuO to increase the CO\(_2\) conversion selectivity in carbon product from 69.4% to 84.5%. The modification of –NH\(_2\) on CDs effectively enhances the chemisorption capacity of CO\(_2\), while the electron sink effect of NCDs increases the electron concentration on catalyst surface. Therefore, the NCDs/Cu/CuO interface generates a higher concentration of CO\(_2\) and charge at the same time, promoting the C–C coupling process [65]. Zhang et al reported a functionalized QDVs which can convert CO\(_2\) to CH\(_4\) with simultaneous high selectivity of 70% and production rate. They found that the electron-donating groups (–OH, –NH\(_2\)) in QDVs can favor the produce of CH\(_4\) while the electron-withdrawing groups (–COOH, –SO\(_3\)) suppress this process [111]. Chen et al prepared a Bi\(_2\)O\(_3\)-NQDVs composite catalyst, which displays nearly 100% Faraday efficiency of CO\(_2\) to formate at 0.7 V. DFT calculation results reveal that the introduction of nitrogen-doped graphene quantum dots (NQDVs) increased the adsorption energy of CO\(_2\) and OCHO\(^-\) intermediate, which is the important factor to maintain the high catalytic activity over a wide negative potential range (–0.9 V to –1.2 V) [112].

5. Deep understanding based on transient photo-induced voltage (TPV) (current) method

Photoelectrocatalysis is a series of multi-scale processes involving photoelectrochemical, chemical and catalytic processes, with which the design and optimize of the catalysts should be built around. The main concerns focus on the following points. (a) The band gap structure regulation. (b) Carrier migration efficiency improvement. (c) Electron transport adjustment. Methods such as doping and defect, phase engineering, surface modification and interfacial construction are wildly used in current catalyst investigations. The commonly used characterization methods of photoelectric properties, including transient absorption spectroscopy, transient fluorescence spectroscopy, and transient surface photovoltage, etc, focus on the analysis and understanding of photochemical processes, which provide important insights into photophysical processes and rapid charge transfer processes. Ultrafast infrared and Raman spectroscopy give information of the surface bonding and active species on the catalyst surfaces. These in-situ signals present the information at a steady state of a catalytic reaction, seldom reflecting the changeable processes. So, the in-situ analysis and kinetics of the catalytic interface are still lack of corresponding characterization analysis methods. It is urgent to illuminate the mechanism of photocatalytic reaction by conducting in-depth study on the interface dynamics of photo- and/or electro-catalytic system. Dynamic in-situ spectroscopy/microscopic imaging is needed to directly determine the intermediate structure that exists on the surface of the catalyst and to obtain the kinetic parameters of the intermediate reaction.

5.1. New methods for transient photoelectrochemical characterization

In-situ dynamic study of a photocatalytic system is subject to many limitations. For example, photo excitation interferes the common spectral measurement techniques. The additional electrical disturbance will cause the performance change of the photocatalyst, leading to the inaccuracy of the test results. Photoelectrocatalysis is a series of multi-scale processes involving photoelectrochemical, chemical and catalytic events, as shown in figure 5 [113–115]. Photophysical characterization of photocatalytic processes provides important information about photophysical and rapid charge transfer processes, which often correspond to very fast time scales. Conventional electrochemical and photoelectrochemical techniques can obtain potential, current and photoelectrochemical response characteristics in relatively slow time scales for catalytic processes. However, the interface behavior of photoelectrocatalytic system connects photophysical and surface catalytic processes, and is in the region of several hundred nanoseconds to several hundred milliseconds on the time scale, which is the weak area of the current in-situ dynamic characterization of catalysis. Due to the limitation of these photoelectrocatalytic systems, new characterization methods need to be established. Considering that photoelectric excitation is a necessary condition of catalytic system, it is a reasonable approximation to simulate catalytic reaction system by using the instantaneous photoelectric stress response of catalyst. Using the instantaneous photoelectric stress response with limited conditions, we can obtain the quantitative information of the transfer orientation of charge distribution, the charge transfer kinetics and the number of electron transfer in catalytic reaction. Next, we briefly introduce new methods for transient photo-induced current/voltage (TPC/TPV) characterization based on instantaneous photoelectric stress response.
5.1.1 Transient photo-induced current (TPC). By combining the rotary counter electrode technology with the instantaneous photoelectrical stress response, the method model of photoelectron directional extraction and in-situ photocatalytic forced dynamic process can be constructed. The basic idea involved in this method is based on directional charge movement in response to photoelectrical stress, hence the method is named TPC (figure 6(a)). Taking the water decomposition reaction as an example, the number of transferred electrons (n) of the photocatalytic semi-reaction can be obtained in situ by means of the current change of the transient photo-induced disk/ring electrode (figure 6(b)).

For the photocatalytic decomposition of water, the intermediates corresponding to the two-electron reaction process and the four-electron reaction process are different in the half reaction of water oxidation. Therefore, TPC technique can be used to measure the number of apparent semi-reactive transferred electrons to determine the reaction path and reaction intermediates. Liu et al demonstrated for the first time using TPC that CDs/C₃N₄ can realize photocatalytic overall water splitting via a 2e⁻/2e⁻ path two-step process [70]. Zhao et al used TPC to measure the electron transfer number of Ni-CAT-CN₆₀ is 4, indicating that the H₂O was oxidized to O₂ follows a typical four-electron path [116]. Li et al reported a CN₁₈/ICT/CDs catalyst to produce H₂O₂ through a dual-channel process via solar-driven water splitting. In this catalysis system, the transfer electron number was calculated to be 2.34 by TPC, suggesting that water participates in the 2e⁻ reaction to generate H₂O₂ [117]. Guo’s group also tested the electron transfer numbers of different photocatalysts using TPC, and their research showed that g-C₃N₄ is thermodynamically favorable for the formation of H₂O₂.
At present, this method has become an important mean to investigate the electron transfer number of photocatalytic decomposition of water and has been widely used [59, 113, 119, 120]. However, this method cannot provide information about the transfer orientation of electron transfer and charge distribution at the photocatalytic interface, the kinetics of transport and the kinetics of in-situ reaction.

5.1.2. Transient photo-induced voltage (TPV). Based on the above analysis, Kang’s group proposed a new characterization method, namely TPV method. The schematic diagram of test principle is shown in figures 7(a) and (b). A pulse laser (355/532 nm) of 4 ns is irradiated on the sample, and the data are collected with time resolution of 50 ns, which can provide detailed information about the charge transfer, storage, recombination processes, and photo-charge-based catalytic reactions. The whole characterization covers reaction time ranging from microsecond to second scales. Through comparison of the parameters such as the maximum of intensity, the shape of the curves, the time of the maximum intensity, the integral area and attenuation constant, we can obtain the interfacial electron transport kinetics and in-situ catalytic process reaction kinetics directly or indirectly. These photoelectric response data help us determine catalytic active sites, the catalytic center and reactants characteristic, which can even be used to discover new properties of catalytic materials beyond expectations.

In a TPV curve (figure 7(c)), we can directly obtain the parameters of the charge extraction rate ($t_{\text{max}}$), maximum charge extraction efficiency ($A$) and electron attenuation constant ($\tau$). The small $t_{\text{max}}$ and large $A$ are corresponding to the fast charge transfer rate and photogenerated charges, while long $\tau$ means low recombination rate of electron–hole pairs. In order to show the combined influence of the three parameters, the surface effective electron number ($n_e$) of the catalyst is defined as $n_e = A \times \tau / t_{\text{max}}$, the value of which can present the charge transfer kinetics rate [119]. This value can help us to select the optimal catalyst in the orthogonal experiments without spending a lot of time to test the catalytic performances. Combined this assessment method with machine learning will provide a highly efficient way for catalyst design in the future [121].

5.2. CDs as an excellent model catalyst characterized by TPV

Photo- and/or electro-catalysis that surrounded solar energy are important technologies to solve the energy and environmental problems. In traditional catalytic systems, carbon is always considered as a good catalyst substrate for it lacks catalytic activity. However, when reducing the size of the carbon materials, the small size effect will bring abundant photo- and/or electro-chemical properties, which may promote them to be an ideal paradigm for catalytic study as active sites or other functions more than substrate. Through heteroatomic doping or surface functional group modification, CDs can be used as catalysts along. Its surface properties also make it a proper component for other photoelectrocatalysis systems, which can be combined with most metals and semiconductors. The main roles of CDs in a compound system are summarized as follows. (a) CDs can facilitate the charge transfer on the interface and lead to high-efficient charge separation. (b) Modulate the bandgap structure of semiconductors, increase the light absorption. (c) Surface reaction activity. These advantages give us an excellent model for TPV
to investigate the interfacial kinetics and build the theoretical basis for other similar catalytic systems (figure 8). The main functions of TPV including four points. (a) It helps us identify the active site in a catalyst. (b) It can be used to determine the type of reactions. (c) It gives clues to illuminate the reaction mechanism. (d) It quantifies the charge transfer kinetics processes. The research on CDs catalysis is developing rapidly, but the specific catalytic mechanism has been given a vague explanation. TPV technology provides a new path for further exploring the photoelectric catalytic mechanism of CDs.

5.3. Application of TPV technology in photocatalysis

TPV curves can be used to identify the active sites of a photocatalyst. When the catalysts are exposed in different environmental conditions including gas atmosphere (O₂ or N₂) and solvent (H₂O or acetonitrile), the intensity of the TPV curves give information of which active sites consume the electrons. Through this method, Wang et al determined that the pyrrolic nitrogen in the nitrogen-doped CDs is the catalytic active sites and substrate binding sites in the enzyme-like catalysis (figures 9(a) and (b)) [122]. Zhou et al demonstrated that g-C₃N₄ is the active site for CO₂ reduction in the COF1-g-C₃N₄ system (COF: covalent organic frameworks) [123].

The TPV curves also can be employed to determine the reaction type. For example, the proportion of oxygen reduction and water oxidation in the photo-induced H₂O₂ production can be calculated through comparing the integral area difference [124]. While in the photocatalysis of organic semiconductor DAnTMS (DAnTMS synthesized from 9,10-dibromoanthracene (DAn) and trimethylsilylacetylene (TMS)), the shapes of the TPV curves in different gas and solvent situations are different, indicating the inconformity of the reaction mechanism for DAnTMS. The difference values of the photovoltage intensity were compared to show that the reaction rate of H₂O reduction is faster than that of H₂O oxidation [125]. Liu et al prepared Ni₂P/CDs composite for water photocatalytic-splitting [126]. Although O₂ reduction showed slow kinetics, the ratio of the number of electrons consumed by the catalyst under water-saturated conditions and saturated O₂ conditions illustrated that the O₂ reduction reaction is dominant when prolonged the reaction time. Zhao et al constructed a C₃N₄ modified Ni-CAT composite. The photovoltage intensity increased slightly in trace water and decreased sharply in O₂, which means this catalyst showed ability of both water oxidation and oxygen reduction. The ORR is the main step and the ratio of oxygen reduction to water oxidation is 6.3 [120].

New reaction mechanism can be illuminated by TPV test. For example, a new photochemical property of CDs, namely electron well effect, is discovered by in-situ TPV test. Wu et al designed and synthesized a non-noble metal photocatalyst based on polymer CDs, which is named as PM-CDs. Due to the salt enhanced electron well effect (figure 9(c)), this catalyst realized the direct high-efficient photo-synthesis of H₂O₂ from seawater and oxygen. Generally, a large amount of photogenerated charges is consumed in terms of salt in seawater, leading to the deactivation of the photocatalysts. In the TPV curves, it is interesting to find that when NaCl is added in the CDs, the intensity of photovoltage increased because of the enhanced electron-withdrawing property of the functional group by ionization increases electron extraction...
rate under the same excitation (figure 9(d)). Also, negative signal region on the TPV curve was observed (figure 9(e)). The ‘trapped’ electrons surrounding adjacent oxygen cannot participate in the electron–hole recombination process in a short time due to the increased energy barrier of the electron sink. The equilibrium time was prolonged as the ‘trapped’ electrons slowly pass through the barrier and recombine with holes. The PM-CDs catalyst exhibited high photocatalytic ability to produce H$_2$O$_2$ with the yield of 1776 µmol g$^{-1}$ h$^{-1}$ in real seawater (figure 9(f)), about 4.8 times higher than the pure polymer [127].

The intensity of TPV represents the relative amount of charge. High TPV intensity also partly indicates the high charge extraction process. But the processes are different in details. For example, in COF1-g-C$_3$N$_4$, the high intensity of the TPV curve showed a sharply decrease in 1.3 µs, and then the attenuation trend tends to be flat, which denotes that the photo-induced electrons undergo extremely fast transfer due to the covalent structure in COF1-g-C$_3$N$_4$ [122].

Fourier transform (FT) can extract the periodic frequency component in signals through decomposing them into alternate representations by sine and cosine. Usually, the TPV curves of materials show obviously non-static characteristic without periodic frequency components, which are more suitable to be analyzed by continuous wavelet transform (CWT). CWT is a time-scale/frequency-scale transformation, giving the contribution of the electron transfer velocity at a certain moment in a catalytic reaction. Han et al employed this analytic method to show that the CDs enhance the interface electron transfer of TiO$_2$ [128]. In the CWT transformed curves, the peak positions of intensity vs time are shown in figure 9(g) at a frequency of 50 Hz. The peak positions on the time scale were different between TiO$_2$ and CD modified TiO$_2$ (TNCD 15 mg). The average of the sets of time differences were shown in figure 9(h). The peak delay times show positive or negative values. By compared the data from CWT, he concluded that N-CDs can accelerate the interface fast electron extraction by about 0.05 ms, and increase the maximum electron storage time by CDs up to 0.56 ms. Similar phenomenon was also observed in the CDs/NiCo$_2$O$_4$ for water splitting [116].

The empirical mode decomposition (EMD) is another TPV data processing method in the situation that when the signals
exhibit irregular oscillation, meaning the excited electrons transport inner the materials back and forth. EMD is an adaptive time-space analysis, which can locally counterbalance white noise and divide the signal sequences into a series of intrinsic mode functions (IMFs) in the case of retaining time information. IMFs show the fast speed transportation with short periods and low speed transportation with long periods. Zhang et al demonstrated that CDs improve the electron transport in the fast speed processes corresponding to the charge transport between CDs and poly (9-vinyl carbazole) (PVK) molecules (figure 9(i)), enhancing the brightness of PVK LEDs (Light-emitting diode) [129]. CDs form the trap states to bound or capture electrons when absorbed on the PVK molecules is also observed at the long period, which may be applied in photocatalysis.

5.4. Application of TPV technology in electrocatalysis

The TPV method also provides new thought for electrocatalytic process characterization. Electrocatalysis involves multiple electron transfer processes. The electron transfer dynamics has important effect to the formation of intermediates and further the final catalytic performance, which is difficult to quantify due the complex catalyst structure and transient behavior of the migration. The decay curves in the TPV test can be used to analyze this process. When a laser is irradiated on the electrocatalyst samples, the excited plasmon-induced hot electrons, which is a useful substitute for simulating electron motion during the electrocatalytic process. Also take CDs as an example. In a CDs modified electrocatalyst, CDs mainly provides two functions. One is modulating the overall electron transfer rate. Another is changing the charge distribution concentration of local environment at the interface of the modified material.

Wu et al adopted the CDs modified PtNi2 (PtNi2-CDs) composite as an electrocatalyst for alkaline hydrogen oxidation reaction (HOR) [130]. The laser-induced hot electrons transfer through the PtNi2-CDs and generate stimuli-response current and exhibit as a typical TPV decay curve. All the signals present trend as declining sharply at first and then leveling off gradually (figures 10(a)–(f)). The decay time of the rapid decrease region and the complete region can be extracted respectively. For PtNi with increasing Ni content, the average electron relaxation time ($\tau_{ave}$) decreases from 0.3644 ms (Pt/C) to 0.0220 ms (Ni/C), indicating that the fast electron transfer occurs on Ni sites and slow electron transfer occurs

Figure 10. The applications of TPV test in electrocatalysis. (a) TPV curve of PtNi2/C; (b) average electron relaxation time of metal-based samples; (c) CWT pattern of PtNi2/C; (d) TPV curve of PtNi2 5 mg CDs/C; (e) average electron relaxation time ($\tau_{ave}$) of PtNi2/C with different amounts of CDs; (f) CWT pattern of PtNi2 5 mg CDs/C [130] (Copyright (2022), with permission from Elsevier). (g) TPV curves of NCDs, CuO and CuO-NCDs-2, (h) Schematic diagram of NCDs regulating electron transfer behavior of Cu/CuO ($v_e$: electron transfer rate; the length of the green arrows indicates the transmission speed) [65] (John Wiley & Sons. © 2022 Wiley-VCH GmbH).
on Pt sites. In HOR, Pt is the main active sites. The slow electron transfer speed is unfriendly to the electrocatalytic process. After introducing CDs, the complete signal decay time for PtNi₂/C 5 mg CdCs/C is 4.5 ms shorter than that of PtNi₂/C, which indicates that the decay process of the curve is effectively modulated. The fast FT and the CWT processed data presented the signal frequency components of different frequency and time-frequency characteristics of the samples. The decay curves have obvious non-static characteristics while after combining with CDs, the signal frequency of PtNi₂/C in range of 0–4500 Hz changes to 0–150 Hz, indicating the wide interface electron-transfer speed distribution of PtNi₂/C catalysts is sharply narrowed by CDs.

The similar function of CDs is also observed in the NH₂-CD modified Cu/CuO catalysts for electrocatalytic reduction of carbon dioxide [65]. The decay constant of Cu/CuO-NCD is much lower than that of Cu/CuO, indicating that CDs increase the charge transfer rate. In Cu/CuO-NCD decay curves, a negative signal region can be observed, which is due to the electron sink effect from NCDs (figure 10(g)). So, the electrons are more likely to be limited at the interface of the composite, leading to a higher concentration of electrons at the local sites, which is conducive to the multi-electron reduction reaction. At the same time, the signals from the CWT were used to extract the differences of electron transfer time at different frequencies. It was found that the influence of CDs on the catalytic system mainly occurred in the low-frequency region, and CDs could effectively improve the slow electron transfer rate in the reaction, thus improving the catalytic performance (figure 10(h)).

6. Outlook

In this paper, the recent research progress of CDs is briefly introduced, including the synthesis, basic structure and properties of CDs, photoelectrocatalytic function and the application of CDs in photoelectrocatalytic field. The unique advantages and great potential of CDs in clean energy conversion and storage cannot be ignored. In addition, photoelectrocatalysis has a very complex interfacial process, so it is very difficult to deeply study the mechanism. The existing characterization technologies are easy to obtain steady-state information in the photoelectro catalysis process, but it is difficult to reflect the change during the reaction process. Therefore, a new method of in-situ analysis and kinetic characterization is introduced, with CDs as an excellent model. TPV technology was used to collect and analyze the dynamic process affected by CDs in photoelectrocatalytic process.

Although CDs has been extensively studied, there are still some major challenges, including controlled preparation and purification, regulation and quantification of chemical structure, quantitative analysis of structure and property relationship, etc. The structure of CDs including size, crystallinity of carbon cores, functional groups and other factors has decisive influence on its physical and chemical properties. The study and analysis of the structure-activity relationship of CDs are important goals of future research, which have theoretical significance for us to deepen the understanding of CDs and expand its practical application.

CDs may not represent the most efficient catalysts, but they bring a revolutionary understanding on catalytic mechanism and catalyst design principle. The TPV technology may not represent the most advance and universal techniques, but it brings a new and specific information on electron transfer kinetics for catalytic mechanism and catalyst design. We believe that with the development of advanced synthesis methods and characterization techniques, it is bound to deepen our understanding of the relationship between the structure and properties of CDs, reveal the mechanism of action of CDs as photoelectric functional units, and promote the further development and application of CDs in photoelectric catalysis and other fields.

Acknowledgments

This work is supported by National MCF Energy R&D Program of China (2018YFE0306105), National Key R&D Program of China (2020YFA0406104, 2020YFA0406101), Innovative Research Group Project of the National Natural Science Foundation of China (51821002), National Natural Science Foundation of China (51725204, 21771132, 51972216, 52041202, 51902217), National Science Foundation of Jiangsu Province (BK20190041), Key–Area Research and Development Program of GuangDong Province (2019B010933001), Collaborative Innovation Center of Suzhou Nano Science and Technology, the 111 Project, and Suzhou Key Laboratory of Functional Nano and Soft Materials.

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