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Computational insights into carbon dots: Evolution of structural models and structure–activity relationships



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ABSTRACT

As researchers have gained a deeper insight into the properties of carbon dots (CDs), their applications gradually spanned from fluorescent probing and bio-imaging to energy storage, catalysis, and other numerous fields in recent years. At the same time, computational methods are also employed to deepen the understanding of CDs on the other sides. In this process, the establishment of the statical atomic model and structure–activity relationship is becoming especially valuable. This review summarizes the progress to date in the construction of structural models referring to CDs and evaluates their significance in establishing structure–activity relationships. Specifically, the modeling strategy of CDs and CDs composites, and the functions of related models in explaining CDs as fluorescent reagents, biological probes, catalytic materials, and energy storage devices will be evaluated, aiming at offering some different insights for the design of more rational and reliable CDs-based models for the exploration of more novel characteristics and phenomena related to CDs.

1. Introduction

From emerging luminescent nanomaterials to robust catalysts, CDs [1] including graphene quantum dots (GQDs) [2], carbon nanodots (CNDs) [3], and carbonized polymer dots (CPDs) [4], have attracted numerous researchers' attention, where their properties have been gradually revealed by an increasing number of in-depth studies. To elaborate, GQDs consist of minute fragments of graphene, composed of single or a few graphene sheets, featuring pronounced graphene lattices and chemical groups located along the edges or within interlayer defects. These characteristics contribute to their unique properties, including the quantum confinement effect and edge effects. GQDs are typically anisotropic, with lateral dimensions usually below approximately 20 nm and heights less than five layers of graphene sheets (around 2.5 nm). It's worth noting that the quantum confinement effect

encompasses both the confinement of GQD sizes and the confinement of conjugated π -domains, which are isolated by defects on the graphene plane [2]. An increase in oxygen content often leads to more defects and, consequently, more conjugated π -domains, serving as fluorescence centers. In contrast, CQDs are spherical structures with distinct crystal lattices and chemical groups on their surfaces. They exhibit intrinsic state luminescence and experience a quantum confinement effect related to their size, making it a meaningful approach to tuning the wavelength of photoluminescence [4]. CNDs are characterized by a high degree of carbonization with some surface chemical groups but usually lack obvious crystal lattice structures and polymer features. Their photoluminescence primarily originates from defect/surface states and subdomain states within the graphitic carbon core, without a quantum confinement effect tied to particle size. CPDs have a hybrid structure consisting of polymer chains and functional groups on the surface

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Scheme 1. Structure schematic diagrams and the classification of CDs, including graphene quantum dots (GQDs), carbon quantum dots (CQDs), carbon nanodots (CNDs), and carbonized polymer dots (CPDs).

surrounding a carbon core [5] (see Scheme 1).

CDs can be readily synthesized through two primary approaches: "top-down" and "bottom-up" methods [3]. In "top-down" methods, CDs are typically derived from larger carbon structures, such as graphite powders. Specific techniques include electrochemical exfoliation, acidic oxidation-exfoliation, and microwave methods, etc. These processes fragment bulk carbon into ultra-fine pieces, resulting in diverse surface states of CDs. On the other hand, "bottom-up" methods involve the efficient synthesis of CDs through processes like microwave treatment, hydrothermal synthesis, and calcination [3–5]. CDs produced via these methods originate from small molecules or oligomers, and as a result, their final products exhibit chemical structures resembling their precursors. These diverse preparation methods yield valuable insights for constructing models of CDs. Following the synthesis, a purification process is essential to remove residual precursors and reaction intermediates. Dialysis and chromatographic purification methods have been developed and play crucial roles in this regard, where the former method can be used for impurity removal, and the latter one is usually used to meet the needs of CDs separation [3,4]. Regardless of the chosen purification method, it contributes to obtaining pure CDs products with specific surface structures. Subsequent characterizations can then be used to confirm the structures of CDs.

When CDs samples with a specific composition are obtained, researchers can hardly wait to explore the physical properties of these novel nanomaterials. It is well recognized that CDs, as a type of nanomaterial with quantum effects, exhibit high luminescence, chemical stability, good solubility, abundant catalytic sites, or controllable surface states, and have huge potential for a wide range of advanced applications spanning from bioimaging [5], biosensors [6] to photo/ electro-catalysis [7], solar cells [8], light-emitting devices [9], and energy storage materials [10] in the next generation. At the same time, relevant theoretical calculations referring to CDs also play a crucial role, greatly helping accelerate the understanding of relevant experimental phenomena. Unlike other carbon allotropes like mesoporous carbons or activated carbons with a large size on a micron scale, CDs, with diameters not larger than 10 nm, suggest they are more easily described by structural models, where the calculation results can better match experimental expectations. Now, computational assistance involving CDs has become an indispensable technical means in relevant experimental papers.



Scheme 2. The general logic of the computational process of CDsbased models.

Till now, numerous outstanding reviews discussing the dramatic photoluminescence (PL) property of CDs have emerged from diverse viewpoints. These reviews mainly contain basic knowledge such as structural features, synthesis approach, PL mechanism, and, most importantly, the explanation for the structure-activity relationship [11–13]. As for the unique theoretical and computational perspectives, Otyepka's group and Lu's group reviewed the PL property and electrocatalytic performance of CDs, mainly focusing on the related computational studies [14,15]. It is also noteworthy that the comprehensive review reported by Carbonaro's group highlights the vast majority of in silico methods involved in the study of CDs in different types [16]. Meanwhile, Iskandar's group reviewed the design and discovery of novel CDs-based nanomaterials with the assistance of promising machine learning techniques that can provide a deep understanding of the synthesis-structure-properties-performance relationship [17]. Compared to existing computational reviews of CDs, which primarily focus on the intrinsic properties of CDs themselves, our work places a greater emphasis on the impact and behavior of CDs as constituents of a broader composite system. Based on our previous work on carbonrelated energy storage materials, we have a good chance to reveal the nature of the structure-activity relationship among CDs-involving systems. This approach allows us to explore how CDs influence and contribute to the overall performance of the corresponding materials, opening up new avenues for the application of CDs-based materials in diverse fields. Furthermore, the establishment of structural models for CDs plays a pivotal role in elucidating the structure-activity relationships governing its chemistry and physical properties, which also deepens our understanding of the functionality of CDs from a theoretical perspective. Despite advances in related research, a consensus on the computational models for CDs remains elusive. Specifically, the design

framework of atomic models is instrumental in elucidating the remarkable capabilities of CDs. A significant challenge lies in achieving a balance: the model must be detailed enough to closely mirror experimental systems, yet sufficiently simplified to highlight key features with reasonable accuracy, and the specific logic is shown in Scheme 2.

In the following parts, a detailed discussion regarding the model construction of CDs and CDs-related composites will be made, involving the basic methods for constructing the CDs model with different modifications or in different composites. Then, the application of CDs models in the exploration of the structure–activity relationship of various materials will be analyzed. Finally, insightful views will be offered for the possibility of further design of theoretical models that are able to overcome the limitation of computational scale.

2. The roadmap for CDs models

2.1. Basic methods for constructing CDs models

As we know, the typical workflow of computational chemistry is to obtain a detailed description of electronic structures for the corresponding system through a set of theories and numerical algorithms based on the Schrödinger equation. The wave function, containing all information about electrons, and the Hamiltonian operator provide the structural information of related particles and contribute to the molecular models.

Limited by the restriction of computational resources and technique, the theoretical approaches in chemistry are categorized based on their scale and scope, encompassing methodologies like Nonempirical Wavefunctional Theory, Density Functional Theory (DFT), Molecular Dynamics (MD), and Monte Carlo (MC). Nonempirical Wave-functional Theory, in particular, can be further classified into two main types: Hartree-Fock (HF) and post-HF methods. The classical HF method is a foundational quantum chemical approach designed to approximate the electronic structure of small molecules. It calculates the quantized energy of a system by solving the Schrödinger equation within the fundamental framework of the HF scheme. However, the energy obtained from HF consistently exceeds the exact ground state energy due to inherent limitations in accurately describing electronic correlation effects. This correlation energy, defined as the difference between the HF limit and the exact (non-relativistic) solution within the Born-Oppenheimer (BO) approximation, highlights the HF method's shortcomings, particularly in capturing strong correlation effects found in multi-electron excited states and strongly correlated compounds. To address these deficiencies, post-HF methods have been developed, incorporating higher-order electronic correlation effects. Examples include the Møller-Plesset (MPn) methods, Configuration Interaction method (CI), multiconfigurational self-consistent field (MCSCF), and coupled cluster method (CC). While these methods partially mitigate the limitations of electronic correlation seen in HF, their detailed treatment significantly increases computational costs, making them more suitable for smaller systems.

The following DFT methods propose a suitable approximation for the exchange–correlation (XC) functional form to address the electronic correlation effects based on electronic density. It leads to the solution of the Kohn-Sham formulation and allows for the determination of the total energy of systems. Local density approximation (LDA) and generalized gradient approximation (GGA) are widely used approximations in describing molecular structures, chemical bonding, and charge distribution with reasonable accuracy at a relatively low computational cost. Subsequently, the limitations of LDA and GGA for neglecting the non-local electron–electron correlation effects could be solved through the modified DFT-based methods such as non-local core, empirical corrections, double-hybrids, random phase approximation (RPA), and *GW* approximation. These methods could provide a better description of the correlation effects with higher accuracy.

Theory (TD-DFT) approach addresses the solution of the time-dependent Schrödinger equation by introducing a time-dependent effective potential, incorporating the adopted exchange–correlation (XC) approximation, where the time-dependent effective potential is derived from the functional derivative of the XC potential with respect to the electron density. With the assistance of the theorem of Runge and Gross, it's readily possible to obtain the time-dependent Hartree potential and further the excitation energy and characteristics of corresponding systems.

Based on current research, we have observed that the accuracy of Time-Dependent Density Functional Theory (TDDFT) methods is critically dependent on the choice of the XC approximation. Especially, longrange corrected functionals and hybrid functionals have proven to be more suitable than pure functionals for calculating excited states. Notably, functionals such as X3LYP, B98, PBE0, and mPW1PW91 exhibit outstanding performance in optical property calculations. Additionally, the basis sets employed to describe electronic wavefunctions can be categorized into two types: plane waves and atomic orbitals. The former includes ultrasoft pseudopotentials and norm-conserving pseudopotentials when periodic conditions are considered, while the latter comprises three types: Gaussian-type orbitals (GTO), Slater-type orbitals, and Numerical-type orbitals (NTO). The suitable choice of diffuse and polarization functions added to the basis set could significantly improve the precision of description for the long-range interactions and covalent bonds within excited states, respectively. In calculations related to CDs, GTO basis sets, particularly the 6-31G and 6-311G basis sets, are widely employed. [16].

Moreover, the influence of the solvent environment on excited states is highly pronounced. Two primary strategies are commonly employed for managing the solvent's impact. The first approach adopts the explicit solvent model, wherein solvent molecules are meticulously constructed and subjected to Quantum Mechanical (QM) calculations concurrently with the solute molecules. Alternatively, the Quantum Mechanics/Molecular Mechanics (QM/MM) method is employed, wherein the surrounding solvent molecules are treated using a molecular force field. An additional approach is the implicit solvent model (ISM), which conceptualizes the solvent as a continuous medium. This method introduces a field or energy term representing the solvent environment to simulate interactions between solute molecules and the solvent. Noteworthy models encompass the Polarizable Continuum Model (PCM), the solvation model based on density (SCM), and the conductor-like screening model (COSMO).

Unlike the former two methods that focus on the description of electronic structures and are widely used for isolated small molecules with high accuracy, the classical MD simulations could provide dynamic insights by modeling the time evolution of atoms and molecules in huge complex systems such as proteins, materials, and solutions. Aided by Newton's equations, it is particularly well-suited for studying energy, electronic structures, vibrational frequencies, and thermodynamic properties through static calculations.

Additionally, molecular dynamic calculations can facilitate the investigation of temperature (T), pressure (P), diffusion, and the time evolution of motion trajectories. These simulations are generally carried out through typical ensembles like the canonical ensemble (NVT), isothermal-isobaric ensemble (NPT), microcanonical ensemble (NVE), and grand canonical ensemble (µVT). To elucidate the intra- and intermolecular interactions within a molecular system, including covalent bonds, non-bonded interactions, and electrostatic forces during simulation processes, the utilization of empirical Force Fields (FF) is typically indispensable. Parameters embedded in these force fields, such as bond lengths, force constants, and potential energy functions, are often determined empirically through Quantum Mechanics (QM) calculations and experimental data. This approach ensures an accurate representation of molecular system properties throughout the simulation. The choice of a specific FF generally hinges on the research focus and the characteristics of the system under investigation, with options including

In the framework of DFT, the Time-Dependent Density Functional



Fig.1. (a) Energy level diagram calculated by structural models, and transition type of CDs with efficient blue RTP behaviors. Adapted with permission from Ref. [24], Copyright 2023, Wiley. (b) Calculated structures, adsorption, and PL spectra of IPCA-like surface molecular centers. Adapted with permission from Ref. [26], Copyright 2019, American Chemical Society. (c) Optimized structures and fluorescence spectra of edge and surface-modified GQDs. Adapted with permission from Ref. [30], Copyright 2023, Elsevier. (d) Construction of 3D models of polymer CDs by MD simulation through layer-by-layer assembly of CA-based building blocks. Adapted with permission from Ref. [38], Copyright 2018, American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

widely recognized ones such as Amber, CHARMM, OPLS, and COM-PASS, among others.

Diverging from classical Molecular Dynamics (MD) simulations, Born-Oppenheimer Molecular Dynamics (BOMD) distinguishes itself by integrating dynamical simulations with ab initio methods, employing the Car-Parrinello (CP) approach. Within this methodology, electronic wavefunctions dynamically optimize to acquire the ground-state electronic structure of the system. This approach proves particularly advantageous when investigating smaller-sized systems, consequently expanding the application scope of dynamical simulations. Describing the BOMD methods offers a more reasoned explanation for the extended applicability of MD simulations.

The MC method is used to simulate the stochastic occurrence of events in a system, primarily at the atomic scale, which investigates the system's dynamical behavior by simulating the randomness of events and is usually applied for the simulation of larger systems, even complicated complexes with fuzzy structural information such as CPDs. These methods come with their own sets of advantages and limitations, and researchers choose the most appropriate approach based on their research topic and system characteristics.

In some cases, combining these methods can lead to a more comprehensive understanding of molecular and material properties. The suitable choice of computational models will lead us to a better understanding of the behaviors and properties of involving atomistic structures, further helping to build integrated quantum-level databases for the screening of descriptors that fit the training models in machine learning technology.

In this section, we will categorize common CDs models into four classes based on their structural characteristics: isolated molecules, graphene-like sheets, stacked models, and mixed systems. Additionally, we will provide a detailed exploration of the establishment rationale and the strengths of each model.

As the standard starting point for calculation and simulation, the construction of the atomic structure model derived from the characterization result plays a vital role in obtaining precise information about electrons, orbitals, and energy for corresponding molecules from a microscopic perspective. For instance, X-ray Diffraction (XRD) provides the basic structural information, serving as the fundamental framework for models. Transmission Electron Microscopy (TEM) gives an unambiguous image of the core region structure, while the Atomic Force Microscope (AFM) is used to study the dimensions and morphology of particles. The combination of X-Ray Photoelectron Spectroscopy (XPS), Nuclear Magnetic Resonance (NMR), and Fourier Transform Infrared Spectroscopy (FTIR) provides information about functional groups and orbital hybridization, making a significant contribution as a reference for model construction. After a reasonable optimization and relaxation process at the appropriate computational level, the calculated results contribute to the explanation of reaction mechanisms and the prediction of novel structures significantly [18–20].

CDs with 0D nanostructures are commonly described through a 'core-shell' model, where the inner core is mainly composed of ordered sp^2 graphitized carbon or graphene, and the outer shell consists of many disordered modified functional groups or polymer chains [21]. While fully detailed structural characteristics have not been illustrated by existing experimental techniques, scientists have made a significant effort to design a reasonable model of CDs with different scales to meet the requirements of calculations. Reduced molecular models with diverse strategies have proven to be a reasonable method to achieve our aim. There emerges a considerable number of structural models with different particle sizes, the capabilities of which have already been

verified. Along with the enlargement of the system scale, isolated small molecules and partial graphite sheets originating from the synthesis process, aggregates of layer structures, and polymer species supported by π - π and van der Waals interactions, respectively, even the spherical model with detailed descriptions of core–shell structure and important modifications like defects, doped heteroatoms, and functional groups are established for the interpretation of structure–activity relationships. This will be discussed further in this section. Other than focusing on the models and properties of CDs themselves, the complex system containing CDs, widely used as energy storage and catalytic materials, also warrants our attention. The remarkable effects brought about by CDs based on the slab model could be revealed by DFT or first-principle calculations, where the construction strategy and reduced logic of the structural model could assist us in obtaining the microstructural parameters of some materials with unique performance.

A most intuitive example was contributed by Strauss and co-workers, where they reported a novel method to synthesize CNDs with narrow and excitation-independent luminescence characteristics. The combination of theoretical analysis and luminescence experiments has perfectly illustrated the photo-physics of such carbon-based nanomaterials [22]. Density Functional Theory (DFT) calculations on six CNDs models with different chemical modifications at @B97X-D/def2-SV(P) has shown that the increasing particle size of CNDs leads to a noteworthy red-shift in absorption and luminescence bands, while the epoxidation and pyridinic nitrogen doping of CNDs went the opposite way. The subsequent molecular dynamics (MD) simulation of the solvated sp²-network of CNDs further confirmed that these structural defects of the model system were responsible for the effect on the resulting optical properties. Together with the charge-transfer properties acquired by time-resolved techniques, theoretical and experimental results collaboratively showed the dynamic of a quenching process to explain the deactivation pathways of luminescence at longer wavelengths. The fundamental structure-property relationship of this novel CNDs was revealed, and its unique advantage could serve as a valuable building block that differs from other quantum dots.

As mentioned earlier, there are two popular routes for the preparation of CDs, one of which is referred to as the 'bottom-up' method. This method involves using carbon-based small molecule precursors to undergo a carbonization reaction, resulting in the final carbon nanoparticles. Polycyclic aromatic hydrocarbons (PAHs), such as citric acid (CA) and imidazo[1,2-a]pyridine-7-carboxylic acid (IPCA), serve as fluorescent species of precursors, intermediates, and byproducts obtained during the reaction process. Sometimes, these species display luminescence properties close to the desired CDs in a range of frequencies [23]. This insight suggests that these isolated molecules may serve as building blocks for reduced CDs models. For example, Song's group conducted first-principal Time-Dependent (TD)-DFT calculations with the assistance of seed-CDs and urea-tread CDs models derived from the synthetic precursor (3-aminopropyl) triethoxysilane. This investigation aimed to explore the room-temperature phosphorescence performance of designed CDs with outstanding fluorescence emission [24]. As depicted in Fig. 1a, the spin-orbit coupling values exhibit a remarkable increase after functionalization on the edge of the molecular model through the introduction of C=O, -NH2, and C=N groups. These alterations in the electronic configuration of CDs make the inter-system crossing (ISC) process from S1 to T3 possible. Additionally, the natural transition orbitals reveal the transition from (π , π^*)-dominated to (n, π^*)-participated in such a CDs system, indicating the transfer of electrons from an excited state to the ground state. This brings about effective room-temperature phosphorescence (RTP), consistent with experimental results showing enhanced phosphorescence efficiency in surface-modified CDs. This microscopic perspective helps us understand the photoluminescence mechanism, revealing that abundant functional groups tend to reduce the energy gap and facilitate ISC from singlet to triplet excited states. This insight suggests to subsequent researchers that isolated molecular models with limited size are sufficient to support

quantum chemistry calculations, providing a supplementary explanation of the hidden phosphorescence mechanism of CDs.

In general, the calculated absorption and fluorescence spectra of the selected isolated molecular models are typically similar to the corresponding experimental results, making the choice of the computational model and level reasonable. From a theoretical perspective, a basic correlation between computational and experimental results always exists, allowing the acquisition of key properties from both, thus ensuring the qualitative accuracy of the calculation framework [25]. To comprehend the mechanisms governing the blue-emissive properties of CDs, Kundelev and coworkers proposed a novel strategy involving the construction of a molecular model based on IPCA. This model represented the surface molecular centers attached to the CDs for quantumchemical DFT calculations [26]. As illustrated in Fig. 1b, the additional conjugated π -electrons result in red-shifts in both absorption and PL spectra. The noncovalent and covalent binding forces in dimer models exhibit the same effect but also a significant decrease in intensity at a similar band. Coupled with the decrease in computed oscillator strengths, it is reasonable to hypothesize that the remarkable weakening of emission intensity is derived from the aggregates of small PAHs on the CDs' surface. Subsequent experiments of PL spectra with variations in synthesis time further confirmed that the modification of surface molecular centers led to a dramatic decrease in PL intensity. Therefore, the bright PL in CDs mostly arises in the early stages of synthesis, between 1 and 2 h.

As pointed previously, other than "bottom-up" route, there is also an inverse method called the "top-down" approach capable of acquiring CDs. This method utilizes physical and chemical techniques to decompose bulk carbon structures into ultra-fine carbon nano pieces with the aid of harsh conditions such as strong oxidants and high temperatures. The obtained graphene sheets or fragments also have the potential to be good candidates contributing to building the detailed atomic model of CDs. Since graphite materials have been extensively studied in recent years, the relevant models have become the most popular choice for investigating GQDs. Concerning common models for theoretical calculations, two possible pathways exist to reach the aim. The simplest way involves directly considering the monolayer graphene within the periodic boundary as the building models, emphasizing the importance of the bulk area of the "core" region in CDs with a larger size of more than 10 nm. This approach is mostly applied to first-principles calculations. The other types of models are constructed using larger PAHs or diamond-shaped clusters, mainly focusing on the edge-functionalized effect. The former models are usually employed to study heterostructures containing CDs, where phenomena like electron-phonon coupling, electron-hole transition, and charge transfer are present. The latter focuses mostly on their own optical and electronic properties [27,28].

Recently, Boukhvalov's group proposed a novel CDs model based on ordered graphene layered structures. The model has different ratios of sp²/sp³ hybridized carbon atoms stranded for the graphic and functionalized areas, respectively. The central 24 sp² hybridized carbon atoms in this model exhibited better accuracy in describing electronic structures than the PAHs model of a similar size [29]. The calculated density of states (DOS) and band gaps have indicated that controlling the oxidation or reduction degree of such nanoparticles through the oxygen contents is a suitable method for tuning CDs to achieve desired PL properties. Additionally, Rani and coworkers [30] reported the fluorescence mechanism of GQDs by introducing heteroatoms and borinic related groups in their structures through a constraint monolayer molecular model shown in Fig. 1c. The calculated absorption and fluorescence spectra of edge modified GQDs both exhibit a red shift compared to the pure structural model and the HOMO-LUMO gap also decrease after the presence of electron-withdrawing groups. While the fluorescence quantum yield of s-B-GQDs containing both edge- functionalized groups and doped Boron atom reach 29 % which bring the possibility for potential bio-imaging application.

It is well documented that the formation of aggregates consisting of fluorescent organic species involved in the synthesis process could govern the optical response of CDs. [31]. Do similar dimer models of graphene sheets possess the same ability? Shi and coworker reported a computational study of stack models based on pyrene and coronene with different sizes to distinguish the differences between diverse reference methods, where the calculated absorption and emission spectra through DFT/Multi Reference Configuration Interaction (MRCI) methods exhibit good agreement to experimental data while the SOS-ADC(2) and CAM-B3LYP methods were able to provide a reasonable description for the excitation energies of four lowest excited states [32]. The involved calculation results of adiabatic excitation energy, vertical emission energies, and charge transfer values enlighten us the extended dimer system of larger PAHs, which is able to help us understand the properties of electronically excited states in the graphitic regions of CDs through the accurate description of charge transfer transitions, electron correlations and polarizability between the ground states and excited states.

Moreover, the first-principles calculation of the dimer model constructed through a bi-layer with different twist angle have shown the interlayer interaction energy was able to decompose into four types, the charge transfer energy of which display a remarkable contribution to the increase of twist angle and play an important role on determining the behavior of inter-layer coupling. This indicates that the physical origin of inter-layer coupling basically depends on the cross-layer overlap of Kohn-Sham orbitals, the clear illustration of which would be useful for the manipulation of optoelectronic properties of corresponding graphene-based CDs [33].

It is clear that simplified models based on small precursor molecules or larger PAHs are an effective way to study the optical properties of CDs. However, with the constant deepening of research, the relevant 3D models also need to describe their structural characteristics as detailed as possible to further ensure the accuracy of calculation results. While the specific atomic structure of CDs has not yet been accurately obtained, according to the results of experimental characterization and reasonable speculation, scientists still try to build more complicated and detailed CNDs models for further theoretical research. Based on the conformational behavior of the IPCA dimer system through classical MD simulations, the randomly distributed IPCAs at the primary stage prefer to form a π -stacking cluster containing 2 or 3 monomers at the first nanosecond time period of the simulation process, which implies the possible configurations of CNDs [34]. In 2018, Otvepka's group reported a dramatic work about the construction of the full model of CDs in a spherical shape that is available for all-atom MD simulations. This unique configuration derives from the stacking of the gradually decreasing size of the hexagonal graphene-like sheet from the middle to terminal position, and the functional groups covered surrounding the edge of the monolayer make the model more accurately approach to the real CDs. The simulated results indicate the CDs model with 2.1 nm of gyration, 0.34 nm of interlayer distance and hydroxyl, carbonyl, or carboxyl groups lead to the stability of spherical structures in water, while the excess internal interlayer hydrogen bonds of CDs in N,N-Dimethylformamide (DMF) suppress the interaction to solvent and present an aggregation of DMF that may affect the geometry or fluorescence of CDs [35]. Afterward, the investigations of CDs as Oxidation Reduction Reaction (ORR) catalysts in flexible Al-air batteries have referred to the above design logic to build CDs to study the detailed reaction procedures through DFT calculation, where the aggregates of three graphene sheets corresponded to the simplified patterns of pure and phosphorus doping CDs. The side-on geometry was proven to be the most energetically favorable configuration for O₂ adsorption on the edge of the graphene plane, the free energy diagrams of reduction steps have revealed the rate-determining step should be the formation of *OOH and the phosphorus-doped CDs exhibited a significant downhill free energy for each step of 4e⁻ transport pathway indicated the improved thermodynamic driving force for O2 dissociation. This suggested the phosphorus-doped CDs was a highly preferred catalyst for ORR in

battery device and confirmed the reliability of the spherical shape CDs model [36].

Unlike GQDs and CNDs, creating atomistic models for Carbonized Polymer Dots (CPDs) presents more challenges due to their intricate structures comprising mixed molecules, oligomers, and polymer clusters. To reveal the unambiguous nature of blue fluorescence and crosslink emission effect in the nano-size polymer CDs, a simplified model based on the aggregates of polymeric units with the stoichiometric formula of C₈H₁₂O₅N₂ obtained through NMR and elemental analyses experimental results was investigated via DFT and TDDFT calculations [37]. The analysis of molecular orbitals indicated an obvious separation from HOMO to LUMO located on amide and carboxylic groups respectively, the corresponding local charge transfer process contribute to the considerable change in dipole moment that led to the large Stokes shift, which was illustrated as the origin of fluorescence phenomena with the support by H-bonds supramolecular interactions. Meanwhile, Sau and coworker reported a 3D model of CPDs consisting of six building blocks based on the assemble of CA molecules in different sizes during the acidcatalyzed condensation reaction, the ultimate model with a compact sphere shape exhibit considerable stability through MD simulation that qualifies to perform the calculation for the description of electronic structure, which was shown in Fig. 1d. The possible electron-transfer pathway between CPDs and menadione was revealed via the distribution of molecular orbitals on different moieties, where the surfaces of CPDs with polymer structures always act as both electron donors and acceptors and the overlapping of π -electron clouds in CPDs contribute to its unusual double-humped periodic excitation-dependent photoluminescence. Obviously, the simplified 3D models of CPDs possess a similar construction logic that the aggregates of small molecules derived from the synthesis process of corresponding carbon nanoparticles satisfied the acquirement of the quantum chemistry calculations [38].

Till now, the construction methods of CDs models have evolved from isolated small molecules to complex structures containing various segments of polymers, essentially encompassing the most typical CDs models. As the demand for accuracy in CDs calculations constantly increases, a universal structural model with corresponding construction and simplification logic for theoretical calculations at different scales becomes necessary. This implies the establishment of a database containing key factors of CDs derived from both experimental and theoretical results, which will be crucial for the effective design of carbonbased quantum materials.

2.2. Basic requirements for constructing functionalized CDs models

It is well documented that photoluminescence (PL), as the most fundamental feature of CDs, commonly emerges with remarkable characteristics such as higher quantum yield (QY), longer emission wavelength, adjustable PL profiles, and controllable PL behaviors. Further investigations into the PL mechanism have revealed that absorption and emission behaviors, PL color, photostability, solvent, pH environment, and molecular states dominate the origin of luminescence in CDs [39]. Meanwhile, the quantum confinement effect determined by the particle size of an sp^2 carbon domain in the core region, the surface states consisting of the carbon backbone and connected functional groups, and heteroatom doping were considered effective methods to regulate the optical performance of CDs through the modulation of electronic configuration, especially the energy level and gap. According to the discussion in the previous section, common theoretical calculations usually simplify the atomic model derived from different synthesis routes, considering the consumption of computational resources, which can meet the demand for qualitative accuracy but may lack some integrality of the structural model. Thus, it is necessary to take the features of particle effect, surface defect, edged chemical groups, and doped heteroatoms into consideration as building blocks for the construction of atomistic models to make the corresponding calculations more reasonable [40,41]. In this section, our emphasis will be on a comprehensive



Fig.2. (a) Structures, HOMOs, and LUMOs of model species of CDs with different sizes. Adapted with permission from Ref. [44], Copyright 2021, American Chemical Society. (b) Absorption spectra of holey GQDs with their corresponding structures and DOS. Adapted with permission from Ref. [45], Copyright 2021, Elsevier. (c) Transition densities for the first bright transitions of the isomers of functionalized square GQDs. Adapted with permission from Ref. [48], Copyright 2022, American Chemical Society. (d) Density profile and structure of the CDs fragment were constructed through the assembly of PAH layers and IPCA anions. Adapted with permission from Ref. [49], Copyright 2020, American Chemical Society. (e) NTO pairs for the prominent excited states of doped GQDs. Adapted with permission from Ref. [52], Copyright 2020, Royal Society of Chemistry.

exploration of the influence of diverse modifications on CDs models and how these modifications can serve as valuable references for optimizing the structure and performance of CDs-related materials.

Chen's group has reported comprehensive research on the PL mechanism of GQDs with different sizes, edge configurations, shapes, connected functional groups, heteroatom doping, and surface defects through the combination of DFT and TDDFT calculations. The emission wavelength varies from deep Ultraviolet Radiation (UV) to near-infrared bands with an increasing diameter from 0.46 to 2.31 nm [42]. GODs with armchair edges could widen the band gaps, leading to a blue-shift of emission compared to hexagonal zigzag-edged structures. The attached oxygenated groups bearing on GQDs exhibited red-shifts on the fluorescence peaks, regardless of the edge or basal plane, similar to the effect caused by vacancy defects. On the contrary, the graphitic, pyridinic, and pyrrolic N atoms on GQDs bring a significant blue shift on the emission bands. These calculations based on fluorescence spectra provide a reasonable explanation for the existing experimental observations, confirming the regulating ability of the mentioned structural factors.

As we already know, the superior optical properties of common quantum dots originate from the quantum confinement effect that emerges when the size of the conjugated π -domain is smaller than their exciton Bohr radius, where the luminescence behaviors under excitation are highly related to the band gap of the crystalline graphite region. Similarly, the size of carbon cores in CDs, strongly coupling with surface functional groups, is closely related to the location, energy, and shape of the emission peak, leading to its unique optical-electric performance [43].

To address the urgent need for a quantitative relationship between electronic configuration and experimental measurements of CDs, Kang's group has proposed a semiempirical equation capable of acquiring HOMOs or LUMOs through their HOMO-LUMO gaps [44]. The equations, based on tight-binding methods with specific adjustments for CDs with various functional groups through work functions, have been shown to be accurate in predicting HOMO/LUMO values compared to the results of theoretical calculations based on CDs models of different sizes (Fig. 2a). The increasing size leads to a remarkable reduction in the band gap of corresponding CDs structures. These simple equations provide important guidance for evaluating the optical and photo-electrochemical properties of future-designed CDs with electro-optical applications.

Furthermore, surface defects introduced through surface oxidation or passivation can serve as capturing centers for excitons, where the non-perfect sp² domains in carbon cores are responsible for the multicolor emissions of CDs through the energy transfer and recombination of electron-hole pairs. Abdelati reported the optical properties of holey GQDs with different sizes, edges, and pore passivation through calculated geometric parameters, adsorption spectra, and DOS. Stable porebased models derived from two-dimensional graphene sheets were categorized based on terminated H atoms replaced by F atoms or the exposed sp² C atoms in the graphite domain saturated by H, O, and N atoms, respectively [45]. It is clear that a mere variation in the terminated atom in holey GQDs only plays a slight role in the position of adsorption peaks and electronic configuration, while the increasing size of the pore with more H-passivated atoms exhibits a significant reduction in the HOMO-LUMO gap and the emergence of a new peak on the absorption spectrum (Fig. 2b). This allows us to obtain GQDs with tunable optical properties controlled through different pores.

In general, carbon-based materials mostly possess similar PL mechanisms, where the specific differences can be distinguished through intrinsic inner structures and attached functional groups. According to plenty of characterization experiments, it is clear that CDs with excellent PL performance are not pure carbon materials. The surface states, consisting of the carbon core domain and adjacent functional groups, play a



Fig.3. (a) Optimized structures and molecular orbitals associated with the intense transition for the DA-functionalized QDs. Adapted with permission from Ref. [55], Copyright 2022, American Chemical Society. (b). Schematic of the synthesis process and calculated free-energy diagram and adsorption energy for the Bi₂O₃-NGQDs. Adapted with permission from Ref. [56], Copyright 2018, Wiley. (c) A computational model of end-on-adsorbed O₂ on FePc/GQD and calculated free energy profiles for the ORR on FePc and FePc/GQD at different cell potentials. Adapted with permission from Ref. [57], Copyright 2019, American Chemical Society. (d) Time-dependent contact area and van der Walls interactions for A₃₀ssDNA absorbing to GQD through molecular dynamic simulations. Adapted with permission from Ref. [60], Copyright 2020, Nature Publishing Group. (e) Optimized structures and corresponding differential charge density iso-surfaces of heterostructures derived from ZnO with different CQDs. Adapted with permission from Ref. [63], Copyright 2023, Elsevier. (f) Geometric structures of reaction intermediate on SCAu-plane, SCAu-plane, SCAu-edge, NC and NC-SCAu along the CO₂ catalytic pathway. Adapted with permission from Ref. [64], Copyright 2018, American Chemical Society.

crucial role in the fluorescence properties. This is readily observed through synthesis and post-treatment routes, whether it be the hydrothermal method for cutting oxidized carbon nanotubes and graphene with defect-based groups or the carbonization reaction of solely molecules and polymers containing hydroxyl, carboxyl, carbonyl, and amino. The obtained CDs with abundant surface functionality could undergo further modification or passivation to improve the QY or modulate the emission bands, meeting the requirements for particle application [46,47].

Recently, Bishop's group reported a DFT investigation of the electronic and optical properties of GQDs with different edged substituents and carbon backbone shapes through the delocalization of electrons and adsorption energy, respectively [48]. The calculation level was set to CAM-B3LYP/6-31G, which was proven to be suitable for single-wall carbon nanotubes like GQDs. The raw atomistic model derived from the square graphene that comprises 120 carbon atoms with four CH₂ groups located in different edged positions leads to seven isomer structures. The different placement of capping units provides distinct energy for the lowest energy transition and first bright transition, respectively. The cooperation of natural transition orbitals and transition densities of such a model reveals the origin of their PL behavior, where isomers B, C, and D exhibit the delocalization of transition densities throughout the carbon backbone, while isomers D and G with similar positions of substituents share similar adsorption spectra and excitonic localization in the electronic characteristic (Fig. 2c). Meanwhile, the edge effects, such as the armchair and zigzag configuration of GQDs, also make a significant difference in the bandgap, electron transition, HOMO-LUMO distribution, and luminescence behaviors. The hexagonal and rhombic with all-zigzag edges models show a similar position of adsorption peaks representing the first excited states, while the rhombic with all-armchair edges model displays a dramatic reduction in low-lying S1 states. The deformation of the latter structure was not as large as the former two when the edged hydrogen atoms were replaced by CH₃, attributed to its unique rigidity of geometrical configuration. It suggests the electronic structure of GQDs is significantly influenced by its shape and edge functionalization, which enlightens us that minor modifications to the structural features of GQDs through the synthesis route could provide finely tuned homogeneous emission for potential optoelectronic devices.

Unlike the simple models derived for the graphene-like segments with restricted atoms, Otyepka's group proposed a spherical CDs model with precise structural features constructed through multilayer hydroxyl functionalized PAHs as the seed to simulate the process of CDs formation through classical all-atom MD (Fig. 2d). In this simulation, IPCA neutral molecules and anions prefer to form adlayers on the exposed surface of CDs. The stability of the intralayer derives from the hydrogen bonds connected through carboxylic groups and water molecules that make these molecular fluorophores aggregate spontaneously and intend to incorporate into the CDs structures, playing an important role in the PL properties of the fully grown CDs.[49].

To improve the functionality of CDs, many researchers have reported that the introduction of atomic impurities with suitable atomic size compatibility like nitrogen, boron, sulfur, phosphorus, etc., was considered an effective way to modulate their geometric and electronic characteristics, where the doping atoms could generate mid-gap states between HOMO and LUMO and result in a significant alteration in absorption and emission behaviors [50,51].

For the purpose of revealing the comprehensive effect of nitrogen dopants on the PL properties of GQDs that further optimizes the doping strategy for optical applications, Li's group performed TDDFT calculations based on pristine GQDs models with different amounts, types, and N/C ratios of dopants [52]. The calculated Partial Density of State (PDOS) shows a new state introduced by nitrogen doping that leads to the reduction of the HOMO-LUMO gap and the red-shift of adsorption peaks. When the N/C ratio increases to the experimental level, graphitic and pyrrolic nitrogen maintain the same change, while the pyrrolic

nitrogen induces an opposite blue shift on the adsorption wavelengths. As shown in Fig. 2e, nitrogen doping destroys the evenly distributed natural transition orbital in the symmetrized hole and particle states, where the hybridization of nitrogen-bonded carbon was changed from sp^2 to sp^3 , accompanied by more delocalized transition compared with the pristine GQDs.

2.3. Basic requirements for constructing CDs composites models

There already emerges plenty of researches focused on the characteristics of CDs as a single component, while the CDs materials as a part of joining the constructions of composited materials will generate more broad attention from scientists. In this way, CDs can play their roles in catalysis, energy storage, and other crucial research fields, which are far beyond the initial understanding of them. In this situation, the heterojunction models of CDs-matrix as dominant methods have deeply connected with related materials properties and experimental phenomena [53,54].

Compared to the isolated CDs models that only focus on the structure features on its own, the structure of CDs-involving complex systems should pay more attention to the binding mode between CDs and other components. Meanwhile, the type, size and location of CDs exhibit a remarkable effect on its adsorption behavior and further the PL property, electrochemical performance and catalytic activity of corresponding systems. Hence, in this section, we will further explore the necessary adjustments to heterojunction models when considering CDs as constituents within composite systems.

The classic heterostructures commonly consist of two sections derived from the unit cell structure of the research system with suitable cleavage or modification. The first-principles calculations of these structures lead us to acquire a micro view. Differing from the mentioned models based on PAHs, graphene sheets, or spherical structures, Foerster reported novel isolated hydrogenated carbon, silicon, and germanium clusters with diamond-like and icosahedral shapes, respectively (Fig. 3a) [55]. The sensing mechanism of dopamine-functionalization was revealed through the HOMO-LUMO gap, excitation energies, absorption spectra, and molecular orbital diagrams computed using TDDFT/CAM-B3LYP methods, where the $6-31 + G^*$ basis sets were used for C-containing quantum dots, and the SRLC basis set was selected for the remaining structures. The quenching of fluorescence would emerge when the energy of occupied orbitals of dopamine in oxidized form is higher than the singly occupied orbitals of quantum dots, leading to a reductive photo-induced electron transfer (PET) process. Despite the carbon-based cluster not meeting the requirement of transition energies for quantum dots-based optical sensors, this type of atomistic model still provides us with a unique route to describe the structural characteristics of CDs, broadening our choices for corresponding calculations in CDsrelated complex systems.

Liu's group reported a series of heterogeneous electrocatalysts consisting of GQDs and Bi_2O_3 nanosheets capable of reducing CO_2 to formate with excellent faraday.

efficiency and good stability, with the assistance of edged functional groups. In this system, GQDs play an important role in increasing CO₂ adsorption ability [56]. After preparation, characterization, and electrochemical experiments, DFT calculations using CP2K with PBE functionals and norm-conserving GTH pseudopotentials were performed to explain the reaction mechanism of formate formation and reveal the origin of the remarkable catalytic activity. The calculated free-energy diagram of the HCOOH formation process exhibited the largest free-energy barrier for the second step of OCHO* formation, implying that the potential limiting step should be this initial proton-coupled electron transfer process (Fig. 3b). The results of the adsorption energy of each particle on the catalyst's surface indicated enhanced adsorption behavior through the introduction of N-doped GQDs. Meanwhile, the higher selectivity of Bi2O3-NGQDs in obtaining formate was confirmed by comparing the energy barrier and limiting potentials of the same step



Fig.4. (a) Collected powders of SiCDs under visible light and 365 nm UV light. (b) Optical photographs of operating SiCDs-based LEDs. (c) The absorption spectra, normalized PL emission spectra and FTIR spectra of four selected SiCDs. (d) Schematic illustration of the four selected SiCDs for their PL mechanism. Adapted with permission from Ref. [67], Copyright 2023, Elsevier.

in CO₂ Reduction Reactions (CO₂RR) and Hydrogen Evolution Reaction (HER), respectively. Thus, the synergistic effect between Bi_2O_3 and NGQDs should be responsible for the high activity of CO₂ reduction with such heterogeneous electrocatalysts.

Similarly, Lee's group conducted a DFT + U study on the ORR performance of iron phthalocyanine (FePc) with the assistance of GQDs. The study focused on the optimized structural features, electronic configuration, and, especially, the free-energy profile of the entire energetically favorable 4e⁻ pathway of the ORR process. In this heterojunction model, the GQDs were represented by a graphene network with hexagonal and zigzag shapes, serving as the carbon support to enhance the ORR catalytic activity of FePc [57] (Fig. 3c). Following the addition of GQDs, the adsorption of O₂ onto the catalyst's surface was significantly enhanced, and the reaction barrier of the rate-determining step was reduced by 0.03 eV compared to pure FePc at the equilibrium potential of 1.23 V. This improvement positions the formed electrocatalyst with the supplementation of carbon materials as a promising candidate for a non-platinum group metal (non-PGM) catalyst for ORR with the desired performance.

Beyond the comprehensive discussion of the unique PL properties of GQDs, we have already covered, their low toxicity, biocompatibility, and stability make these nanoscale carbon-based materials suitable for applications in optical biosensing, delivery, and protein recognition [58,59]. In studies involving biomolecules of general size, the dimensions of corresponding theoretical calculations will also increase. Landry's group conducted a study on how GQDs with different oxidation levels influence the adsorption behavior of single-stranded DNA onto the GQDs' surface, connected with several functional groups. MD simulations were carried out to investigate the adsorption protocols, considering simulation trajectory, non-bonding interaction energies, contact area, center-of-mass distance, and the number of atoms within 5 Å. The GQDs were constructed through the nanotube-builder software in a 5 \times 5 nm size, with the DNA oligomers placed onto it [60]. As shown in Fig. 3d, van der Waals interactions dominate the adsorption of DNA on



Fig.5. (a) DFT calculation models, the calculated HOMO-LUMO levels, and energy level diagrams of CDs@PVA. Adapted with permission from Ref. [68], Copyright 2022, Wiley. (b) The bandgap fluctuations and wavefunctions of COOH-CD and NH₂-CD at different time intervals. Adapted with permission from Ref. [69], Copyright 2020, Nature Publishing Group. (c) The hydrogen-bond interaction and adsorption energy of complexes between chiral CDs and DOPA. Adapted with permission from Ref. [70], Copyright 2022, American Chemical Society. (d) Electron-hole distributions upon optical excitation and densities of electric dipole moments for F-GQDs. Adapted with permission from Ref. [71], Copyright 2022, American Chemical Society. (e) PET-based fluorescence 'turn off' mechanism of the PVDF-HFP containing BH@CDs. Adapted with permission from Ref. [72], Copyright 2021, Elsevier.

the GQDs' surface compared to the hydrogen bonds between biomolecules and the edged oxygen-based groups of carbon sheets. GQDs with a lower degree of oxidation demonstrate stable adsorption, aligning with experimental observations through fluorescence spectra and atomic force microscopy. Additionally, the influence of different nucleotide sequences was revealed through this 100 ns simulation, showing that only the poly-cytosine-based DNA exhibited weak adsorption dynamics on the less oxidized GQDs. This suggests a novel approach to tune the PL of GQDs through the polymer sequence and type when designing sensors for future nanobiotechnology applications. Unlike the typical role CDs play as platforms in heterojunction structures, it is also common for CDs to be positioned on the top of base models, representing their incorporation on the surface of metals or metal oxides [61,62]. Hareesh's group constructed a nanohybrid model consisting of the (100) surface and GQDs with different dopants to investigate the electronic features of the photocatalyst for hydrogen generation through first-principle calculations. The optimized structures, shown in Fig. 3e, illustrate that the geometry of GQDs is bent, and the hydrogen atoms, saturating the edged carbon atoms, tend to approach the exposed oxygen atom of ZnO [63]. The charge density

difference of ZnO with pristine, doped, and N, P co-doped GQDs indicates a strong interaction within the interface. The decrease in work function and band gap facilitates electron transfer, supporting the experimental results that demonstrate the enhanced performance of the formed efficient photocatalysts.

Zhu's group has proposed a heterojunction model containing gold nanoparticles and N-doped GQDs represented by single layer graphene in a periodic box to investigate the mechanism for the electrochemically converting process of CO_2 to CO through the detailed description of the structures in the reaction pathway and its electronic configuration [64]. The free energy diagram demonstrates the formation of COOH* intermediate was the rate-limiting step and the support of NGQDs could reduce its energy barrier significantly. The charge transfer from gold nanoparticles to GQDs has been revealed through DOS, Bader charges, and charge density difference, illustrating the synergistic effect between these two substances, which is responsible for their enhanced catalytic performance (Fig. 3f).

As discussed previously, different structural features usually lead to various properties in CDs. The varying particle size has a significant effect on the absorption and luminescence bands of CDs, while the shape of pores in the non-perfect surface could also influence the position of adsorption peaks. The introduction of edged functional groups could be an effective method to regulate the electronic configuration of CDs and acquire the desired phosphorescence. Additionally, the oscillator strengths are highly related to noncovalent interactions such as hydrogen bonds and π - π stacking in aggregates or bio-systems involving CDs. Furthermore, the oxidation degree of GQDs, which serves as the loading platform, plays an important role in the adsorption behavior of biomolecules. This is verified through MD simulations and provides a reliable explanation for the photoluminescence (PL) dynamics of polymer-based sensors. The structure-activity relationships we have discovered in CDs can provide us with a better understanding for the future design of carbon-based functional materials with specific purposes.

3. The structure-activity relationship of CDs in various applications through computational models

3.1. CDs as luminescent materials

We have discussed the common construction strategy of CDs models with their own intrinsic structure and different modifications, CDs as potential star materials possess a wide range of applications, and the adjustment of computational models for uncovering the structure-activity relationship and key properties of CDs in various fields are also worth our attention. In this section, we will concentrate on the applications of CDs in the realm of fluorescent materials and explore, from a computational standpoint, the impact of various structural features on the luminescent properties of related materials.

Luminescence, as the fundamental properties of CDs, is deeply influenced by the types of CDs and is closely associated with precursor resources and synthetic routes. For instance, bottom-up processes always enable CPDs with a higher QY and specific precursors always generate a different emission wavelength of the final CDs products. Moreover, synthesis conditions are well worth considering, like the amount of reactive solvents and reaction temperature. Besides these, broad photoluminescence profiles and excitation-dependent photoluminescence behaviors are also crucial features of most CDs, which can be used to understand the properties of CDs [65,66]. As a typical example, one work conducted by our group suggests that adjusting the ratio of precursors CA and p-phenylenediamine (p-PDA) can effectively control the luminescent centers, where CDs with different emission wavelengths can be achieved (Fig. 4a-c). Furthermore, silanefunctionalized CDs were formed by (3-aminopropyl) triethoxysilane (APTEs), which can effectively prevent fluorescence quenching of CDs due to aggregation. Accordingly, the high-efficiency fluorescence of CDs in the aggregated state can be achieved with a high QYs of 26–57 % with different luminescence colors (Fig. 4d) [67].

Besides, Lu's group has designed a CDs-based core-shell structure with diverse polymers coated that exhibited excellent QYs and much longer room temperature phosphorescence, the DFT calculations are provided to support the XPS experiment that the crosslink between CDs and coating polymers facilitates the electron transfer process and leads to the intersystem crossing process [68]. According to the results of geometric structures, frontier orbitals, and the energy gap between excited state levels, the abundant hydrogen bonds, activated hydroxyl groups, and emerging covalent interactions within the composites were introduced through polymers should be responsible for enhanced phosphorescence behavior, which also indicate the degree and the degree and strength of crosslinking were capable of tuning phosphorescence properties of such composite materials. (Fig. 5a).

Furthermore, Sargent's group reported the edge amine-based passivation of CDs could provide an effective deep-blue light-emitting behavior and higher QYs for the LEDs application, the calculated wave function exhibits more delocalized feature in the.

CDs model with pure NH_2 groups compare to those models with diverse oxygen-based groups, which also provide a narrow bandgap fluctuation that contributes to the narrow-linewidth emission [69]. (Fig. 5b) More interestingly, Kang's group reported the fabrication of chiral CDs with inverse handedness and two cyclic dipeptides as the spatial structure unit, the DFT calculations based on the appropriate choice of the suitable portion of molecules derived from the unit and short chains of CDs were performed to study the Cotton effects and enantioselective catalytic activity compared to the experiment results [70]. As shown in Fig. 5c, the stronger hydrogen bond between L-CDs to L-DOPA compared to those substances in different charity should be responsible for the enantioselective catalytic activity on DOPA enantiomers oxidation, where the higher adsorption energy leads to the higher catalytic efficiency.

Recently, Zheng's group has proposed a physical mechanism for the fluorescence of functionalized GQDs through the combination of Gaussian and VASP, the nature of chirality and structure–activity relationship were also involved [71]. The calculated model used here is based on a defect-free *ortho*-hexagonal graphene sheet with plenty of edged functional groups such as carboxyl, hydroxyl, and acylamino. (Fig. 5d) The results of absorption, fluorescence, and electronic circular dichroism (ECD) spectra have indicated the occurrence of the photon momentum transfer to the electron system, while the isosurface of electron-hole distribution and densities of electric dipole moments demonstrate the charge transfer length could increase along with the augment in sizes and the destruction of complete π electron system respectively, which could be concluded that the edge functionalization brings the twist geometries, chirality and charge transfer feature that highly related to the PL performance of GQDs.

Moreover, Das' group proposed a PET pathway-based fluorescence mechanism according to the results of TDDFT calculation to understand the detection mechanism of CDs decorated boehmite nanostructure probe in the Cr (VI) environment, the fluorophore part of CDs was taken out to build the atomistic model for concise [72]. The electron in the HOMO-5 state of the selected fluorophore moiety has transferred to LUMO + 2 of the quencher upon excitation, and then go through a nonradiative internal conversion to reach the LUMO state. The fluorescence quenching derived from the radiative transition from LUMO to HOMO-5 lead to the gradual decay in fluorescence lifetime as the experiment observed. (Fig. 5e).

As the previous discussion, benefiting from their unique catalytic and optical properties, large surface area, and functional surface, CDs show great potential in various biologically related applications. From being bioimaging and biosensing reagents at first, CDs now have been broadly used as biocatalysts, tumor inhibitors, antibacterial reagents, antiviral agents, etc. At the same time, relevant issues of quantum chemical calculation of CDs are becoming increasingly important [73].



Fig.6. (a) The optimized adsorption configurations of H_2O_2 on the surface of the g1-1Lc model with the corresponding adsorption energies. Adapted with permission from Ref. [74], Copyright 2021, American Chemical Society. (b) Snapshots of absorption of GQDs on poly(A–T)₂₀ through MD simulation. Adapted with permission from Ref. [75], Copyright 2020, American Chemical Society. (c) Typical photographs of selected bacteria after the treatment with different concentrations of CDs for 24 h and the representative configurations were taken from some key time points to show the terminal base pair denaturation process. Adapted with permission from Ref. [76], Copyright 2018, American Chemical Society. (d) The QTAIM graph, RDG isosurface of complexes model between GQDs and GC, and plots of interaction energy versus simulation time for loading of GC drug on the nanocarrier surfaces. Adapted with permission from Ref. [77], Copyright 2019, Royal Society of Chemistry. (e) MD optimized structure of tau protein-CND complex, with the nearest interacting residues shown on the right. Adapted with permission from Ref. [78], Copyright 2022, Elsevier.

According to the oxidative reaction routes of cholesterol in the presence of cholesterol oxidase, Jarujamrus's group reported the fabrication of a microfluidic paper-based analytical device containing N-doped CDs. The TDDFT calculations were performed to study the optical and electronic properties of calculated models based on pyrene and coronene through the UV–vis adsorption spectrum, molecular orbitals distribution and the adsorption configurations of H_2O_2 on the surface of CDs, where the high electron density concentrate on N-related region demonstrate the existence of nitrogen atom could enhance the electronic charge in a specific area and provide active sites for catalysis of H_2O_2 that prefer to strongly adsorb on the graphitic N position of CDs [74] (Fig. 6a).

To further understand to biosafety, cytotoxicity, and genotoxicity of GQDs, Liang's group have reported a MD simulation study based on DNA with different bases and GQDs of different size saturated by hydrogen atoms to evaluate the potential DNA damage caused by the base mismatch [75]. (Fig. 6b) The snapshots of the simulation trajectory have revealed only the small GQDs model with just seven benzene rings could enter the interior of two chains of DNA fragments and break the

hydrogen bonds between bases leading to the mismatch of A and T bases, while it also prefers to adsorb on the G-C base pair of DNA structures compare to the large size of GQDs which tend to cause the DNA unwinding by its adsorption behaviors.

Similarly, Kang's group reported the achievement of low-toxic and degradable CDs with strong broad-spectrum antibacterial and antifungal activity, the combination of TDDFT and MD calculations were performed to investigate the UV–vis spectrum, excited states, and dynamical process of CDs respectively, where the computed models derive from the dimer of vitamin C molecular structure as the synthesis precursor through the electrochemical method [76]. The MD simulation results indicated that the presence of CDs could destabilize the DNA structures and cause a distinctive distortion in the binding mode of the base pair starting from the terminal position, the newly formed intermolecular interactions between CDs and DNA hairpin become strong at the end of the simulation that reveals the origin of the antibacterial in such nanomaterials (Fig. 6c).

As for drug delivery application of CDs, Shariatinia reported a comprehensive study about N-functionalities GQDs through both MD



Fig.7. (a) TEM image and HRTEM image of CDs, and TEM images of PANI/CDs. (b) Maximum charge extraction time, extraction efficiency of the charge extraction process (t_{max}), and attenuation constants (τ) of the charge recombination process of PANI and PANI/CDs. (c) Comparison of OER LSV curves and Tafel plots of PANI/NF and PANI/CDs/NF, and Amperometric curve of the OER at 1.52 V under dark conditions. (d) Photograph of the two-electrode cell for water splitting. (e) Mechanism diagram of P-EC overall water splitting. Adapted with permission from Ref. [80], Copyright 2021, American Chemical Society.

and DFT calculations, where the binding energy, quantum molecular descriptors, molecular electrostatic potentials, and force–displacement profiles were employed to evaluate the penetration of the gemcitabine-loaded GQDs across the membrane of cell constructed through dipal-mitoylphosphatidylcholine bilayer [77]. As shown in Fig. 6d, the stability of the drug-loaded model where GQDs serve as the platform should be attributed to its face-to-face stacking pattern and the weak vdW interaction in the interface. The plots of interaction energy for both loading and release of the drug from the nanocarriers exhibit the drug molecule is properly loaded on the surface of GQDs, which is consistent with the DFT results and further confirms the rationality of constructed complex models. The results of steered MD indicate the GQDs-based nanocarriers prefer to penetrate in the perpendicular position and the

center of N-GQDs shows better performance for this drug delivery system.

Carbon nitride dots as a unique type of CDs with clear atomistic structures possess basically the same properties compared to the common CDs, which are capable of serving as the potential inhibitors for the aggregation of microtubule-associated protein tau through hydrophobic interaction between the mentioned protein and CDs [78]. The MD simulations were performed to reveal the structure–activity relationship, where the CDs model was constructed through the heptazine rings and surrounded by different charged, neutral, and hydrophobic residues and binding through hydrogen bonding and C-H π interaction respectively. It is consistent with the experimental results and explains the reason why hydrophobic CNDs display more effective in tau aggregation



Fig.8. (a) Plane-averaged charge density difference and diagram of the band edge positions of $C_{32}H_{14}$ -MoS₂, and the band alignment of selected GQDs-MoS₂ heterostructures. Adapted with permission from Ref. [81], Copyright 2022, Royal Society of Chemistry. (b) Illustrations of the adsorption and dissociation of the H₂O molecule on Ru-graphene surfaces. The isosurfaces of transferred charge upon adsorption of Ru (00.1) and graphene-supported Ru cluster. Adapted with permission from Ref. [82], Copyright 2018, Wiley. (c) Local configurations for the corresponding adsorbed hydrogen intermediates and the energy variations for the hydrogen evolution reaction proceeding on C–MoP, 1NC-MoP, 2NC-MoP, and 3NC-MoP structures. Adapted with permission from Ref. [83], Copyright 2020, Elsevier. (d) The reaction paths, corresponding free energies, PDOS, and differential charge density of different models based on FeNi₃. Adapted with permission from Ref. [84], Copyright 2022, Elsevier. (e) Atomic spheres representation of the ORR intermediates (top and side views) for the B, N-GQD models along the associative reaction path and free energy reaction profiles for the 4e⁻ (black line) and 2e⁻ (red line) pathways of the corresponding ORR reaction. Adapted with permission from Ref. [85], Copyright 2015, American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

inhibition (Fig. 6e).

3.2. CDs as advanced catalysts

As a type of nanomaterial with quantum size, small sizes, various surface groups, and tunable surface charge states of CDs allow them to have abundant catalytic sites, which are the key points to improve the catalytic performance [79]. In this section, we will focus on how CDs affect the reaction processes as a novel catalyst, through computational researches that are mainly based on heterojunction models. One of the significant research projects was conducted by Kang's group. In this research, CDs were introduced in the synthesis of Polyaniline (PANI)/CDs composites (Fig. 7a) and played a key role in enhancing the photoelectric effect of the catalysts. Specifically, the addition of CDs would improve visible light absorption, where the higher photo-induced bias voltage (Fig. 7b) generated by CDs will accelerate the HER and OER processes. Moreover, CDs as part of the composited electrode can also hinder the recombination of the electrons and holes (a longer relaxation



Fig.9. (a) Minimum energy paths for the reduction from * CH₂OH to * CH₂ via H-shuttling (squares) mechanisms and the initial, transition-state, and final configurations through corresponding pathways, and the thermodynamic free energy diagram for the conversion of CO₂ to CO on different N-doped carbon materials. Adapted with permission from Ref. [88], Copyright 2017, American Chemical Society. (b) Band structures, PDOS and interfacial electron transfer of the composite model based on g-C₃N4 and CDs. Adapted with permission from Ref. [89], Copyright 2018, American Chemical Society. (c) Schematic diagram of photocatalytic CO₂ reduction by the ^mCD/CN and sCD/CN and the most stable configuration of H₂O on ^mCD constructed through coronene and pyrene. Adapted with permission from Ref. [90], Copyright 2020, Nature Publishing Group. (d) Proposed reaction paths for CO₂ reduction reaction over NG/Cu (111) and reaction Gibbs free energy diagram from the adsorbed C₂H₃O intermediate on corresponding heterostructures based on N-GQDs. Adapted with permission from Ref. [91], Copyright 2020, Wiley.

time, Fig. 7b), therefore, a lower over-potential can be accomplished by PANI/CDs composited system (Fig. 7c). Meanwhile, CDs additives with clear graphite lattices (Fig. 7a) always means stable inner-structures, which ensure strongly continuous functions of CDs during the long-term cycling test (Fig. 7c) [80].

MoS₂ as a type of promising 2D semiconducting materials that are

widely used in photocatalytic reactions especially the HER via water splitting, the activities of which are able to be enhanced significantly with the assistance of GQDs in different modification. Wang's group constructed several models based on the vdW heterojunctions structures containing 0D GQDs represented by C_6H_6 , $C_{24}H_{12}$, and $C_{32}H_{14}$ with tunable size respectively, where the aromatic rings were placed

parallelly above the plane consisting of exposed O atoms derive from the monolayer MoS_2 [81]. The optimized structures and electronic properties were obtained through first-principle calculations to reveal the photocatalytic properties of such hetero-structures. As shown in Fig. 8a, the results of charge density difference point out the electron transfer from GQDs to MoS_2 that promotes the separation of electrons and holes, the formation of heterostructures brings the significant movement of band edge positions illustrates the flow direction of photogenerated electrons derive from MoS_2 under visible-light irradiation. The band alignment of such heterostructure with different types reveals the possible excitation process of electrons from valance bands to respective conduction bands, while the unique staggered alignment of $C_{32}H_{14}$ – MoS_2 with opposite hole flow leads to the separated charge carriers that make this heterojunction a good candidate for a promising photocatalyst.

Except for electronic configuration, the relative Gibbs energy diagram that consists of the adsorption energy between catalytic systems and isolated species based on small molecules such as H2, O2, H2O or CO₂, etc. in each step along the catalytic reaction process could provide more specific information of the activity of constructed catalysts. Lu's group proposed a novel HER electrocatalyst-based carbon-loaded ruthenium nanoparticle where the CDs serve as the key carbon component for the enhancement of catalytic ability [82]. The DFT calculations were performed to reveal the origin of excellent HER catalytic performance, where the model of CDs was built based on the single-layer graphene sheets that serve as the carrier below the Ru cluster (Fig. 8b). Compared to the isolated CDs model, the CDs-Ru system exhibits remarkable low energy barrier of the HER process that attributes to the electron transition from Ru cluster to CDs before the adsorption of H₂O molecules, which indicate the collaborative effect between Ru and Ndoped CDs should responsible for its superior HER activity. Soon after, this group reported another CDs-based HER electrocatalyst with excellent H₂ production performance during the electrolysis of alkaline solution, the computational heterojunctions model was built through the same logic that the metal clusters were put above the modified CDs that derive from the graphene (Fig. 8c) [83]. The results of carbon vacancy formation energy and partial density of state have stated that N doping could facilitate the formation of C defect while the interaction between defect sites and Mo atoms contribute to the enhancement of charge transfer along the interface of metal and CDs. Moreover, the energy evolutions of the HER process based on different modified CDs have shown strong hydrogen adsorption and large HER overpotential, where the increasing of N content benefits its catalytic performance. It is also worth noting that the preliminary DFT calculation could provide vital information that can guide the design of novel nanomaterials with a specific purpose.

A similar computational system could also be appropriate for other catalytic reactions like Oxygen Evolution Reaction (OER) that are commonly used in the study of electrolytic water splitting. Tian's group reported advanced OER electrocatalysts by introducing GQDs to FeNi₃ alloys that are able to promote electron transfer from metal atoms to carbon materials [84]. The DFT calculation used here through the heterostructure model we mentioned before where the alloy part occupies the main position while the CDs were represented through a fragment of graphene without periodicity that adsorb on the exposed surface of FeNi₃ (Fig. 8d). The free energies diagram of typical four-electron transfer steps for OER in different set potentials have exhibited the emergence of GQDs is capable of reducing the energy barrier from *OH to *O thus improve the catalytic activity. The electronic configuration of such heterojunctions is investigated through PDOS and charge density difference, the introduction of GQDs could bring a significant change in d-band shape, d-orbitals of metal atoms and the charge flow from Fe and Ni sites to C sites, the synergistic effect of which could enhance the adsorption of intermediated species and facilitate OER process.

Other than the nanomaterials containing CDs, the individual GQDs are also able to act as the catalysts for the selective production of H_2O_2

through the ORR. Agnoli's groups reported the study about how dopants affect the activity of GQDs-based catalytic system, the DFT calculation provides the optimized atomic structural models for the adsorption position of oxygen-related species like *O₂, *OOH, *O and *OH with different oxidation degree, based on which the free energy profiles of reactant, intermediates, and products along the 2e⁻ and 4e⁻-path of ORR were calculated respectively (Fig. 8e) [85]. The results indicate the introduction of doped GQDs plays a vital role in its remarkable catalytic activity under reducing conditions, where the ORR prefers to proceed through the 4e⁻ path relatively that consistent with the experimental observations.

To meet the urgent requirement of the imminent climate change and depletion of fossil energy resources, the conversion of atmospheric CO₂ through a unique catalytic system to carbon-based products like CO, methane, methanol, and formic acid become a hot topic that plenty of researchers chasing for, where the CDs could act as the considerable part due to its excellent catalytic ability [86,87]. Yakobson's group reported a theoretical study about the origin of the catalytic activity of N-doped GQDs that were able to facilitate the reduction of CO₂ to hydrocarbons and oxygenates through the first-principle calculation, the climbing image nudged elastic band (CI-NEB) method was performed to assist the description of the possible energy pathways for the CO₂RR [88]. As shown in Fig. 9a, N-doped GQDs exhibit a highly competitive energy barrier along the conversion of CO₂ to CO while the *COOH serves as the intermediate state that due to the enhanced binding of carboxylate radicals. According to the thermodynamic analysis, the formation of *CH₂ preferred the H-shuttling pathways with a significantly lower energy barrier in only 0.6 eV after the introduction of additional H₂O molecule, which led to the selective generation of CH₄ rather than CH₃OH.

As a more complicated catalytic system, Kang's group reported a novel ternary Au-CDs- C_3N_4 electrocatalyst with excellent Faradaic efficiency, density and stability that is able to convert CO_2 to CO, the DFT calculations of electronic configuration through band structure, PDOS and charge density difference (CDD) of corresponding computational models were performed to reveal the synergetic effect of different components that lead to the potential mechanism of CO_2RR [89] (Fig. 9b). The obtained results demonstrate the decrease of band gap as the consequence of the participation of CDs, which is constructed through the commonly used model that derive from graphene sheets. The loading of Au brings the enhanced electron mobility of the corresponding composite where the electron from C_3N_4 prefers to accumulate around the metal particles and CDs, which also provides the significant corrugated alteration to the planar structures of C_3N_4 that is able to facilitate the CO_2RR process due to the decrease of energy barrier.

As an effective solution to the sluggish water oxidation reaction that is able to support the conversion of CO₂ to methanol, the microwavesynthesized CDs decorated C₃N₄ reported by Tang's group exhibited the remarkable conversion efficiency and unique selectivity in a metalfree route, where the DFT calculation was employed to illustrate the vital role of such co-catalyst [90] (Fig. 9c). To describe the atomic structures of CDs, the stacking model consisting of coronene and pyrene molecules was chosen here to provide the results of adsorption energy of CO2, CH3OH and H2O on the constructed heterostructure with the assistance of common and protonated C3N4. The calculated results indicate the mentioned small molecules prefer to adsorb on the surface of C₃N₄ except for H₂O, which contributes to the establishment of a potential photo-conversion mechanism that microwave-synthesized CDs are capable of capturing holes from C3N4 to oxidize H2O into O2 compared to the sonication-based method CDs with obvious slow oxidation rate that result in the amazing selectivity of this carbon-based photocatalyst.

Other than the electronic configuration we have discussed adequately, the energy diagram containing each intermediate and transition state structure during the catalytic process is also an important method that contributes to gaining detailed information for the



Fig.10. (a) CDs with nitrogen, phosphorus, and oxygen-containing groups and PAM hydrogels are the precursors of the porous carbon. (b) Scheme of the attraction of functional groups and defects to different cations. (c) Pore size distributions and nitrogen adsorption–desorption isotherms (inset). (d) DFT calculation results of the charge distributions of nitrogen (N-6) and phosphorus (~CPO₃) doped functional groups. CV curves of NPOCD/HPC and free-HPC (blank sample) at a scan rate of 10 mV s⁻¹ in (e) alkaline, (f) acidic, and (g) neutral aqueous solutions, respectively. Adapted with permission from Ref. [93], Copyright 2019, Wiley.

origin of the excellent performance of CDs-based catalysts. Han's group performed the DFT calculation based on the composite model consisting of Cu (111) and N-doped GQDs, where the latter was represented by a part of single-layer graphene with periodic conditions [91]. As shown in Fig. 9d, the CH₂CHO species were chosen as the key intermediate that was able to distinguish the pathway from ethylene to ethanol due to the same intermediate during the reduction process, the results of free energy difference have indicated the production of ethanol was more favorable under the participation of N-doped GQDs and bias potential compare to the significant high energy barrier exhibited in adsorption model for pure Cu (111) surface, which mainly attributes to the strong oxophilicity properties of CDs and show good agreement to the experimental results in high selectivity.

3.3. Cds as robust energy storage materials

Similar to the catalytic reactions, the interface processes of the electrodes and electrolytes are also important to energy storage performance, where CDs also play important roles in regulating related reactions [92]. Using the work of our group as an example, an innovative solution to improve the performance of negative electrodes (based on electronic double-layer capacitance) in hybrid batteries: constructing electron-rich regions by CDs with specific functional groups, so the surface will form "electron-rich" regions to adsorb different cations and accelerate the charge-transfer at the same time (Fig. 10a-b). Based on the charge-distributions obtained by DFT simulation Fig. 10d), part of surface groups like phosphate-type group (~CPO₃), carboxyl, or pyridine-

type nitrogen certainly introduce a significant change of charge in the surrounding regions. Compared with that, the functions of some other group types like oxidized nitrogen or quaternary nitrogen are relatively limited. By CDs, good carriers with great advantages in adjustable compositions and controllable surface groups, numerous electron-rich regions can be constructed on the surface of porous carbon. And related influence can be verified by cyclic voltammetry (CV) tests. According to the related results, in acidic, neutral and alkaline electrolytes, the capacitance of NPOCD/HPC (hierarchical porous carbon made from porous hydrogels combined with nitrogen, phosphorus, and oxygen codoped CDs, the optimal sample) is surprisingly increased up to 40 % over that of sample free-HPC (hierarchical porous carbon derived from polyacrylamide (PAM) hydrogels with porous structures as the blank sample). Particularly, in neutral solutions with unobvious faradaic processes, ion absorption will mainly contribute to the specific capacitance, and it suggests that CDs can be used as efficient tools for adjusting the properties of electrode interfaces [93]. In the following sections, we will discuss how different computational models, when CDs serve as energy storage materials, reveal the structure-performance relationships inherent in the materials. Furthermore, we will also explore how these corresponding computational results connect to the variations in the key electrochemical properties of such systems.

At the same time, CDs also can be employed as a part of electrolytes to further optimize the interface reaction process of batteries. Ultrastable cycling performance of aqueous zinc ion batteries (ZIBs) is achieved by just adding a small amount of nitrogen-doped and sulfonated carbon dots (NSCDs) into the ZnSO₄ aqueous solution. Such types of X. Zhao et al.



Fig.11. (a) Schematic diagrams for Zn deposition in 2 M ZnSO₄ electrolyte with and without NSCDs additive. (b) Confocal luminescence image of Zn plate. (c) Schematic structure for NSCDs. (d) Binding energies of Zn^{2+} absorption on different function groups by DFT calculations. (e) Absorption energy comparison of H₂O and NSCDs on the Zn (002) crystal plane. (f) Comparison of long-term charging/discharging and (g) rate performance of Zn//Zn symmetric cell in Zn-NSCDs0 and Zn-NSCDs0.1. (h) Coulombic efficiency measurements of Zn//Ti cells using different electrolytes, and (e) the corresponding voltage profiles at certain cycles. Adapted with permission from Ref. [94], Copyright 2023, Wiley.

NSCDs exhibit multi-functions in ameliorating ZIBs according to DFT calculations. Firstly, the abundant strong polar groups (–COOH, –NH₂, –OH, and -SO₃H) on NSCDs can effectively regulate the Zn²⁺ solvation structure by decreasing the coordinated active H₂O molecules (Fig. 11a). Secondly, partial NSCDs are adsorbed on Zn anodes to form a protective layer, which isolates the corrosion from H₂O/SO₄²⁻ and avoid side-reactions. As a result, the symmetric Zn//Zn batteries exhibit a remarkable cyclic performance (4000 h at current densities of 0.5, Fig. 11f). Besides, the corresponding Zn//Ti half-cell achieves a high average coulombic efficiency of 99.5 % after 1200 cycles (Fig. 11h) [94].

Despite there are obvious differences in experimental characterization methods of the diverse application field, the theoretical calculations for corresponding systems generally have similar content such as geometric structures and electronic configuration that usually serve as a start for the exploration of underlying structure–property relationships for objective models [95,96]. Parasuk's group reported a DFT study about the adsorption behaviors of Li ion/atom on GQDs with different size and charge to illustrate the origin of higher loading capacity when GQDs serves as the anode for lithium-ion battery [97]. The results of adsorption patterns and energy have shown Li ions could only bind to negatively charged GQDs or positively charged GQDs in large size, while



Fig.12. (a) Adsorption energy per ion (E_{ads}/n) and number Li ions (n) for neutral and negatively charged GQDs. Adapted with permission from Ref. [97], Copyright 2020, Cell Press. (b) Schematic diagram of the energy storage process based on the Mn–Co LDH@CD model, and the 2D slice view of ELF and SCD through DFT calculations. Adapted with permission from Ref. [98], Copyright 2021, American Chemical Society. (c) Relation between calculated redox potential (vs Li/Li+) and the number of carbonyls and hydroxyls for the surface/edge functionalized CQD models with the MESP map of both gas-phase and solution phase models. Adapted with permission from Ref. [99], Copyright 2022, Wiley. (d) Differential charge density of Li adsorbed on the V site of graphene and the diffusion path and barrier on the outer surface of bismuthine. Adapted with permission from Ref. [100], Copyright 2021, American Chemical Society. (e) The geometrical configuration of N-GQDs/NiCo₂S₄/CC (311) surface model and the relative Gibbs free energy diagram of different catalysts for the ORR/OER at zero potential. Adapted with permission from Ref. [102], Copyright 2019, Wiley. (f) Synthetic routes and digital photographs of White ZnO Nano Rods and the models of CDs derivatives and ZnO crystals (100). When combination happens, a Brønsted acid site of CDs derivatives is substituted by a Zn²⁺ ion which changes to be Zn⁺. Adapted with permission from Ref. [103], Copyright 2021, Elsevier.

the Li atom prefers to interact with positively charged GQDs especially $C_{96}H_{24}^+$ (Fig. 12a). The charge transfer process observed here could proceed in both direction where the GQDs can act as both electron donor and acceptor, and the following added Li-related species mostly located on the opposite side of the hexagonal plane up to 4 and 5 ions which bring the higher loading capacity of small GQDs and make it suitable for electrode materials for Li-ion batteries.

Moreover, Wang's group reported the surface spatial confinement on

the Mn-Co Layered double hydroxides (LDH)@CDs that were mostly driven by the charge transfer and interaction, where the CDs model was constructed through a C_4 chain cluster that possesses a similar logic of small molecules from "bottom-up" routes and the ab initio molecular dynamics (AIMD) of the integrated structures further confirm the reasonability of this design strategy based on the stable total energy within the 200 fs simulations [98]. The calculated results of electron localization function (ELF) and spin-charge density (SCD) shown in



Fig. 13. Modeling approaches for CDs or CDs-related structures.

Fig. 12b have indicated the effective charge transport between LDH and CDs, where the localized and delocalized electrons are accumulated on metal-O bonds and hydroxyl groups respectively and the quantitative charge distribution also calculated through Mulliken charge that the carbon and oxygen atom of LDH layer varies of + 0.05 e and -0.18 e respectively. Together with the enhancement of LDH conductivity verified through DOS, it is clear that the remarkable interaction provided by CDs makes a vital contribution to the surface spatial confinement effect and leads to the high capacitance and long stability for the high-performance supercapacitors.

As for energy storage devices, CDs also play a vital role in the electrochemical properties of different alkali-ions. Lee's group reported a hybrid carbon framework containing reduced graphene oxide and GQDs as an organic cathode material for Li-, Na-, and K-ions storage [99]. The DFT calculations used here focus on the variation of redox potential along with the increasing size of functionalized GQDs in the coronene model, the removal of carbonyl and hydroxyl groups could lead to the diverse decrease or increase in redox potential respectively that confirms the character of corresponding groups (Fig. 12c). Also, the ESP of such groups was lower during the hydrothermal reduction of GQDs that able to attract the alkali metal atoms, which is further confirmed by the decreased LUMO energies and binding energies in the solution phase that brings the enhanced reactivity and conductivity for these CDs-based materials that could be modulated through its functional groups. Besides, the heterostructures consisting of bismuthene and graphene are also able to be the potential anode materials for Li-ion and Na-ion batteries, the differential charge density and diffusion path and barrier of the computed models show in Fig. 12d exhibit that most of the charges are accumulated in the middle of Li/Na atoms and four adjacent Bi while the bonding between Bi and Li/Na exhibit the characteristics of metal bonds, the diffusion barrier of Li/Na is significantly decreased from 0.48/0.12 eV to 0.14/0.10 eV in the emergence of carbon layer that bring this heterostructures superior properties and better stabilities as the promising anode materials.

Zn-air batteries have drawn much attention due to their dramatic performance of theoretical energy density, flat working voltage, and safety that was capable of serving as a potential energy storage system [100,101]. Chen's group reported the air cathode of a flexible Zn-air battery device containing NiCo₂S₄ nanoarray and N-doped GQDs with abound defects that exhibited the superior electronic chemical performance and catalytic activity for both OER and ORR process, the supported DFT calculation based on NiCo₂S₄ (311) crystal plane and N-

modified graphene-like fragment model were performed to reveal the origin of enhancement for the catalytic activity of such CDs-based system [102] (Fig. 12e). The results of Gibbs free energy profile have indicated the 4e[•] ORR process is spontaneously exothermic, where the rate-limiting step is changed from $O_2 \rightarrow OOH^*$ to $OOH^* \rightarrow O^*$ after the introduction of GQDs and provide the electron transfer from NiCo₂S₄ to GQDs. The adsorption energy of OH* on the surface of different catalytic systems also reveals the facilitation of the OH* removal process that is responsible for the reduction of ORR overpotential and enhancement of ORR activity.

To cover shortcomings of the short lifespan of nickel-zinc alkaline batteries, our group proposed novel anode materials consisting of ZnO nanorods and CDs with excellent cycling stability and rate capability, where the forming univalent zinc (Zn⁺) species after the participation of CDs and calcination in N₂ could accelerate the electron transfer thus make the ZnO anodes advantageous electronic structures for electrochemical reaction processes, which help enhance the reversibility of anodes and suppress side reactions at once [103]. The calculation shown in Fig. 12f suggests the formation of Zn⁺ starts with Brønsted acid sites interacting between hydroxyl groups of CDs and O atoms of ZnO, where the Zn²⁺ ions are able to acquire electrons from charged CDs or CDs derivatives and stabilize as Zn⁺ and further accelerate the decisive step of the charging. Thus, it is clear that the coated carbon layer makes a significant contribution to the electrochemical storage process and gives practical applications for these commercial Ni-Zn secondary batteries.

4. Summary and outlook

In this review, we comprehensively discuss the modeling of various types of CDs, encompassing molecular clusters, aggregated states, graphene fragments, diamond-like structures, stacked configurations, and amorphous forms. Different CDs models incorporate additional modifications, such as size effects, defects, surface functionalization, and heteroatom doping, depending on the specific research focus. In the case of CDs as components in composite materials, their models predominantly take the form of heterojunctions. These simplified models can be classified into two types: pure CDs models or composite models where CDs are incorporated as constituents. With the advancing landscape of cOps have progressed from simplistic representations capturing only the hot regions to comprehensive models that encompass the most crucial structural features, bringing them closer to experimental reality. These X. Zhao et al.

Table 1



advancements, discussed in previous sections, are elucidated through modeling approaches outlined in Fig. 13, aiding in the review of pertinent content. Additionally, we explore the integration of computational techniques, ranging from basic geometric structures and electronic properties to frontier orbitals, absorption-emission spectra, adsorption energy, and energy barrier profiles in reaction systems. By aligning computational findings with experimental results, we elucidate the structure-performance relationships of CDs-related systems.

The current computational research on CDs remains in its nascent stages, still facing three crucial challenges. Firstly, due to the intricate nature of CD structures and the difficulties in their characterization, an accurate and comprehensive structural model is yet to be fully revealed. Currently, models are constructed based on distinctive structural features, previous research experience, and simple benchmark tests for the computational level. Therefore, more advanced characterization techniques and computational methods, such as quantitative

structure-activity relationship or high-throughput screening, are required to assist in achieving complete CD structural elucidation [104]. Secondly, commonly used models in calculations predominantly rely on GQDs, regardless of the specific CD type involved in the experiments. Although large model sizes and computational resources remain major limitations, the rationality of the constructed models also needs to be corroborated with the synthesis routes, necessitating the establishment of unified standards for each type of CD [105]. Lastly, while accurate structural models for CDs are relatively large, their applicability is restricted to MD studies involving biomacromolecules. Therefore, a significant challenge for future research lies in proposing logical simplification approaches that retain CDs core/edge structural features and stacking characteristics, enabling their application in composite systems, particularly in catalysis and energy storage fields. To facilitate the review of elements about CDs models and the key considerations in model construction, Table 1 centrally summarizes various CD models with distinct structural features.

To this end, the establishment of universal and reliable CDs models for theoretical calculations on different scales (isolated systems, complex systems, or bio-related systems) is crucial. The selection of key parameters, such as bonding descriptors, frontier orbitals, excitation characteristics, and reaction activity, that can describe the intrinsic structure of CDs and their related modifications is essential for uncovering inherent regularities, bridging abstract numerical results to concrete physicochemical properties of CDs. This process requires a substantial amount of calculation data and mature mining and analysis technology. With substantial support from comprehensive experimental and computational datasets in iterative learning control, researchers have successfully enhanced and optimized the functionals, basis sets, and force fields frequently utilized in the computational modeling of CDs. These refinements contribute to the development of more efficient and precise computational strategies, specifically tailored for various scales [106–108]. Therefore, they should enable nuanced adjustments to meet the specific demands of diverse application scenarios, thereby ensuring a smooth progression in the simulation and design of novel CDs-based materials in the future. As computational models continue to advance, the realization of CDs with remarkable performance is imminent. Moreover, quantum dots have gained increased attention, particularly with the awarding of the Nobel Prize in chemistry. CDs, as members of the quantum dots family, will also continue to receive attention due to their unique characteristics, such as size effects and surface states. Throughout this developmental process, the dimensions of theoretical models for CDs or relevant composites will undoubtedly need to closely approximate real sizes, allowing for a more accurate representation of the actual surface state of CDs. Therefore, establishing large-scale models based on CDs to better explain their applications in complex chemical systems such as self-formation mechanisms, photoluminescence, and interfacial chemical processes will not be an unimaginable thing.

In summary, we firmly believe that the ongoing maturation and widespread application of machine learning, deep learning, neural networks, artificial intelligence, and high-throughput screening techniques will provide profound insights into the structure-performance relationships of CDs.

CRediT authorship contribution statement

Xiao Zhao: Writing – original draft, Software, Methodology, Formal analysis, Data curation, Conceptualization. Jishi Wei: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. Tianbing Song: Visualization, Validation, Resources, Methodology, Formal analysis. Zhengren Wang: Methodology, Formal analysis, Data curation. Dawei Yang: Validation, Software, Resources, Data curation, Conceptualization. Xirong Zhang: Visualization, Validation, Resources, Formal analysis, Data curation. Feng Huo: Visualization, Validation, Project administration, Investigation. Yanqiang Zhang: Validation, Funding acquisition, Formal analysis, Data curation. Huan-Ming Xiong: Writing – review & editing, Supervision, Resources, Project administration, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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