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CARBON QUANTUM DOTS FOR SUSTAINABLE ENERGY AND OPTOELECTRONICS

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Preface

In congruence with all progress made by human society, the thrust on natural resources has escalated incessantly, which has had a detrimental impact on the health of ecosystems and the well-being of people. Hence, striking a balance between progressive industrialization led economic development and consumption of natural resources is the only way forward for the sustainability of the evolution of society. Sustainable development is defined by the United Nations as the development of present society keeping in view the generations to come. As natural resources are limited, they should be used judiciously and optimally to ensure that there is enough left for future generations as well, without affecting the present quality of life. A sustainable society must thrive to be socially responsible, technologically accessible, and economically feasible keeping in view environmental protection and dynamic equilibrium between human and natural ecosystems. The main pillars of sustainable development are energy, water, and health care. The United Nations has declared them as the goals in the United Nations Sustainable Development Goals SDG7 and SDG6 to ensure access to affordable, clean, reliable, sustainable, and modern energy and to ensure availability and sustainability of clean water and sanitation to all without affecting the environment. Scientific community should focus their research toward attaining these goals. Nanotechnology, a recently developed innovative technology dealing with the science and technology in a nano dimension, is established as a promising tool for achieving these goals. Nanotechnology has the potential to fulfill the overwhelming demand for energy and basic commodities and advancing technology without affecting our environment, climate, and natural resources. The global sustainability challenges our world faces today can be solved by nanotechnology as an environmentally acceptable technique. The main components of nanotechnology in the battle are the nanomaterials and quantum dots. Quantum dots, few nanometers in size, are particles where quantum mechanics are predominant, with the associated quantum mechanical waves confined in nano-dimensions and generating size-dependent discrete energy levels. Generally, in a quantum dot, the energy gap between the conduction band and the valence band or the gap between the HOMO and LUMO is dependent on the particle size. The electronic waves associated with the free electrons on the particles are confined within the boundary of the particle (dimension of the particle) and the energy associated with them is quantized according to the size of the particle. So, the optical and electronic properties of the quantum dots differ largely from their bulk counterparts. The quantum dots have the properties lying somewhere between the bulk and the atom/molecules, and they vary with size and shape. Now the carbon quantum dots (CQDs) have emerged as a game changer among different quantum dots and other allotropes of nanocarbon because of simple and sustainable fabrication methods involved. There are different types of allotropes of nanocarbon such as carbon nanotube, buckminsterfullerene, graphene and nanodiamond used in nano-engineering facilitating sustainable development. Carbon, the group 14 member of the periodic table, has a very interesting electronic structure and multiple valance and coordination numbers. Because of different oxidation numbers and catenation properties of carbon, there exist a large variety of allotropes with orbital hybridization along with the structure, governing their properties. Among the nanocarbon allotropes, CQDs are attracting a good deal of research interest because of their ease of synthesis and versatile applications. The CQDs can be synthesized from carbon-containing materials, mainly biomaterials, by a simple chemical reduction process. The simple technique for surface passivation and functionalization adds to the host of characteristics of CQDs for applications in different fields for sustainable development.

This book solely focuses on the different aspects of CQDs facilitating sustainable development of our society. First, this book discusses the structure−property relationship of CQDs in optical domains in detail. As the photophysical properties of CQDs are the most interesting and studied ones, we focused on understanding the photophysical properties and their origin. This book also discusses the theoretical modeling of the CQDs from a basic to an advanced level. The synthesis of CQDs is more beneficial compared to other nanomaterials, especially carbon nanomaterials like CNT and graphene, as it does not require sophisticated instrumentation and technology. A facile and cost-effective synthesis method for CQDs makes them very popular among researchers. The third chapter of the book delivers the details of the synthesis method of CQDs. Following the synthesis, the physical properties and different characterization techniques of CQDs are covered. As the properties of the CQDs are predominantly controlled by the surface states of the CQDs, this book pays special attention to the surface functionalization of CQDs in the next chapter. Most of the fabrication methods of CQDs are sustainable ones, but if we want to highlight the role of CQDs in sustainable development, it is mainly derived from the different application aspects of the CQDs. We focus on the application of CQDs in energy harvesting, energy storage, and wastewater treatment to biosensing in other chapters. Biomedical applications of CQDs ranging from bioimaging to theranostics are covered in subsequent chapters. The magnetic applications of CQDs and composites of CQDs are also discussed. Finally, the CQD-based optical and electronic nanodevices are discussed with a special focus on terahertz applications and single electron transistor applications. Another form of carbon nanoparticle, nano-diamond, is explored for photonic and biomedical applications. The book concludes with a summary of recent advancements and future prospects of CQDs for sustainable applications.

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Contents

Photocatalytic applications of carbon quantum dots for wastewater treatment

13

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13.1 Overview on advanced oxidation process and photocatalysis

The excessive discharge of industrial effluent, worldwide production, and utilization of chemical products, as well as expanding world population contributes significantly to the increasing accumulation of bio recalcitrant organic pollutants in the environment [1]. In developing countries, this unpleasant trend is widespread due to the improper enforcement of environmental regulations and monitoring frameworks. A proportion of these organic pollutants remains unregulated and causes serious deterioration of the freshwater ecosystem. Presently, a large amount of various chemical pollutants containing wastewater are produced from domestic and industrial activities, which eventually pollute the environment [2,3]. Fresh, uncontaminated, and enough sanitary measures remain critical tohuman health and socioeconomic sustainability as these two are becoming endangered commodity at present [1,4,5]. In accordance with solving the present water crisis globally and acquiring more economic gain, an alternative for new water treatment technology that can completely remove organic pollutants is henceforth significant and necessary [6]. Owing to the expanding worldwide concern for environmental protection, advanced oxidation technology (AOT) pointed out the prominent role of a special class of oxidation technology defined as advanced oxidation process (AOPs) was developed. To date, studies have shown that AOPs still upheld as one of the favorable and reasonable methods for treating the water and wastewater to remove the contaminants [7−9]. AOPs stand out as one of the most environmentally friendly techniques used to remove bio recalcitrant organic pollutants that are not easily

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treatable by existing conventional treatment technologies due to their chemical stability [10]. The advantages and disadvantages of the existing water treatment method and photocatalytic system are summarized in Table 13.1.

AOPs allude to a set of chemical treatment procedures for removing organic pollutants in water and wastewater by oxidation. AOPs were first proposed for portable water treatment in the 1980s [9,11,12], which were then defined as oxidation processes involving the generation of hydroxyl radicals (OH-) in adequate amounts for water purification. The main mechanism of the AOPs function is the generation of highly reactive free radicals. AOPs include two phases of oxidation process: formation of strong oxidants (e.g., hydroxyl radicals) and the reaction of these oxidants with organic contaminants in water [13−15]. Table 13.2 depicts the oxidants used in different wastewater treatment techniques with corresponding oxidation potential values [16]. Among o them, OH- has stronger oxidation power than normally used oxidants and decomposes the organic compounds into moderately harmless compounds, such as CO_2, H_2O, or HCl.

To measure the effectiveness of the treatment, it is necessary to understand the selected type of AOPs, physical and chemical properties of pollutants, and operating parameters of the process. A variety of techniques were classified under the broad definition of AOPs. A list of possible techniques offered by AOPs are given in Fig. 13.1

Photocatalysis was included in the family of AOP, which enlisted many advantages and can likely provide solutions for many environmental problems faced by the modern world. This is because photocatalysis allocates a simple way of utilizing

Table 13.1 The advantages and disadvantages of existing water treatment technologies.

Water treatment technology	Advantages	Disadvantages
Biological	High reliability High load operation can be processed	Difficulty in securing stable process High level of sludge Operating management requires expertise
Coagulation/ precipitation	High efficiency of processing Low sites	Excessive sludge produced Difficult to maintain
Fenton	Wide coverage Treatment process is simple and easy to manage Effective colored discoloration of wastewater	High operating cost over the use of the Fenton's reagent Removal of the equipment needs iron salts
Photocatalytic advanced oxidation	Low operational and installation cost No sludge produces Possible for nonbiodegradable wastewater treatment	Limited lamp life when UV lamp is used Limitation on photocatalyst recovery facility

Source: Adapted from Lim, S.Y., Shen, W., & Gao, Z. (2015). Carbon quantum dots and their applications. Chemical Society Reviews, 44(1), 362–381. https://doi.org/10.1039/c4cs00269e.

summarizes some of the CQDs-TiO_2 composite that has been conducted as photocatalyst for the degradation variety of target pollutants [29].

As reported in Table 13.6, Sun et al. outlined the fabrication of CQDs-TiO_2 nanotubes photocatalyst with improved visible light absorption and photoelectrochemical response [70]. The result shows that the prepared composite of CQDs-TiO_2 nanotubes exhibited higher degradation efficiency than TiO_2 nanotubes arrays by 14% in 100 min under given experimental condition (MB = 15 mL, 5 mg/L). From this study, it was clear that CQDs-TiO_2 nanotubes composite enhanced photocatalytic activity when illuminated with visible light compared to TiO_2 nanotubes. Subsequently, in 2014, Yu and coworkers reported that CQDs-TiO_2 nanosheets (CQDs-TNS) and CQDs-P25 composite exposed an enhancement in photocatalytic activities, especially CQDs-TNS compared to CQDs-P25. Besides, an increasing amount of CQDs solution from 2.5 to 10 mL increases the degradation efficiency gradually from 27.2% to 95.4%, which indicates that utilization of a suitable amount of CQDs can effectively improve the visible light photocatalytic activity of TNS for RhB degradation [38].

Jun et al. attributed the improvement of the degrading efficiency of CQDs-TiO_2 powder, which is notably higher than the controlled pure TiO_2. At the point when the volume of CQDs utilized was 10 mL, catalytic activity is most noteworthy, up to 90%, which is almost 3.6 times higher than that of pure TiO_2. It is fascinating that, with the increase in CQDs from 5 to 10 mL, the catalytic activity of the CQDs-TiO_2 increased drastically due to improved absorbance of visible light and increased separation efficiency of photogenerated charge carriers. However, further increment of CQD content to 15 mL leads to an apparent decrease in photocatalytic performance due to the distribution of CQDs on the surface of TiO_2 [40].

Even though the reported studies successfully improved the visible light photocatalytic efficiency, the research gap still involves combining TiO_2 with CQDs derived from biomass as the carbon precursor, and the utilization of harmless sunlight irradiation for photocatalytic activity needs to be explored. This is because, the former studies were done using graphite rod and I-ascorbic acid as the precursor. The precursor is not cost-effective, not easily available, and meanwhile, the usage of chemicals as the precursor is considered not environmentally friendly [29,38,40,70]. The previous studies also involved harsh and multiple steps procedures, which were time-consuming and sometimes produced poor phase structure and bigger size of photocatalyst that effect the photocatalytic activity [29,40,70].

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