

# Chapter 3

## Metal and Carbon Quantum Dot Photocatalysts for Water Purification



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**Abstract** Carbon quantum dots are zero-dimensional carbon nanomaterials having a size of less than 10 nm with  $sp^2$ -/ $sp^3$ -hybridized carbon atom containing a variety of functional groups at basal plane and periphery. Carbon quantum dots are a new

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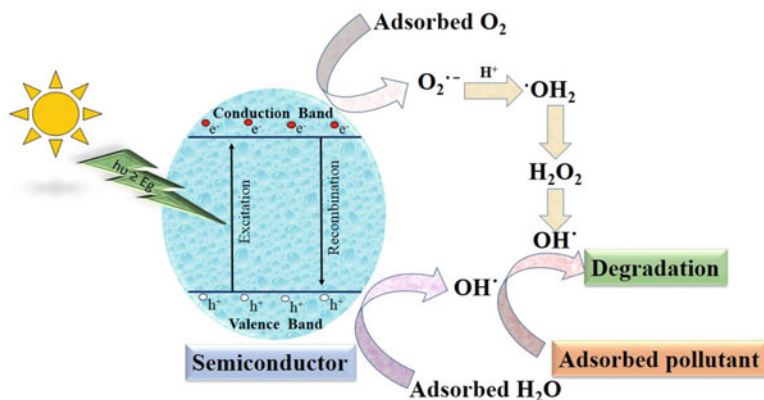
class of carbonaceous material which are recently developed and attracted appreciable importance due to their superlative properties and significant applications in different fields. By virtue of their unique optical, electronic, and efficient light harvesting, tunable photoluminescence, and up-conversion property, carbon quantum dots displayed huge applications in bio-sensing, bio-imaging, drug delivery, photocatalysis, photovoltaics and optoelectronics. Today, contamination of water is one of the biggest and most alarming problems that demands an immediate solution, and non-availability of economical method for water treatment makes it more significant. The potential pollutants of water pollution are heavy metal ions, sewage, pesticide, pharmaceutical waste, and industrial waste. The most abundant carbon as photocatalytic nanomaterial could be a better choice among previously reported conventional photocatalyst and quantum dots.

The book chapter aims to demonstrate top-down method and bottom-up method for the fabrication of carbon quantum dots. Further, the basic mechanism of photocatalysis, disadvantages of conventional quantum dots, classification of carbon quantum dots, and the concept behind up-conversion phenomena were also reviewed. The photocatalytic degradation and antimicrobial application of carbon quantum dot-based photocatalyst were also explored. Lastly, conclusion and future perspective were considered and speculated. The design of photocatalytic system with high photo-efficiency is still challenging, and the area remains open to carry out future research.

**Keywords** Carbon quantum dots · Graphene quantum dots · Photocatalyst · Nanocomposites · Up-conversion · Water purification

### 3.1 Introduction

The need of a promising approach to meet the global energy requirement of the future generation as well decreasing environmental pollution by utilizing renewable solar energy is the most prominent method. The idea of bringing out an effective usage of solar energy makes scientists to explore such material which is capable of both energy conversion and environmental pollutant degradation (Chandel et al. 2019; Gautam et al. 2017; Zhu et al. 2017). The semiconductor photocatalysts become an evident material with immense potential for solving water pollution (Singh et al. 2014; Raizada et al. 2017a; Shandilya et al. 2018a). Thus, various semiconductor photocatalytic materials such as titanates (He et al. 2018; Kumar et al. 2019), vanadates (Adan et al. 2015), tungstates (Huang et al. 2014), zirconates (Chen et al. 2015), chalcogenides (Nie and Zhang 2017), oxyhalides (Sharma et al. 2019a; Priya et al. 2016a; Singh et al. 2016), ferrites (Sonu et al. 2019; Singh et al. 2019a, b), and borates (Huang et al. 2013) have been investigated. However, these materials are associated with certain limitations like inefficient solar light harvesting



**Fig. 3.1** Mechanistic view of semiconductor-based photocatalysis indicating generation of electron–hole pair under solar irradiation; the holes in the valence band oxidizes water molecule into hydroxyl radical, whereas the electron in the conduction band reduces oxygen into superoxide radical. The generated reactive oxygen species oxidizes adsorbed pollutant into innocuous product

due to wide band gap, complex synthetic procedure, high cost, high toxicity, and leaching.

The basic mechanism for photocatalytic reaction can be understood from Fig. 3.1. The electron–hole pair generation is mainly stimulated when light of certain frequency with energy greater than or equal to the band gap of semiconductor is made incident on its surface (Singh et al. 2018; Raizada et al. 2017b; Priya et al. 2016b; Gautam et al. 2016; Shandilya et al. 2019). The charge carrier generated may either recombine or assort individually to render hydroxyl radical in the valence band and superoxide radical in the conduction band (Singh et al. 2013). The electron exhibit a strong reductive potential of +0.5 to  $-1.5$  V *w.r.t.* normal hydrogen electrode, whereas holes possess strong oxidative potential of +1.0 to +3 V *w.r.t.* normal hydrogen electrode. The reactive oxidation species is a strong oxidizing agent that can oxidize the pollutant into innocuous product. Further, electron reduces the oxygen into superoxide anion in the conduction band, and holes oxidize the water molecule into hydroxyl radical in the valence band (Raizada et al. 2014a, b, 2019a, b; Sudhaik et al. 2018a).

Both superoxide anion and hydroxyl radical are highly reactive oxidation species that can bang up all types of pollutant along with biomolecules and can be used to disinfect and deodorized air and water (Singh et al. 2017, 2018; Hasija et al. 2019a; Sudhaik et al. 2018b). The continuous attack by reactive oxidation species finally brings about the abasement of pollutant present in water. All impurities in water were oxidized by reactive oxidation species ( $\text{OH}\cdot$ ,  $\text{O}_2^{\cdot-}$ , and  $\text{H}_2\text{O}_2$ ) generated during photocatalysis (Hasija et al. 2019b; Dutta et al. 2019; Raizada et al. 2019c, d).

However, ineffective utilization of solar spectrum due to wide band gap, higher rate of recombination of photogenerated charge carrier, difficulty in separation/recovery, complex synthetic procedure, high cost, high toxicity, and leaching are certain disadvantages possess by bare metal oxide-based semiconductor (Raizada

et al. 2016; Tian et al. 2014). One of the effective ways to minimize these limitations is to assemble carbon-coated nanostructure where the carbonaceous material enhances the charge carrier mobility by acting as an electron sink/acceptor. Further, the codoping of carbon framework with nitrogen and sulfur induces the surface defects which increase the delocalization of electron (Wu et al. 2007; Pang et al. 2015; Raizada et al. 2018). Thus, one of the prominent nanomaterials ruling nanotechnology is the metal-free carbon-based photocatalytic system employed for the degradation of pollutant from water. After oxygen, carbon is the second highest abundant element in the periodic table and also the major constituent of organic compound. The usage of the most abundant carbon as photocatalytic nanomaterial makes them more economical and advantageous in which carbon quantum dots acquire a significant attention.

Earlier, the survey was confined to CdSe/CdS and CdSe/ZnS and ZnSe/CdSe quantum dots. In these traditional quantum dots, cadmium is the chief constituent which leads to cytotoxicity due to the leakage of cadmium ions (Xu et al. 2010). Thus, scientists emphasize to develop cadmium-free quantum dots, for example, graphene quantum dots, carbon quantum dots, and silicon quantum dots (Al Awak et al. 2017). Quantum dots have been utilized in a variety of applications including bio-sensing, bio-imaging, and biomarkers and in medicine (Sharma et al. 2019b; Jamwal et al. 2015). However, potential cytotoxicity, environmental hazards, and tedious synthesis procedure were certain limitations that hindered the large-scale applicability of quantum dots. Conventional quantum dots like PbS, PbSe, HgTe, CdSe, InAs, and InP (Cademartiri et al. 2006; Moreels et al. 2007; Keuleyan et al. 2011; Guzelian et al. 1996; Micic et al. 1997) have various properties. However, metal-based quantum dots face major challenges of depositing on the support, recycling, and extremely hazardous nature which need to be addressed. Limitation of conventional quantum dots can be obviated by using organic quantum dots as an alternative; hence, many researchers nowadays are extensively working on it.

Currently, quantum-sized carbon has attracting much attention due to its tunable band gap with broader absorption range; good conductivity; strong photoluminescence emission; large-scale synthesis at low cost; less complex synthetic procedure; most abundant and thus inexpensive; high photostability; remarkable optical, electronic, and magnetic property; good biocompatibility; low toxicity; and high chemical stability that make them chemically inert (Chen et al. 2018b; Ma et al. 2017; Lim et al. 2015) (Fig. 3.2). All these properties make them widely utilized in different fields, for example, in optoelectronics, biosensor, drug delivery, bio-imaging, biomedical engineering, and photocatalysis (Luo et al. 2016; Namdari et al. 2017). Further, the excellent electronic property of carbon quantum dots makes them good electron donors and acceptors, resulting in their wide application in catalysis, semiconductor devices, and sensor (Fig. 3.3).

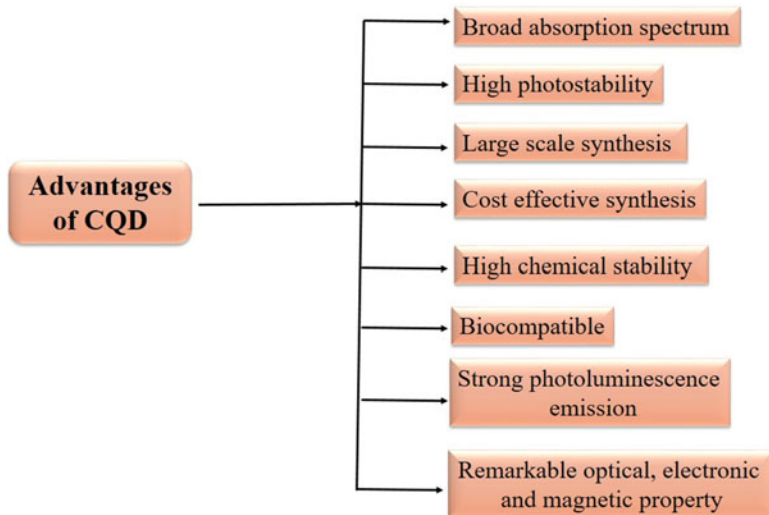


Fig. 3.2 Various advantages of carbon quantum dots

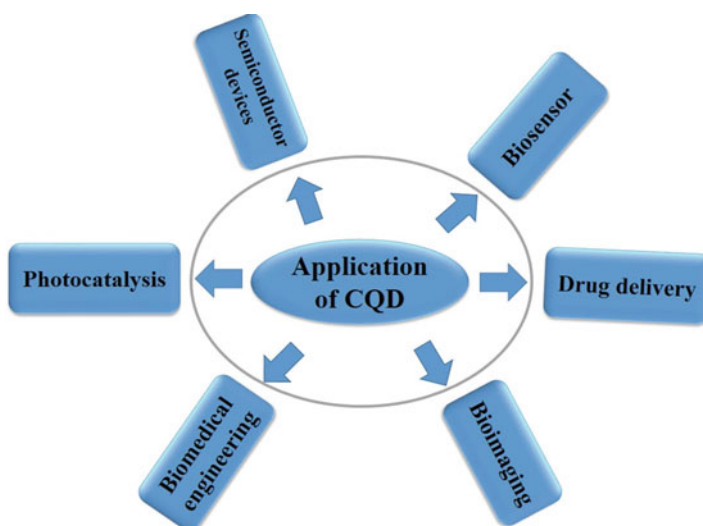


Fig. 3.3 Different applications of carbon quantum dots

## 3.2 Classification of Carbon Quantum Dots

Various allotropic forms of carbon are graphene, fullerene, carbon nanotubes, carbon onions, carbon nano-horns, and carbon quantum dots. On the basis of dimension, carbon nanomaterials are classified into zero-dimensional (carbon quantum dots,

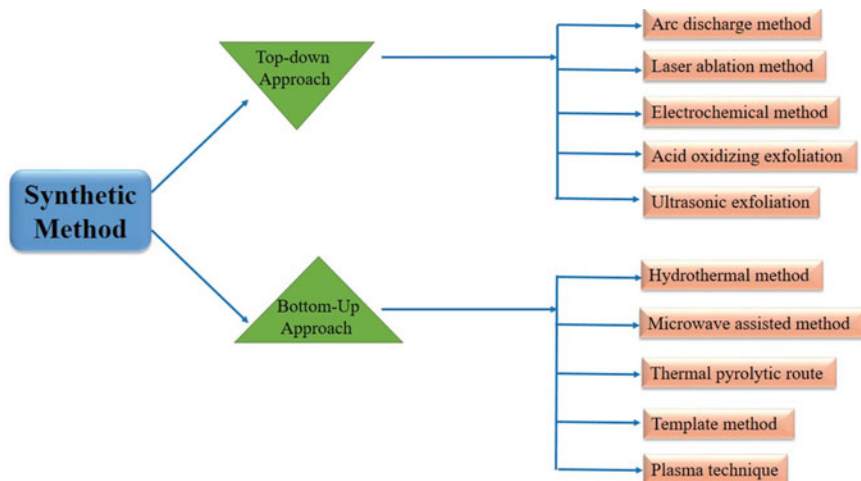
fullerene, carbon onions, nano-diamonds), one-dimensional (carbon nanotubes, single-walled carbon nanotubes, carbon nanofibers), and two-dimensional materials (graphene, graphene nanoribbons, few layered graphenes) (Shandilya et al. 2018b).

Xu et al. (2004) firstly isolated carbon quantum dots from the crude soot while preparing single-walled carbon nanotubes (Xu et al. 2004). Sun et al. (2006) isolated carbon quantum dots from graphite powder and cement using laser ablation method (Sun et al. 2006). Pan et al. (2018) fabricated CdS/BiOCl heterojunction via selective deposition of CdS quantum dots on BiOCl nanosheets. Various characterization techniques indicate the uniform dispersion of CdS quantum dots. The photocatalytic performance was carried out against methyl orange and phenol, which shows 4.0 and 4.8 times higher efficiency of nanocomposites as compared to bare BiOCl. The increased visible light absorption and high migration efficiency of charge carrier are attributed for high efficiency. Due to the narrow band gap of CdS of 2.4 eV, CdS can be easily coupled with bismuth-based photocatalyst so as to inhibit rate of recombination by promoting charge carrier separation. Earlier, BiOI, BiOCl coupled with CdS quantum dots, and photocatalytic activity were evaluated against rhodamine B and methyl orange (Kandi et al. 2017; Liu et al. 2014).

There are many review articles published highlighting the synthetic approaches, properties, surface functionalization, and application of carbon quantum dots. Here, top-up and bottom-down approaches for the synthesis of carbon quantum dots with their advantages and disadvantages were reviewed. Then, the mechanism of some novel photocatalysts is also proposed followed by the general discussion of Z-scheme photocatalyst and later on the up-conversion phenomena of carbon quantum dots which are basically responsible for the higher photo-efficiency of nanocomposites by broadening the region of solar light absorption.

### 3.3 Method of Preparation of Carbon Quantum Dot-Modified Photocatalysts

Generally, there are two synthetic methods by which carbon quantum dots can be prepared: “bottom-up” and “top-down” approaches (Roy et al. 2015; Zhu et al. 2015). The main problems taken into account while synthesizing carbon quantum dots are agglomeration, surface functionalization, size control, and uniformity. The top-down approach includes the fragmentation of large based precursor (graphite, graphene, graphene oxide, carbon nanotube, carbon fiber) into carbon nanomaterial via arc discharge, laser ablation, electrochemical approach, acid oxidizing exfoliation, and ultrasonic exfoliation (Yuan et al. 2016). However, bottom-up approach includes hydrothermal/solvothermal method, microwave-assisted method, thermal pyrolytic route (oil bath), reverse micelle technique, template method, and substance oxidation (Zuo et al. 2016) (Fig. 3.4 and Table 3.1). Bottom-up approach is a template strategy which is used to construct carbon quantum dots by using citric



**Fig. 3.4** Schematic diagram of various synthetic methods of top-down and bottom-up approach for the synthesis of carbon quantum dots

acid, glucose, xylose, and resin as carbonaceous materials (Yang et al. 2018; Tang et al. 2012).

### 3.3.1 Top-Down Method

#### Arc Discharge Method

In arc discharge method, a helium gas of 660 mbar pressure is electrically broken down to generate plasma using electric current at the anode and cathode. The pure graphite rod acts as the cathode which is 16 mm in diameter and 40 mm in length, while the anode is also made up of graphite rod which is 6 mm in diameter and 100 mm in length. The anode is further drilled to make a hole of 3.5 mm in diameter and 40 mm deep filled with carbon precursor along with catalysts. The arc discharge was generated by applying 100 A current and 30 V potential between the anode and cathode kept at a constant distance of 3 mm. Mixtures of metals, Ni–Co, Co–Y, and Ni–Y, in different atomic percentages were used as catalysts. The high-temperature plasma sublimes the carbon precursor. The carbon vapor moves toward the cathode where it cools down due to temperature gradient and is collected from the walls of the chamber (Journet et al. 1997). Xu et al. (2004) devised arc discharge method for the preparation of single-walled carbon nanotube exploiting soot which is condensed on the chamber walls.

**Table 3.1** Advantages and disadvantages of synthetic method of carbon quantum dots

Sr. no.		Synthetic method	Advantages	Disadvantages	References
1.	Top-down approach	Arc discharge method	Most attainable method	Harsh condition, low quantum yield, composite method	Xu et al. (2004) and Journet et al. (1997)
		Laser ablation method	Rapid, effective, varied size carbon quantum dots can be synthesized, effective technique	Low quantum yield, poor size control, large amount of carbon precursor is required	Xiao et al. (2017) and Liang et al. (2014)
		Electrochemical method	Stable one-step method, size and nanostructure are controllable, hydrophilic carbon quantum dots can be synthesized, amount of carbon quantum dots can be increased by changing current density	Complex method	Bao et al. (2011) and Ahirwar et al. (2017)
		Acid oxidizing exfoliation	Most accessible	Harsh condition, multistep process, poor control over size	Dong et al. (2012) and Zhu et al. (2010)
2.	Bottom-up approach	Hydrothermal/solvothermal method	Hydrophilic carbon quantum dots can be synthesized, cost-effective, non-toxic method, and eco-friendly	Poor control over size	Zuo et al. (2016) and Sarkar et al. (2016)
		Microwave-assisted method	Rapid, scalable, inexpensive, and eco-friendly method	Poor control over size	Qin et al. (2013) and Yang et al. (2013b)
		Thermal pyrolytic route	Easy and simple method	Low quantum yield, high temperature requirement	Wang et al. (2011) and Liu et al. (2011)
		Template method	Synthesized carbon quantum dots are bio-compatible and exhibit good colloidal stability	Low quantum yield, highly expensive method, time-consuming	Grun et al. (2000) and Lai et al. (2012)



### Laser Ablation Method

In laser ablation method, carbon precursors firstly absorb the high-energy laser pulse, and then electrons are removed through photoelectric and thermionic emission from the atom followed by generation of high electric field which produces strong repulsive forces and thus breaks down the carbon quantum dots (Xiao et al. 2017). Laser ablation method is a chemically simple and facile method and generates very little by-products. Also, laser ablation method does not require extreme temperature and pressure, and also there is no need of catalysts for the process to be carried out. Further, preparation of carbon quantum dots was done using carbon nanoparticles in organic solvent ethanol and acetone (Li et al. 2010a). Here, carbon nanomaterial was dissolved in organic solvent, with subsequent ultrasonication. The suspension was then conserved in a glass cell irradiated with laser followed by continuous magnetic stirring so as to avoid settling of nanoparticles. Other than carbon quantum dots, fluorescent carbon nanoparticles were also prepared by laser irradiation of carbon suspension in organic solvent (Hu et al. 2009).

Sun and co-worker (2006) also synthesize carbon dots by using laser ablation method in argon using water vapor. Carbon precursor was prepared by stepwise baking, curing, and annealing of the mixture of graphite powder and cement in an argon flow. The obtained sample was treated with aq.  $\text{HNO}_3$  solution to oxidize surface carbon with refluxing for 12 h followed by surface passivation of carbon particle through organic species which exhibit luminescence property. Thus, the surface passivation of carbon precursor by organic molecule polyethylene glycol to prepare carbon quantum dots can activate the surface and become highly photoactive in visible and IR region (Wang et al. 2009). Not only carbon quantum dots but one-dimensional iron-based bimetallic magnetic nanoparticles such as FePt, FeCo, and FeNi were also synthesized by laser ablation method (Liang et al. 2014). Laser ablation method is mainly associated with low productivity problem which strongly depends upon laser power density and liquid medium. Because nanoparticles have strong absorption and scattering effects in liquid medium, determining their productivity is an important parameter.

### Electrochemical Approach

Electrochemical method involves a nonselective top-down approach using various carbon precursors for the synthesis of carbon quantum dots. Electrochemical method is a unique method since the size of quantum dots can be adjusted by regulating potential. Ahirwar et al. (2017) synthesize graphene and graphene oxide quantum dots via electrochemical exfoliation method with 2–3 nm in size. The two electrodes used were made up of graphite which is dipped in the solution of electrolyte made up of combination of weak and strong electrolytes. Further, Devi et al. (2018) synthesize carbon quantum dots via electrochemical method using graphite electrode acting as the anode and cathode, respectively, and mixture of NaOH/EtOH as an electrolyte

solution. Depending upon applied current and time, different particle-sized carbon quantum dots are synthesized which is further confirmed by various spectroscopic techniques.

Deng et al. (2014) prepared carbon nanodots by one-pot electrochemical carbonization of alcohol under basic condition. Uniform carbon dots were prepared using low molecular weight alcohol. Herein, a three-electrode system is used where two platinum sheets were used as working and counter electrodes placed 3 cm apart, and calomel electrode was used as reference electrode. After electrolysis, the obtained mixture was evaporated at 800 °C until a yellow-colored powder was obtained followed by dialysis using dialysis membrane. Shinde and Pillai (2012) prepared uniform size graphene quantum dots from multi-walled carbon nanotube in nonaqueous solvent via electrochemical method. Due to high photostability, non-toxicity, and biocompatibility, graphene quantum dots are a promising candidate for various applications in nano-electronics and as biomarkers and chemosensors. The uniform-sized carbon dots can be further prepared from the bundle of carbon fiber using three-electrode system at constant potential (Bao et al. 2011). Here, carbon fiber was used as the working electrode, Pt sheet as the counter electrode, and Ag wire as the quasi-reference electrode, respectively. Among these methods, electrochemical method is a green method with large yield, less time-consuming, and operated at low temperature.

Further, zero-dimensional graphene quantum dots with sizes ranging from 3 to 5 nm were synthesized via electrochemical method (Li et al. 2011b). Firstly, the graphene film was prepared by direct filtration (pore size 220 nm) of colloidal suspension of reduced graphene oxide. Then, dried graphene was mechanically peeled to obtain graphene film, which is further treated with oxygen plasma for just 10 s to increase hydrophilicity. In the electrochemical preparation, three electrodes were used: a graphene film (working electrode), Pt wire (counter electrode), and Ag/AgCl (reference electrode). The mono-dispersed graphene quantum dots are much smaller in size (3–5 nm) as compared to graphene quantum dots (10 nm) synthesized by hydrothermal method (Li et al. 2008).

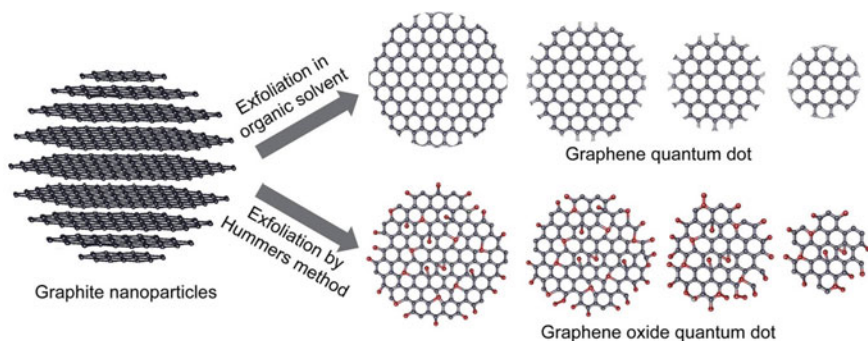
Other than carbon quantum dots, simple metal oxide or metal sulfide quantum dots were also synthesized by electrochemical method. Gopalakrishnan et al. synthesize MoS<sub>2</sub> luminescent quantum dots of sizes ranging from 2.5 to 6 nm from bulk solution using aqueous ionic liquid (Gopalakrishnan et al. 2015). Similarly, Valappil et al. (2017) synthesize transition metal dichalcogenides quantum dots WS<sub>2</sub> via electrochemical method with a wide application in optoelectronic devices. Earlier, various methods for the synthesis of quantum dots are available. Synthesis of potassium intercalation followed by ultrasonication is quite complicated and laborious; thus, it needs further purification for the removal of potassium ion (Lin et al. 2013). Another way is simple ultrasonication of WS<sub>2</sub> nanosheets but the size of the product cannot be determined easily.

## Acid Oxidizing Exfoliation

In acid oxidizing exfoliation method, carbon quantum dots were synthesized by controlled oxidation using strong oxidizing acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Using harsh and drastic condition is necessary for the formulation of carbon quantum dots and one of the major disadvantages of acid oxidizing exfoliation method. Graphene quantum dots have promising application in nanotechnology and can be synthesized by chemical breakdown of graphene oxide (Zhu et al. 2010; Terrones et al. 2010). Peng et al. (2012) prepared graphene quantum dots in large scale by acid exfoliation followed by etching of carbon fibers having resin-rich surface. Different sized graphene quantum dots which can be accessed by easily varying the reaction temperature were observed.

Various strategies are focused on regulating the size of the carbonaceous material not more than 10 nm which is called carbon quantum dots that attributes to the quantum confinement effect. Liu et al. (2013) employed graphite nanoparticle as a starting material to prepare graphene and graphene oxide quantum dots as illustrated in Fig. 3.5. For the synthesis of graphene quantum dots, graphene nanoparticles were directly exfoliated and centrifuged at 4000 rpm for 30 min, and for graphene oxide quantum dots, modified hummer method is used followed by exfoliation. Various graphene layers well-adjusted by van der Waals forces and pi-pi interaction were exfoliated to obtain homogeneous and single-layered graphene quantum dots and graphene oxide quantum dots with high yield. Further, the exfoliation of graphite was also reported in various organic solvents (Hernandez et al. 2008).

Further, Peng et al. (2012) described graphene quantum dot synthesis through acid treatment and chemical exfoliation using carbon fibers as precursor, which produces graphene quantum dots with different sizes ranging from 1 to 4 nm. Dong et al. also detailed easy, cheap, and high yield approach to prepare graphene



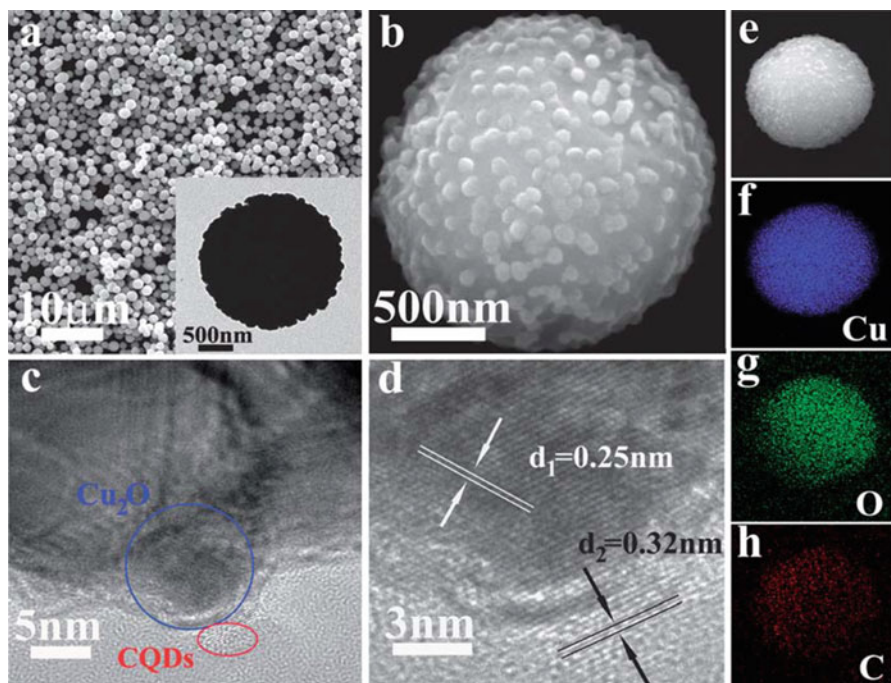
**Fig. 3.5** Synthesis of graphene quantum dots and graphene oxide quantum dots via chemical exfoliation method. The exfoliation in organic solvent without an oxidizing agent yields a few layered graphene quantum dots, and the exfoliation by hummer's method in the presence of an oxidizing agent yields graphene oxide quantum dots using graphite nanoparticles as precursor (oxygen sites in graphene quantum dots are shown in red dots). (Reprinted with permission from Liu et al. (2013) copyright©2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

quantum dots employing CX-72 carbon black as the starting material by refluxing with conc.  $\text{HNO}_3$  for 24 h (Dong et al. 2012). Single-layered graphene quantum dots can effectively penetrate the cell without any bio-conjugation which enables them to be utilized in bio-imaging and drug delivery, whereas multilayered graphene quantum dots exhibit broad solar absorption, rendering promising candidate in optoelectronic devices.

### Ultrasonic Exfoliation

The synthesis of carbon quantum dots through ultrasonication can generate alternate waves in liquids of low and high pressure liable for the generation and collapsing of vacuum bubbles in the reaction medium. It also prevents agglomeration and creates strong hydrodynamic shear forces. Li et al. (2012) synthesize carbon quantum dot-based  $\text{Cu}_2\text{O}$  nanostructure via facile one-step ultrasonic treatment using glucose as carbon precursor in alkali medium. Higher productivity of nanostructure is due to the high light reflecting capability of  $\text{Cu}_2\text{O}$  and up-conversion photoluminescence of carbon quantum dots. IR light comprises nearly 53% of solar spectrum which has not been utilized effectively. For the first time, Li et al. (2012) demonstrated that carbon quantum dot-based  $\text{Cu}_2\text{O}$  photocatalytic system could harness the near-infrared region of the solar spectrum. The photocatalytic activity of nanostructure was evaluated against methyl blue. The spherical-shaped nanostructure protruding  $\text{Cu}_2\text{O}$  particle could be clearly seen in scanning electron microscope images in Fig. 3.6.

The ultrasonic waves had the potential to convert macroscopic carbonaceous material into nanoscale carbon quantum dots. Li et al. (2011a) synthesize water-soluble fluorescent carbon quantum dots by using hydrogen peroxide-assisted ultrasonic method using activated carbon as precursor. The hydrophilic character of carbon quantum dots was attributed to the occurrence of hydroxyl group. To prepare a suitable amount of activated carbon, an appropriate amount of  $\text{H}_2\text{O}_2$  was added and subjected to 40 KHz ultrasonic treatment for 2 h at room temperature. The obtained suspension was then vacuum-filtered using 20 nm pore cellulose membrane. Park et al. (2014) described green synthesis based on carbon quantum dots using waste food via ultrasonic method at room temperature (Scheme 3.1). The usage of renewable resources for large-scale production of carbon quantum dots is a cost-effective method and useful in energy conversion and biomedical and industrial application. The synthetic procedure involves the following steps: dehydration, polymerization, carbonization, and passivation (Jeong et al. 2012). In a typical procedure, waste food and ethanol were mixed followed by ultrasonication to 45 min at 40 KHz. The obtained sample was centrifuged to separate heavy and agglomerated particle. The supernatant was then filtered twice through 0.22  $\mu\text{m}$  membrane to separate carbon quantum dots and further dried at 45  $^\circ\text{C}$ . The uniform spherical shape carbon quantum dots with average size of 4.6 nm were synthesized and further confirmed by high-resolution transmission electron microscope and atomic force microscopy images Fig. 3.7.



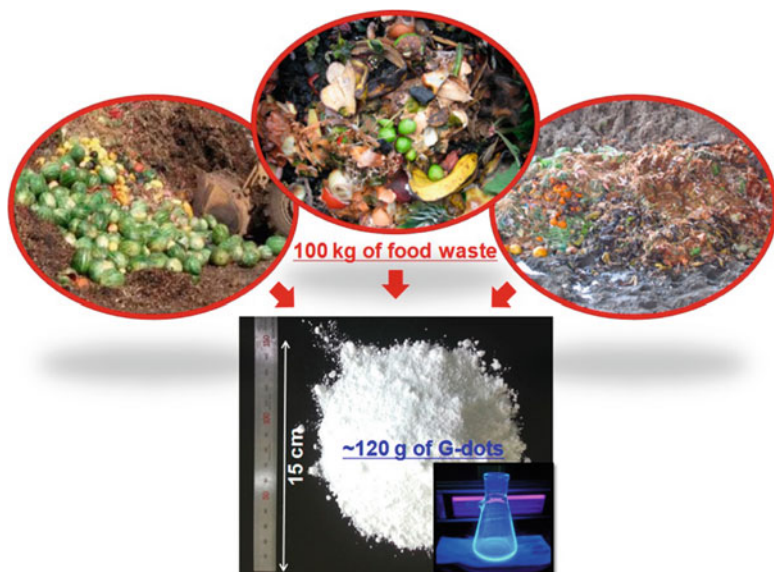
**Fig. 3.6** (a–c) Spherical-shaped scanning electron microscopy images of carbon quantum dots/ $\text{Cu}_2\text{O}$  composite at different resolutions: 10 nm, 500 nm, and 5 nm, respectively (inset of a). Transmission electron microscopy images of carbon quantum dots/ $\text{Cu}_2\text{O}$  composite. (d) High-resolution transmission electron microscopy images of the carbon quantum dots/ $\text{Cu}_2\text{O}$  prepared by one-step ultrasonic treatment with 0.25 nm and 0.32 nm d spacing values. (e) Scanning electron microscopy image of a single carbon quantum dots/ $\text{Cu}_2\text{O}$  particle for energy-dispersive X-ray spectroscopy. (f–h) Element mapping data of Cu, O, and C elements throughout a single carbon quantum dots/ $\text{Cu}_2\text{O}$  particle. (Reprinted with permission from Li et al. (2012) copyright@2012, The Royal Society of Chemistry)

### 3.3.2 Bottom-Up Approach

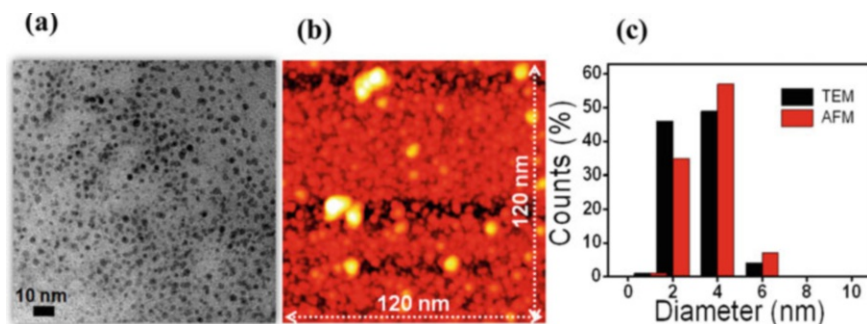
#### Hydrothermal Method

Chen et al. (2018a) develop green one-pot hydrothermal method for graphene quantum dot synthesis with a diameter ranging from 2.25 nm to 3.50 nm using starch as a natural polymer. Hydrothermal method is free from usage of any strong acid or metal impurities. The reaction mechanism during the synthesis follows hydrolyzation of starch mainly into glucose followed by ring closure to generate graphene quantum dots which is separated through centrifugation. Graphene is a promising building block for graphene quantum dot synthesis. Pan et al. (2010a) develop a hydrothermal method for piercing peroxidized graphene sheets into ultrasmall graphene quantum dots. The graphene sheet is prepared by thermally reducing the graphene oxide.





**Scheme 3.1** Schematic description of the large-scale synthesis of graphene dots by utilizing food waste. These nanodots represent the efficient transition from large food waste to valuable carbon-based nanomaterials. (Reprinted with permission from Park et al. (2014) copyright@2014, American Chemical Society)



**Fig. 3.7** (a) High-resolution transmission electron microscopy image of graphene dots at 10 nm resolution. (b) Atomic force microscopy image of graphene dots with a thickness of 120 nm. (c) Size distribution of graphene dots which indicates that the amount of graphene dots with a diameter of 2 nm was less than 45%, with a diameter of 4 nm is less than 60%, and with a diameter of 6 nm is less than 10% (*TEM* transmission electron microscopy, *AFM* atomic force microscopy). (Reprinted with permission from Park et al. (2014) copyright@2014, American Chemical Society)

Shen et al. (2018) prepared carbon quantum dots coupled with  $\text{TiO}_2$  via hydrothermal method using glucose and citric acid as precursors. The heterojunction exhibits enhanced photocatalytic activity against phenol under ultraviolet light. Carbon quantum dots–glucose/ $\text{TiO}_2$  heterojunction was synthesized using glucose

and carbon quantum dots–citric acid/TiO<sub>2</sub> by using citric acid as precursor. Among these two heterojunctions, carbon quantum dots–glucose/TiO<sub>2</sub> has better crystalline property which is responsible for facile charge carrier migration and hence responsible for higher photocatalytic activity. Sarkar et al. (2016) prepared water-soluble carbon quantum dots from sucrose by using cost-effective and environment-friendly hydrothermal technique. Mixture of sucrose solution and ethanol was taken in Teflon autoclave and heated to 175–180 °C for 2 h and then cooled. The yellow-colored solution is obtained which is centrifuged at 16,000 rpm. Moreover, graphene quantum dots were also synthesized by a hydrothermal method using graphene sheets which are obtained by thermal oxidation of graphene oxide sheets at 200 °C (Pan et al. 2010a). The synthesized graphene quantum dots were used in organic photovoltaic devices.

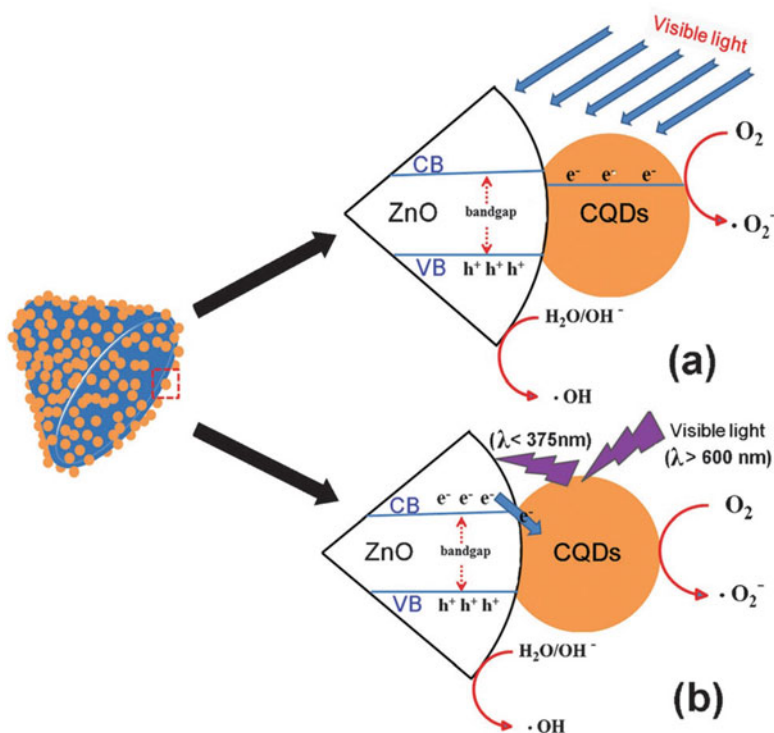
Mehta et al. (2014) devised a highly cost-effective and green hydrothermal technique to synthesize fluorescent quantum dots using plant-based precursor *Saccharum officinarum*. These quantum dots were used in cellular imaging of bacteria and yeast. Several green techniques have been devised for the preparation of carbon dots by utilizing inexpensive renewable precursor. Researchers developed green synthetic approach for the synthesis of carbon dots from watermelon peel and pomelo peel using hydrothermal method (Zhou et al. 2012a; Lu et al. 2012). Prasannan and Imae (2013) also reported the synthesis of fluorescent quantum dots by hydrothermal method at 180 °C using orange peel. Orange peel used mainly consists of various carbohydrates, glucose, fructose, sucrose, and cellulose, which are used as carbon sources. The morphology and chemical composition were characterized by various spectroscopic techniques. The carbon dots prepared were amorphous in nature with large quantity of functional group. Typically, orange waste was firstly washed with water and then in H<sub>2</sub>SO<sub>4</sub> solution and again rinsed with water followed by drying in hot air oven at 150 °C for 10 h. The secured product was further treated with sodium hypochlorite solution and kept for 4 h at room temperature followed by washing with water several times till pH 7 is attained. Lastly, the oxidized orange peel was kept in autoclave for heating, followed by washing with dichloromethane to remove extra organic species followed by centrifugation. Hydrothermal carbonization is considered as a green and effective method avoiding the usage of strong toxic chemical.

Kapitonov et al. (2018) present a new method for carbon dot synthesis using hydrothermal method by choosing different precursors: berry juice, birch bark soot, glucose, and citric acid which are reported earlier. Various functional groups present on the surface of carbon dots are epoxy, carbonyl, hydroxyl, and carboxyl providing hydrophilic character to carbon dots. The carbon dots can be functionalized by doping with heteroatom to improve the surface property and also the quantum yield. Thus, nitrogen-doped carbon quantum dots were synthesized by hydrothermal method used for the selective sensor for the detection of Hg<sup>2+</sup> (Liu et al. 2015), Fe<sup>3+</sup> (Wu et al. 2013), and Ag<sup>+</sup> (Li et al. 2017). Wang et al. (2018b) prepared nitrogen-doped carbon dots utilizing mandelic acid together with ethylenediamine as carbon and nitrogen source, respectively. The solution of mandelic acid and ethylenediamine were mixed ultrasonically at room temperature with subsequent

hydrothermal treatment followed by dialysis for 24 h. The obtained powder after dialysis was dried by adding ethanol and centrifuged at 10,000 rpm for 20 min.

Yu et al. (2012) synthesize ZnO/carbon quantum dot nanocomposites by using one-step hydrothermal method. The nanocomposites exhibit superior photoactivity under solar light for the decomposition of benzene and methanol, both toxic gases, and benzene binds by  $\pi$ - $\pi$  interaction in conjugation between the two moieties. The higher efficiency of nanocomposites was attributed to the up-conversion emission by carbon quantum dots under visible region. ZnO loading on carbon quantum dots constructs a “dyad structure” where the electron is simultaneously transferred to carbon quantum dots’ surface and the hole remains at the ZnO surface (Scheme 3.2).

The simultaneous transfer of electron onto carbon quantum dots inhibits charge carrier recombination and increases the lifetime of electron-hole pair. The adsorbed  $O_2$  on the surface of carbon quantum dots converts into superoxide radical anion, which is a strong oxidizing agent and easily oxidized the adsorbed toxic gases on the surface. The up-conversion of emission light means the conversion of longer



**Scheme 3.2** Schematic model for the photocatalytic process of ZnO/carbon quantum dot composites under visible light. ZnO loading on carbon quantum dots constructs a “dyad structure” where electrons simultaneously migrate to the carbon quantum dot surface and holes remain at the ZnO surface. (CQDs carbon quantum dots). (Reprinted with permission from Yu et al. (2012) copyright@2012, The Royal Society of Chemistry)

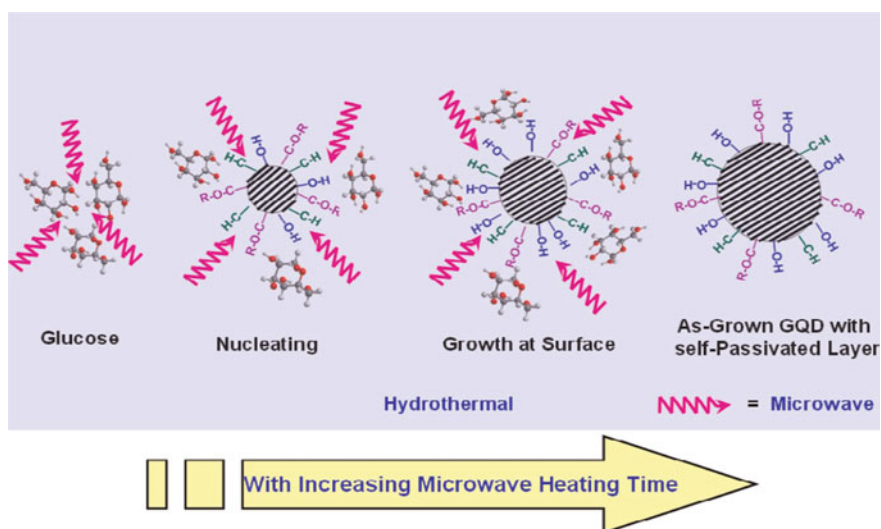


wavelength visible light into short wavelength ultraviolet light which can now generate electron–hole pair on the surface of ZnO nanoparticle (Scheme 3.2b). As the band gap of ZnO is 3.3 eV which lies in ultraviolet region, therefore light of shorter wavelength can only initiate the excitation process.

### Microwave Method

Microwave method is a low-cost, facile, rapid, and green method with high quantum yield efficiency in comparison to hydrothermal method (Yang et al. 2013b). Photoluminescent carbon dots were also synthesized by using flour as a source of carbon by microwave-assisted method (Qin et al. 2013). Tang et al. (2012) prepared water-soluble crystalline graphene quantum dots derived from glucose through microwave-facilitated hydrothermal method that utilizes the assets of both these methods (Scheme 3.3). Firstly, the glucose molecule is paralyzed followed by dehydration under hydrothermal method. The glucose solution was subjected to microwave oven at a different power of 280 to 700 W for a different period of time, 1–11 min. The transparent color of the solution changes to pale yellow which indicates the formation of graphene quantum dots. The microwave provides uniform heating responsible for consistent size distribution of graphene quantum dots.

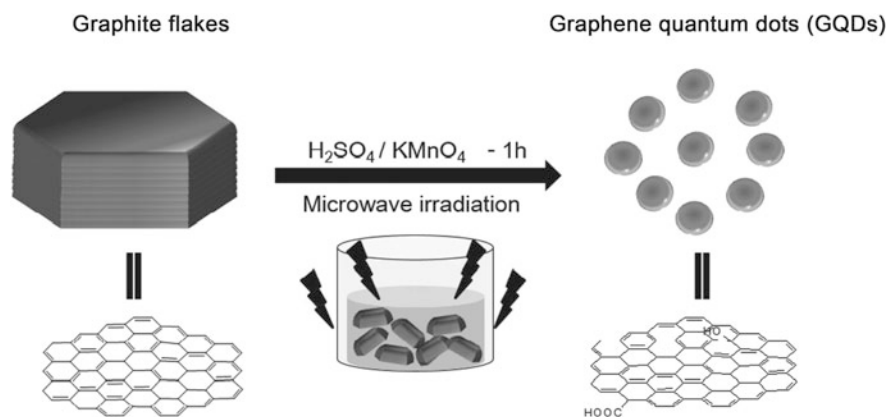
Zhu et al. (2009) also prepared carbon nanoparticle via microwave pyrolysis method which is a cheap and convenient method for large-scale production. For solution of polyethylene glycol and monosaccharide's glucose and fructose that



**Scheme 3.3** Preparation of graphene quantum dots by microwave-assisted hydrothermal method using glucose as precursor followed by nucleation and microwave heating. (GQD graphene quantum dots). (Reprinted with permission from Tang et al. (2012) copyright@2012, American Chemical Society)

were heated in microwave oven of 500 W for 2–10 min, a yellow-colored solution changes to dark brown which indicates the formation of carbon nanoparticles. Microwave method was very less time-consuming as the nanoparticles were synthesized in just 10 min. Umrao et al. (2015) reported microwave carbonization followed by aromatization of acetyl acetone as a precursor to prepare graphene quantum dots having tunable size and surface functionalities. Graphene quantum dots can be modified for specific application by tailoring the size, surface, and band gap. Acetyl acetone is weakly acidic in nature, which is why dehydration and decomposition reaction under microwave irradiation proceed in a controlled manner followed by aldol condensation and cycloaddition reaction.

Further, doping of carbon quantum dots with heteroatom boron, nitrogen, sulfur, and fluorine is a potent approach for adjusting optical and electronic property of carbonaceous material. Kundu et al. (2015) also used one-step microwave technique for the preparation of codoped nitrogen, fluorine, and luminescent graphene quantum dots with average size of 2 nm by using multi-walled carbon nanotubes as precursor in ionic liquid. The coupling of ionic liquid with microwave technique enables ultrafast process and also increases the quantum yield to nearly 70%. Due to short reaction times, microwave irradiation method is extensively utilized for the preparation of carbon quantum dots. Graphite, a well-known precursor, comprised of stacked graphene sheets is one of the readily available and inexpensive materials for the synthesis of graphene quantum dots. Shin et al. (2014) synthesize graphene quantum dots via highly powered microwave irradiation using graphite under acidic condition followed by oxidative cleavage (Scheme 3.4). Carbon quantum dots can also be prepared by using amino acid as the starting material in the presence of acid or alkali. Histidine is dissolved in ortho-phosphoric acid followed by microwave irradiation to 700 W for nearly 3 min (Jiang et al. 2012). The resultant carbon



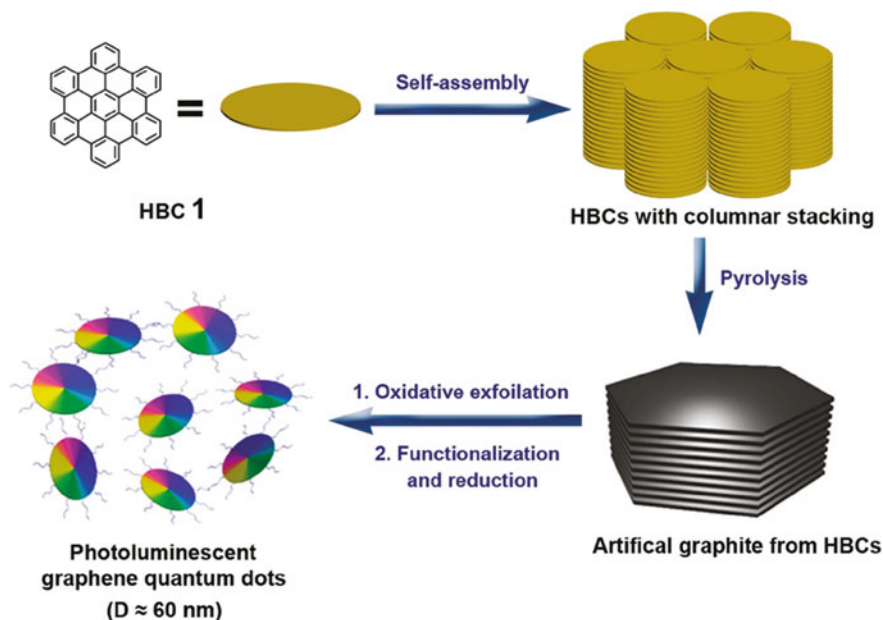
**Scheme 3.4** Schematic representation of the fabrication of a few layered graphene quantum dots from multilayered graphite powder by one-pot microwave irradiation under acidic conditions. (Reprinted with permission from Shin et al. (2014) copyright©2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

quantum dots were dispersed and purified with ultrapure water using dialysis membrane to remove the impurities.

### Pyrolytic Route

Liu et al. (2011) for the first time synthesized mono-dispersed disklike graphene quantum dots with 2–3 nm thickness and ~60 nm in diameter. The graphene quantum dots are synthesized by pyrolytic method using un-substituted hexa-peri-hexabenzocoronene as carbon source. The process involves various steps, carbonization, oxidation, surface functionalization, and reduction, as illustrated in Scheme 3.5.

Pan et al. (2010b) described the preparation carbon quantum dots via pyrolysis of ethylenediaminetetraacetic acid at low temperature. Typically, ethylenediaminetetraacetic acid was calcined at 400 °C for 2 h with a heating rate of 10 °C per minute in an inert atmosphere, and the product obtained is then dispersed in acetone followed by centrifugation. Ethylenediaminetetraacetic acid possesses stable carboxylate ion which persists during pyrolysis and enables carbon quantum dots to be hydrophilic and soluble in various polar organic solvents. Also, the highly sensitive and selective carbon dots were also prepared by pyrolysis of ethylenediaminetetraacetic acid, which is used as sensor for the detection of  $\text{Hg}^{2+}$  ion and biothiols (Zhou et al. 2012b). Guo et al. (2012) also prepared one-step

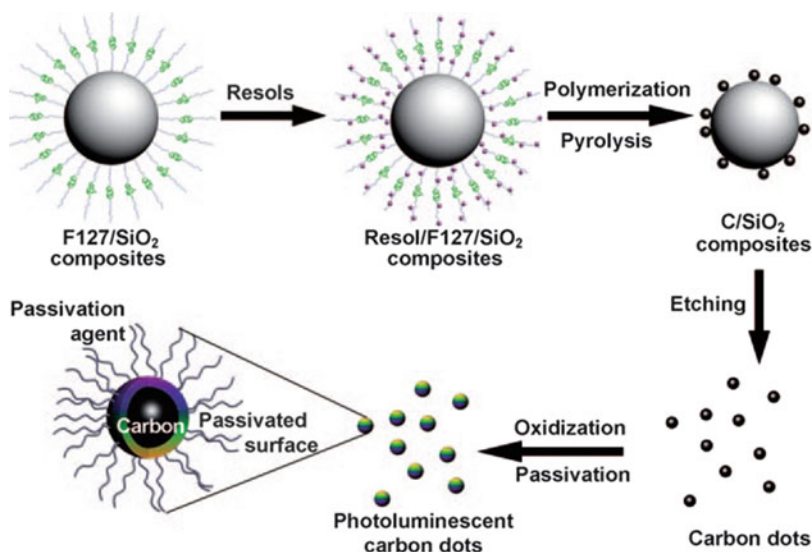


**Scheme 3.5** Processing diagram for the preparation of photoluminescent graphene quantum dots using hexa-peri-hexabenzocoronene as carbon source. (HBC 1 hexa-peri-hexabenzocoronene). (Reprinted with permission from Liu et al. (2011) copyright©2011, American chemical society)

pyrolytic method for the synthesis of carbon dots by chemical unzipping of epoxy-enriched polystyrene photonic crystal.

Liu et al. (2009) reported novel route for the synthesis of nanosized carbon dots typically 1.5–2.5 nm. The preparation method includes polymerization, pyrolysis, oxidation, and surface passivation as illustrated in Scheme 3.6. Firstly, SiO<sub>2</sub> suspension was added to the aqueous solution amphiphilic triblock copolymer, and the sample was stirred overnight. Here, resols (i.e., phenol/formaldehyde resins) are used as carbon source. Further, high-temperature treatment removes silica carrier and generated nanosized carbon dots. Here, the surfactant-modified silica is utilized as carrier, anchors resols during polymerization, and also prevents aggregation of carbon dots during pyrolysis.

The surface-functionalized carbogenic nanoparticles with size less than 10 nm can be synthesized by thermal dissipation or by 4-aminoantipyrine route (Bourlinos et al. 2008). The organophilic nanoparticles were prepared by citrate route while, carbonization of 2-(2-aminoethoxy)-ethanol in another route prepare hydrophilic nanoparticles. In both these methods, amide linkage (–NH–CO–) ties the organic moiety to the core, and the precursor was pyrolyzed at 300 °C for 2 h. Wang et al. (2010) synthesize oil-soluble carbon dots by carbonization of carbon precursor and water-soluble carbon dots by simply altering the solvent and capping reagent. For oil-soluble carbon dot preparation, octadecane was used as the non-coordinating solvent, 1-hexadecylamine as the capping agent, and citric acid as the carbon source. The mixture of octadecane and 1-hexadecylamine was heated up to 300 °C under



**Scheme 3.6** Processing diagram for the synthesis of multicolor photoluminescent carbon dots by polymerization, pyrolysis, oxidation, and surface passivation. Resols were used as carbon source. (Reprinted with permission from Liu et al. (2009) copyright©2009, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

inert atmosphere with addition of citric acid. The obtained product is purified with acetone several times. The oil-soluble carbon dots are appreciably soluble in organic solvents like toluene, hexane, and chloroform. Wang et al. (2011) synthesize amorphous carbon dots via pyrolytic method using anhydrous citric acid in the presence organosilicane as the coordinating solvent at 240 °C for 1 min. The ultrasmall carbon dot with a size of 0.9 nm was prepared with high quantum yield of 47%. Simple heating is required for the preparation of carbon dots from organosilicane as compared to other method where addition of polymer or inorganic compound is needed.

### Template Method and Substance Oxidation

Mesoporous templates have been employed to confine the carbon dots in pores to gain a narrow size distribution, but effectively restricting the pore size of templates is challenging. In template method, carbon quantum dots are prepared by calcination using mesoporous template like silicon sphere or by etching to obtain nanosized carbon quantum dots. The uniform, spherical mesoporous silica was prepared using tetra-ethoxysilane as the precursor, *N*-hexadecylamine as the surfactant, and ammonia as the catalyst with particle size of 1.3 μm in diameter and pore size of 3.60 nm (Grun et al. 2000). Further, the nanosized hydrophilic carbon dots are synthesized by impregnated method by performing calcination of mesoporous silica with mixture of complex salts and citric acid solution (Zong et al. 2011). The mesoporous silica was used as support to prevent the aggregation of carbon dots, and also the small pore size of silica enables synthesis of nanosized carbon dots with sizes ranging from 1.5 nm to 2.5 nm.

Yang et al. (2013a) reported combination of copolymer pluronic and mesoporous silica as soft–hard template for the synthesis of mono-dispersed photoluminescence carbon dots. Soft–hard template method overcomes the disadvantages of using mesoporous silica alone and synthesizes carbon dots with narrow size distribution and well-defined morphology. The organic molecules with different aromatic framework like diaminebenzene, pyrene, 1,3,5-trimethylbenzene, and phenanthroline are used as carbon precursors. The use of different organic precursors is beneficial to modify the size, structure, composition, and photoluminescent property of carbon dots. Briefly, organic precursor was enwrapped into micelles of soft template with mesoporous silica followed by carbonization, template removal through etching, and passivation. Here, a soft template provides nano-space for the formation of nanosized carbon dots and mesoporous silica, while a hard template prevents aggregation of carbon dot particle. In another method free from catalysts, mesoporous silica was blended with polyethylene glycol and glycerol as carbon source (Lai et al. 2012). The majority of top-down techniques involve tedious methods and usage of extensively harsh chemicals which generate more chemical waste and high temperature for a prolonged time. On the other hand, bottom-up approach is a time-consuming process and complicated synthetic scheme and

requires costly and special equipment. Thus, there is an urgency of developing an adequate and cost-effective synthetic strategy for carbon quantum dot preparation.

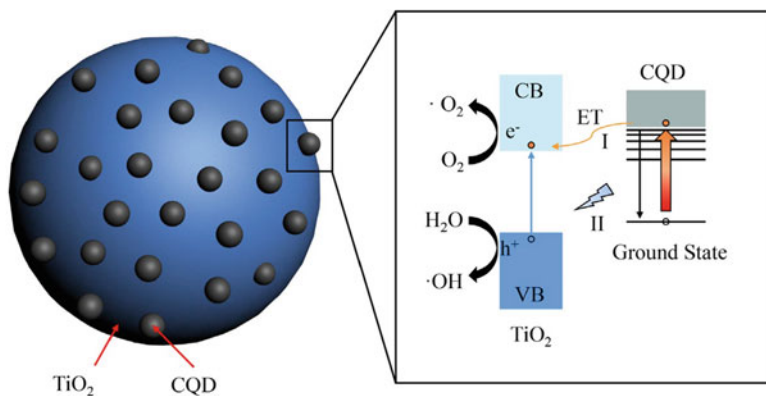
### 3.4 Photocatalytic Activity of Carbon Quantum Dot-Based Nanocomposites

As per the previously reported literature, fabrication of carbon quantum dots, metal oxide, and metal sulfide-based carbon quantum dots has gained substantial attention. A remarkable efficiency is assigned because of broader range of solar spectrum. The aim of enhancing the photo-efficiency can be achieved by constructing a heterojunction system between the carbon quantum dots and the semiconductor. Li et al. (2010b) reported facile one-step electrochemical technique for uniform and mono-dispersed carbon quantum dots synthesized in alkaline medium with sizes ranging from 1.2 to 3.8 nm. Further, the design of carbon quantum dots is based on TiO<sub>2</sub> and SiO<sub>2</sub> nanocomposites by sol-gel strategy and utilized for the photodegradation of methyl blue. The complete photodegradation was observed in 25 min and 15 min for TiO<sub>2</sub>/carbon quantum dots and SiO<sub>2</sub>/carbon quantum dots, respectively. The excitation of TiO<sub>2</sub> and SiO<sub>2</sub> photocatalyst is due to the up-conversion process. Similarly, tetraethyl orthosilicate was added for the preparation of SiO<sub>2</sub>/carbon quantum dots in a similar fashion. The photocatalytic activity was evaluated against methyl blue. The photodegradation analysis was carried out in 3100 mL conical flask containing 50 mgL<sup>-1</sup> dye solution with 10 mg nanocomposites, and 300 W halogen lamp was used as light source.

Deng et al. (2015) synthesize 2D BiOCl/carbon quantum dot composites by template-free coprecipitation method. The composites exhibit enhanced efficiency, and almost 100% removal of 2-nitrophenol was observed. The higher efficiency of the composites was attributed to excellent light absorption capacity in the visible region and effective electron-hole pair separation which slows the rate of recombination. Carbon dots/ZnO composites were also used for the photodegradation of various azo dyes under visible light using 250 W Xe lamp (Ding et al. 2016). The photodegradation follows the trend methyl blue > rhodamine B > methyl orange, respectively.

Feng et al. (2015) synthesized porous nanorods of carbon dots/ZnO by solvothermal deposition method. The photocatalytic activity was assessed against phenol under visible light. The pollutant was 94% degraded in 60 min. Further, Li et al. (2013) synthesized carbon dot/ZnO heterostructure via sol-gel method followed by spin coating method and evaluated the photo-efficiency against rhodamine B dye. Thirty percent of rhodamine B was photodegraded in 120 min using 18 W ultraviolet lamp. The heterostructure exhibit three times higher photo-efficiency as compared to base ZnO.

Besides ZnO, TiO<sub>2</sub> is also a promising photocatalyst to be utilized in photodegradation of various pollutants due to its high oxidizing ability and high



**Fig. 3.8** Proposed mechanism for up-conversion photocatalytic process in carbon quantum dots/ $\text{TiO}_2$ , where high-energy photo emitted by carbon quantum dots generates the electron-hole pair over  $\text{TiO}_2$  surface. (CQDs carbon quantum dots) (Reprinted with permission from Ke et al. (2017) copyright@2017, Published by Elsevier Inc.)

thermal and chemical stability. Nitrogen-doped carbon dot/ $\text{TiO}_2$  composites synthesized via hydrothermal method degraded 95% of rhodamine B in 30 min using 500 W Xe lamp (Zhang et al. 2013). Similarly, photodegradation analysis using carbon dot/ $\text{TiO}_2$  nanocomposites synthesized by hydrothermal method or sol-gel method was carried out by various researchers against methyl blue, methyl orange, and rhodamine B photodegradation (Saud et al. 2015; Wang et al. 2015; Li et al. 2010b, 2018a).

Ke et al. (2017) prepared carbon quantum dots via hydrothermal method and carbon quantum dots/ $\text{TiO}_2$  via sol-gel method, and photo-efficiency was observed against methyl blue dye under visible light. About 90% of methyl blue was degraded in just 120 min, and carbon quantum dots/ $\text{TiO}_2$  reveal nearly 3.6 times higher efficiency as compared to bare  $\text{TiO}_2$ . On the other hand, the unique up-conversion property of carbon quantum dots which could convert low-energy photons into high-energy photons is utilized for the construction of heterojunction (Jia et al. 2012). Generally, conventional semiconductor quantum dots absorb high-energy photon and then emit low-energy photon which may be further thermally dissipated. But using carbonaceous-based quantum dots, low-energy photons convert into high-energy photons which is further utilized to generate charge carrier on the surface of  $\text{TiO}_2$  (Fig. 3.8).

For carbon quantum dots/ $\text{TiO}_2$  composites that generate charge carrier under visible light irradiation, the photoinduced electron migrates to the conduction band of  $\text{TiO}_2$  and further produces superoxide radical, whereas holes stay at ground state and generate hydroxyl radical. Some of the photoinduced electrons may recombine with holes in the ground state which emit photons of higher energy. That emitted photon of higher energy could excite the host  $\text{TiO}_2$  and further generate electron-hole pair. Thus, up-conversion property of carbon quantum dots efficiently utilizes



solar energy and enhances the photo-efficiency. The carbon quantum dots were also loaded with  $\text{Bi}_2\text{WO}_6$  and applied for the degradation of various organic pollutants.

Wang et al. (2018a) fabricated 0D and 2D carbon dots on  $\text{Bi}_2\text{WO}_6$  nanosheets, and the photodegradation study was carried out on methyl orange and bisphenol A. The composites show three times higher efficiency as compared to  $\text{Bi}_2\text{WO}_6$  alone. The excellent photocatalytic activity was ascribed to the up-conversion and electron reservoir property of carbon quantum dots. The high ability of charge carrier separation is further confirmed by density functional theory calculation. Further, electron spin resonance measurement and quenching experiment reveals hydroxyl radical, superoxide radical, and holes are the active species in photodegradation. Zhang et al. (2018) design nitrogen-doped carbon quantum dot-mediated  $\text{Ag}_3\text{PO}_4/\text{BiVO}_4$ , a Z-scheme photocatalyst, via solvothermal precipitation method. Tetracycline, an antibiotic, was used to assess the photocatalytic performance under visible light, and nearly 88.9% was degraded in just 30 min. The higher performance was due to the fabrication of Z-scheme photocatalyst which increases the effective utilization of solar light.

Zhang et al. (2017) fabricated carbon quantum dots/ $\text{Bi}_2\text{WO}_6$  nanocomposites and successfully studied photodegradation of rhodamine B and phenol and hydrogen production using solar light. Di et al. (2015a) design visible light-driven carbon quantum dots/ $\text{Bi}_2\text{WO}_6$  hybrid having a sphere-like structure. The competence was assessed against rhodamine B; ciprofloxacin, a colorless antibiotic agent; tetracycline hydrochloride; and bisphenol A, an endocrine interrupting agent. Further, electron spin resonance and trapping experiment studies explore that the active species were superoxide radical and holes, respectively. Other than  $\text{Bi}_2\text{WO}_6$ ,  $\text{Bi}_2\text{MoO}_6$  having a band gap of 2.5–2.8 eV, high chemical stability, resistance to corrosion, and low cost is also of much importance. Di et al. (2015b) distributed carbon quantum dots having an average size of 7 nm over  $\text{Bi}_2\text{MoO}_6$  via hydrothermal method and investigated the photodegradation of ciprofloxacin. The photo-efficiency was assessed using ciprofloxacin, bisphenol A, tetracycline hydrochloride, and methylene blue as targeted pollutant. The enhanced photo-efficiency is due to the more adsorption active species, visible light absorption, and slower rate of recombination.

Zhang et al. (2018) prepared carbon dot/ $\text{BiPO}_4$  photocatalytic system via hydrothermal followed by calcination method. The photocatalytic activity was assessed against indomethacin a nonsteroidal anti-inflammatory drug under solar light. The photocatalytic efficiency of nitrogen-doped carbon quantum dot/ $\text{BiPO}_4$  synthesized by ionic liquid-assisted solvothermal method was also tested against ciprofloxacin, enrofloxacin, tetracycline, and 4-chlorophenol, a colorless antibiotic, under ultraviolet radiation (Di et al. 2017). Zhang et al. (2018) prepared novel carbon quantum dots/ $\text{Bi}_2\text{O}_2\text{CO}_3$  using simple dynamic adsorption method and chosen methyl blue and phenol as targeted pollutants for degradation. Here,  $\text{Bi}_2\text{O}_2\text{CO}_3$  photocatalyst exists in different morphological flower, porous ball, sponge, and slice-like structure.  $\text{Bi}_2\text{O}_2\text{CO}_3$  has very unique layered structure consisting of  $\text{CO}_3^{2-}$  layer interwoven



among  $[\text{Bi}_2\text{O}_2]^{2+}$  layers. The composites exhibit efficient photocatalytic performance, and nearly 94% and 61% of methyl blue and phenol were degraded within 2 h.

Wang et al. (2017) successfully loaded nitrogen-doped carbon dots onto the surface of g- $\text{C}_3\text{N}_4$  composites via polymerized method to design nitrogen-doped carbon dots/g- $\text{C}_3\text{N}_4$  photocatalysts. Graphitic carbon nitride is a visible light active metal-free photocatalyst with a band gap of 2.7 eV with various applications in  $\text{CO}_2$  reduction,  $\text{H}_2$  production, and pollutant degradation. The photocatalytic activity of nitrogen-doped carbon dots/g- $\text{C}_3\text{N}_4$  was remarkably higher as compared to g- $\text{C}_3\text{N}_4$  and was assessed against indomethacin under visible light. Novel carbon quantum dots/g- $\text{C}_3\text{N}_4$  metal-free nanocomposites were synthesized via electrostatic self-assembly method, facile low temperature process, and impregnation-thermal method (Jian et al. 2016; Hong et al. 2016; Zhang et al. 2016). Carbon quantum dots/g- $\text{C}_3\text{N}_4$  exhibits excellent electron transfer properties, and its photocatalytic activity was assessed against methyl blue, tetracycline hydrochloride, rhodamine B, and phenol under visible light. By using electrostatic self-assembly method, the size, composition, porosity, and surface functionality can be easily modified. An effective harvesting of solar light due to up-conversion process by carbon quantum dots is one of the reasons why carbon quantum dots/g- $\text{C}_3\text{N}_4$  is highly efficient.

Hu et al. (2019) synthesize mesoporous nitrogen-doped carbon quantum dot/BiOCl composites via solvothermal reduction method. The composites exhibit excellent photocatalytic activity against organic pollutant under visible region and near-infrared light. The photodegradation process is mainly dependent on holes and superoxide radical. Qu et al. (2019) fabricated graphene oxide/carbon dot/BiOI ternary nanocomposites by using simple one-step solvothermal method. The ternary nanocomposites exhibit excellent photocatalytic activity against the photodegradation of 4-chlorophenol in the visible region. The synergistic effect of nonmetallic graphene oxide, carbon nanodots, and BiOI is responsible for high efficiency. The photodegradation efficiency decreases in the order graphene oxide/carbon dot/BiOI > carbon dot/BiOI > graphene oxide/BiOI > BiOI, respectively, in 3 h under visible light.

Xie et al. (2018) construct graphene oxide/g- $\text{C}_3\text{N}_4$ /MoO<sub>3</sub> Z-scheme photocatalysts and photocatalytic activity against tetracycline antibiotic. The high efficiency is ascribed to the synergistic effect of Z-scheme heterojunction. Further, a ternary composite, carbon quantum dots/CdSe/reduced graphene oxide, is fabricated by hydrothermal method (Huo et al. (2017)). The optical and electronic properties were analyzed by transmission electron microscope, x-ray diffraction, and photo-electrochemical testing. The photocatalytic performance is investigated for the photodegradation of tetracycline hydrochloride. Although the carbon quantum dots have a promising application in nanotechnology and nanomedicine, a lot of work is still needed to be explored for the designing of smart materials.

### 3.5 Antibacterial Activity of Carbon Quantum Dot-Based Nanocomposites

Microbial pollution is the biggest and most challenging menace for individuals as overusing fluoroquinolone, chloramphenicol, and trimethoprim antibiotics makes multiple drug-resistant bacteria which are difficult to remove (Levy and Marshall 2004). With the advancement in nanoscience, antimicrobial nanomedicine also becomes a prominent field for the researcher to devise some nanomaterial for microbial pollution. Previously, metals (Ag and Au) or metal oxide (CuO, ZnO and Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were reported having antibacterial properties (Hoseinnejad et al. 2018; Pare et al. 2008, 2009; Raghunath and Perumal 2017). These earlier devised nanomaterials suffer with limitation of biological toxicity, generation of secondary pollutant, low efficiency, and poor degradation.

Recently, less toxic, environmental-friendly, and biocompatible carbonaceous materials have identified as promising antimicrobial agents. Li et al. (2018b) fabricated less toxic, biodegradable, and broad-spectrum antibacterial and antifungal carbon dots from vitamin C using electrochemical technique. Carbon dots displayed antibacterial activity, by destroying bacterial cell wall even at lower concentration. At the end, carbon dots are completely degraded into innocuous product in the visible region or at low temperature. The antibacterial activity of carbon dots is evaluated against Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative (*Bacillus* sp. WL-6 and *Escherichia coli*) bacteria, whereas their antifungal properties were evaluated against two pathogenic fungi, *Rhizoctonia solani* and *Pyricularia grisea*.

Kovacova et al. (2018) investigated the photocatalytic and antibacterial activity of hydrophobic carbon quantum dots/polyurethane nanocomposites synthesized by swell-encapsulation-shrink method. The nanocomposites had shown bactericidal effect against *Staphylococcus aureus* and *Escherichia coli* for 60 min of irradiation of blue light, whereas the photocatalytic degradation of Rose Bengal dye was observed for 180 min. Habiba et al. (2015) fabricated Ag nanoparticle-decorated graphene quantum dots via pulse laser method. The antibacterial activity of Ag-graphene quantum dots, bare graphene quantum dots, and Ag nanoparticle were compared. The symbiotic effect of Ag and graphene quantum dots in Ag-graphene quantum dot nanocomposites enhances the antibacterial property in comparison to Ag and graphene quantum dots.

Dong et al. (2017) employed carbon dots with other antibacterial agents such as H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>COOH, and Na<sub>2</sub>CO<sub>3</sub>. The photoactivated technology for antibacterial property is a rapidly growing field to prevent microbial pollution. Carbon quantum dot nanocomposites possess bactericidal property and can be utilized to remove photocatalyzed antimicrobial pollution. The antibacterial property of carbon-based nanocomposites can be easily tailored by surface modification. Liu et al. (2018) fabricated ZnO/graphene quantum dot nanocomposites using hydrothermal method and assessed their antibacterial property through minimum inhibitory concentration, and decreases in bacterial colony were counted by plate count method. The

antibacterial property was enhanced under ultraviolet photo-irradiation, which is attributed to the production of reactive oxidation species responsible for membrane damage as confirmed by paramagnetic resonance and fluorescence microscopic measurements. The ZnO/graphene quantum dot nanocomposites exhibit higher bactericidal effect as compared to ZnO and graphene quantum dots, which may be accounted due to the interfacial charge transfer from graphene quantum dots to ZnO surface that enhances the generation of reactive oxidation species.

### 3.6 Conclusion

Carbon quantum dots recently emerge as important nanomaterials among various available carbonaceous materials due to their unique properties. Carbon quantum dots are visible light-driven photocatalysts which exhibit special up-conversion phenomena in which they convert longer wavelength light into shorter wavelength with high-energy photon that is efficiently employed for the excitation of charge carrier from the surface of wide band gap semiconductor. The property of up-conversion validates carbon quantum dot usage as photosensitizer as well as photocatalyst. Besides their many applications in different fields, carbon quantum dot-based nanocomposites can also be efficiently used as antimicrobial agents. Carbon quantum dots displayed not only antibacterial but also antifungal property. The antibacterial activity of carbon quantum dot-based nanocomposites is basically due to the generation of reactive oxidation species which may cause oxidative stress as well as disruption of the cell membrane. The book chapter provides a basic review of various synthetic methods for the preparation of carbon quantum dot-based nanocomposites and utilization as photocatalyst. Though significant efforts have already been done on carbon quantum dots over the past 15 years, they are still facing many challenges. From the future prospective, understanding the concept behind up-conversion mechanism of carbon quantum dots, increasing yield of carbon quantum dots, optimization of synthetic procedure for better control over size, increasing photostability of carbon quantum dots, or minimizing photo-bleaching and green method to avoid chemical pollution need to be addressed before practical application. The literature survey reveals that studies were limited to certain basic pollutants like methylene blue, methyl orange, rhodamine B, and phenol. Thus, photodegradation by carbon quantum dots needs further extension to other pollutants as well, applying it to pollutants belonging in the real world. Lastly, photo-efficiency and separation of carbon quantum dots are also important issues, as no such photocatalyst is designed yet which shows high efficiency for degradation of pollutants. Despite the many challenges associated with carbon quantum dots, numerous opportunities are still waiting to explore endless potential to be employed in various technologies.

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