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Photocatalytic Activity of Quantum Dots

Hamid Reza Rajabi

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Abstract

In recent years, nanoscale semiconductors have attracted great interest due to their unique structural, optical and electronic properties, which arise due to their large surface-to-volume ratio and quantum confinement effect. Quantum dots (QDs) as zero-dimensional semiconductor nanomaterials, which are confined to a size of 2–8 nm in three dimensions, are defined as particles with physical dimensions smaller than the exciton Bohr radius. One of the attractive research fields in recent years is the synthesis of various sizes and shapes of semiconductor material nanoparticles as doped with different dopants. The aim of this chapter is to focus on the photocatalytic activity of QDs as new, green and efficient nanophotocatalysts.

Keywords: quantum dots, nanophotocatalyst, pollutants, band gap, semiconductors

1. Introduction

Nowadays, nanotechnology is a field of applied science and technology whose theme is the control of matter and the fabrication of devices or materials on the atomic and molecular scale, generally between 1 and 100 nm. This is a highly multidisciplinary field, benefiting from the efforts and developments in many fields, including applied physics, materials science, interface and colloid science, supramolecular chemistry, chemical engineering, mechanical engineering, biological engineering and electrical engineering. Since the birth of cluster science and the invention of the scanning tunneling microscope in 1980s, nanotechnology has been prosperously developed with the ability to measure and visualize the novel phenomena and to manipulate and manufacture the materials and devices with nanostructures of 100 nm or smaller. In a subfield of nanotechnology, researchers study and develop nanomaterials which are reduced to the nanoscale dimension showing very different properties compared to what they exhibit

on a macroscale. For example, as the size of the system decreases, the "quantum size effect" becomes pronounced where the electronic properties of solids are altered. Meanwhile, the increase of surface area-to-volume ratio changes the mechanical, optical, chemical, thermal and catalytic properties of materials significantly. The distinct properties enable unique applications of nanomaterials [1].

Especially, the semiconductor nanocrystals, the so-called quantum dots (QDs), are a newly emerging nanomaterial, which have attracted many interests. Having excitons confined in all three spatial dimensions, quantum dots have properties that are between those of bulk semiconductors and those of discrete molecules. After excitation of the QDs, the emitted energy by QDs can be adjusted by controlling the composition and the particle size of QDs, due to the well-known effect of quantum size confinement effect. [2].

In the past decades there has been a growing interest in photo-assisted catalysis using semiconductors as an advanced oxidation process for the elimination of many organic pollutants in wastewater systems. Among various physical, chemical and biological techniques, photocatalyst-based degradation process has been considered as an alternative technique for water treatment due to its advantages over the traditional techniques, such as simplicity, quick oxidation, high efficiency and no formation of polycyclic products. Photocatalytic decolorization of pollutants using semiconductors as metal oxides and sulfides, such as TiO_2, ZnO, Fe_2O_3, WS_2, ZrO_2, WO_3, V_2O_5 and CeO_2, has received much attention because of possible practical applications [3]. Among the most extensively studied catalysts, zero-dimensional semiconductor nanomaterials (i.e., quantum dots), as well-known multifunctional materials, have received considerable attentions for degradation of pollutants. Moreover, QDs get more and more attention because their confinement by the excited electrons and holes leads to optical and electronic properties different from those in bulk semiconductors [4]. Moreover, QDs as new semiconductor particles in the nanosized scales possess a higher surface area-to-volume ratio than their bulk counterparts, and thus allows for greater photon absorption on the photocatalyst surface. Furthermore, recombination of the electron–hole pair within the semiconductor particle drastically reduces as particle size decreases. Therefore, the nanoscale semiconductor is expected to have higher photocatalytic activity than its bulk [5].

This material has been proved as a better photocatalyst due to rapid generation of electron–hole pairs with photoexcitation as it is a direct wide band gap semiconductor material [6]. Furthermore, it possesses high negative reduction potential of excited electrons due to its higher conduction band (CB) position in aqueous solution as compared to other extensively studied photocatalysts [7]. It has also been used in UV detectors due to its high resistivity at ambient conditions and fast switching time upon UV light illumination, thus exhibiting the highest potential for a UV-light detector.

On the other hand, surface modification of QDs can change their optical, chemical and photocatalytic properties. Surface modification possibility and capability of the band gap of QDs are the potential advantages of the colloidal QDs. It can also cause an improvement in the photostability of QDs, the generation of new traps on the surface of the QD leading to the appearance and efficiency of light-induced reactions occurring on the surface of QDs [8].

2. Semiconductor quantum dots

Luminescent QDs are zero-dimensional semiconductors that may be used in a wide array of fields and which will, along with rod and tetrapod nanoparticle semiconductors, see use in applications such as electrooptical devices, spectral bar coding, light filtering and computing applications. QDs are nanometer-scale semiconductor crystals composed of groups II–VI or III–V elements and are defined as particles with physical dimensions smaller than the exciton Bohr radius [9]. A typical QD has a diameter ranging from 2 to 20 nm containing roughly 200–10,000 atoms, with size comparable to a large protein. Quantum dots, rods and tetrapods have diameters that fall below the material's Bohr-exciton radius. When a photon hits such a semiconductor, some of their electrons are excited into higher energy states. When they return to their ground state, a photon of a frequency characteristic of that material is emitted [10].

Quantum confinement is the phenomenon which is the widening of the band gap energy of the semiconductor material when its size has been shrunken to nanoscale. The band gap of a material is the energy required to create an electron and a hole with zero kinetic energy at a distance far enough apart that their Columbic attraction could be ignored. A bound electron-hole pair, termed exciton, would be generated if one carrier approaches the other. This exciton behaves like a hydrogen atom, except that a hole, which is not a proton, forms the nucleus. The distance between the electron and hole defined as the exciton Bohr radius (r_B), which can be expressed by:

$$r_B = \frac{\hbar^2 \varepsilon}{e^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

(1)

where m_e and m_h are the effective masses of electrons and holes, and ε, $\hbar$ and e are the dielectric constant, reduced Planck constant and the charge of an electron, respectively. If the radius (R) of a quantum dot shrinks to r_B, especially when $R<r_B$, the motion of the electrons and holes is strongly confined spatially to the dimension of the quantum dot. Consequently, the exciton-ic transition energy and the band gap energy will increase, which results in the blue shift of the emission of the quantum dot [11].

If excitons in a solid are confined to a two-dimensional thin layer of the order of the exciton Bohr radius, one needs to treat the excitons as particles in a quantum well. Such a quantum well can be made using two different semiconductors, where a nanometer scale thin layer of semiconductor is sandwiched between two identical semiconductors which have a higher band gap compared to that of the thin layer. Also, the valence band edge and conduction band edge of the thin layer (the quantum well) must fall between the valence band edge and the conduction band edge of the second semiconductor (the barrier). This type of structure is known as a 2D nanostructure because excitons are restricted to move only along a 2D plane. Further confinement can be achieved if the excitons are confined along one more direction so that excitons are able to move only in the other direction. This structure is called a 1D nanostructure or quantum wire. This structure consists of nm² cross-section and long tube of

the lower band gap semiconductor surrounded by larger gap semiconductor. In a 0D nanostructure or quantum dot, excitons are confined in all directions. Here the quantum dots are made using lower band gap semiconductor surrounded by higher band gap semiconductor. The electronic and optical properties of these nanostructures are significantly different from the bulk semiconductor material. A schematic representation of these nanostructures is shown in **Figure 1** [12].
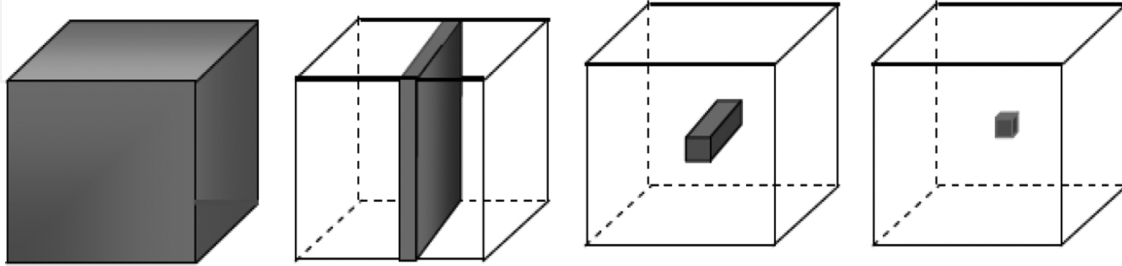
Figure 1. A schematic of bulk, quantum well, quantum wire and quantum dot (from left to right).

The separation between the valence band maximum and the conduction band minimum becomes smaller when the QD size increases. Consequently, one important advantage of semiconductor QDs is the tunability of the emission wavelength, simply by changing the QD size. The origin of the energy gap of QDs is described primarily as a perturbation that results from the Columbic interaction between the electron and the hole and the confinement of this exciton. Therefore, quantum confinement effects of quantum dots can be described as:

$$E \sim E_g + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} \tag{2}$$

where E is the band gap energy of QDs, E_g is the bulk band gap and R is the radius of QDs. The quantum confinement terms follow R2 and shift E to higher energy as the radius decreases; oppositely, the Coulomb term shifts E to lower energy as R decreases. In this equation, the correlation between electron and hole positions induced by the Coulomb interaction is not strong, and the major effect is the electron and hole confinement energy. Therefore, the QD energy gap increases as the particle size is reduced [13].

2.1. Optical properties of QDs

As it has already been stated, due to quantum size confinement, decreasing the particle size results in a hypsochromic (blue-) shift of the absorption onset [14, 15]. While its position depends on the band gap and, consequently, on the particle size, its form and width are strongly influenced by the distribution in size, as well as the form and stoichiometry of the nanocrystals [16]. In **Figure 2**, the absorption and photoluminescence spectra of a series of CdSe nanocrystals differing in size are depicted.
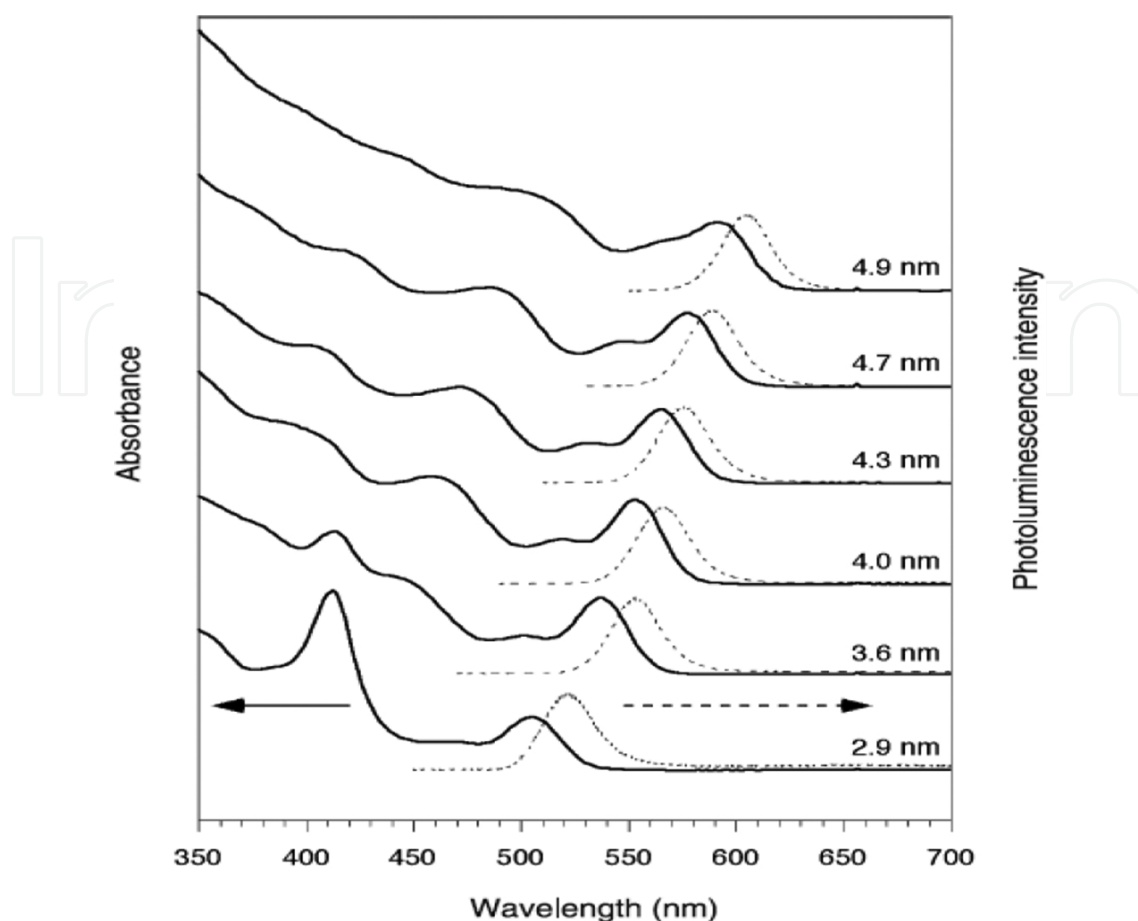
Figure 2. Absorption and normalized photoluminescence spectra of a series of CdSe NCs differing in size.

From the position of the absorption edge the mean particle size can be determined using the well-established relation between particle size and absorption onset [17]. The optical direct band gap values of the nanoparticles were determined by Tauc's relation [18], $\alpha h\upsilon = \alpha_0 (h\upsilon - E_g)^{1/2}$, where $h\upsilon$, α_0 and E_g are photon energy, a constant and optical band gap of the nanoparticles, respectively. Therefore, in the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$, extrapolating the straight-line portion of the plot to zero absorption coefficient gives the corresponding E_g values. The bulk materi-al band gap which is a characteristic of a semiconductor material becomes a size-dependent property. These particles then show a quantum confinement effect due to localization of charge carriers here after called QDs or quantum particles [19]. As the size of a semiconductor particle falls below the critical radius, the charge carriers begin to behave quantum mechanically and the charge confinement leads to a series of discrete electronic states. Free-standing nanopar-ticles are therefore preferred in order to understand basic quantum size effects in these materials [20]. According to the above discussion, the blue-shifted absorption edge and the increase in the band-gap energy of semiconductor are the results of decreasing the particle size and doping of nickel and copper ions. The increase in the band gap energy of a semiconduc-tor is due to increase in the lifetime of electrons and holes; thus, it is expected that photocata-lyst reactivity will increase (**Figure 3**) [21].
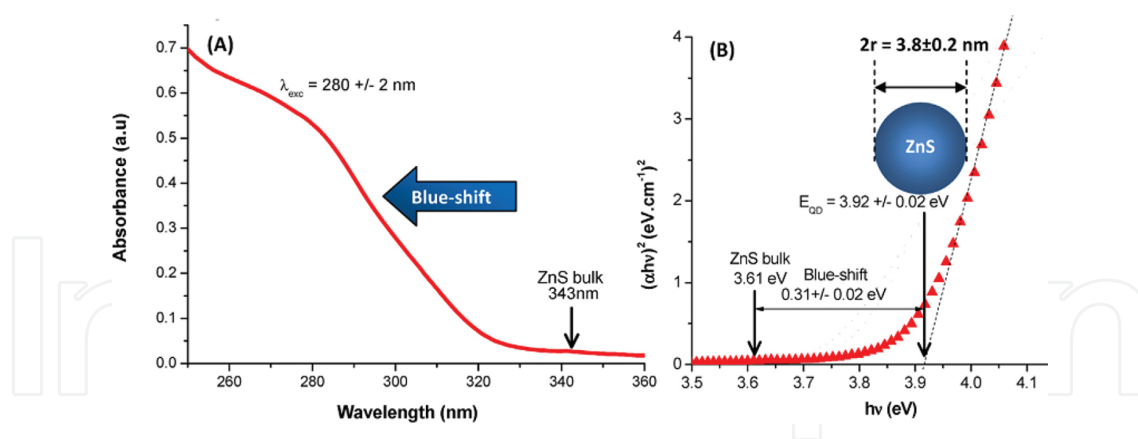
Figure 3. (A) UV-vis spectra and (B) optical band gap plot using Tauc's equation of the ZnS/chitosan conjugates [21].

In photoluminescence behavior of semiconductors, after the excitation by photons with an energy hv_e superior to its band gap, the emitted photons have an energy corresponding to the band gap of the nanocrystals; thus, the emission color can be tuned by changing the size of particle [22]. Due to spectral diffusion and the size distribution of nanocrystals, the luminescence line widths of CdSe NCs are in the range of 20–25 nm (FWHM), which the observed redshift is usually referred to as Stokes-shift [23].

2.2. Photocatalytic activity of QDs

Up to now, many nanoscaled semiconductors have been used as nanophotocatalysts for water treatment. For example, due to some advantages such as low cost, chemical stability and abundance and suitable optical absorption in the UV region, titanium dioxide (TiO_2) has been most extensively applied for photodegradation of pollutants [24]. However, a major cause of the slow reaction kinetics in TiO_2 nanoparticle-photocatalysis systems is the fast recombination of e^- and h^+ [25]. Among the alternative cases for low-dimensional materials for photocatalytic applications, ultrasmall semiconductor nanocrystals (i.e., QDs) have recently emerged as a novel class of nanomaterials with unique physicochemical, electronic, magnetic and optical properties. Surprisingly, despite exhibiting very interesting properties, the use of QDs in environmental applications has only recently attracted attention from scientists [26–31].

QDs designed for environmental monitoring, sensing and testing would need to fulfil requirements similar to those used in biological applications, such as biocompatible fluorescent labels for diagnosis and imaging of cells, tissues and organs under physiological conditions. However, the unique properties of QDs made them as efficient semiconductor nanophotocatalysts especially for environmental applications. It has been shown to be useful and durable nanophotocatalysts for a variety of problems of environmental interest such as water and air purification. Due to higher surface area-to-volume ratio than their bulk counterparts, the recombination of the electron–hole pair within the QDs drastically reduces as particle size decreases. Therefore, QDs are expected to have higher photocatalytic activity than its bulk [32]. Moreover, QDs get more and more attention because their confinement by the excited electrons and holes leads to optical and electronic properties different from those

in bulk semiconductors. For QDs, the transportation length of electron/hole from crystal interface to the surface is short, which it helps to accelerate the migration rate of electron/hole to the QDs' surface to participate in the reaction process [33]. This pointer and increasing accessible surface of photocatalysts as nanoparticles lead to increasing photocatalytic activity of QDs.

Other advances key of QDs is the recent advances on the surface chemistry of QDs by conjugation with appropriate functional molecules [34]. The surface modification of QDs can enhance their luminescent quantum yields, their stability and prevent them from aggregating [35]. Moreover, by surface modifications of QDs, it is possible to make QDs available for interactions with target analytes [36] for various applications. However, modification of QDs by highly toxic organic reagents may restrict the application of this method [37]. Therefore, proper surface modification is a critical challenge to keep QDs colloidal and photostable under intracellular or intercellular conditions. On the other hand, surface modification of QDs can change their optical, chemical and photocatalytic properties. Being coated on any surface and capability of the band gap to be tuned by changing the size, and the shape of the particle are the potential advantages of colloidal QDs [34]. It can also cause an improvement in the photostability of QDs, the generation of new traps on the surface of the QD leading to the appearance and efficiency of light-induced reactions occurring on the surface of QDs. For the above reasons, QDs have great potential in analytical applications in aqueous media [38].

Quantum confinement effect of photogenerated electrons and holes was experimentally observed and theoretically justified. One of the most striking observations regarding the quantum confinement effect is the 'blue shift' in optical absorption spectra and enhancement of excitonic peak with reduction in particle size. The particle size below which the blue shift occurs is often termed as 'critical size' which is the Bohr radius of excitons in semiconductors [39, 40].

It is well known that the growth of a nanostructure is due to two processes namely Ostwald ripening and oriented attachment (OA). It is reported that the capping agents, as they directly modify the nanoparticle surface can largely influence the OA processes [41]. The molecular weight of the capping ligand also makes a remarkable contribution in the assembly behaviors of the capped nanoparticles on the surface of the nanoparticle restricts the growth of the nanoparticles which results in quantum confinement. The type of growth mechanism that will occur is largely based on the monomer concentration formed, the type of metal being used and the type and amount of capping agent present to induce nucleation. Monomer attachment growth typically provides the best route for single crystalline material, whereas coalescence growth often forms nanoparticles with multiple twin structures and/or high-energy facets [42]. Moreover, most of the organic capping molecules are distorted in shape and larger than a surface site. As a result, coverage of surface atoms with the organic capping molecules may be sterically hindered [43].

On the other hand, surface defects in QDs, due to the presence of capping agents, act as temporary 'traps' for the electron, hole or excitons, quenching radiative recombination and reducing the quantum yields. Surface passivation of QDs can confine the carrier inside the core

and changes the size and optical properties of QDs. Therefore, capping or passivation of the surface is crucial for development of photostable QDs [44].

In the capping agent effect on the morphology of QDs, it is possible to suggest that the capping agents can cover the particles, and therefore, the particles do not coalesce to form bigger particles, even after an extensive period of time [45]. However, some aggregations between the particles may be occurring, lead to larger particles. The key point is that the capping agent must be able to suppress the growth of certain crystal facet by binding with metal cations [46]. Additionally, based on the spatial conformations of capping agents, they play an important role in controlling size and morphology of QDs (**Figure 4**) [47].
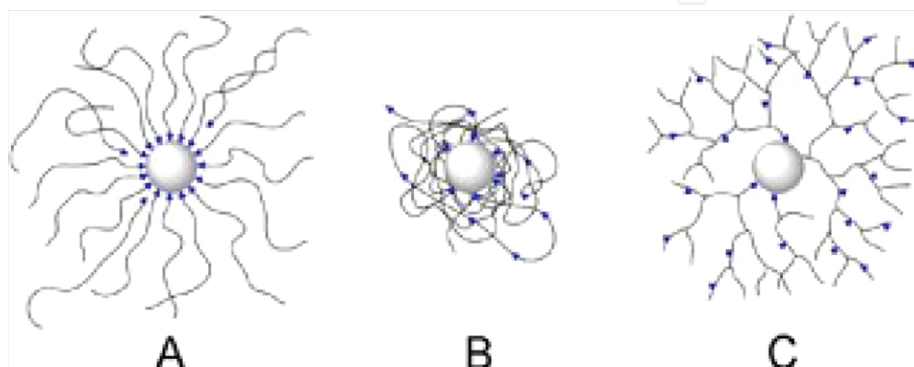
Figure 4. Spatial conformations of capping agents on nanoparticle (gray ball) surface: (A) linear long-chain hydrocarbons; (B) unbranched polymers and (C) branched polymers and dendrimers. Blue triangle represents the anchoring sites of capping agents [47].

2.3. Mechanisms of QD photocatalysis

The possible mechanism in the QD-based photocatalytic process is not yet fully understood. However, Pirkanniemi et al. [48] suggested five steps for the removal of pollutants in heterogeneous photocatalysis reaction:

(i) diffusion of reactants to the surface of photocatalyst particles,

(ii) adsorption of reactants onto the surface,

(iii) reaction on the surface,

(iv) desorption of products from the surface and

(v) diffusion of products from the surface to the bulk solution.
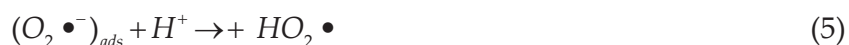
In homogeneous photocatalysis (for example, graphene quantum dots (GQDs)), both photocatalytic degradation and photosensitization degradation pathways may be occurring (**Scheme 1**). The light can be absorbed efficiently by both the QD and the pollutant molecule (P). According to the proposed pathway for the photocatalytic activity of the QDs, electrons in the valence band of QDs could be excited to the conduction band and electron–hole pairs are generated (Eq. (3)). Then the molecular oxygen (O_2) near the interface photocatalyst could

be quickly reduced to the superoxide radical ($O_2(\bullet^-$ and hydrogen peroxide radical ($\bullet OOH$) by the photogenerated electrons (Eqs. (4)–(7)), whereas the valence band holes can directly oxidize organic pollutants adsorbed on the surface of catalyst (QDs) or mineralized them indirectly through hydroxyl radicals$\bullet$) OH) generated by the reaction of holes and water molecules (H_2O) or chemisorbed (OH^-) (Eqs. (8)–(10)) [49]. For example, in the self-photosensitization pathway for the new fuchsin dye, photodegradation in the presence of QDs under visible light irradiation as shown in **Scheme 1b**. Firstly, the large surface area of GQDs can effectively adsorb molecules. Then, under vis-light irradiation, some photogenerated electrons can transfer from excited-state of adsorbed molecules to the conduction band (CB) of QDs. Thus, it would facilitate for the photoinduced active species (e.g., $O_2\bullet^-$, $\bullet OOH$, $\bullet OH$) to oxidize or degrade the surface-absorbed organic pollutants. Subsequently, $P^{\bullet+}$ readily reacts with these oxygen radicals to finally dissociate (Eqs. (11)–(13)).

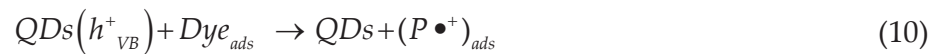$$QDs + hv \rightarrow QDs\left(e^-_{CB} + h^+_{VB}\right) \tag{3}$$
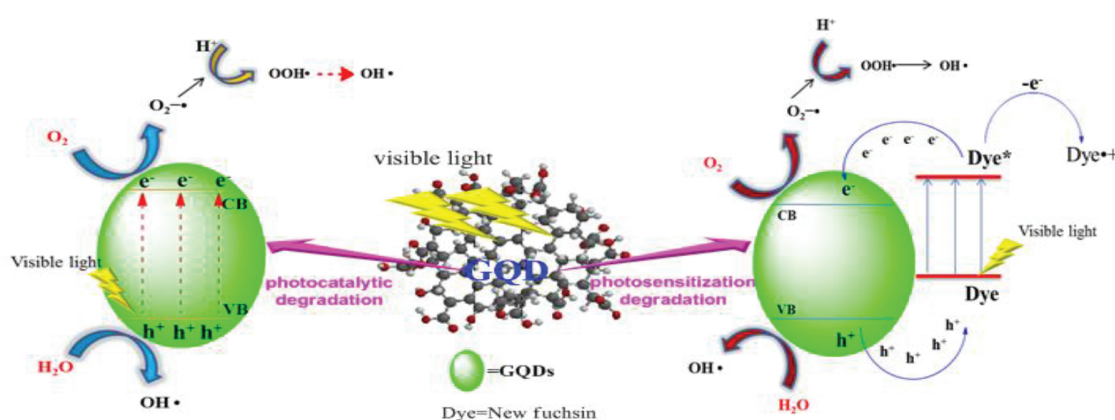
Scheme 1. Schematic representation of the proposed mechanism for degradation of New Fuchsin (NF) under visible light irradiation by (a) photocatalytic and (b) photosensitization pathways.

When the irradiation energy exceeds the energy difference between the valence and conduction bands (band gap) of a semiconductor, electron-hole pairs will be generated. This is referred to as the photoexcited state of the semiconductor [50]. The photogenerated charges (i.e., e^- and h^+ carriers) cause oxidation reactions on the particle surface, giving rise to free radicals, which in turn degrade the organic molecules. The photogenerated holes are highly oxidizing than the conventional oxidizing agents as the redox potential for the photogenerated holes is +2.53 V against the standard hydrogen electrode (SHE) in neutral (pH=7) solution.
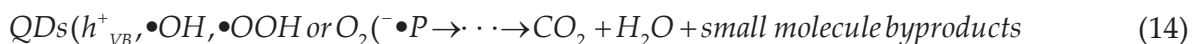
$$QDs\left(e^-_{CB}\right) + \left(O_2\right)_{ads} \rightarrow QDs + (O_2^-\bullet)_{ads} \tag{4}$$

$$\left(O_2\bullet^-\right)_{ads} + H^+ \rightarrow + HO_2\bullet \tag{5}$$

$$2HO_2 \bullet \rightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 + e^- \rightarrow OH^- + OH \bullet \tag{7}$$

These holes react with water to produce hydroxyl radicals (OH•), whose redox potential is only slightly decreased [51]. Moreover, the high oxidative potential of h^+ in the catalyst permits direct oxidation of organic matter to reactive intermediate, or it can react with chemisorbed H_2O molecules to form reactive species such as hydroxyl radicals (OH•) [31, 33], as illustrated in the following equations:

$$QDs\left(h^+_{VB}\right) + \left(H_2O\right)_{ads} \rightarrow QDs + \left(HO\bullet\right)_{ads} + \left(H^+\right)_{ads} \tag{8}$$

$$QDs\left(h^+_{VB}\right) + \left(HO^-\right)_{ads} \rightarrow QDs + \left(HO\bullet\right)_{ads} \tag{9}$$

$$QDs\left(h^+_{VB}\right) + Dye_{ads} \rightarrow QDs + \left(P\bullet^+\right)_{ads} \tag{10}$$

$$P + h\upsilon \rightarrow P^* \tag{11}$$

$$P^* + QDs \rightarrow P\bullet^+ + QDs\left(e^-_{CB}\right) \tag{12}$$

On the other hand, e^- in the conduction band can reduce molecular oxygen to superoxide anion, then the superoxide anion can react with H_2O to form other active radicals [52]. Depending upon the exact experimental conditions, the holes, electrons, hydroxyl radicals, super oxide radicals and oxygen itself can play an important role in the photocatalytic reaction mechanism [53]. Therefore, the produced hydroxyl radicals can cause organic matter mineralization:

$$\left[OH^\bullet / O_2^{\bullet-} + dye \rightarrow CO_2 + H_2O + small\,/\,lesstoxicspecies \right] \tag{13}$$

$$QDs(h^+_{VB}, \bullet OH, \bullet OOH \, or \, O_2(^-\bullet P \rightarrow \cdots \rightarrow CO_2 + H_2O + small\,molecule\,byproducts \tag{14}$$

In doped QDs with proper elements, the energy from absorbed photons can be efficiently transferred to the impurity, quickly localizing the excitation and suppressing undesirable reactions on the nanocrystal surface [26]. For example, incorporation of ZnS with other transition metals such as manganese, nickel and copper can have a beneficial effect on the

photoreactivity of photocatalysts. These doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays and optical sensors. As mentioned, the number and the lifetime of free carriers (electrons/holes) are particle size- and dopant-dependent. Doping of ZnS with other transition metal ions offers a way to trap charge carriers and extend the lifetime of one or both of the charge carriers (Scheme 2) [54]. **Table 1** illustrates the application of some prepared QDs by different methods in the photocatalytic degradation of pollutants [55–69].
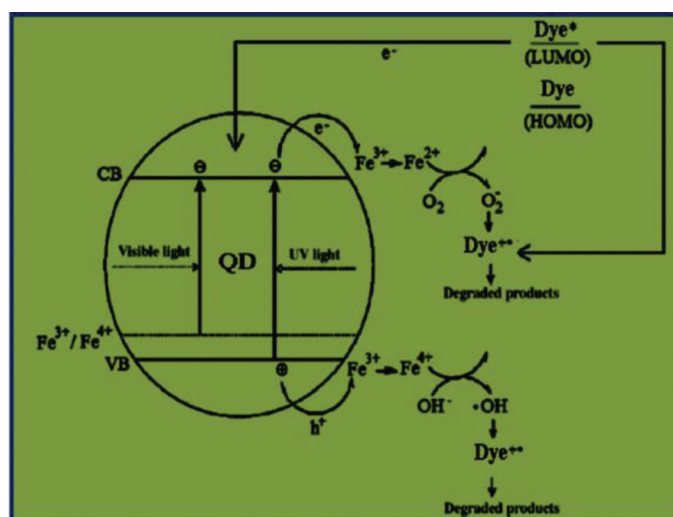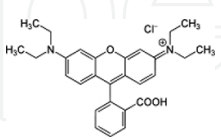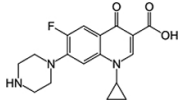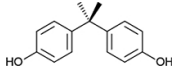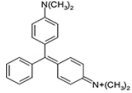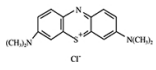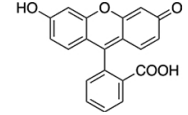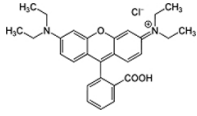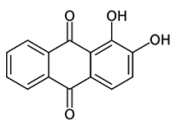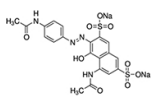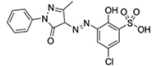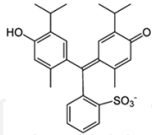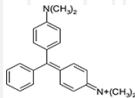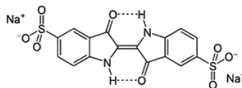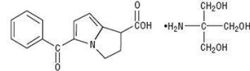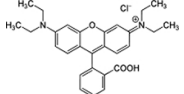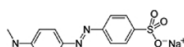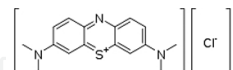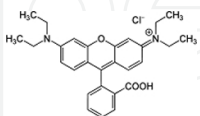
Scheme 2. Proposed mechanism for dye degradation under UV or visible light irradiations in the presence of doped QDs, such as iron-doped ZnS QDs [7].

Type of QDs	Synthesis method	Characterization methods	Name of the tested pollutant	Chemical structure	References
ZnS QDs, as pure and doped with different metal ions such as Cu, Mn, Ni, Co and Fe	Chemical precipitation	XRD, TEM, SEM, colorimetry, UV-vis absorption spectroscopy, fluorescence and atomic absorption spectroscopy	Methyl violet		[31]
			Victoria blue		[6, 28, 30]
			Malachite green		

Type of QDs	Synthesis method	Characterization methods	Name of the tested pollutant	Chemical structure	References
			Thymol blue		
			Congo red		[55]
			Methylene blue		[54]
			Safranin		
			Congo red		[32, 56, 57]
			HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)		[58]
			RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)		
Graphene QDs	Pyrolyzing	Colorimetry, UV -vis absorption spectroscopy, Raman and fluorescence spectroscopy andzeta potential measurements	New fuchsin		[5]
	Chemical exfoliation of multi wall carbon nanotubes	TEM, XRF, UV-vis spectro photometry and thermal gravimetry	Rhodamine B		[59]
			Methyl orange		
Graphene quantum dots	One-step hydro	XRD, TEM FT-IR, Raman spectroscopy,	Methyl orange		[60]

Type of QDs	Synthesis method	Characterization methods	Name of the tested pollutant	Chemical structure	References
(GQDs) -polyvinyl pyrrolidone (PVP)-CdS nano composite	thermal method	X-ray photoelectron spectroscopy and UV-vis spectroscopy			
Carbon quantum dots/BiOX (X = Br, Cl) hybrid nano sheets	Ionic liquid-induced strategy	SEM, TEM and XRD	Phenol rhodamine B (RhB)		[61]
			Ciprofloxacin		
			Bisphenol A (BPA)		
Carbon quantum dots/N-doped zinc oxide (CQD/N-ZnO)	One-step chemical method	Raman and X-ray photo electron spectroscopy	Malachite green		[62]
			Methylene blue		
			Fluorescein		
Graphitic carbon nitride quantum dots decorated self-organized TiO$_2$ nanotube arrays	Electro chemical anodiza tion technique followed by a facile organic molecular linkage	SEM, TEM, XPS and UV–vis spectrophoto metry	Rhodamine B		[63]
CdS QDs	Chemical precipi tation	TEM, XRD and absorption and fluorescence spectroscopy techniques	Alizarin		[64]
			Acid violet		

Type of QDs	Synthesis method	Characterization methods	Name of the tested pollutant	Chemical structure	References
			Mordant red		
			Thymol blue		
CdSe/ZnS quantum dots	Chemical synthesis based on Schlenk reaction	UV/vis spectroscopy	Methyl green		[65]
TiO₂ quantum dots	Simple sol-gel, template free	UV-light irradiation, TEM and XRD images	Indigo carmine		[66]
	Facile ultrasonic-assisted hydro thermal process	FTIR spectrum, TEM and XRD images	Ketorolac tromethamine		[67]
ZnO foam /carbon quantum dots	Combus tion method	TEM, XRD EDAX, UV-vis spectrophoto metry and fluorescence	Rhodamine B		[68]
			Methyl orange		
			Methylene blue		
Ag@AgCl QDs sensitized Bi2WO6	Oil-in -water self- assembly method	XRD, TEM, SEM, DRS and XRF	Rhodamine B		[69]

Table 1. Characteristics of some prepared QDs by different methods in the photocatalytic degradation of pollutants.

2.4. Toxicity of QDs

Although QDs offer potentially invaluable societal benefits such as in vivo biomedical imaging and detection, they may also pose risks to human health and the environment under certain

conditions. Generally, there are at least three different pathways by which QDs can interfere with organism function and lead to metabolic disability or death. First and most important is the composition of QDs. Upon corrosion inside the organism, toxic ions could be released from QDs and poison the cells. Compared with the bulk material, nanoparticles are more likely to have partial decomposition and release of ions due to their high surface-to-volume ratio. Another possible negative effect of QDs results from their small size, regardless of the composition of material. Particles can stick onto the surface of cell membranes, or can be ingested and retained inside cells, causing the impairing effects. The shape of particles may cause some adverse problems as well [70]. To date, most commercial QDs contain toxic elements, such as Cd, Pb, Hg and As. It was reported that the Cd-core QDs were indeed cytotoxic, especially when surface oxidation through exposure to air or UV irradiation led to the formation of reduced Cd on particle surface and the release of free Cd^{2+} ions. The cells cultured with CdSe QDs for 7 days were damaged with poorly defined cell boundaries and diffused nuclei. It was also shown that CdTe QDs exerted deleterious effects on cellular processes, and the smaller ones with green emission were more harmful than the larger red-emitting ones [71].

Meanwhile, studies suggest that the QD toxicity depends on multiple factors such as size and charge of particles, initial concentration of used QDs and type, structure and shape of the outer coating bioactivity (capping material and functional groups). To alleviate the toxicity of QDs, a variety of synthesis, storage and coating strategies have been proposed. Surface coatings such as ZnS, bovine serum albumin and vitamin E were shown to reduce, but not eliminate the cytotoxicity. With different surface modifications including mercaptopropionic acid, silanization and polymer coating, there were always quantitative concentration limits of QDs for the onset of cytotoxic effects to occur. Therefore, QDs with toxic elements will eventually induce cell death due to their inherent chemical composition. They can never be considered as 100% biocompatible or safe, but depending on the experimental conditions under which the toxicity can be tolerated [72, 73]. Another potential disadvantage arises from the possible toxicity of the II–VI semiconductors that are commonly used to prepare QDs (e.g., CdS, CdSe, PbS and PbSe). There are concerns that the toxicity of these materials may, for example, hinder in vivo applications of QDs [13].

Biography

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