Perspective

Construction of vesicle CdSe nano-semiconductors photocatalysts with improved photocatalytic activity: Enhanced photo induced carriers separation efficiency and mechanism insight

Jiangsu Wen¹, Changchang Ma¹, Pengwei Huo², Xinlin Liu³, Maobin Wei², Yang Liu², Xin Yao², Zhongfei Ma¹,4,⁎, Yongsheng Yan²,⁎

1. School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China. E-mail: wenjiangshu@sina.cn
2. School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China
3. School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, China
4. State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, Xuzhou 221008, China

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ABSTRACT

Visible-light-driven photocatalysis as a green technology has attracted a lot of attention due to its potential applications in environmental remediation. Vesicle CdSe nano-semiconductor photocatalyst are successfully prepared by a gas template method and characterized by a variety of methods. The vesicle CdSe nano-semiconductors display enhanced photocatalytic performance for the degradation of tetracycline hydrochloride, the photodegradation rate of 78.824% was achieved by vesicle CdSe, which exhibited an increase of 31.779% compared to granular CdSe. Such an exceptional photocatalytic capability can be attributed to the unique structure of the vesicle CdSe nano-semiconductor with enhanced light absorption ability and excellent carrier transport capability. Meanwhile, the large surface area of the vesicle CdSe nano-semiconductor can increase the contact probability between catalyst and target and provide more surface-active centers. The photocatalytic mechanisms are analyzed by active species quenching. It indicates that $h^+$ and $O_2^-$ are the main active species which play a major role in catalyzing environmental toxic pollutants. Simultaneously, the vesicle CdSe nano-semiconductor had high efficiency and stability.

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Introduction

In the last few years, one of the major purposes of material researchers is to create routes of controlling the structure of materials on specific nanomorphologies. The structure and size of inorganic micro and nanomaterials are well known to have a significant impact on their widely varying electrical and optical applications. Owing to the special structure, vesicle inorganic micro and nanomaterials as novel materials have paid increasing attentions in various fields of modern science and technology (Nguyen et al., 2014; Liu et al., 2010; Wu and Crudden, 2012; Wu et al., 2013). Their regular vesicle

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structure shows an enhanced surface area and shrinks transport distances for charge transport (Lai et al., 2012). So, they have been widely applied in photocatalysis (Dinh et al., 2014; Xue et al., 2013; Ye et al., 2014), solar cells (Dong et al., 2014), adsorption (El-Toni et al., 2014), and separation (Wei et al., 2014; Zhu et al., 2014). In the specific nanomorphologies, vesicle nano-semiconductor has caused widespread concern due to their specific structure and potential applications. Now, a large number of researchers have devoted themselves to examining versatile methods to prepare vesicle materials (Cao et al., 2010; Fang et al., 2011).

Semiconductor nanocrystals have gained a lot of attention because of the ability to tune their photosresponse by size and surface treatment (Kongkanand et al., 2008). Recently, utilizing semiconductor nanomaterials for obtaining photocatalytic performance has attracted wide attentions in sewage systems (Liu et al., 2013; Zhu et al., 2015; Dong et al., 2015).

The tailored structure of vesicle nano-semiconductor will have bright prospects in application in environment and chemistry. Responding to technology needs, a great deal of methods to synthesize versatile vesicle nano-semiconductor has been proposed (Niu et al., 2010). These methods can be roughly divided into two forms: soft template and hard template methods. Hard template included silica, polystyrene, latex and resin sphere (Kang et al., 2014; Zhang et al., 2014), post-processing was necessary in hard template method, for example, heat treatment and acid or alkali dissolution, which might impair the morphology and structure of the vesicle nano-semiconductor. While soft template generally touched on vesicle, droplet, and gas bubble to form vesicle structure materials (Sanetuntikul et al., 2014; Wickramaratne and Jaroniec, 2015; Girija et al., 2015). Compared to the hard template method, the synthesis pathway of the soft template method was simplified and the post-processing was needless. Up to now, researchers have made great progress in synthesizing vesicle nano-semiconductor and plenty of proud achievements have been gained. However, it is still a daunting challenge about exploring effective and proportionate ways to prepare vesicle nano-semiconductor materials with appropriate size and good dispersion for promising applications.

CdSe is a n-type semiconductor. Its bandgap energy is reported to be in the range from 1.65 to 1.8 eV (Scherhorn et al., 2008), which makes it widely used in applications in catalysis, sensor and solar cells. In the meantime, we report a moderate, simple and green liquid phase method to prepare vesicle CdSe nano-semiconductor with controlled diameters based on the soft template (H2 vesicles) method. Vesicle CdSe nano-semiconductor was one-step prepared under open air condition in aqueous solution. The CdSe nanoparticles had a promise of aggregating around the liquid–liquid interface between H2 vesicles and water, which resulted in the formation of vesicle structure. The outstanding features of the present work were as follows: (1) Se powder was used as Se source, which avoided an extra process to prepare the inappropriate Se precursor; (2) all reactions were completed under inert atmosphere protection; (3) the reactions proceeded in aqueous solution, so minimizing the pollution damage to the environment; (4) compared to granular CdSe, vesicle CdSe exhibits more superior photocatalytic performance; (5) the prepared vesicle CdSe nano-semiconductor has been implemented in remediation of residual antibiotics in water and displayed higher removal efficiency. In addition, the optical properties of the obtained nano-semiconductor were also evaluated.

1. Experimental section

1.1. Chemicals and materials

Cadmium chloride (CdCl2·2.5H2O), sodium borohydride (NaBH4), 3-mercaptopropiononic acid (C3H6O2S) and cetyltrimethyl ammonium chloride (C15H34ClN) were purchased from Shanghai Aladdin biochemical Technologies Inc., China. Selenium powder (Se) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were analytical grade and used as received without further purification.

1.2. Preparation of vesicle CdSe nano-semiconductor

In a typical procedure, 0.09134 g CdCl2·2.5H2O was added into a 100 mL flask dissolving with 30 mL deionized water. Then, 0.65 mmol of 3-mercaptopropiononic acid (3-MP) and different qualities of cetyltrimethyl ammonium chloride (CTAC) as a cationic surfactant were added with stirring rate of 450 r/min and stirring time of 5 min. Meanwhile, 0.0592 g Se powders were mixed with 0.3783 g sodium borohydride in a 20 mL round bottom flask and then added with 5 mL deionized water stirring under nitrogen atmosphere until the transparent solution was obtained. When the solution turns clear with white precipitate appeared, the clear liquid was quickly injected into the above solution. Afterward, the solution was continuously stirred for 3 hr in 80°C water bath conditions. The final orange precipitates were collected, washed with distilled water and absolute ethanol, and then dried in vacuum at 40°C for 4 hr.

1.3. Characterizations

X-ray diffraction (XRD) patterns were obtained with a D/max-RA X-ray diffractometer (Rigaku, Japan) equipped with Ni-filtered Cu Kα radiation (40 kV, 200 mA). The 2θ scanning angle range was 10–80° at a scanning rate of 5°/min. The morphology, microstructure and size of vesicle CdSe nanomaterials were confirmed by high resolution transmission electron microscopy (HRTEM) (JEM-2100, HR, Electronic Co., Ltd., Japan). UV–vis diffuse reflectance spectra (UV–vis DRS, UV2450, Shimadzu, Japan) of catalyst powder was obtained for the dry-pressed disk samples using Specord 2450 spectrometer (Shimazu, Japan) equipped with the integrated sphere accessory for diffuse reflectance spectra, using BaSO4 as the reflectance sample.). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR (America thermo-electricity Company) with 2 cm−1 resolution in the range 400–4000 cm−1, using Potassium bromide (KBr) pellets. Thermogravimetric analysis (TGA) curve of catalyst powder was obtained with a comprehensive thermal analyzer (STA499C, Tolerance, Germany). X-ray photoelectron spectroscopy (XPS) data were collected on a PHI5300 analyzer (Perkin Elmer, USA) with aluminum Kα radiation.
1.4. Photocatalytic activity test

The photocatalytic performance of the re-prepared catalyst was tested by photocatalytic degradation of 20 mg/L tetracycline hydrochloride solution in an inner-irradiation-type reactor. The inner-irradiation-type reactor equipped with 500 W Xe lamp was fixed with a quartz jacket and a water cooling system to prevent temperature overheat and to maintain the temperature below 40°C, and included the reaction solution. The 0.05 g catalyst was added into 100 mL tetracycline hydrochloride solution (20 mg/L) under vigorously magnetic stirring. Before the start of illumination, the target solution was vigorously magnetic stirred for 10 min to establish the adsorption equilibrium between the catalyst and target. After given time intervals, 6 mL samples were collected and filtered. The degradation efficiency was indicated by describing change in absorbance of tetracycline hydrochloride. The decrease in the characteristic absorption peak (357 nm) of tetracycline hydrochloride with time illustrates the photocatalytic degradation of tetracycline hydrochloride (Zhou et al., 2015).

The degradation rate \( r \) (\%) can be calculated by Eq. (1):

\[
r = \frac{C_0 - C}{C_0} \times 100
\]

where, \( C_0 \) (mol/L) is the initial concentration of tetracycline hydrochloride and \( C \) (mol/L) is the concentration at time \( t \) (min) (Mazloom et al., 2015).

2. Results and discussion

2.1. Formation mechanism of CdSe hollow nano-semiconductor

During the samples synthesis process, a conjecture was raised that H2 bubbles played a soft templates role to form vesicle CdSe nano-semiconductor. The formation process of vesicle CdSe nano-semiconductor was described in Fig. 1. First of all, H2 bubbles were producing via the reduction reaction between Se powder and sodium borohydride. In the meanwhile, Cd(OH)2 as precursors was generated and reacted with sodium hydrogen selenide forming CdSe nanoparticles. The possible formation process of CdSe nanoparticles in aqueous solution could be speculated as shown in the following reactions:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \cdot\text{H} + \cdot\text{OH} \\
3\text{H}_2\text{O} + \text{Se} + \text{BH}_4^- & \rightarrow \text{HSe}^- + \text{H}_3\text{BO}_3 \downarrow + \text{H}_2 \uparrow \\
\text{Cd(OH)}_2 + \text{HSe}^- & \rightarrow \text{CdSe} + \text{OH}^- + \text{H}_2\text{O} \\
n(\text{CdSe}) & \rightarrow (\text{CdSe})_n
\end{align*}
\]

During reaction process, plenty of Cd(OH)2 precursors existed on the surroundings of H2 bubbles. Moreover, various active sites such as vacancies, defects, traps existed on the surface of precursors to form CdSe nuclei. Finally these CdSe nuclei would transform into stable CdSe nanoparticles. As all CdSe nuclei generated on the surface of H2 bubbles, vesicle CdSe nano-semiconductor was forming when H2 bubbles were emptying. The advantage of utilizing such a template is that it is automatically removed at the end of the reaction. This method avoids the step of removing the template to obtain the pure product (Zhou et al., 2013; Khan et al., 2013).

2.2. Structure and morphology analysis

Fig. 2a and b showed the transmission electron microscope (TEM) images of the as-prepared products. As can be seen from the picture, the samples that have been prepared have obvious vesicle structure characteristics; then the majority of the vesicle CdSe nano-semiconductors present irregular shapes and a handful of samples are roughly spherical particles. Besides, the vesicle CdSe nano-semiconductor with different inner and outer diameters is 6–10 nm and 20–25 nm. The special structure of vesicle CdSe catalysis could make them greedily adsorbed target molecules as much as they can, and then increase the possibility of interactions between target molecules and catalysis. Ultimately the photocatalytic
efficiency was improved reasonably. Fig. 2c showed the XRD patterns of as-prepared vesicle CdSe nano-semiconductor. The diffraction peaks at 2θ values 25.48°, 42.21° and 49.96° are indexed as (111), (220) and (311) planes corresponding to those of hexagonal CdSe, and no other diffraction peaks related to impurities, such as oxides, were detected, indicating phase purity of CdSe (Mi et al., 2012). The diffraction peaks along with their relative intensities were found to be in good agreement with standard data of JCPDS card No. 19-0191. The approximate dimensions \( D \) (nm) of CdSe nanoparticles were calculated from the broadening of the (111) diffraction peak according to Debye–Scherrer’s Equation (Eq. (2)):

\[
D = \frac{0.9\lambda}{\beta \cos\theta}
\]

where, \( \lambda \) is the wavelength of the X-ray radiation, \( \beta \) is the full-width half maximum and \( 2\theta \) is the diffraction angle. It could be summarized that the grain size of CdSe nanoparticles is estimated to be 5–7 nm (Ma et al., 2015; Subramonian et al., 2016; Teh et al., 2015).

2.3. FT-IR spectra analysis

The as-prepared vesicle CdSe nano-semiconductor was analyzed by means of FT-IR spectra and the results were shown in Fig. 3. The peaks at about 2400 cm\(^{-1}\) and 3400 cm\(^{-1}\) could be assigned to the stretching vibration of C–SH and stretching vibration of O–H, indicating that the vesicle CdSe nano-semiconductor surface has been successfully covered with 3-mercaptopropionic acid. Characteristic bands of C–H, C–N and C–Cl stretching located at 1733 cm\(^{-1}\) and 1221 cm\(^{-1}\) are very visible, demonstrating that the dodecyl trimethyl ammonium chloride vesicles served successfully as cationic surfactant for increasing surface charge (Islam et al., 2014).

2.4. Thermogravimetric analysis

Fig. 4 showed the thermogravimetric analysis (TGA) curve of re-prepared catalyst. As can be seen from Fig. 4, when the temperature increased to 700°C, the total mass losses of
14.84% could be observed. It is evident from Fig. 5 that the mass loss (150°C) was caused by the evaporation of water molecules, and the mass loss between 150 and 700°C was attributed to re-prepared material’s surface organic mulches and the organic cationic surfactant (Lu et al., 2014).

2.5. UV–Vis–NIR absorption properties analysis

The optical absorption spectra of the granular and vesicle CdSe nano-semiconductor are also measured by characterization, as well as displayed in Fig. 5. Compared with the granular CdSe, it is clear that the optical absorption intensity in the UV–vis region of vesicle CdSe is stronger than that of granular CdSe, particularly when wavelength is less than 700 nm. Therefore, the improvement of the absorption efficiency of catalysts can raise light energy utilization ratio, which may be caused by the absorption edge that was red shifted when wavelength is smaller than 700 nm and the excellent photocatalytic properties in vesicle CdSe.

2.6. BET surface area analysis

In order to further research the contact probability between the catalyst and the target pollutant, the corresponding nitrogen adsorption/desorption isotherm and pore size distribution of vesicle CdSe nano-semiconductor were displayed in Fig. 6a. The vesicle CdSe nano-semiconductor has isotherms of type IV based on the IUPAC classification (Yu et al., 2015), illustrating the existence of mesopores, the pore size mainly distributes in the range of 2 to 20 nm. However, as shown in Fig. 7b, the granular CdSe is the non-porous material. The BET surface area, pore volume, total pore volume, pore diameter of vesicle CdSe nano-semiconductor and granular CdSe were given in Table 1.

2.7. XPS spectra analysis

The XPS spectra displayed in Fig. 7 provided further information for the chemical composition and element valence of solid catalyst. Every peak was verified through taking C(1s) (289 eV) peaks as the standard. The XPS spectrum of the vesicle CdSe nano-semiconductor illustrates that the sample compose of Cd, Se (Fig. 7a). The two peaks observed at 404.6 and 411.4 eV were attributed to Cd 3d5/2 and Cd 3d3/2 as well as the binding energies of Se3d core levels for the vesicle CdSe situated in 53.6 eV, which confirm the existence of CdSe QDs (Fig. 7b and c) (Wang et al., 2016).
2.8. Photocatalytic activity study

The photocatalytic performance of the granular CdSe and vesicle CdSe samples was tested by the photocatalytic degradation of tetracycline hydrochloride, as displayed in Fig. 8a and b. The “Dark environment” displayed that tetracycline hydrochloride hardly can be degraded using photocatalysts without the visible light illumination. The “Blank environment” displayed that the degradation ratio of tetracycline hydrochloride without any catalyst is nearly invariable in 30 min, illustrating that the self decomposition of tetracycline hydrochloride could be ignored. The vesicle CdSe possesses the higher photocatalytic performance compared with the granular CdSe. On the one hand, it is because of the fact that the vesicle structure can provide larger surface area which can guarantee the catalyst and target in sufficient contact with each other and the vesicle structure is more beneficial to carrier transport; on the other hand is because of the stronger optical absorption of visible and UV-light through vesicle structure. Consequently, the vesicle CdSe material revealed better photocatalytic performance than granular CdSe material. The photocatalytic degradation of tetracycline hydrochloride with various catalysts fits pseudo-first-order kinetics which was displayed in Fig. 8c, \( \ln(C/C_0) = kt \), where, the slope \( k \) is the apparent reaction rate constant. The reaction rate constant of vesicle CdSe (0.04867 \(\text{min}^{-1} \)) was about four times higher than that of granular CdSe (0.01077 \(\text{min}^{-1} \)). Based on experiment and characterization data mentioned above, it leads to the conclusion that vesicle structure is propitious to advance the photocatalytic performance of materials.

The influences of adding dosage of CTAC on the photocatalytic performance of vesicle CdSe nano-semiconductor was shown in Fig. 9. Vesicle CdSe synthesized with 0.4 g CTAC showed higher activity than that synthesized in the absence of CTAC. This behavior could be attributed to the fact that the CTAC not only led to vesicle structure but also made the solid catalyst in a kind of ideal state that a large number of positive charges are formed on the catalyst surface. Since the tetracycline hydrochloride surface charge is negative in water, this leads to a large number of target molecules that were adsorbed on the surface of catalyst, and then increased the contact chance of catalyst with target molecule. Consequently, with the increase of positive charges, the adsorption capacity of solid catalyst was gradually enhanced, and then photocatalytic activity of solid catalyst was improved. However, when the adding dosage of CTAC was more than 0.4 g, the ability to remove target molecules of catalysts was severely reduced. One reason for this may be the catalysts and free target molecular were repulsive from each other since too many target molecules were adsorbed on the surface of catalysts. On the other hand, the active sites on catalyst surface were occupied excessively by target molecules which were adsorbed on the surface of catalysts, thus resulting in target molecules that cannot be removed sufficiently (Hu et al., 2015).

The ability for recycling is one of the most key properties for an excellent catalyst. Hence, the stability of the vesicle CdSe catalyst was detected through cycling experiment. The photocatalytic behavior of tetracycline hydrochloride by the catalyst for four cycles was shown in Fig. 10. After each circulation, the reclaimed solid samples were cleaned through ultrasonic washing when ultrasonic frequency is 80 kHz and ultrasonic time is 10 min. The cycling experiment reveals that the stability of catalyst was very superior, as the degradation efficiency almost maintained constant after fourth cycles.

2.9. Proposed mechanisms of the vesicle CdSe nano-semiconductor

It is well known that the active species such as \( \cdot \text{OH} \) and \( \text{h}^+ \) are the key influencing force, which influences the removal efficiency of the target pollutant. The quenching experiment system included 0.05 g catalyst, 1 mmol scavenger and 100 mL tetracycline hydrochloride solution (20 mg/L), and the concentration was detected by a UV–vis spectrophotometer with the maximum absorption wavelength at 357 nm. Fig. 11a showed the quenching experiment of active species during the photocatalytic process. It was obvious that the degradation efficiency of tetracycline hydrochloride was small scope weakened by the addition of 1 mmol tert-butanol (a quencher of \( \cdot \text{OH} \)) (Martinez et
In the meantime, the degradation efficiency of tetracycline hydrochloride significantly reduced with the presence of EDTA-2Na (a quencher of $h^+$) and $p$-benzoquinone (a quencher of $O_2^-$) (Jiang et al., 2014; Chen et al., 2015; Ding et al., 2013). Thus, it comes to a conclusion that $h^+$ and $O_2^-$ are the main active species of vesicle CdSe in aqueous solution under visible light irradiation (Liu et al., 2014).

To elucidate the photocatalytic microprocess mechanism, conduction band minimum (CBM) and valence band maximum (VBM) potentials of vesicle CdSe should be proved. Generally speaking, the CBM and VBM of a semiconductor can be estimated according to an empirical equation (Eq. (3)) (Ye et al., 2012):

$$E_{CM} = X - E_e - 0.5E_g$$

where, $E_{CB}$ (eV) is the CBM edge potential; $X$ is the electronegativity of the semiconductor, which is the geometric mean of the absolute electronegativities of the constituent atoms; $E_e$ is the energy of free electrons on the hydrogen scale (about 4.5 eV); $E_g$ is the band gap energy of the semiconductor; and $E_{VM}$ can be calculated by $E_{VM} = E_{CB} + E_g$. The values applied to calculate the CM and VM potentials of vesicle CdSe nano-semiconductor and granular CdSe were presented in Table 2.

![Fig. 8 - Photocatalytic degradation rate of tetracycline hydrochloride test during irradiation with visible-light radiation: (a) tetracycline hydrochloride concentration changes as a function of irradiation time, (b) the comparison of degradation rate after 30 min of visible-light radiation pseudo first-order reaction kinetics and (c) pseudo first-order reaction kinetics.](image)

![Fig. 9 - The influence of adding dosage of CTAC on the catalyst performance of vesicle CdSe nano-semiconductor. CTAC: cetyltrimethyl ammonium chloride.](image)

![Fig. 10 - Repeated experiment of photocatalytic degradation of tetracycline hydrochloride over the vesicle CdSe nano-semiconductor under visible-light irradiation (concentration of tetracycline hydrochloride, 20 mg/L).](image)
The possible photocatalytic microprocess mechanism of vesicle CdSe nano-semiconductor was displayed in Fig. 11b. At the presence of visible light, the vesicle CdSe is excited and producing photogenerated electrons (e\(^{-}\)) and holes (h\(^{+}\)). The photogenerated electrons (e\(^{-}\)) transfer from valence band (VB) to the conduction band (CB) and living holes (h\(^{+}\)) in the valence band (VB) (Chen et al., 2014). For vesicle CdSe nano-semiconductor, because of unique vesicle structure which is similar to pearl necklace, the carrier transporting properties of vesicle CdSe nano-semiconductor is extremely excellent. Ultimately, holes (h\(^{+}\)) are remained in the valence band (VB). Yet, h\(^{+}\) on the VB of catalyst, which cannot directly react with H\(_{2}\)O to form .OH for the EVB, is more negative than \(E(\text{OH/OH}^{-})\) (2.38 eV vs. NHE) (Wang et al., 2014). Thus, the photogenerated h\(^{+}\) participates in the oxidation reaction directly. Besides, the electrons on the CBM can react with O\(_{2}\) to produce .O\(_{2}\)\(^{-}\) and then the \(E_{CB}\) of vesicle CdSe catalyst (−0.325 eV) is more negative \(E(\text{O}_2/\text{O}_2^{-})\) (−0.32 V vs. NHE), which can oxidize the hazard pollutants. Consequently it is compliant with the conclusions of the previous quenching experiment. Meanwhile, the \(E_{CB}\) of granular CdSe catalyst (−0.355 eV) is more negative than the vesicle CdSe, but the band gap energy is larger than the vesicle CdSe. Consequently, the vesicle CdSe was more likely to be excited by visible light and had a higher photocatalytic activity.

3. Conclusions

To sum up, vesicle CdSe nano-semiconductors had been successfully prepared through a soft template method and using H\(_{2}\) bubbles generated during the reaction as soft templates. The preparation process was controllable, efficient and environment-friendly. Based on their efficient catalytic performance, the vesicle CdSe nano-semiconductor catalysts could be widely applied in environmental removal of toxic pollutants in aqueous solution. Meanwhile the degradation mechanism of toxic pollutants was analyzed through free

<table>
<thead>
<tr>
<th>Sample</th>
<th>X</th>
<th>(E_g) (eV)</th>
<th>(E_{CB}) (eV)</th>
<th>(E_{VB}) (eV)</th>
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</thead>
<tbody>
<tr>
<td>Vesicle CdSe</td>
<td>5.05</td>
<td>1.75</td>
<td>−0.325</td>
<td>1.425</td>
</tr>
<tr>
<td>Granular CdSe</td>
<td>5.05</td>
<td>1.81</td>
<td>−0.355</td>
<td>1.455</td>
</tr>
</tbody>
</table>

\(E_{CB}\) (eV) is the CB edge potential; \(E_{VB}\) (eV) is the VB edge potential; \(X\) is the electronegativity of the semiconductor; \(E_g\) is the band gap energy of the semiconductor. CB: conduction band; VB: valence band.
radical quenching experiments. The fact has been proved that \( h^+ \) and \( O_2 \) are the main active species which play a major role in catalyzing environmental toxic pollutants.

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