

Carbon-nanodot-coverage-dependent photocatalytic performance of carbon nanodot/TiO₂ nanocomposites under visible light*

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(Received 9 January 2017; revised manuscript received 31 January 2017; published online 6 April 2017)

Carbon nanodots (CDs) with visible absorption band and TiO₂ are integrated to enhance the photosensitivity of TiO₂. The CD/TiO₂ nanocomposites show obvious CD-coverage-dependent photocatalytic performance. The CD/TiO₂ nanocomposites with moderate CD coverage exhibit the highest photocatalytic activity after being irradiated with visible light, which is more excellent than that of TiO₂. Too little CD coverage could result in poor visible light absorption, which limits the photocatalytic performance of CD/TiO₂ nanocomposites. While, too much CD coverage weakens the photocatalytic activity of CD/TiO₂ nanocomposites by restraining the extraction of conduction band electrons within TiO₂ to generate active oxygen radicals and the electron transfer (ET) process from CDs to TiO₂. These results indicate that rational regulation of CD coverage and the realization of efficient ET process are important means to optimize the photocatalytic performance of CD/TiO₂ nanocomposites.

Keywords: carbon nanodots, TiO₂, photocatalysis, electron transfer

PACS: 81.05.U-, 82.65.+r, 78.47.jd, 78.67.Sc

DOI: 10.1088/1674-1056/26/5/058101

1. Introduction

Recently, great attention has been paid to solar energy conversion, due to the problems of environment and energy.^[1–3] Semiconductor TiO₂ has been widely used in the field of photocatalysis, which is attributed to its unique features such as low cost, good stability, and environmental friendliness.^[4–6] While, the large bandgap of TiO₂ (~ 3.2 eV) severely restricts its practical application progress of photocatalysis,^[4–7] considering the fact that TiO₂ responds only to the ultraviolet region (lower than 5% of the full solar spectrum).^[8] Therefore, it is important to expand the photo-sensitive spectrum range of TiO₂ to visible region. In recent years, great efforts have been made to sensitize the narrow bandgap quantum dots (QDs) and organic dyes on TiO₂ for improving the performance of TiO₂ photocatalysts.^[9–12] However, most of QDs with superior performances contain heavy metal elements and the photochemical stability of organic dyes is generally unsatisfactory.^[13,14]

Carbon nanomaterials, which include carbon nanotubes, fullerene, graphene, carbon nanodots (CDs), and so on, are expected to replace the use of QDs and organic dyes in bioimaging, optoelectronics, photovoltaics and photocatalysis.^[14–19] Especially, CDs have received significant attention due to their low toxicity, biocompatibility, good stability and water solubility.^[20–24] Moreover, CDs could be easily coupled to TiO₂ by many methods.^[25–28] Recently, a lot of efforts have been made to employ the CD/TiO₂ nanocomposites in

photocatalysis. The photocatalytic performances of CD/TiO₂ nanocomposites were pretty excellent under visible light in comparison with TiO₂.^[25–33] For example, Yu *et al.* prepared CD/TiO₂ nanocomposites with a simple hydrothermal process and reported that the photocatalytic H₂ evolution rate of the CD/TiO₂ nanocomposites was obviously improved compared with that of TiO₂ after being irradiated with visible light, due to the sensitization effect of CDs.^[25] Ming *et al.* designed a new CD/TiO₂ hybrid photocatalyst by integrating CDs with TiO₂ through an easy hydrothermal method, which exhibited an excellent photocatalytic performance under visible light.^[32]

It is known that the exposure of active sites on TiO₂ surface is essential for excellent photocatalytic activity.^[31] In addition, the sensitization of CDs on the surface of TiO₂ could expand the absorption band of TiO₂ photocatalysts to visible region and enhance the interfacial charge separation process, which can improve the photocatalytic performance of CD/TiO₂ nanocomposites.^[28,29,31,34] While, the sensitized CDs could also occupy some active sites on TiO₂ surface, which play an important role in photocatalysis.^[31] Therefore, rational regulation of CD coverage has a great influence on the photocatalytic activity of CD/TiO₂ nanocomposites, which is proposed as an urgent consideration for the design of CD/TiO₂ nanostructure photocatalysts. However, the influencing mechanisms of CD coverage are less explored and understood in CD/TiO₂ nanocomposites.

In this work, we prepare CDs with visible absorption band

*Project supported by the Scientific Research Starting Fund for Doctor of Mudanjiang Normal University, China (Grant No. MNUB201508), the Youth Science Foundation of Heilongjiang Province, China (Grant No. QC2016007), and the National Natural Science Foundation of China (Grant No. 61604065).

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locating in the range from 400 to 600 nm by the microwave synthesis method and design the CD/TiO₂ nanocomposites with different CD coverages. The CD/TiO₂ nanocomposites exhibit expanded photosensitive spectrum range compared with TiO₂ and the photocatalytic performance of CD/TiO₂ nanocomposites is measured by photodegradation experiment of Rhodamine B (RhB) dye molecules after being irradiated with visible light. The experimental results are well reproducible. CD-coverage-dependent photocatalytic performance of the CD/TiO₂ nanocomposites is studied and possible mechanisms are analyzed through time-resolved photoluminescence (PL) spectrum.

2. Experiment

2.1. Chemicals and materials

TiO₂ nanoparticles (P25, average size 25 nm, 20% rutile and 80% anatase phase) were purchased from Degussa. Urea (99.5%), citric acid (99.8%), and RhB (99%) were all purchased from Aladdin.

2.2. Synthesis of CDs

The CDs were synthesized with the microwave synthesis method.^[23,35] The urea of 4 g and citric acid of 2 g were loaded into a beaker. Some deionized water (~ 15 mL) was added and then a clear solution was formed. For the formation of CDs, the obtained clear solution was then heated for about 10 min in a 750 W microwave oven. In the process of heating, the reaction mixture gradually evolves from clear solution to dark-brown solid. After that, the dark-brown solid CDs were dispersed in deionized water and purified five times with a centrifugal speed of 10000 rpm to remove clustered CDs.

2.3. Fabrication of CD/TiO₂ nanocomposites with different CD coverages

The CD/TiO₂ nanocomposites with different CD coverages were prepared by changing the mixing mass ratio of CDs and P25 TiO₂ from 1:10, 1:50, 1:200, 1:500 to 1:1000. Specifically, they were that 2, 0.4, 0.1, 0.04, and 0.02 mL of CD solutions in deionized water (5 mg/mL) were simply dispersed in 20 mL of TiO₂ solution in deionized water (5 mg/mL). The mixed solutions were magnetically stirred for about 24 h to complete the adsorption process of CDs on TiO₂ surface. After that, the reaction products were dispersed in some deionized water and then purified to eliminate unbonded CDs several times until no fluorescence was detected in the supernatant with the centrifugal speed of 4000 rpm. The obtained CD/TiO₂ nanocomposites were dried at a temperature of 80 °C in a vacuum oven.

2.4. Photocatalytic experiment

The photodegradation rates of RhB dye molecules under visible light were measured to evaluate the photocatalytic performances of CD/TiO₂ nanocomposites with different CD coverages. The CDs, P25 TiO₂ and CD/TiO₂ nanocomposite solutions (5 mg/mL) were prepared in deionized water. Each (100 μL) of these solutions, 100 μL of RhB solution in deionized water (100 mg/L) and some deionized water (2.8 mL) were mixed in a 1 cm×1 cm quartz cuvette. After that, the obtained mixed solutions were kept in darkroom with constant stirring to achieve the balance between adsorption and desorption of RhB dye molecules. After being kept in darkroom for 2 h, the mixed solutions were irradiated under visible light ($\lambda > 420$ nm) from a solar simulator (Zolix SS150) equipped with a 420 nm cut-off filter, during which magnetic stirring was constantly kept. The absorption spectra of RhB dye molecules were in situ measured once every 10 min with the USB4000 spectrometer. The reference light for measuring the absorption spectra of RhB dye molecules was from a HL-2000 light source (Ocean Optics) and imported by a QP8-2-SMA-BX fiber (Ocean Optics). The transmission light was then exported by a QP1000-2-SR fiber (Ocean Optics) and collected by USB4000 spectrometer. 510 nm cut-off filter was used to avoid exciting the CDs by reference light.

2.5. Characterization

The absorption spectrum of CD aqueous solution was measured with Shimadzu UV-3101PC UV-Vis-NIR spectrophotometer. The PL spectra of CDs and CD/TiO₂ nanocomposites in deionized water were recorded in a 10 mm×1 mm quartz cuvette by Hitachi F-7000 spectrophotometer. The diffuse reflectance spectra of CD/TiO₂ nanocomposites with different CD coverages were also measured by Hitachi F-7000 spectrophotometer with an integrating sphere scanning from 200 to 700 nm with BaSO₄ used as the reference. The morphology of CD/TiO₂ nanocomposites was recorded on TECNAI G2 transmission electron microscope (TEM). The time-resolved PL spectra were recorded on LifeSpec-II PL lifetime spectrometer (Edinburgh Instruments) with a diode laser (with a picosecond pulse, laser wavelength of 405 nm, pulse width of 74.5 ps) used as an excitation source. The detector was Hamamatsu H5773-04 photomultiplier (response time: 250 ps) and the instrument response function was about 440 ps.

3. Results and discussion

The CDs are prepared with microwave synthesis method.^[23,35] As seen from Fig. 1(a), the CDs own a visible absorption band located in a range from 400 to 600 nm, ensuring that the potential of the CDs acts as a photon harvester. The integration of CDs and TiO₂ is significant for enhancing the

photosensitivity of TiO₂ and improving the charge separation process between CDs and TiO₂ under visible light.^[28,29,31] The CD/TiO₂ nanocomposites are prepared by mixing CDs and TiO₂ powder in deionized water with magnetic stirring for 24 h. The reaction products are dispersed in some deionized water and then purified to eliminate unbonded CDs several times by centrifugation. The coverage of CDs on TiO₂ surface is regulated through gradually changing mixing mass ratios of CDs to TiO₂ powder from 1:10, 1:50, 1:200, 1:500, to 1:1000. The absorption spectra of TiO₂ and CD/TiO₂ nanocomposites are measured and shown in Fig. 1(a), which are converted from

the diffuse reflection spectra of them. As seen from Fig. 1(a), pure TiO₂ has hardly any absorption ability in the visible region ($\lambda > 400$ nm), and the sensitization of CDs could expand the absorption band of TiO₂ to the visible spectrum range from 400 to 600 nm. The absorption band in visible region gradually extends with the CD content increasing, indicating larger coverage of CDs on TiO₂ surface. To visually observe the structure of the CD/TiO₂ nanocomposites, high-resolution TEM image of them is recorded as seen from Fig. 1(b), which demonstrates the integrating of CDs with TiO₂ nanoparticles.

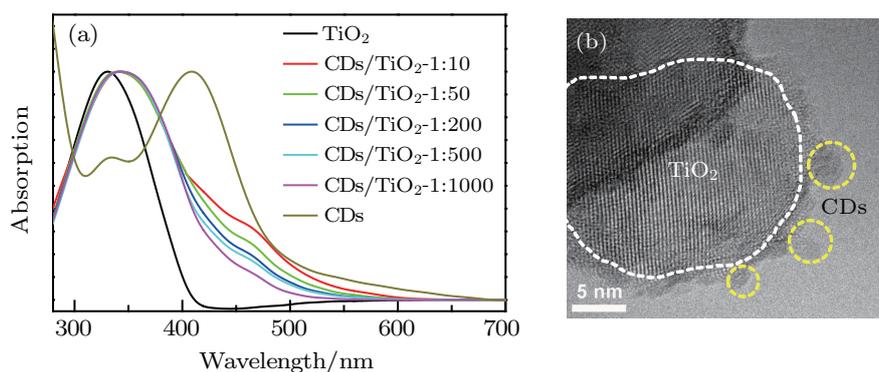


Fig. 1. (color online) (a) Absorption spectra (normalized) of the CDs, TiO₂, and CD/TiO₂ nanocomposites with different CD coverages, (b) TEM image of the CD/TiO₂ nanocomposites.

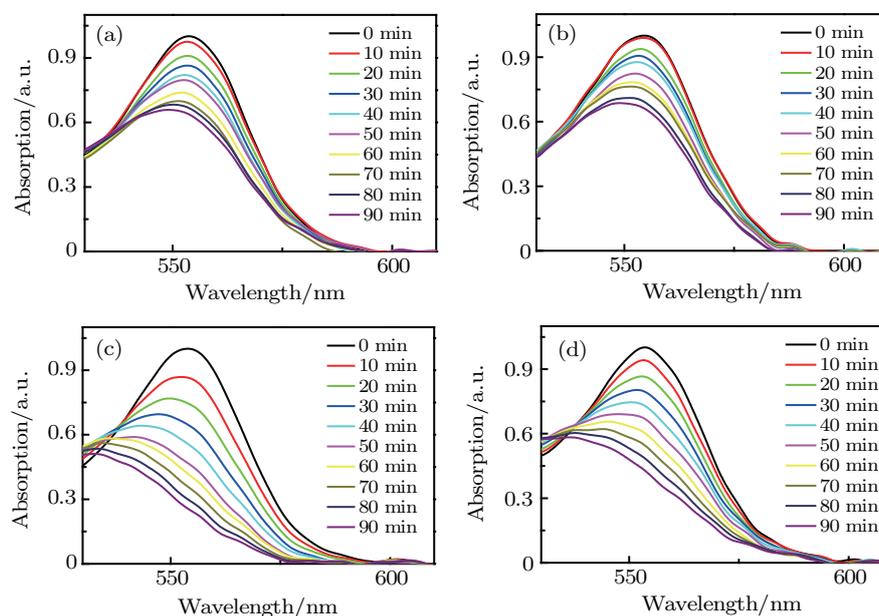


Fig. 2. (color online) Absorption spectra of the RhB dye molecules mixed with (a) TiO₂ and CD/TiO₂ nanocomposites (mass ratios: (b) 1:50, (c) 1:500, and (d) 1:1000) in deionized water after different visible light irradiation times.

The photodegradation rates of RhB dye molecules after being irradiated with visible light ($\lambda > 420$ nm) are measured to evaluate the photocatalytic performance of CD/TiO₂ nanocomposites. In the photodegradation process, it is generally considered that photogenerated electrons and holes within CD/TiO₂ nanocomposites under visible light are extracted by O₂ and OH⁻ in water to generate active oxygen (O₂⁻) and hy-

droxyl (\cdot OH) radicals, respectively, thereby degrading the RhB dye molecules.^[28,29,32-34] Figure 2 shows the absorption spectra of the RhB dye molecules mixed with TiO₂ and CD/TiO₂ nanocomposites in deionized water after different visible light irradiation times. As seen from Fig. 2(c), the characteristic absorption peak (554 nm) of RhB dye molecules drops quickly with an obvious blue shift at peak wavelength under visible

light irradiation when CD/TiO₂ nanocomposites are added. The decrease in the characteristic absorption peak of RhB dye molecules results from the cleavage of conjugated ring structure chromophore by CD/TiO₂ nanocomposites, which is major part of photodegradation.^[36,37] The blue shift at peak wavelength may be attributed to the de-ethylation of RhB dye molecules.^[36,37]

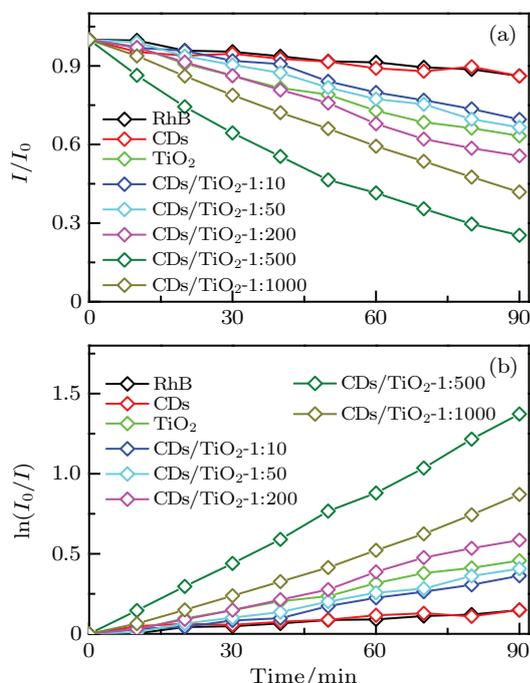


Fig. 3. (color online) Time-dependent photocatalytic performances of (a) I/I_0 and (b) $\ln(I_0/I)$ for the CDs, TiO₂, and CD/TiO₂ nanocomposites with different CD coverages after being irradiated with visible light ($\lambda > 420$ nm).

Figure 3(a) shows the ratios between the absorption peak (554 nm) intensity of RhB dye molecules under visible light for a certain period of time (I) and that before irradiation (I_0). The degradation dynamic results ($\ln(I_0/I)$) of the RhB dye molecules by these photocatalysts are shown in Fig. 3(b).^[28,29] The RhB dye molecules have an about 14% self-degradation after visible light irradiation for 90 min as seen from Fig. 3(a). The photodegradation rate of RhB dye molecules by CDs is similar to that of pure RhB, indicating that CDs have almost no photocatalytic ability under visible light. It is about 35% for the photodegradation of RhB dye molecules after TiO₂ has been added. While, the photodegradation rate caused by the CD/TiO₂ nanocomposites with a mass ratio of 1:500 is much faster than those of TiO₂ and CDs, which indicates that the excellent photocatalytic performance of CD/TiO₂ nanocomposites should be attributed to the sensitization effect of CDs on TiO₂ as seen from Figs. 3(a) and 3(b). Most of RhB dye molecules (75%) could be photodegraded by the CD/TiO₂ nanocomposites (optimized mass ratio: 1:500) after being exposed to visible light for 90 min. In addition, the CD/TiO₂ nanocomposites exhibit obvious CD-coverage-dependent photocatalytic activity as seen from Figs. 3(a) and 3(b). The

photodegradation rate is raised from 30% to 75% and then dropped to 58% with the coverage of CDs on TiO₂ surface decreasing. Too little or too much CD coverage is adverse to the high photocatalytic activity.

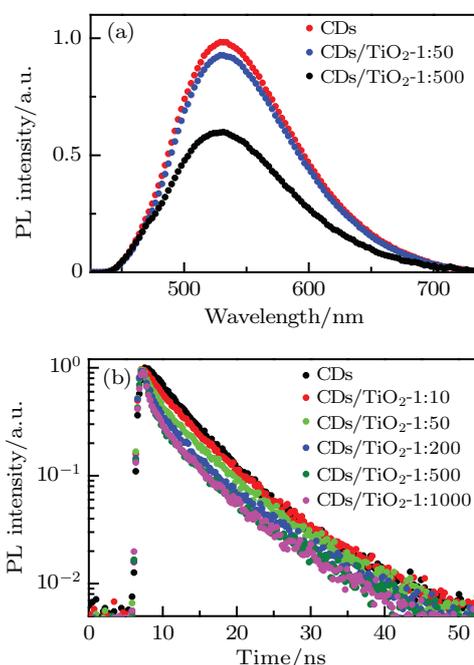


Fig. 4. (color online) (a) PL spectra of CDs and CD/TiO₂ nanocomposites with mixing mass ratios of 1:50 and 1:500 in deionized water in a 10 mm×1 mm quartz cuvette under 405 nm excitation, the samples for PL spectrum measurement are prepared by mixing the CDs and TiO₂ with magnetic stirring for 24 h, the concentrations of the CDs in the three samples are all the same (10 mg/L), (b) PL decays of CDs and CD/TiO₂ nanocomposites with different CD coverages in deionized water, excited with 405 nm, measured at 530 nm.

Charge separation in CD/TiO₂ nanocomposites under visible light is considered to be the crucial process to improve photocatalytic performance of TiO₂, because it is a key step for the generation of O₂^{·-} and [·]OH to photodegrade organic dye molecules.^[25,28–31,34] The dynamic behaviors of electron transfer (ET) from CDs to TiO₂ give rise to primary photo-physical processes to achieve charge separation between them after being irradiated with visible light.^[28,38] Thus, there is a strong need to study the ET dynamic processes between CDs and TiO₂ for better understanding the effect of CD coverage on the photocatalytic activity of CD/TiO₂ nanocomposites. Figure 4(a) exhibits the PL spectra of CDs and CD/TiO₂ nanocomposites with the same concentration of CDs in deionized water. The emission of CDs could be significantly quenched by TiO₂ when the coverage of CDs is relatively low (mass ratio: 1:500) as shown in Fig. 4(a), indicating the possibility of ET from CDs to TiO₂. To acquire an in-depth understanding of CD-coverage-dependent photocatalytic performance of CD/TiO₂ nanocomposites, the PL dynamic behaviors of CD/TiO₂ nanocomposites with different CD coverages are investigated with the excitation of 405 nm and measured PL decay spectra are exhibited in Fig. 4(b). As

seen from Fig. 4(b), obvious shortening is observed in PL decay spectra of the CDs after being integrated with TiO₂, which results from photoinduced ET from the CDs to TiO₂.^[28,29,39] It should be noted that the coverage of CDs on TiO₂ surface has a significant effect on the PL decay of CDs as shown in Fig. 4(b). The PL decay of the CDs slows down gradually with the coverage of CDs on TiO₂ surface increasing, indicating that the ET process is suppressed. To quantify these results, ET rate (k_{ET}) and efficiency (η_{ET}) are evaluated from the following equations:^[28,38–40]

$$k_{ET} = \frac{1}{\tau_{ave}(CD-TiO_2)} - \frac{1}{\tau_{ave}(CD)}, \quad (1)$$

$$\eta_{ET} = 1 - \frac{\tau_{ave}(CD-TiO_2)}{\tau_{ave}(CD)}, \quad (2)$$

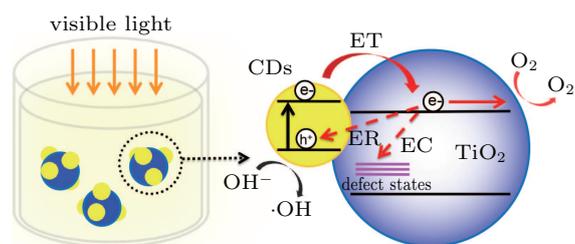
Table 1. Fitting results for the PL dynamic behaviors of CDs and CD/TiO₂ nanocomposites in deionized water and calculation values of k_{ET} and η_{ET} .^a

Samples	τ_1 /ns	a_1 /%	τ_2 /ns	a_2 /%	τ_3 /ns	a_3 /%	τ_{ave} /ns	$k_{ET}/10^7 \text{ s}^{-1}$	η_{ET} /%
CDs/water	5.01	70.54	10.42	29.46			6.60		
CDs/TiO ₂ -1:10	0.95	4.64	4.69	55.81	9.94	39.55	6.59	0.02	0.15
CDs/TiO ₂ -1:50	0.76	11.24	4.52	44.78	10.06	43.98	6.53	0.16	1.06
CDs/TiO ₂ -1:200	0.72	15.76	4.05	41.93	10.28	42.31	6.16	1.08	6.67
CDs/TiO ₂ -1:500	0.82	24.38	4.66	38.85	10.56	36.77	5.89	1.83	10.76
CDs/TiO ₂ -1:1000	0.81	22.57	4.57	42.32	10.05	35.11	5.65	2.55	14.39

^aThe average PL lifetimes are calculated by $\tau_{ave} = \sum_{i=1}^n a_i \tau_i$,^[41,42] a_1 , a_2 , and a_3 are fractional contributions of decay lifetimes τ_1 , τ_2 , and τ_3 , respectively.

Three feasible consumption ways for conduction band electrons of TiO₂ exist in the CD/TiO₂ nanocomposites, which are electron extraction by O₂ in water, electron recombination back to the CDs, and electron capture into TiO₂ defect states^[28,29] as seen from Fig. 5. When the CDs are excited by visible light, electron-hole pairs are generated. In the CD/TiO₂ nanocomposites with low coverage of CDs, the photoexcited electrons within the CDs could be injected into TiO₂ conduction band and then extracted by O₂ in water,^[28,29] which quenches the PL of CDs. In the nanocomposites with high coverage of CDs, the active sites on the surface of TiO₂ nanoparticles are mostly covered by CDs,^[25,31] leading to inefficient electron extraction by O₂ in water and then causing a suppression of the ET from CDs to TiO₂, which should be responsible for the unsatisfactory photocatalytic performance of the CD/TiO₂ nanocomposites with high CD coverage. This result also accords with the negligible PL quenching (Fig. 4(a)) of the CD/TiO₂ nanocomposites with high CD coverage (mass ratio: 1:50). As discussed above, when the CD coverage on TiO₂ nanoparticles is low, many surface active sites of TiO₂ will be exposed. The extraction of conduction band electrons of TiO₂ to generate O₂^{·-} is effective and ET process from photoexcited CDs to TiO₂ is feasible. Nonetheless, the poor visible light absorption consequentially limits the photocatalytic activity of the CD/TiO₂ nanocomposites with low CD coverage. While, too much CD coverage could restrain the ex-

traction of conduction band electrons of TiO₂ injected from photoexcited CDs to generate O₂^{·-} and ET process from CDs to TiO₂ by reducing the surface active sites of TiO₂, which weakens the photocatalytic activity of CD/TiO₂ nanocomposites.



CD/TiO₂ nanocomposites in water

Fig. 5. (color online) Schematic illustration for the ET process and possible consumption ways (electron extraction by O₂ in water, ER for electron recombination back to the CDs and EC for electron capture into TiO₂ defect states) for injected electrons into TiO₂ conduction band within the CD/TiO₂ nanocomposites in water after being irradiated with visible light.

By the way, the electron recombination back to the CDs and electron capture into TiO₂ defect states are inferred to be less effective than electron extraction by O₂ in water, which is important for efficient photocatalytic activity. Because the effective electron recombination back to the CDs and electron capture into TiO₂ defect states could also consume conduction band electrons of TiO₂ injected from photoexcited CDs and then promote the ET from CDs to TiO₂, which cannot cause

the PL decay of the CD/TiO₂ nanocomposites with low CD coverage (mass ratio: 1:1000) to be much shorter than that of CD/TiO₂ nanocomposites with high CD coverage (mass ratio: 1:10). This accords well with the fact that the PL quenching (Fig. 4(a)) of the CD/TiO₂ nanocomposites with high CD coverage (mass ratio: 1:50) is much weaker than that of the CD/TiO₂ nanocomposites with low CD coverage (mass ratio: 1:500).

4. Conclusions

In this work, we expand the photosensitive spectrum range of TiO₂ to visible region by the sensitization of CDs. The CD/TiO₂ nanocomposites show obvious CD-coverage-dependent photocatalytic performance under visible light. The CD/TiO₂ nanocomposites with moderate CD coverage exhibit the best photocatalytic performance under visible light, which is more excellent than that of pure TiO₂. The PL dynamic study demonstrates that too little CD coverage results in poor visible light absorption, which limits the photocatalytic activity of the CD/TiO₂ nanocomposites, while too much CD coverage could restrain the extraction of conduction band electrons of TiO₂ injected from photoexcited CDs to generate O₂ and ET process from CDs to TiO₂ by reducing the surface active sites of TiO₂, thus weakening the photocatalytic activity of CD/TiO₂ nanocomposites. These results indicate that rational regulation of CD coverage and the realization of efficient ET process are important means to optimize the photocatalytic performance of CD/TiO₂ nanocomposites. We think that a clear understanding of the CD-coverage-dependent photocatalytic activity is significant for further designing the excellent CD/TiO₂ nanostructure photocatalysts.

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