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Towards efficient photoinduced charge separation in carbon nanodots and TiO$_2$ composites in the visible region†

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In this work, photoinduced charge separation behaviors in non-long-chain-molecule-functionalized carbon nanodots (CDs) with visible intrinsic absorption (CDs-V) and TiO$_2$ composites were investigated. Efficient photoinduced electron injection from CDs-V to TiO$_2$ with a rate of 8.8×10^8 s^{-1} and efficiency of 91% was achieved in the CDs-V/TiO$_2$ composites. The CDs-V/TiO$_2$ composites exhibited excellent photocatalytic activity under visible light irradiation, superior to pure TiO$_2$ and the CDs with the main absorption band in the ultraviolet region and TiO$_2$ composites, which indicated that visible photoinduced electrons and holes in such CDs-V/TiO$_2$ composites could be effectively separated. The incident photon-to-current conversion efficiency (IPCE) results for the CD-sensitized TiO$_2$ solar cells also agreed with efficient photoinduced charge separation between CDs-V and the TiO$_2$ electrode in the visible range. These results demonstrate that non-long-chain-molecule-functionlized CDs with a visible intrinsic absorption band could be appropriate candidates for photosensitizers and offer a new possibility for the development of a well performing CD-based photovoltaic system.

Introduction

Carbon-based nanomaterials, including fullerene, graphene, carbon nanotubes, and carbon nanodots (CDs), have been regarded as a viable alternative to organic dyes and traditional semiconductor quantum dots (QDs) in bioimaging and biosensing, photocatalysis, optoelectronics, and photovoltaics (PVs).[1–8] Especially, CDs, owing to their superior performance in terms of water solubility, stability, toxicity, resistance to photobleaching, and biocompatibility, have recently drawn significant attention.[9–15] The electron injection from CDs to TiO$_2$ was demonstrated to be feasible and the CD-sensitized TiO$_2$ photoelectrodes have been applied in photocatalysis and PVs.[10,16–21] However, it is still a challenge to achieve efficient electron injection from CDs to TiO$_2$ under sunlight,[21] which is a primary

photophysical process in generating photocurrent in CD-based PVs.[22,23] To date, the power conversion efficiency of CD-based PVs has been only 0.13%, as reported by Mirtchev and co-workers.[21] The authors pointed out that the low power conversion efficiency was possibly due to inferior electron injection from CDs to TiO$_2$. Most of the CDs, such as those prepared by laser ablation, electrochemical oxidation, and hydrothermal synthesis, have the main absorption band in the ultraviolet region,[10] which is unfavorable for efficient absorption of solar energy. The CDs used by Mirtchev *et al.* in the CD-based PVs have absorption bands mainly in the ultraviolet region with a tail in the visible region.[21] The long tail absorption band possibly arises from surface defect states.[24,25] The surface defects are unstable and dissipative in energy, which are unfavorable for efficient electron injection in PVs.[23,26–28] In addition, the reported CDs are generally passivated with insulating long chain molecules,[10,12,29] which act as tunneling barriers and are against efficient electron injection and well performing CD-based optoelectronic devices.[22,30] To realize efficient CD-sensitized TiO$_2$ PVs under sunlight, the CDs should exhibit intrinsic absorption in the visible region and be integrated effectively with TiO$_2$. Thus, it is of significant interest to exploit such photoelectrodes based on CD/TiO$_2$ composites to demonstrate the possibility of developing a well performing CD-based PV system.

Previously, we prepared non-long-chain-molecule-functionlized CDs with a strong and specific absorption band in the visible region (CDs-V) extending to 500 nm, which exhibited superior

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† Electronic supplementary information (ESI) available: Measurement section. Optical images of pure TiO$_2$ and CDs-V/TiO$_2$ composites. The normalized absorption spectra of RhB solution and RhB solutions mixed with CDs-V, pure TiO$_2$, CDs-U/TiO$_2$ and CDs-V/TiO$_2$ composites after different visible light irradiation times. The normalized absorption spectra of CDs-U and CDs-V. See DOI: 10.1039/c5cp00444f

photostability compared with organic dyes.[12,29,31,32] Amplified spontaneous green emission and lasing were achieved from the CDs-V.[29] Green photoluminescence (PL) was proposed to be intrinsic state emission and the visible absorption was from intrinsic absorption rather than from surface defect states.[29] In this work, we demonstrated that the CDs-V could be integrated with TiO$_2$ with the absorption band extending to the visible region. Efficient photoelectrodes were prepared by integrating the CDs-V with the TiO$_2$ film on the fluorine-doped tin oxide (FTO) substrate with fast and efficient electron injection from CDs-V to TiO$_2$ with a rate of 8.8×10^8 s^{-1} and an efficiency of 91%. The electron injection properties and charge separation processes for the CDs-V/TiO$_2$ composites were investigated through regulating the surrounding environment. The CDs-V/TiO$_2$ composites exhibited excellent photocatalytic activity under visible light, much better than pure TiO$_2$ and the CDs with the main absorption band in the ultraviolet region (CDs-U) and TiO$_2$ composites, indicating that visible photoinduced electrons and holes in CDs-V/TiO$_2$ composites could be effectively separated. The CD-sensitized TiO$_2$ solar cells were prepared. The incident photon-to-current conversion efficiency (IPCE) results also agreed with efficient charge separation between CDs-V and the TiO$_2$ electrode in the visible range. These interesting results demonstrate that the non-long-chain-molecule-functionlized CDs with visible intrinsic absorption could be appropriate photosensitizers and offer new opportunities for developing a well performing CD-based PV system.

Experimental section

Chemicals and materials

Citric acid (99.5%) and urea (99%) were purchased from Beijing Chemical Works. TiO$_2$ powder (P25, a mixed phase of 80% anatase and 20% rutile; average size 25 nm) was purchased from Degussa. CdSe/ZnS core/shell QDs were purchased from Ocean Nano Tech LLC. All chemicals were used without further purification. The water used in all experiments was purified using a Millipore system.

Synthesis of CDs-V

3 g of citric acid and 6 g of urea were added to 20 mL of deionized water to form a transparent solution. Then the mixed solution was heated in a domestic 750 W microwave oven for about 5 minutes, during which the solution changed from a colorless liquid to a light brown and finally dark brown clustered solid, indicating the formation of CDs. The solid was then dissolved in water and centrifuged to remove agglomerated particles with a speed of 8000 rpm for 20 min three times.

Synthesis of CDs-U

3 g of citric acid and 6 g of urea were added to 20 mL of deionized water to form a transparent solution. The mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave. Then the sealed autoclave was heated to 160 °C and kept for about 4 h.

Fabrication of CD/TiO$_2$ composites

The CD/TiO$_2$ composites were prepared by simply dispersing P25 powder in CDs-U or CDs-V aqueous solution (5 mg mL^{-1}) with constant stirring for 24 h. All the reaction mixtures were washed with water and centrifuged to remove unadsorbed CDs with a speed of 5000 rpm until the supernatant was non-fluorescent. The samples were then dried at 80 °C and kept in a vacuum oven for further experiments and measurements. The color of TiO$_2$ changes from pure white to light brown after integrating with the CDs-V as shown in Fig. S1 (ESI†).

Fabrication of CDs-V/TiO$_2$ composites on glass and FTO substrates

The TiO$_2$ films were spread on glass and FTO substrates by spin-coating P25 paste onto the substrates with a speed of 2500 rpm for 60 s, and the obtained substrates were calcined at 500 °C in air for 60 min and cooled to room temperature naturally. The TiO$_2$ films on glass and FTO substrates were immersed in the aqueous solution of CDs-V with a concentration of 5 mg mL^{-1} for 24 h and then rinsed thoroughly with water.

Fabrication of CD-sensitized solar cells

TiO$_2$ mesoporous films were spread on FTO substrates by successive screen printing of P25 paste as the transparent layer (9.5 ± 0.5 μm) and 30 wt% 200–400 nm TiO$_2$ mixed with 70 wt% P25 paste as the light scattering layer (6.5 ± 0.5 μm). The obtained substrates were calcined at 500 °C in air for 60 min and cooled to room temperature naturally. A modification of the TiO$_2$ mesoporous films with an aqueous solution of TiCl$_4$ (0.04 M) was then performed. For the integration of CDs-V with TiO$_2$ film electrodes, the TiO$_2$ mesoporous films on FTO substrates were immersed in the aqueous solution of CDs-V with a concentration of 5 mg mL^{-1} for 24 h and then rinsed thoroughly with water. Platinum coated FTO was chosen as the counter electrode. The solar cells were prepared by sealing the platinum coated FTO counter electrode and CD-sensitized TiO$_2$ film electrode with a binder clip using a Scotch spacer. Then, a small amount of I$^-$/I$_3^-$ electrolyte was infiltrated into the cell through a pre-drilled hole in the platinum coated FTO counter electrode.

Photocatalytic activity measurements

The photocatalytic activity of the samples was tested through measuring the decomposition rate of Rhodamine B (RhB) molecules under visible light irradiation ($\lambda > 400$ nm) from a Zolix SS150 solar simulator with a 400 nm cut-off filter. The CDs-V, P25 TiO$_2$, CDs-U/TiO$_2$ and CDs-V/TiO$_2$ composites were dissolved in water at a 5 mg mL^{-1} concentration. Each solution (0.1 mL) was mixed with 0.1 mL of RhB aqueous solution (100 ppm), and 3 mL of deionized water was added. The mixed solutions were then transferred into a quartz cuvette and kept away from any source of light for 1 h with magnetic stirring for the adsorption/desorption equilibrium between catalysts and RhB. Then the solutions were exposed to visible light irradiation with continuous stirring. The decrease in the absorbance

value at the characteristic absorption peak of RhB (554 nm) was measured after irradiation for a constant time interval with visible light. The absorption spectra were measured *in situ* using the absorbance mode of a USB4000-UV-VIS Spectrometer with reference light from an Ocean Optics HL-2000 light source. A 510 nm cut-off filter was placed on the light source to prevent the excitation of CDs-U and CDs-V. The reference light was imported from an Ocean Optics QP8-2-SMA-BX fiber and exported from an Ocean Optics QP1000-2-SR fiber.

Results and discussion

The CDs-V were synthesized according to our previous work with the starting materials of 3 g of citric acid and 6 g of urea.[12,29] The CDs-V have a specific intrinsic absorption band in the visible region ranging from 400 to 500 nm (Fig. 1a). The mass extinction coefficients of the CDs-V are much higher than those of CdSe/ZnS core/shell quantum dots (QDs) in the entire absorption band, especially in the visible region as shown in Fig. 1a, which indicates that the CDs could be a good photosensitive material for PVs. A compact integration of CDs-V with TiO$_2$ nanoparticles is necessary for efficient electron injection. The CDs-V/TiO$_2$ composites were prepared by simply mixing them in water under constant stirring for 24 h. The reaction mixtures were diluted with water and centrifuged to remove unadsorbed CDs-V with a speed of 5000 rpm until the supernatant was non-fluorescent. The color of TiO$_2$ changed from pure white to light brown after the integration of CDs-V with TiO$_2$ nanoparticles as shown in Fig. S1 (ESI†), verifying the success in integrating the CDs-V with TiO$_2$ nanoparticles. Fig. 1b shows the UV-Vis absorption spectra (converted from diffuse reflection spectra) of TiO$_2$ and CDs-V/TiO$_2$ composites. Pure TiO$_2$ has almost no absorption above 400 nm, while the CDs-V/TiO$_2$ composites have continuous broad absorption in the visible region ranging from 400 to 600 nm, indicating the adsorption of CDs-V on the surface of TiO$_2$. To further confirm the integration of CDs-V with TiO$_2$ nanoparticles, high resolution

transmission electron microscopic (HRTEM) images of the CDs-V/TiO$_2$ composites were recorded (Fig. 1c and d). As seen from Fig. 1d, the interplanar spacing of 0.35 nm is assigned to the (101) lattice plane of anatase TiO$_2$, while the 0.21 nm lattice fringes agree well with the (102) plane of graphitic carbon, demonstrating the integration of CDs-V with TiO$_2$ nanoparticles. It should be mentioned that no long chain molecules were functionalized on the CDs-V. Thus, the cores of the CDs-V could be closely anchored to the surface of TiO$_2$, resulting in compact integration, as shown in Fig. 1d, which is beneficial for efficient electron injection.

To clearly illustrate the electron injection properties of the CDs-V/TiO$_2$ composites, the PL properties of the CDs-V/TiO$_2$ composites in water were studied. The emission of CDs-V could be quenched by TiO$_2$ after integrating CDs-V with TiO$_2$. The PL dynamics of CDs-V and CDs-V/TiO$_2$ composites in water were collected as shown in Fig. 2. After integration with TiO$_2$ nanoparticles, a shortening in the PL decays of CDs-V was observed. This shortening is ascribed to electron injection from CDs-V to the conduction band of TiO$_2$.[33] The electron injection rate (k_{EI}) and efficiency (η_{EI}) can be calculated from eqn (1) and (2):

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

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

where $\tau_{ave}(CD)$ and $\tau_{ave}(CD/TiO_2)$ are the average lifetimes of the CDs-V and CDs-V/TiO$_2$ composites, respectively.[33–35] The PL decay curves of the CDs-V and the CDs-V/TiO$_2$ composites were fitted with bi- or tri-exponential decay kinetics and the calculated k_{EI} and η_{EI} are summarized in Table 1. The k_{EI} and η_{EI} from CDs-V to TiO$_2$ in water were estimated to be $\sim 0.15 \times 10^8$ s^{-1} and 8.8%, respectively.

To acquire a deep understanding of the electrical interaction between the CDs-V and TiO$_2$, the PL dynamics of the CDs-V/TiO$_2$ composites in air were measured, as shown in Fig. 2.
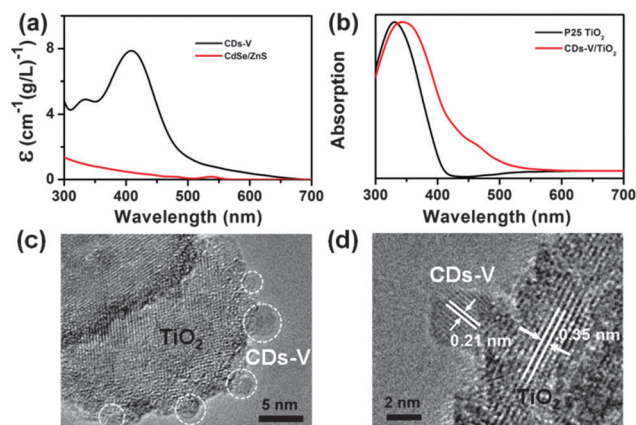

Fig. 1 (a) The mass extinction coefficient spectra of CDs-V in water and CdSe/ZnS core/shell QDs in toluene. (b) Normalized UV-Vis absorption spectra of TiO$_2$ and CDs-V/TiO$_2$ composites. HRTEM images of CDs-V/TiO$_2$ composites (c and d).
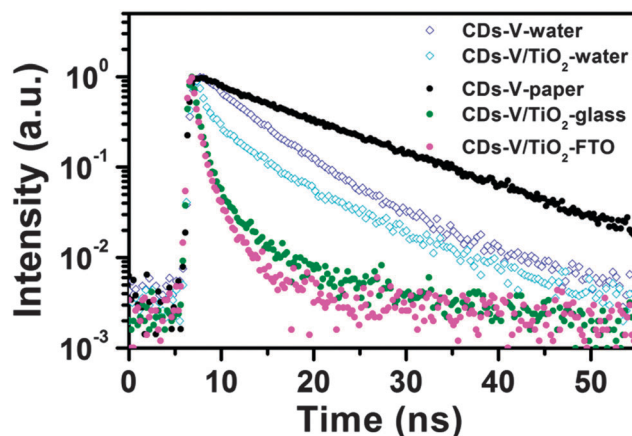

Fig. 2 PL decay curves of the CDs-V and CDs-V/TiO$_2$ composites in water (empty symbols) and the CDs-V integrated with paper and TiO$_2$ films on glass and FTO substrates in air (solid symbols), excitation at 405 nm, monitored at 530 nm.

Table 1 Fit parameters of the PL decay curves of the CDs-V and CDs-V/TiO$_2$ composites in water and CDs-V integrated with paper and TiO$_2$ films on glass and FTO substrates in air. CDs-V-water and CDs-V-paper are the reference samples in water and air, respectively[a]

Samples	τ_1 (ns)	a_1 (%)	τ_2 (ns)	a_2 (%)	τ_3 (ns)	a_3 (%)	χ^2	τ_{ave} (ns)	k_{EI} (10^8 s^{-1})	η_{EI} (%)
CDs-V-water	4.96	74.70	11.02	25.30			1.42	6.49		
CDs-V/TiO$_2$-water	0.60	22.05	4.29	40.14	10.75	37.81	1.25	5.92	0.15	8.8
CDs-V-paper	5.37	11.55	13.10	88.45			1.06	12.20		
CDs-V/TiO$_2$-glass	0.24	50.01	1.51	34.02	9.42	15.97	1.21	2.14	3.9	82
CDs-V/TiO$_2$-FTO	0.15	52.25	1.02	35.40	4.89	12.35	1.12	1.04	8.8	91

[a] The average lifetimes were calculated using the equation $\tau_{ave} = \sum_{i=1}^{n} a_i \tau_i$.[36,37]

The CDs-V/TiO$_2$ composites were prepared by immersing mesoporous TiO$_2$ films on glass or FTO substrates in aqueous solution of the CDs-V with a concentration of 5 mg mL^{-1} for 24 h and then rinsing thoroughly with water to avoid the aggregation of CDs-V. The CDs could be separately adsorbed on paper with enhanced fluorescence as shown in our previous report.[12] The reference sample was prepared by dispersing the aqueous solution of the CDs-V with low concentration on commercially available filter paper, which is an insulator and there is no electron transfer process in the CDs-V/paper composites. As seen from Fig. 2, the PL decay of the CDs-V/TiO$_2$ composites on the glass substrate is significantly shortened, which can be further shortened in the CDs-V/TiO$_2$ composites on the FTO substrate. The k_{EI} and η_{EI} for the CDs-V/TiO$_2$ composites on the glass substrate in air were 3.9×10^8 s^{-1} and 82%, respectively. When the CDs-V were integrated with the TiO$_2$ film on the conductive FTO substrate, k_{EI} and η_{EI} were further increased to 8.8×10^8 s^{-1} and 91%. These results demonstrate that efficient electron injection in the CDs-V/TiO$_2$ composites can be achieved. k_{EI} and η_{EI} from the CDs-V to TiO$_2$ in water were estimated to be $\sim 0.15 \times 10^8$ s^{-1} and 8.8%, respectively, which were much lower than those for the CDs-V/TiO$_2$ composites in air. There are three possible dissipative channels for the electrons in the conduction band of TiO$_2$ in the CDs-V/TiO$_2$ composites, which are electron extraction by O$_2$,[16] electron capture by defect states in TiO$_2$, and electron recombination from TiO$_2$ to the CDs-V, as shown in Fig. 3. It can be inferred that the content of O$_2$ in

air is much higher than that in water, which could efficiently extract the photoinduced injected electrons in the conduction band of TiO$_2$ from the CDs-V. The photoinduced injected electrons in the conduction band of TiO$_2$ from the CDs-V could not be efficiently extracted by O$_2$ in water, due to low concentration of O$_2$ in water (~ 8 mg L^{-1}). So the electron injection from the CDs-V to TiO$_2$ in water was less efficient than that in the composites in air. It can be concluded that the electron capture by defect states in TiO$_2$ and electron recombination from TiO$_2$ to the CDs-V are unfavorable compared with electron extraction by O$_2$. Effective electron capture by defect states in TiO$_2$ and electron recombination from TiO$_2$ to the CDs-V would also extract the photoinduced injected electrons in the conduction band of TiO$_2$ and then promote the electron injection from CDs-V to TiO$_2$ nanoparticles, which cannot lead to such obvious oxygen-content-dependent electron injection properties. After replacing the glass substrate with the conductive FTO substrate in the CDs-V/TiO$_2$ composites, k_{EI} and η_{EI} in air were further increased. This is because the FTO substrate enhances the electron extraction from the conduction band of TiO$_2$ due to the role of the FTO conductive film as another dissipative channel for the electrons. It can be inferred that the visible photoinduced charges in the CDs-V/TiO$_2$ composites could be efficiently separated and collected through an effective loop in the CD-based PVs.

We further investigated the photoinduced charge separation processes in the CDs-V/TiO$_2$ composites by photocatalytic experiments on the CDs-V/TiO$_2$ composites. The decomposition rates of RhB by the CDs-V/TiO$_2$ composites were measured under visible light irradiation ($\lambda > 400$ nm). The absorption spectra of RhB solutions mixed with pure TiO$_2$ and the CDs-V/TiO$_2$ composites measured at different visible light irradiation times are shown in Fig. S2a–e (ESI†). The characteristic absorption peak of RhB aqueous solution (554 nm) mixed with CDs-V/TiO$_2$ composites decreased quickly with peak wavelength exhibiting a blue shift under visible light irradiation (Fig. S2e, ESI†), which might be due to two concomitant photodegradation processes: cleavage of the conjugated chromophore ring structure and de-ethylation of RhB.[38,39] The intensity ratios of the characteristic absorption peak of RhB (554 nm) after irradiation under visible light for a constant time interval (C) and prior to irradiation (C_0) were calculated as shown in Fig. 4a. Fig. 4b shows the photodegradation kinetics ($\ln(C_0/C)$) of RhB solutions containing different components.[16] As seen from Fig. 4a and b, pure CDs-V have almost no degradation of RhB under visible light. The decomposition rate constant of RhB by the
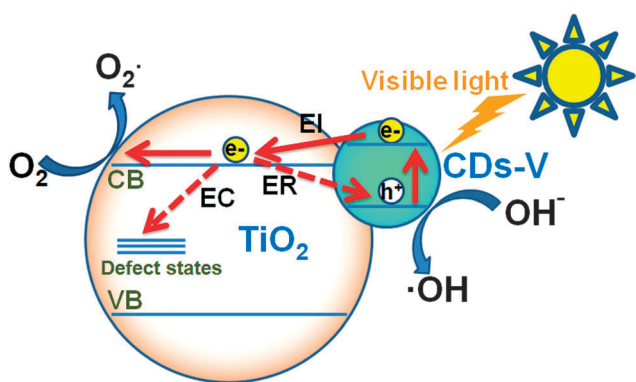

Fig. 3 Schematic illustration for the visible photoinduced electron injection (EI) and possible dissipative channels for the photoinduced electrons in the CDs-V/TiO$_2$ composites (electron extraction by O$_2$, electron capture by defect states in TiO$_2$ (EC) and electron recombination from TiO$_2$ to the CDs-V (ER)) under visible light irradiation. CB: the conduction band of TiO$_2$, VB: the valence band of TiO$_2$.
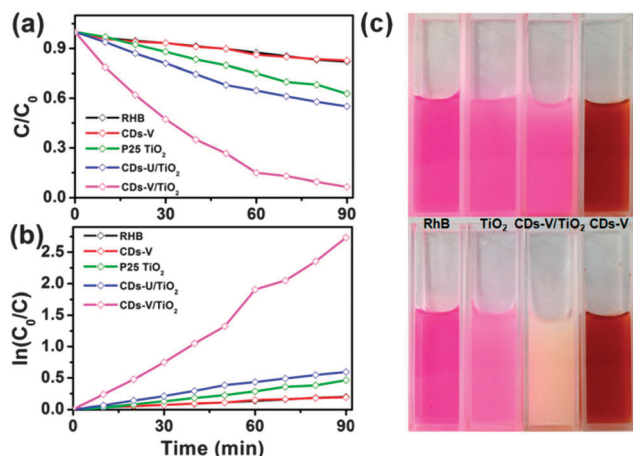
CDs with a visible intrinsic absorption band are appropriate candidates as photosensitizers and indicate that the visible photoinduced charges in the CDs-V/TiO$_2$ composites could be efficiently separated and collected through an effective loop in the CD-based PV system.

Acknowledgements

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