Supporting Information

Rational Design of Carbon and TiO₂ Assembly Materials: Overcover or Strew, Which is better for Photocatalysis?

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1. Chemicals

Tetrabutyl titanate (TBOT), hexanoic acid (HA), glucose and methylene blue (MB) dye were purchased from Sinopharm Chemical Reagent Company. All the chemicals were of AR grade. Resols with low molecular weight (500~1000) was amicably afforded by Shandong Shengquan Chemical Co. LTD. Ultrapure water used in the experiment was purified with Mill-Q (electric resistivity 18.2 MΩ·cm) water purification system.

2. Synthesis Process

2.1 Catalyst Preparation

Synthesis of spherical anatase TiO$_2$

A uniform spherical anatase TiO$_2$ particles with diameter of 200~300 nm was fabricated by a hydrolysis of metal alkoxide method in the presence of alkyl chain carboxylic acids.$^{[1]}$ In a typical procedure, 0.46 g hexanoic acid was dissolved in 230 ml ethanol, and 1.7 g TBOT (10% ethanol solution) was added with stirring at room temperature. 35 ml H$_2$O was dropped into the mixed solution with vigorous stirring at room temperature, and the mixture was allowed to react at room temperature for 12 h. The products were obtained after centrifugal separation and washed with ethanol for three times, which was ready for the next modification with carbon materials. The as-prepared TiO$_2$ sample used for photoactivity comparison was calcined at 550$^\circ$C for 5 h to remove the remaining organic ligand.

Synthesis of TiO$_2$-Cdot and TiO$_2$@C

The as-prepared TiO$_2$ without calcination was easily strewed with carbon nanodots by using resols as carbon precursor. Typically, 0.4 g colloidal TiO$_2$ suspension was dispersed in 300 mL pH 12 NaOH aqueous solution. Resols with low molecular weight (500~1000) dissolved in pH 12 NaOH aqueous solution. Then, the two solutions were mixed and stirred at 60 $^\circ$C for 12 h to allow for the polymerization of the resol precursors on the surface of TiO$_2$. Khaki-colored composite was obtained by centrifugation (4000 rmp, 15 min) and washed with water for several times to remove the excessive NaOH, then, dried at 80$^\circ$C. Subsequently, it was calcined at 550$^\circ$C for 5h under Ar conditions. The carbon nanodots content can be controlled by simply increasing or decreasing the mass ratio of resols and TiO$_2$.

TiO$_2$@C was prepared by hydrothermal method using glucose as carbon precursor to obtain ultrathin carbon layer. Typically, the as-prepared calcined TiO$_2$ (0.4 g) and 0.5 g glucose were dissolved in 35mL water. The solution was subsequently transferred to a 40 mL autoclave and hydrothermally treated at 180$^\circ$C for 4 h. Then, the samples were collected via centrifugation and dried in an oven at 80$^\circ$C for 4 h. Finally, it was calcined at 550$^\circ$C for 5h under Ar conditions.
3. Catalyst Characterization

3.1 Instruments

A HITACHI S-4800 Scanning Electron Microscope (SEM) equipped with a field-emission gun operated at 5.0 kV was used to characterize the morphology of the as-obtained product. Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images were obtained using a TECNAI G2 high resolution transmission electron microscope operating at 200 kV.

Powder X-ray diffraction data were collected on polycrystalline products mounted on Si (111) zero background sample holders with a Bruker D8 Advance diffractometer. PXRD patterns were acquired using Cu Kα radiation with a step width of 0.02 in a 2θ range from 10 to 85 degree. The scan speed, applied voltage and current were 0.2, 40 kV and 40 mA, respectively.

X-ray photoelectron spectroscopy (XPS) spectra were performed with a Phobios 100 electron analyzer (SPECS GmbH) equipped with 5 channeltrons, using an unmonochromated Mg Kα X-ray source (1253.6 eV). C 1s energy binding peaks centered at 284.6 eV was used for calibration. The Deconvolution of the XPS peaks was done by a XPS Peak fitting program (version 4.1).

The UV-Vis-NIR diffuse reflectance spectrum was measured on a VARIAN Cary 5000 spectrophotometer with BaSO4 powder used as a reference (100% reflectance). Nitrogen adsorption–desorption isotherm measurements were carried out on a Micromeritics ASAP2020 Surface Area and Porosity Analyzer. The relative pressure value (P/Po) used for estimation of the BET surface areas was in the range from 0.0572 to 0.3005.

ZETA potential measurements were performed on a Zetasizer NanoZS Malvern Instrument equipped with a 633nm wavelength laser. The samples were dispersed in water in a content of 0.4mg/mL.

The solid fluorescence spectrum was carried out with an Edinburgh FLS920 spectrofluorimeter (Edinburgh Instruments Ltd, England) equipped with a xenon lamp.

3.2 IR spectrum for TiO2-HA(1); TiO2-HA-Resol(2); TiO2-Cdot(3) and TiO2(4)
As shown in Figure S1, the FTIR spectrum distinctly showed that the absorbance band at 2960–2860 cm$^{-1}$, 1531 cm$^{-1}$, 1441 cm$^{-1}$, 1376 cm$^{-1}$ ascribed to the remained hexanoic acid (Figure S1, Line 1) disappeared and the absorbance band peaked at 3448.8 cm$^{-1}$ ascribed to the hydroxyl group of resols obviously increased after intertwined with the polymerized resol (Figure S1, Line 2). After calcination at 550°C, the polymerized resols were carbonized with the disappearance of the absorbance band peaked at 1345–1012 cm$^{-1}$ ascribed to benzene ring of resol (Figure S1, Line 3) and uniform carbon nanodots with diameter of 20–30 nm were formed on the surface of TiO$_2$.

3.3 TGA measurements

![Figure S2. The weight loss of the as-prepared TiO$_2$-Cdot nanoparticles by the thermogravimetric analysis](image)
3.4 HRTEM of TiO$_2$-Cdot and TiO$_2$@C

![HRTEM of TiO$_2$@C](image1)

**Figure S3.** HRTEM of TiO$_2$@C

![HRTEM Patterns of TiO$_2$-Cdot.](image2)

**Figure S4.** HRTEM Patterns of TiO$_2$-Cdot.

The as-prepared TiO$_2$@C had an ultrathin carbon shell with 2–3 nm thickness (Figure S3). As shown in Figure S4, there were three lattice spacing observed from the carbon dots anchored on the TiO$_2$ surface: one broad centered at 0.43 nm was attributed to highly disorder carbon and another observed at 0.41 nm was ascribed to the inter-chain distance of densely packed alkyl chains$^{[2]}$; the lattice spacing observed at 0.23 nm was ascribed to the (100) facet of graphite.$^{[3]}$

3.5 XRD, Raman spectrum and XPS
Figure S5. XRD patterns of TiO$_2$(Red), TiO$_2$@C(Blue) and TiO$_2$-Cdot(Black).

Figure S6. Raman spectrum of TiO$_2$ (Black), TiO$_2$-Cdot (Red) and TiO$_2$@C (Blue).

Figure S7. XPS of TiO$_2$-Cdot

Figure S8. XPS of Ti2p
The X-ray diffraction (XRD) patterns of the as-prepared TiO2-Cdot composites, TiO2@C and TiO2 are shown in Figure S5. They almost have the same XRD peaks localized at 20 values of 25.3, 37.8, 48.0, 53.9, 55.1, 62.7, 68.8, 70.3, and 75.0° ascribed to TiO2 with typical anatase phase (JCPDS card No.21-1272) regardless of the presence of carbon materials. It was reported that there was strongest (002) reflection of graphite layers located at 2θ = 25.9° (JCPDS 26-1079). However, due to the amorphous phase or being shielded by the stronger diffraction peak localized at 25.3° of TiO2, no discriminable diffraction peaks belonging to the carbon nanodots are observed in the TiO2-Cdot nanocomposites. Then, Structural properties of the TiO2-Cdot composites materials were further investigated by Raman scattering as shown in Figure S6. Both TiO2-Cdot and TiO2@C has the same four Raman lines located at 149.4, 392.5, 507.2 and 627.9 cm\(^{-1}\) which were ascribed to TiO2 anatase phase. Compared with the pure TiO2, discriminable displacements for the four peaks were observed, which was consistent with the previously reported carbon-doped TiO2 material.\(^{[4]}\)\(^{[5]}\) The two adjacent strong peaks located at 1379 cm\(^{-1}\) (D-band) and 1585 cm\(^{-1}\) (G-band) in the Raman spectra confirm the presence and partial graphitization of carbon,\(^{[4]}\) in agreement with the results observed from the HRTEM images (Figure S4).

The chemical state of surface species in TiO2-Cdot samples was analyzed by XPS. As shown in Figure S7, the XPS survey scan spectra demonstrated that Ti, C and O elements existed in the surface layer of the as-papered nanostructures. The peak located at 464.6 eV corresponds to the Ti 2p1/2 and another one located at 458.67 eV was assigned to Ti 2p3/2(Figure S8).\(^{[1,6]}\) C1s and O1s peaks were analyzed by XPS Peak fitting program (version 4.1). Four peaks were observed in the C 1s binding region peaks centered at 284.6eV, 282.9eV, 286.5eV, and 289.1ev which were ascribed to C–C, C*-O/Ti, C*-O and -C*=O groups, respectively (Figure S9).\(^{[1,6]}\) O1s fitting peaks spectrum indicated that four chemical states peaks centered at 530.0 eV, 531.9 eV and 528.4 eV were ascribed to crystal lattice oxygen (Ti-O*), surface –*OH species, and C-O*/Ti, respectively (Figure S10).
3.6 BET measurements

Figure S11. Isotherm of low temperature nitrogen adsorption and desorption of TiO$_2$

Figure S12. Isotherm of low temperature nitrogen adsorption and desorption of TiO$_2$@C
Figure S13. Isotherm of low temperature nitrogen adsorption(1) and desorption(2) of TiO₂-Cdot

Nitrogen adsorption–desorption isotherm measurements showed that the as-prepared TiO₂-Cdot, TiO₂@C and TiO₂ samples have an average BET surface area of approximately 62.9 m²g⁻¹, 19.2 m²g⁻¹ and 10.4 m²g⁻¹, respectively (Figure S11~S13).

3.7 UV-Vis-NIR Diffuse Reflectance Spectra

Figure S14. Diffuse reflectance spectra of (1) TiO₂, (2) TiO₂-Cdot, (3) TiO₂@C.

4.1 Adsorption and Photoactivity Measurement
Figure S15. Bar plots showing the remaining MB dyes in solution (Initial concentration of MB, 30mg/L): (1) Blank, (2) TiO$_2$, (3) TiO$_2$@C, (4) TiO$_2$-Cdot.

Figure S16. MB dyes photodegradation Plots of TiO$_2$-Cdot with different carbon contents under sunlight.

Figure S17. MB dye photodegradation Plots of TiO$_2$, TiO$_2$-Cdot and TiO$_2$@C under visible light.
The photodegradation of methylene blue (MB) dyes was performed on a reformative XPA-7 photocatalytic reaction instrument. The degradation effect was measured by the absorption spectroscopic technique. In a typical process, aqueous solution of the MB dyes (50 mg/L, 30 mL, unless specialized) and the as-prepared photocatalysts (TiO$_2$, TiO$_2$-Cdot and TiO$_2$@C, 30 mg) were mixed in a 50 mL cylindrical quartz tubes for overnight in darkness to test their adsorption capacity for MB dyes(Figure S15). Then, it was exposed to the visible light or sunlight irradiation produced by a 1000 W Xe lamp with or without the light cutoff filters(λ >420 nm) under ambient conditions and magnetic stirring. At given time intervals, the reaction solution was sampled and analyzed by a UV-Visible spectrophotometer at λ$_{max}$=664nm(Figure S19).(UV 2250, Shimadzu).
It has been well demonstrated that photochemical degradation of methylene blue (MB) dye by TiO$_2$ or carbonaceous TiO$_2$ materials was approximated fitted to a pseudo first order reaction at low dye concentrations$^{[7]}$. In this paper, the degradation rate constant was determined from the equation $\ln(C/C_0) = -kt$, where $C_0$ and $C$ are the dye concentrations at times 0 and $t$, respectively, and $k$ is the pseudo-first-order rate constant (min$^{-1}$). Figure S17 and Figure S18 show the linear fit between the $-\ln(C/C_0)$ and irradiation time that supports this conclusion.

4.2 Photocurrent Measurement

![Graph of photocurrent density](image1)

**Figure S20.** Photocurrent density of (1)TiO$_2$, (2)TiO$_2$@C, (3) TiO$_2$-Cdot under visible light

![Graph of photocurrent density](image2)

**Figure S21.** Photocurrent density of TiO$_2$@C under sunlight (1) and visible light (2)

Photocurrent measurement was carried out on an electrochemical analyzer (CHI660D Instruments) by a standard three-electrode system. The as-prepared samples(TiO$_2$, TiO$_2$-Cdot and
TiO$_2@$(C), Pt sheet and saturated calomel electrode were used as working electrodes, counter electrode and reference electrode, respectively. The working electrode was prepared as follows: 0.05 g of the sample was grinded with 0.1 g terpinol to make slurry. Then, the slurry was coated onto a 4 cm×1 cm Indium Tin Oxide-coated glass (ITO glass) electrode by doctor blade technique. Next, these electrodes were dried in an oven and calcined at 290°C for 30 min under Ar conditions. Then the electrode was immersed in 0.1 M NaClO$_4$ aqueous solution to measure the transient photocurrent under 300W Xe arc lamp irradiation at 0.6V vs. saturated calomel electrode.

5. Zeta Potential Measurement

![Zeta Potential Distribution](image)

**Figure S22.** Zeta Potential of TiO$_2$-Cdot(1,-33.4mV), TiO$_2$(2,-39.5mV) and TiO$_2@$(C(3, -11.4 mV) under irradiation by a 633nm wavelength laser

6. Solid Fluorescence Measurement

![Solid Fluorescence Spectra](image)

**Figure S23.** Solid fluorescence spectra of TiO$_2$(1), TiO$_2$-Cdot(2), TiO$_2@$(C(3) and SiO$_2$-Cdot(4)
As shown in Figure S23, after strewed with carbon nanodots or overcovered with carbon layer, the fluorescence emission ($\lambda_{ex}=260$nm) of TiO$_2$ centered at 398nm, 426nm and 468nm was markedly quenched. Moreover, compared with the SiO$_2$-Cdot contrast material, in which SiO$_2$ is light inert, the emission peaks of TiO$_2$-Cdot and TiO$_2$@C centered at 385nm which were ascribed to the carbon species$^8$, were markedly quenched in different degree, which was probably caused by the injection of electrons photogenerated from carbon species into CB of TiO$_2$.

7. References