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Article

In-situ route for the graphitized carbon/TiO₂ composite photocatalysts with enhanced removal efficiency to emerging phenolic pollutants

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ARTICLE INFO

Article history:

Received 17 January 2020

Accepted 23 February 2020

Published 5 September 2020

Keywords:

Titanium dioxide

Carbon

Visible-light photocatalysis

Composite

Phenolic compound

Water treatment

ABSTRACT

TiO₂ is the most photoactive material because of its superstrong photooxidizing ability, and TiO₂ photocatalysis has been widely applied in sustainable water treatment and environmental remediation. However, poor sunlight or visible-light harvesting efficiency and fast recombination rate of the photogenerated charge carriers severely limit the practical applications of TiO₂. To overcome these problems, the present work demonstrates a facile *in-situ* co-condensation method combined with hydrothermal treatment to prepare a series of graphitized carbon/TiO₂ composite photocatalysts, and anatase TiO₂ phase and π - π -conjugated polycyclic aromatic carbon structure are created simultaneously. As-prepared TiO₂/C composites exhibit remarkably high visible-light photocatalytic activity in the degradation of aqueous emerging phenolic pollutants, acetaminophen (APAP) and methylparaben (MPB), and apparent rate constant of the TiO₂/C composite with carbon doping level of 10.3% for APAP and MPB removal is 7.6 and 2.8 times higher than that of bare TiO₂, and 6.2 and 2.6 times higher than that of Degussa P25 TiO₂. Based on the results of photoelectrochemical experiments, indirect chemical probe measurements, and ESR spectroscopy, it is verified that doping TiO₂ with graphitized carbon is responsible for this enhanced photocatalytic activity, which renders the improved visible-light harvesting ability, the accelerated separation of the photogenerated charge carriers, and enlarged BET surface areas. Through analyzing the intermediates yielded in the photodegradation process, the pathway of visible-light photocatalytic degradation of APAP and MPB over the TiO₂/C composite is proposed.

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1. Introduction

Green photocatalytic technology has a wide range of applications in sustainable water treatment and environmental remediation, including photodegradation of persistent organic pollutants, photoreduction of toxic heavy metals and water disinfection [1,2]. For various photocatalytic processes, the photocatalytic efficiency strongly depends on the performance

of photocatalysts, and titanium dioxide (TiO₂) [3], bismuth oxyhalides (BiOX, X = Cl, Br or I) [4,5] and graphitic carbon nitride (g-C₃N₄) [6–8] are the prevalent and excellent photocatalysts applied in water treatment and environmental remediation. Moreover, till now, TiO₂ is the most photoactive material in the degradation of organic pollutants owing to its superstrong photooxidizing ability, chemical stability and low cost [1,3,9–14]. Different from BiOX and g-C₃N₄ photocatalysts, TiO₂

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This work was supported by the National Natural Science Foundation of China (21573038 and 51608102).

DOI: 10.1016/S1872-2067(20)63565-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 9, September 2020

possesses unique energy band structure, and both hydroxyl radicals ($\cdot\text{OH}$) and superoxide radicals ($\cdot\text{O}_2^-$) can be directly generated on TiO_2 under suitable light irradiation and act as important oxidative species for the complete degradation of organic pollutants. Specifically, the valence band (VB) edge potential of TiO_2 (ca. +2.90 V vs. NHE) [15] is the most positive, rendering it the strongest oxidizing ability. The photogenerated holes (h_{VB}^+) on the VB level of TiO_2 can easily oxidize OH^- ion or H_2O molecule to produce $\cdot\text{OH}$ radicals because the VB edge potential of TiO_2 is more positive than the redox potential of $\text{OH}^-/\cdot\text{OH}$ (+1.99 V vs. NHE) [16] or $\text{H}_2\text{O}/\cdot\text{OH}$ (+2.27 V vs. NHE) [17]; meanwhile, the conduction band (CB) edge potential of TiO_2 (ca. -0.30 V vs. NHE) [18] is more negative than the redox potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.046 V vs. NHE) [19], and the photogenerated electrons (e_{CB}^-) on the CB level of TiO_2 can reduce oxygen to yield $\cdot\text{O}_2^-$ radicals. However, low quantum efficiency due to fast recombination of $e_{\text{CB}}^- - h_{\text{VB}}^+$ as well as poor sunlight utilization efficiency because of wide band gap severely limit the practical applications of TiO_2 in water treatment and environmental remediation [1]. Till now, extensive research work has focused on the improvement of the photocatalytic efficiency of TiO_2 by extending its visible-light absorption and reducing the recombination of $e_{\text{CB}}^- - h_{\text{VB}}^+$. For this purpose, metal doping, surface modification with metal elements, modification with non-metal elements as well as coupling TiO_2 with other semiconductors or metal-complex are the popular strategies [20,21]. Recently, great attention has been devoted to doping TiO_2 with carbon materials, including carbon dots, graphene, carbon nanotubes, active carbons and carbon spheres. The enhanced photocatalytic activity of the resulting TiO_2/C composites is attributed to the synergistic effect of increased visible-light harvesting ability contributed from C 2p states and the accelerated separation of $e_{\text{CB}}^- - h_{\text{VB}}^+$ caused by interfacial charge transfer [22–27].

In the present work, a facile one-step sol-gel co-condensation method combined with low temperature hydrothermal treatment is developed to fabricate TiO_2/C composite photocatalysts, and anatase TiO_2 phase and graphitized carbon with π - π -conjugated polycyclic aromatic carbon structure are created simultaneously during the above process. Meanwhile, compared with anatase TiO_2 prepared by calcination at high temperature, the as-prepared TiO_2 and TiO_2/C composites exhibit micro/mesoporosity with large surface areas, which can not only provide high population of active sites but also improve the utilization efficiency of the incident light through repeatedly reflected inside the mesopores. Additionally, current one-step preparation strategy may ensure intimate contact between anatase TiO_2 nanocrystals and polycyclic aromatic carbon sheets, which is expected to further promote $e_{\text{CB}}^- - h_{\text{VB}}^+$ separation. All of these advantages are anticipated to improve the visible-light photocatalytic activity of TiO_2 in degradation of organic pollutants. To study the visible-light photocatalytic activity of the as-prepared TiO_2/C composites, two emerging phenol derivatives, acetaminophen (APAP) and methylparaben (MPB), were chosen as the target pollutants. APAP is a well-known analgesic and antipyretic pharmaceutical, and it has been frequently detected in surface

water and can lead to the severe hepatotoxicity and nephrotoxicity. MPB is widely used as preservative, and it is regarded as an endocrine disrupting chemical and can cause adverse effects on human health and ecological security [28–32]. Therefore, it is urgent to search for efficient and sustainable approaches to remove phenolic pollutants in water environments. Both APAP and MPB show light absorption in the range of 200–300 nm, and therefore the visible-light photosensitized effect in TiO_2/C -photocatalyzed organic pollutant degradation process can be excluded. The present studies find out that the visible-light photocatalytic activity of as-prepared TiO_2/C composites is superior to bare TiO_2 and Degussa P25 TiO_2 in degradation of APAP and MPB; and carbon doping level influences the activity obviously. On the basis of the results of the photoelectrochemical experiment, indirect chemical probe method and DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) electron spin resonance (ESR)-trapping measurement, the enhanced visible-light photocatalytic activity of TiO_2 after doping graphitized carbon species is reasonably explained. Additionally, the pathway of visible-light photocatalytic degradation of APAP and MPB over the TiO_2/C composite is tentatively put forward through analyzing the intermediates yielded in the photodegradation process. The present work therefore provides some new hints on designing and developing efficient TiO_2/C composite photocatalysts for sustainable water treatment and environmental remediation.

2. Experimental

2.1. Preparation of the TiO_2/C composite photocatalysts

Typically, titanium isopropoxide (TTIP, 98%, 6 mL) was added to isopropanol (30 mL) dropwise under stirring, while a suitable amount of glucose (0.05760, 0.1728, 0.2880 and 0.5760 g, respectively, to adjust carbon doping levels in the composite) was dissolved in deionized water (2 mL). Subsequently, the above aqueous glucose solution was added to the TTIP/isopropanol solution under vigorous stirring. The resulting suspension was adjusted to pH 1–2 with HCl (8 mol L⁻¹) solution, and the suspension was continuously stirred at room temperature for 1 h. After being heated at 45 °C for 1 h, the formed homogeneous white hydrogel was transferred into a Teflon-lined autoclave and heated at 200 °C for 1 h. Finally, the obtained brown precipitate was centrifuged and then washed with water and absolute ethanol completely. After being dried at 80 °C for 10 h, the TiO_2/C -x composite photocatalyst was obtained, where x refers to carbon doping level (wt%) in the composite.

For comparison, pure TiO_2 was also prepared following the above process in the absence of glucose, and the acidity of the system was adjusted to pH $\approx$ 2 with HCl (8 mol L⁻¹) solution.

2.2. Characterization of the TiO_2/C composite photocatalysts

Carbon doping levels in the composites were determined with a PerkinElmer Pyris Diamond thermogravimetric analysis (TGA) instrument under air atmosphere. X-ray diffraction

(XRD) patterns were recorded on a Japan Rigaku D/max 2000 X-ray diffractometer. FESEM observation was performed on a XL-30 ESEM-FEG field emission scanning electron microscope. Transmission electron microscopy (TEM) images were obtained using a JEM-2100 high resolution transmission electron microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were observed on a VG-ADES 400 instrument with Mg $K\alpha$ -ADES source at a residual gas pressure of lower than 10^{-8} Pa. Nitrogen gas porosimetry measurement was performed on a Micrometrics ASAP 2020M PLUS HD88 surface area and porosity analyzer. UV-vis diffuse reflectance spectra (UV-vis/DRS) were obtained using a Cary 500 UV-vis-NIR spectrometer.

2.3. Evaluation of photocatalytic performance of TiO_2/C composites

Photocatalytic degradation of aqueous APAP and MPB over the TiO_2/C composites was tested at ambient temperature in a self-made quartz photoreactor with the starting concentrations of APAP and MPB at 10 mg L^{-1} , and stirring was applied throughout the reaction process. The external visible-light irradiation was supplied by a PLS-SXE300 Xe lamp (300 W) with IR and 400 nm cut filters. The catalyst mass was 50 mg, and aqueous APAP or MPB solution volume was 50 mL. Before light irradiation, the suspension containing the catalyst powder and aqueous pollutant solution was ultrasonically dispersed for 10 min followed by stirring in the dark for 60 min to accomplish adsorption-desorption equilibrium between the catalyst and reactant. At given time intervals during the reaction, 2 mL of suspension was taken out and centrifuged, followed by passing through a $0.22 \mu\text{m}$ filter membrane. Changes of the concentrations of APAP or MPB during the degradation process were monitored by an Agilent 1260 HPLC equipped with a C18 column and UV detector at $\lambda = 242$ or 255 nm . Mobile phase for APAP or MPB determination was water/methanol (80/20) or water/acetonitrile (50/50), respectively. The intermediates generated were identified by a Thermoscientific Q EXACTIVE Focus HPLC-MS. The mineralization ability of the TiO_2/C composites was studied by monitoring the changes of total organic carbon (TOC) values during the process of photocatalytic degradation of APAP (initial concentration of 20 mg L^{-1}). After stirring the suspension of aqueous APAP and TiO_2/C powder for 120 min, 5 mL of suspension was taken from the reactor at the irradiation time of 0, 120, 240 and 360 min, respectively, followed by centrifugation and passing through a $0.22 \mu\text{m}$ filter membrane. The obtained clear solution was analyzed on a German analytikjena multi N/C 3100 TOC analyzer. To exclude possible interference of the catalyst on the TOC determination, a blank test in the absence of APAP was also performed under the same process mentioned above. Indirect chemical probe technique was applied to identify the active species yielded during the process of TiO_2/C -photocatalyzed degradation of APAP or MPB, and *tert*-butyl alcohol (*t*-BuOH, 1 mmol L^{-1}), ethylenediaminetetraacetic acid (EDTA-2Na, 1 mmol L^{-1}) and nitrogen were used as the scavengers of hydroxyl radical ($\cdot\text{OH}$), $h\nu\text{B}^+$ and superoxide radicals ($\cdot\text{O}_2^-$), respectively. DMPO

(5,5-dimethyl-1-pyrroline-*N*-oxide) electron spin resonance (ESR) spectra were recorded on a JES-FA200 ESR spectrometer.

2.4. Photoelectrochemical measurements

All photoelectrochemical measurements were conducted on a conventional three-electrode electrochemical workstation (CHI 660E, China) equipped with an Ag/AgCl (saturated KCl) and a Pt wire as the reference electrode and the counter electrode, respectively. A PLS-SXE300 Xe lamp (300 W) was used as a light source. The fluorine-doped tin oxide (FTO) coated with the photocatalyst film was used as the working electrode. The transient photocurrent response was determined by the amperometric *I*-*t* curves with a bias voltage of +1.0 V for 200 s in 0.01 mol L^{-1} Na_2SO_4 solution, electrochemical impedance spectroscopy (EIS) Nyquist analysis was performed by applying an alternating current voltage amplitude of 5 mV in 0.5 mol L^{-1} Na_2SO_4 solution within a frequency range of 1000–50 kHz, and the Mott-Schottky (MS) plot was obtained in a 0.5 mol L^{-1} Na_2SO_4 solution by impedance measurement at a fixed frequency of 1 kHz.

3. Results and discussion

3.1. Preparation and characterization of TiO_2/C composite photocatalyst

Generally, TiO_2 photocatalysts are prepared by the heat treatment of amorphous titania precursor (550–750 °C). However, high temperature treatment for attaining crystallinity often leads to particle agglomeration, small surface area and sintering associated with the collapse of mesoporous structure [33], which result in a remark decrease in the photocatalytic activity. In comparison to a variety of chemical preparation methods, hydrothermal treatment is a suitable low-temperature (120–200 °C) strategy to prepare TiO_2 photocatalysts with large surface area and nanometer sizes [34]. Here, TiO_2/C composite photocatalysts are simply prepared *via* one-step hydrolysis and condensation of TTIP (titanium source) at acidic condition (pH = 1–2) in the presence of glucose (carbon source) followed by hydrothermal treatment. After the above steps, TiO_2 with mainly anatase phase is formed; meanwhile, glucose is suffered from incomplete carbonization to yield graphitized carbon with π - π -conjugated polycyclic aromatic carbon structure. By adjusting the initial glucose adding amount from 0.0576, 0.1728, 0.2880 to 0.5760 g, the carbon doping levels in the TiO_2/C composites are well adjusted, and they are 4.0%, 5.6%, 10.3% and 13.1%, respectively, estimated by TGA analysis (Fig. S1 in the electronic Supplementary Information, and weight loss from 200 to 500 °C corresponds to the complete decomposition of the graphitized carbon framework). The results are consistent with the expected values. More importantly, the current process not only produces the TiO_2/C composites with large BET surface areas but also ensures the intimate contact between anatase TiO_2 nanocrystals and carbon materials at the interface. The struc-

ture, morphological and porosity properties as well as optical absorption properties of the TiO_2/C composites are characterized and shown below.

3.1.1. Structural information

The phase structures of as-prepared TiO_2 and TiO_2/C composite photocatalysts are characterized by XRD measurements. As shown in Fig. 1a, bare TiO_2 shows pure anatase phase with the characteristic diffraction peaks appearing at 25.3° , 37.8° , 48.0° , 53.9° , 55.1° , 62.7° , 68.8° , 70.3° , and 75.0° [JCPDS 21-1272] [35]. In the cases of TiO_2/C composites with lower carbon doping level (4.0 wt% and 5.6 wt%), they exhibit major anatase phase with the characteristic diffraction peaks positioning at 25.3° , 37.8° , 48.0° , 53.9° , 55.1° , 62.7° , 68.8° , 70.3° , and 75.0° , respectively; additionally, three weak diffraction peaks found at 27.4° , 36.1° , and 41.2° are assigned to rutile phase [JCPDS 21-1276] [36], reflecting that the $\text{TiO}_2/\text{C-4.0}$ and $\text{TiO}_2/\text{C-5.6}$ also have minor rutile phase. As for the other two TiO_2/C composites with higher carbon doping level (10.3 and 13.1 wt%), they exhibit pure anatase phase. The above result is caused by the adding amount of glucose, which affects the acidity of the preparation system and thus the phase structure of TiO_2 . At a lower adding amount of glucose, the acidity of the preparation system is much higher ($\text{pH} \approx 1.0$), which leads to that the $\text{TiO}_2/\text{C-4.0}$ and $\text{TiO}_2/\text{C-5.6}$ composites possess some rutile phase except major anatase phase. This is due to the fact that the strong acidity of the system is favorable for the formation of rutile phase [37]. However, the acidity of the system

($\text{pH} \approx 1.5\text{--}2.0$) decreases after further increasing the adding amount of glucose, along with the $\text{TiO}_2/\text{C-10.3}$ and $\text{TiO}_2/\text{C-13.1}$ having pure anatase phase. As for bare TiO_2 , it is prepared at $\text{pH} \approx 2.0$, as expected, it exhibits pure anatase phase.

The anatase phase structure of the TiO_2/C composites is further confirmed by the Raman scattering spectroscopy analysis; more importantly, the Raman scattering spectrum also provides an important evidence to verify the π - π -conjugated graphitic carbon structure of the doped carbon materials in the TiO_2/C composites. The Raman scattering spectrum of the representative sample, $\text{TiO}_2/\text{C-10.3}$, is presented in Fig. 1b. Four characteristic Raman scattering peaks with high intensities found at 154.8 (E_g), 398.5 (B_{1g}), 504.0 (B_{1g}) and 629.8 cm^{-1} (E_g) are originated from anatase TiO_2 [38], while other two bands with relatively weak intensities centered at 1319.6 and 1585.2 cm^{-1} are indexed to the disordered (D) and graphitic (G) bands of the sample, respectively. D band reflects disordered portion or defective graphitic structure that is ascribed to edges, other defects and disordered carbon, corresponding to A_{1g} D breathing mode of sp^3 -bonded carbon atoms. G band is originated from E_{2g} G vibrational mode that presents in sp^2 -bonded graphitized carbons [38–42]. However, owing to extremely strong Raman scattering peaks of anatase TiO_2 and low doping level of graphitized carbons, these peaks are relatively weak. We therefore further confirm the graphitic carbon structure of the doped carbon materials in the TiO_2/C composites by XPS surface probe analysis, and the three TiO_2/C composites, $\text{TiO}_2/\text{C-5.6}$, $\text{TiO}_2/\text{C-10.3}$, and $\text{TiO}_2/\text{C-13.1}$, are all

Fig. 1. XRD patterns of TiO_2 and various TiO_2/C composites (a), Raman scattering spectrum of the $\text{TiO}_2/\text{C-10.3}$ (b), XPS survey spectra (c) and high-resolution XPS spectra of TiO_2 , $\text{TiO}_2/\text{C-5.6}$, $\text{TiO}_2/\text{C-10.3}$, and $\text{TiO}_2/\text{C-13.1}$ composites in the C 1s (d), Ti 2p (e), and O 1s (f) binding energy regions.

tested; additionally, as a reference, commercial graphene is also tested. XPS survey spectra of three TiO_2/C composites shown in Fig. 1c clearly indicate the presence of oxygen, titanium and carbon elements. As displayed in Fig. 1d, high resolution XPS spectrum of graphene in the C 1s binding energy region shows only one strong peak at 284.6 eV, which is assigned to sp^2 -bonded carbon atoms in the π -conjugated graphitic carbon framework. The result indicates the perfect graphitic carbon structure of graphene. This strong peak is also found in the C 1s XPS spectra of three tested TiO_2/C composites; additionally, some weak peaks still appear in the C 1s XPS spectra of the composites, and they are attributed to small amount of sp^3 -bonded carbon atoms (285.8 eV) as well as carbon species from oxygen-containing C–O (286.4 eV) and C=O (288.5 eV) groups at the edges of the graphitic carbon framework [25,43]. The above result firmly confirms that the primary graphitic carbon structure is formed after sol-gel process followed by hydrothermal treatment of both Ti and carbon sources; meanwhile, somewhat structural imperfection of the graphitized carbon exists in the TiO_2/C composites. It is generally accepted that the carbon materials with graphitic structure is a good conductor of electricity, and thus doping TiO_2 with graphitized carbon materials is anticipated to be beneficial to further improve the photocatalytic activity of TiO_2 via facilitating the transfer of e_{CB}^- . It should be noted that the characteristic XPS signal of Ti–C bonds at 281.9 eV is absent in the C 1s XPS spectrum of $\text{TiO}_2/\text{C}-10.3$ composite, suggesting that the carbon doping in the anatase TiO_2 lattice is impossible. This is due to the mismatching of the electronegativity of carbon (2.55) and oxygen atom (3.44), accordingly, only weak mixing of C 2p bands with O 2p bands can be expected in the TiO_2/C composite [44].

High resolution XPS spectrum of pure TiO_2 in the Ti 2p binding energy regions is deconvoluted into two individual peaks positioned at 458.6 and 464.3 eV (Fig. 1e), which are assigned to Ti 2p_{3/2} and Ti 2p_{1/2} state, respectively. The splitting between Ti 2p_{3/2} and Ti 2p_{1/2} state is 5.7 eV, indicating a normal state of Ti^{4+} in anatase TiO_2 [45]. After the formation of $\text{TiO}_2/\text{C}-10.3$ composite, the peak positions still remain unchangeable (Fig. 1e), reflecting that the anatase phase structure is not disturbed after doping graphitized carbon species.

Fig. 1f presents high resolution XPS spectra of pure TiO_2 and $\text{TiO}_2/\text{C}-10.3$ composite in the O 1s binding energy regions. Both TiO_2 and $\text{TiO}_2/\text{C}-10.3$ show two peaks at 529.9 and 531.8 eV, which are assigned to oxygen species from the Ti–O–Ti (lattice oxygen) and Ti–OH groups, respectively [46,47]. Additionally, compared with pure TiO_2 , a new weak peak appeared at 531.2 eV is found in the $\text{TiO}_2/\text{C}-10.3$ composite, which is originated from C=O groups in polycyclic aromatic carbon sheets [43].

3.1.2. Morphological and porosity properties

The morphology of TiO_2 and TiO_2/C composites are revealed by both SEM and TEM observations (Fig. 2). As shown in Fig. 2a and 2b, pure TiO_2 is composed of tiny nanoparticles with relatively high dispersion, and the estimated particle size are in the range of 5–8 nm. From HRTEM image shown in Fig. 2c it is found that the lattice fringe used for phase determination is

Fig. 2. SEM, TEM and HRTEM images of TiO_2 (a–c), $\text{TiO}_2/\text{C}-4.0$ (d–f), $\text{TiO}_2/\text{C}-5.6$ (g–i), $\text{TiO}_2/\text{C}-10.3$ (j–l) and $\text{TiO}_2/\text{C}-13.1$ (m–o).

0.35 nm, reflecting the lattice spacing of (101) plane in the anatase phase. As for four TiO_2/C composites, the particle size of TiO_2 in the composites remains unchangeable, and graphitized carbon uniformly covers on the surface of TiO_2 nanoparticles; meanwhile, anatase TiO_2 nanocrystals and polycyclic aromatic carbon sheets has an intimate contact at the interface of both components (Fig. 2d, e, g, h, j, k, m and n). However, agglomeration of TiO_2 nanoparticles happens, which is possibly due to the strong van der Waals force between the doped surface graphitized carbon [48]. In addition, the lattice fringes corresponding to both lattice spacings of (101) plane in the anatase phase and (111) plane in the rutile phase (0.22 nm) are found in the HRTEM images of $\text{TiO}_2/\text{C}-4.0$ (Fig. 2f) and $\text{TiO}_2/\text{C}-5.6$ composites (Fig. 2i). As for $\text{TiO}_2/\text{C}-10.3$ (Fig. 2l) and $\text{TiO}_2/\text{C}-13.1$ (Fig. 2o), only the lattice fringes corresponding to the lattice spacing of (101) plane in the anatase phase are found. The above results are consistent with those of XRD analysis.

The porosity properties of TiO_2 and TiO_2/C are characterized by nitrogen gas porosimetry measurements, and the obtained nitrogen gas adsorption/desorption isotherms and BJH pore size distribution curves are shown in Fig. 3a and 3b.

Fig. 3. Nitrogen gas adsorption/desorption isotherms (a) and BJH pore size distribution curves (b) of TiO₂ and TiO₂/C composites.

Five tested samples, including TiO₂ and four TiO₂/C composites, all exhibit combined characteristics of types I and IV isotherms with considerably large nitrogen gas uptakes occurring at both low ($P/P_0 < 0.1$) and medium-to-high ($P/P_0 = 0.40$ – 0.80) relative pressure (P/P_0), reflecting their both micro and mesoporosity properties; moreover, the samples show H2 hysteresis loops, suggesting that their mesopores are produced by the accumulation of nanoparticles. The determined textural parameters including BET surface areas, pore volumes and pore diameters of the samples are summarized in Table 1. It shows that the micro/mesoporous structure of TiO₂ and TiO₂/C renders them large BET surface areas, and the BET surface areas of the TiO₂/C composites increase somewhat as compared with bare TiO₂. For example, the BET surface areas of bare TiO₂ is 219 m² g⁻¹, much larger than Degussa P25 TiO₂ (50 m² g⁻¹); the BET surface area of the TiO₂/C composites increase gradually from 222, 248, 255 to 263 m² g⁻¹ as increasing carbon doping level from 4.0 wt%, 5.6 wt%, 10.3 wt% to 13.1 wt%. Similar increasing trend is also found in their pore volumes, *i.e.*, the pore volume of TiO₂/C-4.0, TiO₂/C-5.6, TiO₂/C-10.3 and TiO₂/C-13.1 is 0.28, 0.34, 0.37 and 0.42 cm³ g⁻¹, respectively. Both results imply that the graphitized carbon are doped to TiO₂, which can enlarge the space between the aggregated TiO₂ nanoparticles.

The narrowed BJH pore size distribution curves displayed in Fig. 3b suggest that the mesopores of the five tested samples are well-distributed, and they mainly center at *ca.* 5 nm. Such morphological and porosity properties of TiO₂/C composites are favorable to improve the accessibility to the pollutant molecules, to facilitate charge transfer and to increase the population of the active sites. All of these advantages are expected to enhance the photocatalytic activity of TiO₂ in the

degradation of organic pollutants.

3.1.3. Light absorption properties

The light absorption properties of TiO₂ and TiO₂/C are characterized by the UV-vis/DRS method. As shown in Fig. 4a, TiO₂ exhibits light absorption in the range of 200–400 nm, originating from the intrinsic band gap absorption of TiO₂ due to the electron transitions from the VB (O 2p) to CB (Ti 3d) [49]. As for the TiO₂/C composites, their light absorption continuously extends to 800 nm; meanwhile, the absorption edge of TiO₂/C composites gradually redshifts with the increase of carbon doping levels from 4.0 wt%, 5.6 wt%, 10.3 wt% to 13.1 wt%, together with gradually enhanced visible-light harvesting ability. From the UV-vis/DRS, the absorption edges of TiO₂, TiO₂/C-4.0, TiO₂/C-5.6, TiO₂/C-10.3 and TiO₂/C-13.1 are estimated, and they are 396, 447, 468, 480 and 496 nm, respectively; additionally, the corresponding band gaps (E_g) of the samples are estimated by the Tauc plots shown in Fig. 4b, and they are 3.13 (TiO₂), 2.77 (TiO₂/C-4.0), 2.65 (TiO₂/C-5.6), 2.58 (TiO₂/C-10.3) and 2.50 eV (TiO₂/C-13.1), respectively. The formation of interband C 2p states close to O 2p states of TiO₂ structure is responsible for this band gap narrowing and the absorption edge redshifting after doping TiO₂ with graphitized carbon materials. The isolated C 2p states position above the VB level of O 2p, which can reduce energy for the VB to the CB electronic transition, one of the most important parameters leading to an enhancement in visible-light photocatalytic activity of TiO₂.

Besides a suitable E_g value, the CB and VB edge potentials (E_{CB} and E_{VB}) of the semiconductor also play a key role to the photocatalytic reaction because they dominates the redox capacity of e_{CB}^- and h_{VB}^+ . Here, MS plots are recorded to determine the flat band potentials of TiO₂ and TiO₂/C, which are applied to estimate the CB edge potentials of semiconductor photocatalysts [50]. As shown in Fig. 4c, all samples exhibit a positive slope in the linear region, implying their *n*-type semiconductor structure. The estimated flat band potentials are -0.28 (TiO₂), -0.11 (TiO₂/C-4.0), -0.14 (TiO₂/C-5.6), -0.22 (TiO₂/C-10.3) and -0.16 V (TiO₂/C-13.1) vs. Ag/AgCl, respectively. Normally, the E_{CB} of *n*-type semiconductor is more negative about -0.2 V than its flat band potential [51], and therefore, the E_{CB} values of various samples are *ca.* -0.48 (TiO₂), -0.31

Table 1

BET surface area (A_{BET}), pore volume (V_p), pore diameter (D_p) and band gap energy (E_g) of TiO₂ and TiO₂/C composites.

Photocatalyst	A_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	D_p (nm)	E_g (eV)
TiO ₂	219	0.26	4.1	3.13
TiO ₂ /C-4.0	222	0.28	4.6	2.77
TiO ₂ /C-5.6	248	0.34	4.6	2.65
TiO ₂ /C-10.3	255	0.37	4.6	2.58
TiO ₂ /C-13.1	263	0.42	5.2	2.50

Fig. 4. UV-vis/DRS (a), Tauc plots (b), MS plots (c) and energy band structures (d) of various TiO₂-based photocatalysts.

(TiO₂/C-4.0), -0.34 (TiO₂/C-5.6), -0.42 (TiO₂/C-10.3) and -0.36 V (TiO₂/C-13.1) vs. Ag/AgCl, respectively, or *ca.* -0.28 (TiO₂), -0.11 (TiO₂/C-4.0), -0.14 (TiO₂/C-5.6), -0.22 (TiO₂/C-10.3) and -0.16 V (TiO₂/C-13.1) vs. NHE, respectively [52]. The above result shows that the E_{CB} value of TiO₂/C become less negative as compared with TiO₂, implying the slightly weaker reduction ability of the TiO₂/C than TiO₂. Nevertheless, e_{CB^-} on the CB level of the TiO₂/C still can reduce oxygen to yield $\cdot O_2^-$ radicals because of more negative E_{CB} of TiO₂/C than the redox potential of $O_2/\cdot O_2^-$ (-0.046 V vs. NHE) [53]. The E_{VB} of TiO₂ and TiO₂/C are calculated by subtracting E_{CB} from E_g , and they are +2.85 (TiO₂), +2.66 (TiO₂/C-4.0), +2.51 (TiO₂/C-5.6), +2.36 (TiO₂/C-10.3) and +2.34 V (TiO₂/C-13.1) vs. NHE, respectively. The results suggest that the oxidation ability of the TiO₂/C is somewhat weaker than that of TiO₂. However, $h\nu_{VB^+}$ on the VB levels of TiO₂/C still can oxidize OH⁻ ion or H₂O to produce $\cdot OH$ radicals because E_{VB} values of all TiO₂/C composites are more positive than the redox potential of OH⁻/·OH (+1.99 V vs. NHE) [54] or H₂O/·OH (+2.27 V) [55]. On the basis of the above discussion, the energy band structures of TiO₂ and TiO₂/C are illustrated in Fig. 4d.

3.2. Visible-light photocatalytic degradation of aqueous APAP and MPB over the TiO₂/C composite

3.2.1. Photocatalytic activity and reusability

The TiO₂/C composites with advantages of the narrowed band gaps, excellent porosity properties and fast separation of the e_{CB^-} - $h\nu_{VB^+}$ pairs are expected to show excellent visible-light photocatalytic activity in degradation of organic pollutants.

Here, the visible-light photocatalytic activity of the TiO₂/C composites is studied by the degradation of two emerging light-insensitive phenolic pollutants, APAP and MPB, and as-prepared bare TiO₂ and commercial Degussa P25 TiO₂ are also tested under the same conditions for comparison.

As shown in Fig. 5a and b, dark conditions without visible-light irradiation or irradiation in the absence of photocatalyst does not result in the photocatalytic decomposition of APAP and MPB in water. Significant decomposition of APAP (Fig. 5a) and MPB (Fig. 5b) is clearly observed in the presence of both photocatalyst and visible-light irradiation. The results clearly indicate that the decomposition of APAP and MPB is caused by the photocatalytic reactions on the TiO₂ or TiO₂/C powders under visible-light irradiation. For visible-light photocatalytic degradation of APAP (Fig. 5a), four TiO₂/C composites show obviously higher activity than TiO₂ and Degussa P25 TiO₂; moreover, the visible-light photocatalytic activity of TiO₂/C composites increases rapidly as increasing carbon doping level from 4.0 wt%, 5.6 wt% to 10.3 wt%. However, further increasing the doping level to 13.1 wt%, the photocatalytic activity of the resulting TiO₂/C-13.1 is slightly lower than that of the TiO₂/C-10.3. For the most active TiO₂/C-10.3, it can degrade APAP (10 mg L⁻¹) completely only under visible-light irradiation for 20 min. Under the same conditions, conversion of APAP reaches 94.0% (TiO₂/C-13.1), 81.5% (TiO₂/C-5.6), 71.0% (TiO₂/C-4.0), 50.1% (Degussa P25 TiO₂) and 41.1% (TiO₂), respectively. To provide a direct evidence of fast photo-degradation of APAP over the TiO₂/C-10.3, temporal evolution of the UV-vis absorption spectra of APAP during the degradation process is recorded by an HPLC-diode-array detection

Fig. 5. Visible-light photocatalytic activity of various TiO_2 -based catalysts in the degradation of APAP (a) and MPB (b). The corresponding time-resolved absorption spectra (c, d) and kinetic rate constants (e, f). Catalyst 50 mg; c_0 (APAP or MPB) = 10 mg L^{-1} ; volume 50 mL.

(DAD). As shown in Fig. 5c, the characteristic absorption peak of APAP at 242 nm decreases promptly as prolonging visible-light irradiation time, and the absorption peak disappears after the irradiation for 20 min.

In the case of visible-light photocatalytic degradation of MPB, TiO_2 and TiO_2/C composites still follow the similar activity order to that of APAP, and conversion of MPB reaches 92.9% after visible-light irradiating the most active $\text{TiO}_2/\text{C}-10.3$ for 180 min (Fig. 5b). Under the same conditions, the conversion of MPB is 86.2%, 82.4%, 75.0%, 64.5% and 60.0%, respectively, over the $\text{TiO}_2/\text{C}-13.1$, $\text{TiO}_2/\text{C}-5.6$, $\text{TiO}_2/\text{C}-4.0$, Degussa P25 TiO_2 and TiO_2 . Temporal evolution of the UV-vis absorption spectra measured by HPLC-DAD during visible-light photodegradation of MPB over the $\text{TiO}_2/\text{C}-10.3$ further confirms its excellent photocatalytic activity, and the characteristic absorption peak of MPB at 255 nm gradually reduces with continuous visible-light irradiation, and the peak vanishes almost after the irradiation for 180 min (Fig. 5d).

The reaction kinetics of APAP and MPB degradation over the visible-light irradiated various TiO_2 -based photocatalysts are then studied. As shown in Fig. S2, each plot of $-\ln(c_t/c_0)$ vs. t exhibits a good linearity, suggesting that APAP (Fig. S2a) and MPB (Fig. S2b) degradation reactions follow pseudo-first-order kinetics. Accordingly, apparent rate constant (k) for APAP and MPB degradation reactions over various photocatalysts are quantitatively evaluated. As shown in Fig. 5e, various TiO_2 -based photocatalysts follow the k value order of $\text{TiO}_2/\text{C}-10.3 > \text{TiO}_2/\text{C}-13.1 > \text{TiO}_2/\text{C}-5.6 > \text{TiO}_2/\text{C}-4.0 > \text{Degussa P25 TiO}_2 > \text{TiO}_2$ in APAP degradation. Specifically, k value in APAP degradation over the $\text{TiO}_2/\text{C}-10.3$ (0.2038 min^{-1}) is 7.6,

6.2, 3.5, 2.6 and 1.5 times higher than that of TiO_2 (0.0267 min^{-1}), Degussa P25 TiO_2 (0.0330 min^{-1}), $\text{TiO}_2/\text{C}-4.0$ (0.0578 min^{-1}), $\text{TiO}_2/\text{C}-5.6$ (0.0789 min^{-1}) and $\text{TiO}_2/\text{C}-13.1$ (0.1354 min^{-1}). Similarly, the determined k value for MPB degradation over the $\text{TiO}_2/\text{C}-10.3$ (0.01465 min^{-1}) is 2.8, 2.6, 1.8, 1.5 and 1.3 times higher than that of TiO_2 (0.00527 min^{-1}), Degussa P25 TiO_2 (0.00571 min^{-1}), $\text{TiO}_2/\text{C}-4.0$ (0.00795 min^{-1}), $\text{TiO}_2/\text{C}-5.6$ (0.00977 min^{-1}) and $\text{TiO}_2/\text{C}-13.1$ (0.01123 min^{-1}) (Fig. 5f). The above results indicate that the $\text{TiO}_2/\text{C}-10.3$ exhibits the fastest reaction rate among six tested catalysts in two target reactions.

The mineralization ability to organic pollutants is an important issue to evaluate the performance of the photocatalysts because poor mineralization ability of the photocatalysts may yield more toxic organic intermediates than the pollutants themselves. The mineralization of organic pollutants is a complicated process, and it generally needs much longer time to mineralize them completely. Here, the mineralization ability of the TiO_2/C composites is studied by monitoring the changes of TOC values during the process of the $\text{TiO}_2/\text{C}-10.3$ -photocatalyzed degradation of APAP (initial concentration of 20 mg L^{-1}). As shown in Fig. S3, continuous decrease of TOC values is found as prolonging the visible-light irradiation time, reflecting continuous mineralization of APAP. After visible-light irradiation for 360 min, the mineralization efficiency of APAP reaches ca. 90.0%. The above result therefore provides direct evidence of the excellent mineralization ability of the TiO_2/C composite photocatalysts. The reusability of the photocatalyst is a critical issue in practical applications, and adsorption of the intermediates on the surface-active position as well as drop of the active components are two main factors that deteriorate the re-

usability of the photocatalyst.

To evaluate the reusability of as-prepared TiO_2/C composites, $\text{TiO}_2/\text{C}-10.3$ is selected as a representative photocatalyst, and visible-light photocatalytic degradation of APAP and MPB over the $\text{TiO}_2/\text{C}-10.3$ is cycled for five consecutive cycles. After each catalytic cycle, the catalyst is separated and then washed completely with water and ethanol, and the recovered catalyst is applied to the next cycle. As shown in Fig. 6a, the conversion of APAP is 98.0% (1st), 97.5% (2nd), 97.0% (3rd), 88.7% (4th) and 87.3% (5th), respectively, after visible-light irradiation for 20 min. Similar trend is also found in the degradation of MPB over visible-light irradiated $\text{TiO}_2/\text{C}-10.3$, and the conversion of MPB is 92.9% (1st), 90.7% (2nd), 89.1% (3rd), 81.5% (4th) and 78.5% (5th), respectively, after visible-light irradiation for 180 min (Fig. 6b). XRD and TEM analysis shown in Fig. 6c and d indicates that the fifth time spent $\text{TiO}_2/\text{C}-10.3$ photocatalyst still remains anatase phase structure and morphology of nanoparticles. Slight activity loss after the third cycle is therefore due to the adsorption of some residual intermediates on the catalyst surface, which occupy some active positions and thus decreasing the accessibility to the substrates. Nevertheless, TiO_2/C composites still show good reusability, and they can work as recoverable visible-light-driven photocatalysts in decomposition of aqueous organic pollutants.

3.2.2. Photocatalytic activity interpretation and reaction mechanism considerations

To understand the origin of the enhanced visible-light photocatalytic activity of TiO_2 after doping graphitized carbon materials, a series of studies including photoelectrochemical experiment, indirect chemical probe method (free radical and hole trapping experiment) and DMPO-ESR measurement are carried out. At first, the interface charge transfer and separation efficiency of $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$ pairs on the TiO_2 and TiO_2/C composites is investigated by the photoelectrochemical experiment, including transient photocurrent response and EIS Nyquist measurements. As shown in Fig. 7a, under the irradiation of full-spectrum of Xe lamp, TiO_2/FTO and various $\text{TiO}_2/\text{C}/\text{FTO}$ electrodes all show a stable and reproducible photocurrent response, and the photocurrent of each $\text{TiO}_2/\text{C}/\text{FTO}$ electrode is obviously higher than that of TiO_2/FTO electrode. The photocurrent originates from the transfer of e_{CB}^- during light irradiating the photocatalyst electrode, and therefore the enhanced photocurrent response of the $\text{TiO}_2/\text{C}/\text{FTO}$ electrodes than the TiO_2/FTO electrode reflects more e_{CB}^- exist in the systems under the light irradiation. This is due to the fact that the graphitized carbon with huge π - π -conjugated structure can act as the electron reservoir by capturing the e_{CB}^- , which effectively enhances the transport of e_{CB}^- and thus reduces the recombina-

Fig. 6. Reusability tests of the $\text{TiO}_2/\text{C}-10.3$ in visible-light photocatalytic degradation of APAP (a) and MPB (b). Catalyst 50 mg, $c_0 = 10 \text{ mg L}^{-1}$, volume 50 mL. (c) XRD patterns of fresh and the fifth time spent $\text{TiO}_2/\text{C}-10.3$. (d) TEM of the fifth time spent $\text{TiO}_2/\text{C}-10.3$.

Fig. 7. Transient photocurrent responses (a) and the fitted EIS Nyquist plots (b) of TiO_2 and TiO_2/C composites electrodes in aqueous Na_2SO_4 electrolyte solution under Xe lamp irradiation. Inset in (b): Equivalent circuit model (R_s refers to the series resistance, and R_{ct} and CPE are the charge transfer resistance and the constant phase element, respectively).

tion probability of e_{CB}^- and h_{VB}^+ through their spatial separation at the interface between TiO_2 nanoparticles and polycyclic aromatic carbon sheets [56]. Owing to continuously increased carbon doping level, the photocurrent response increases gradually from $\text{TiO}_2/\text{C}-4.0/\text{FTO}$, $\text{TiO}_2/\text{C}-5.6/\text{FTO}$ to $\text{TiO}_2/\text{C}-10.3/\text{FTO}$. However, further increasing carbon doping level to 13.1 wt%, the photocurrent of the $\text{TiO}_2/\text{C}-13.1/\text{FTO}$ electrode becomes lower as compared with the $\text{TiO}_2/\text{C}-10.3/\text{FTO}$. The reduced photocurrent at high carbon doping level is due to the following two reasons. On the one hand, excessive carbon species may shield the light absorption of TiO_2 , resulting in less e_{CB}^- and h_{VB}^+ are excited; on the other hand, excessive carbon species can act as massive recombination centers of e_{CB}^- and h_{VB}^+ , leading to lessened number of the e_{CB}^- in the system.

EIS Nyquist analysis (Fig. 7b) supports the above photocurrent determination result. The electrochemical impedances of various $\text{TiO}_2/\text{C}/\text{FTO}$ electrodes are represented by the curvature diameters of the obtained EIS Nyquist plots, which reflect the electron transfer resistances of the photocatalyst. The smaller curvature diameter of the EIS Nyquist plot indicates more effective separation of e_{CB}^- – h_{VB}^+ pairs and faster interfacial charge transfer occurring on the photocatalyst [57,58]. The tested electrodes follow the electrochemical impedance order of $\text{TiO}_2/\text{FTO} > \text{TiO}_2/\text{C}-4.0/\text{FTO} > \text{TiO}_2/\text{C}-5.6/\text{FTO} > \text{TiO}_2/\text{C}-13.1/\text{FTO} > \text{TiO}_2/\text{C}-10.3/\text{FTO}$, in line with that of their photocurrent response. The equivalent circuit has been shown in the inset of Fig. 7b, and the fitted charge transfer resistances (R_{ct}) based on the equivalent circuit are summarized in Table S1 of electronic supplementary information. It shows that the R_{ct} value of $\text{TiO}_2/\text{C}-10.3$ (4553 Ω) and TiO_2 (17893 Ω) is the smallest and the largest among all five tested samples, which implies that the $\text{TiO}_2/\text{C}-10.3$ and TiO_2 system possess the highest and the lowest quantity of free electrons (e_{CB}^-) and thus the smallest and the highest charge transfer resistances, respectively. The result further confirms that more effective separation of the e_{CB}^- – h_{VB}^+ pairs after doping TiO_2 with suitable amount of graphitized carbon.

Subsequently, the reactive species including h_{VB}^+ , $\cdot\text{OH}$ and

$\cdot\text{O}_2^-$ radicals involved in the process of $\text{TiO}_2/\text{C}-10.3$ -photocatalyzed degradation of aqueous APAP are identified by indirect chemical probe method. In this study, scavengers such as *t*-BuOH and EDTA are added in the system to capture $\cdot\text{OH}$ radicals and h_{VB}^+ , respectively [59], while nitrogen gas is purged to test the possibility of the involvement of $\cdot\text{O}_2^-$ radicals [60,61]. Firstly, influence of the scavengers on the photocatalytic activity of TiO_2 in degradation of APAP is studied. As shown in Fig. 8a, compared with scavenger-free TiO_2 photocatalytic system, the degradation of APAP is inhibited in the presence of EDTA, *t*-BuOH or nitrogen gas; moreover, the inhibition degree to the photocatalytic activity of TiO_2 follows the order of EDTA > *t*-BuOH > nitrogen gas. The result indicates that h_{VB}^+ , $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals are all the active species that are responsible for the photooxidation of APAP, and the yielded h_{VB}^+ plays the most important role to degrade APAP.

In the case of the $\text{TiO}_2/\text{C}-10.3$ photocatalytic system, the degradation of APAP is suppressed completely after purging nitrogen gas, which is different from that of bare TiO_2 photocatalytic system (Fig. 8b). The result indicates that O_2 is of critical importance for a photocatalytic degradation system in that it not only traps e_{CB}^- to suppress the recombination of the e_{CB}^- – h_{VB}^+ pairs but also is essential for the generation of $\cdot\text{O}_2^-$ radicals. More important role of O_2 in the $\text{TiO}_2/\text{C}-10.3$ than pure TiO_2 system is due to more e_{CB}^- are generated in the $\text{TiO}_2/\text{C}-10.3$ system, contributed from more effective separation of the e_{CB}^- – h_{VB}^+ pairs. Additionally, the presence of EDTA or *t*-BuOH inhibits the degradation of APAP in some extent, indicating that both h_{VB}^+ and $\cdot\text{OH}$ radicals participate in current photocatalytic reaction. Contribution of the reactive species to the photocatalytic degradation of APAP over $\text{TiO}_2/\text{C}-10.3$ follows the order of $\cdot\text{O}_2^- \gg h_{\text{VB}}^+ > \cdot\text{OH}$.

ESR technology is used to further confirm that $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals are indeed generated in $\text{TiO}_2/\text{C}-10.3$ photocatalytic system, and DMPO-ESR spectra of $\text{TiO}_2/\text{C}-10.3$ measured in methanol dispersion for DMPO– $\cdot\text{O}_2^-$ adduct and aqueous dispersion for DMPO– $\cdot\text{OH}$ adduct are shown in Fig. 8c and d. In the dark, any ESR signals of DMPO– $\cdot\text{O}_2^-$ and DMPO– $\cdot\text{OH}$ adducts are hardly identified. Under Xe lamp irradiation, obvious signals

Fig. 8. Influence of various scavengers on the visible-light photocatalytic activity of TiO_2 (a) and $\text{TiO}_2/\text{C}-10.3$ (b) in degradation of APAP. Catalyst 50 mg, $c_0 = 10 \text{ mg L}^{-1}$, volume 50 mL. DMPO-ESR spectra of $\text{TiO}_2/\text{C}-10.3$ in methanol dispersion for DMPO- O_2^- adducts (c) and aqueous dispersion for DMPO- OH adducts (d).

related to DMPO- O_2^- adduct with an intensity ratio of 1:1:1:1:1 [62] are found in the DMPO-ESR spectrum of $\text{TiO}_2/\text{C}-10.3$ dispersed in methanol solution (Fig. 8c); additionally, the signals related to the DMPO- OH adducts with an intensity ratio of 1:2:2:1 [63] are also visibly observed in the DMPO-ESR spectrum of $\text{TiO}_2/\text{C}-10.3$ dispersed in aqueous solution. The above results are consistent with those of the indirect chemical probe method.

On the basis of the above experimental results it is inferred that the enhanced visible-light photocatalytic activity after doping TiO_2 with graphitized carbon species is attributed to the synergistic effects induced by the interfacial interaction of anatase TiO_2 nanocrystals with the graphitized carbon structures, and this synergy renders the improved visible-light harvesting ability and the accelerated separation of $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$. Specifically, doping TiO_2 with graphitized carbon can improve the light harvesting ability of TiO_2 by narrowing the band gap and extending the light absorption in the visible-light region, which can reduce energy for the VB to the CB electronic transition and thus higher population of $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$ pairs are excited. On the other hand, for currently prepared bare TiO_2 and TiO_2/C composites, the determined VB and CB edge potentials are in the range of 2.85 to 2.34 V (E_{VB}) and -0.28 to -0.16 V (E_{CB}) vs. NHE, respectively (Fig. 4d), while the calculated Fermi energy level of graphitized carbon materials is *ca.* -0.08 V vs. NHE [25]. Because the Fermi energy level of graphitized carbon is less negative than the CB edge potentials of TiO_2 or TiO_2/C , the graphi-

tized carbon can act as a sink for the e_{CB}^- . It is thus energetically feasible that the e_{CB}^- on the CB of TiO_2 transfer to graphitized carbon. The transferred e_{CB}^- accumulate in the huge π - π framework of polycyclic aromatic carbon sheets in the composites, significantly retarding the recombination of $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$ on TiO_2 [3]; meanwhile, one-step prepared TiO_2/C composites can ensure intimate interaction between anatase TiO_2 nanoparticles and carbon sheets, which provides a good spatial condition for e_{CB}^- transfer from TiO_2 to graphitized carbon *via* the interfaces. This efficient $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$ separation stabilizes the $\text{e}_{\text{CB}}^- - \text{h}_{\text{VB}}^+$ pairs and slows down the charge carrier recombination.

Finally, the TiO_2/C composites with large BET surface areas and porous structure can also provide more plentiful active sites and enhance the visible-light harvesting ability *via* multi-

Scheme 1. Schematic illustration of the mechanism of visible-light photocatalytic degradation of APAP and MPB over the graphitized carbon/ TiO_2 composite.

step reflections. All these factors lead to the increased number of e_{CB}^- and h_{VB}^+ reacting with oxygen and OH^-/H_2O to produce more $\cdot O_2^-$ and $\cdot OH$ radicals, respectively. Since the $\cdot O_2^-$ and $\cdot OH$ radicals possess the strong oxidation ability, they play a crucial role to decompose APAP and MPB completely. However, although the $TiO_2/C-13.1$ shows more narrowed band gap than that of the $TiO_2/C-10.3$, its photocatalytic activity in the degradation of aqueous APAP and MPB is lower than the latter. One of the reasons is that excessive carbon species may shield the light absorption of TiO_2 , resulting in less e_{CB}^- and h_{VB}^+ are excited. The other reason is due to excessive carbon species can act as massive recombination centers of e_{CB}^- and h_{VB}^+ , which increases the recombination opportunity of e_{CB}^- and h_{VB}^+ .

Based on the above discussion, a reasonable mechanism of visible-light photocatalytic degradation of APAP and MPB over the TiO_2/C composites is put forward and illustrated in Scheme 1. Under the visible-light irradiation, the increased number of e_{CB}^- and h_{VB}^+ are generated on the TiO_2/C . Next, the e_{CB}^- are captured by polycyclic aromatic carbon sheet framework and

then accumulate on them, leaving h_{VB}^+ locating on the VB of TiO_2 . This electron transfer process significantly promotes the separation of $e_{CB}^- - h_{VB}^+$, giving rise to abundant e_{CB}^- on carbon sheets to react with dioxygen to produce $\cdot O_2^-$ radicals, while plentiful h_{VB}^+ on CB of TiO_2 react with OH^- or H_2O to produce $\cdot OH$ radicals. Under the attack of the oxidative species including $\cdot O_2^-$, $\cdot OH$ and h_{VB}^+ , APAP and MPB are decomposed completely.

At last, to understand the reaction process of visible-light photocatalytic degradation of APAP and MPB over the TiO_2/C composites deeply, LC-MS is applied to identify the intermediates generated during the above process (Fig. S4). Combination of the identified intermediates and active species involved in current system, the pathway of visible-light photocatalytic degradation of APAP (Scheme 2a) and MPB (Scheme 2b) over the TiO_2/C composite is reasonably proposed. As shown in Scheme 2a, the photodegradation of APAP over the TiO_2/C may follow two parallel pathways. In path I, APAP (compound 1) suffers from successive hydroxylation, demethylation and cleavage of C–N bonds under the attack of active species in-

Scheme 2. Pathway of visible-light photocatalytic degradation of APAP (a) and MPB (b) over the TiO_2/C composite.

cluding $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and $h\nu_{\text{VB}}^+$ to produce compounds **2–4**, accompanying with the release of NO_3^- ion. In path II, under the attack of active species, APAP firstly undergoes decarbonylation to compound **5**. After further hydroxylation and deamination successively, hydroquinone (compound **6**) and benzoquinone (compound **7**) are produced, and the process also associates with the release of NO_3^- ion. Afterwards, continuous photooxidation of compounds **4** and **7** leads to the opening of aromatic ring, together with the formation of a series of aliphatic acids, including *trans*-2-butene-1,4-dicarboxylic acid (compound **8**), succinic acid (compound **9**), 2-hexenoic acid (compound **10**), malonic acid (compound **11**), oxalic acid (compound **12**) and acetic acid (compound **13**). Eventually, under continuous attack by the active species, these aliphatic acids are mineralized to CO_2 and H_2O .

Scheme 2b illustrates the photodegradation pathway of MPB over the TiO_2/C , and two possible paths are proposed. In path I, MPB (compound **1**) is firstly hydroxylated by $\cdot\text{OH}$ radicals to yield compound **2** or **3**, further decarboxylation followed by hydroxylation, compound **4** is yielded. In the other path (path II), MPB suffers from demethylation to produce 4-hydroxybenzoic acid (compound **5**). After further decarboxylation and then hydroxylation, hydroquinone (compound **6**) is produced. Subsequently, benzoquinone (compound **7**) is yielded after photooxidation of hydroquinone. Similar to the degradation pathway of APAP, both compounds **4** and **7** are further photooxidized to generate a series of aliphatic acids, including maleic acid (compound **8**), tartaric acid (compound **9**) and acetic acid (compound **12**); additionally, two small intermediates like 2-pentanone (compound **10**) and propyl acetate (compound **11**) are also found. Ultimately, further photooxidation of these compounds leads to the mineralization of MPB to CO_2 and H_2O .

4. Conclusions

The present work designs a simple one-step co-condensation-hydrothermal treatment route to prepare

TiO_2/C composite photocatalysts with large surface areas, and carbon doping levels in the composites can be well adjusted by changing the initial adding amount of glucose. The TiO_2/C composites display excellent visible-light photocatalytic activity in the degradation of aqueous APAP and MPB, and their activity outperforms bare TiO_2 and Degussa P25 TiO_2 . Such excellent photocatalytic activity is attributed to the synergistic effects induced by the interfacial interaction of anatase TiO_2 nanocrystals and the graphitized carbon structures, giving rise to the improved visible-light harvesting ability, the accelerated separation of $\text{e}_{\text{CB}}^- - h\nu_{\text{VB}}^+$ and easier accessibility to the pollutant molecules. The active species including $\cdot\text{OH}$ radicals, $h\nu_{\text{VB}}^+$, and especially large amount of $\cdot\text{O}_2^-$ radicals involved in the TiO_2/C photocatalytic system are responsible for the photooxidation of APAP and MPB completely. The present work provides some new hints on designing and developing efficient TiO_2/C composite photocatalysts for sustainable water treatment and environmental remediation.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1378–1392 doi: 10.1016/S1872-2067(20)63565-3

***In-situ* route for the graphitized carbon/ TiO_2 composite photocatalysts with enhanced removal efficiency to emerging phenolic pollutants**

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Graphitized carbon/ TiO_2 composites were prepared by an *in-situ* co-condensation-hydrothermal treatment route and exhibited remarkably high visible-light photocatalytic activity in degradation of aqueous emerging phenolic pollutants, which is attributed to the improved light harvesting ability and fast photogenerated charge carrier separation.

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原位法制备石墨相碳/TiO₂复合光催化剂及其高效降解新兴酚类污染物性能

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摘要: 绿色光催化技术在可持续水处理和环境修复领域具有广阔的应用前景。光催化效率在很大程度上取决于光催化剂, 其中二氧化钛(TiO₂)因具有超强的光氧化能力、化学稳定性和低成本等优点而广泛应用于光催化降解水中各类有机污染物。然而, TiO₂的光催化效率仍然受限于其自身比表面积小、太阳光利用率低以及光生载流子复合速率快等缺点。

为了克服以上缺点, 进一步提高 TiO_2 的光催化效率, 本研究采用简单易行的原位共缩合结合水热处理技术, 以葡萄糖为碳源, 四异丙氧基钛(TTIP)为钛源, 成功制备了一系列由锐钛矿相 TiO_2 与石墨相碳组成的 TiO_2/C 复合光催化剂, 它们在水中新兴酚类污染物的降解中表现出了优异的可见光光催化活性. 通过X射线衍射、热重分析、X射线光电子能谱、孔隙率分析、扫描电镜、透射电镜、紫外-可见漫反射光谱等表征手段对催化剂的组成和结构、形貌、孔隙率性质及光吸收特性进行了表征. 结果显示, TiO_2/C 复合光催化剂具有独特的微孔/介孔结构, 以及比 TiO_2 更大的比表面积($222\text{--}263\text{ m}^2\text{ g}^{-1}$)和更窄的带隙能($2.50\text{--}2.77\text{ eV}$).

通过水中新兴酚类污染物如乙酰氨基酚(APAP)和对羟基苯甲酸甲酯(MPB)的可见光光催化降解实验研究了 TiO_2/C 的光催化性能. 结果显示, TiO_2/C 复合光催化剂表现出优于纯 TiO_2 和商用P25- TiO_2 的可见光光催化活性. 其中, 性能最佳的 TiO_2/C -10.3(碳掺杂量为10.3%)在可见光照射下20 min即可完全降解APAP, 180 min可降解90%以上的MPB; TiO_2/C -10.3光催化降解APAP和MPB的表观速率常数分别是纯 TiO_2 的7.6和2.8倍, 是商用P25- TiO_2 的6.2和2.6倍. TiO_2/C 复合光催化剂表现出良好的稳定性, 能够在完成五次光催化循环实验后仍然保持其良好的光催化活性.

通过光电化学实验、间接化学探针测试和电子自旋共振光谱分析并结合表征结果, 揭示了 TiO_2/C 可见光光催化活性提高的原因. 首先, 石墨相碳的掺入降低了材料的带隙能, 拓宽了材料的可见光吸收范围, 同时石墨相碳可作为电子阱促进光生电子从 TiO_2 的价带转移到自身, 从而有效抑制光生载流子的复合; 其次, 在复合催化剂中, 锐钛矿相 TiO_2 与石墨相碳密切接触有利于光生载流子的有效分离, 也可起到抑制光生载流子复合的作用; 最后, 复合催化剂较大的比表面积和独特的微孔/介孔双孔结构为APAP和MPB降解反应提供了充足活性位点, 同时入射光在孔道内多次反射又进一步提高了催化剂对光能的利用率. 在 TiO_2/C 光催化降解体系中检测到的主要活性物种有羟基自由基、光生空穴和超氧自由基, 三者共同参与APAP和MPB的降解和矿化过程. 通过对光催化降解中间产物的分析, 分别提出了 TiO_2/C 复合光催化剂可见光催化降解APAP和MPB的路径.

本研究为设计高效降解水中有机污染物的碳掺杂 TiO_2 光催化材料提供了新思路.

关键词: 二氧化钛; 碳; 可见光光催化; 复合材料; 酚类化合物; 水处理

收稿日期: 2020-01-17. 接受日期: 2020-02-23. 出版日期: 2020-09-05.

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基金来源: 国家自然科学基金(21573038, 51608102).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).