Facile Fabrication of C–TiO$_2$ Nanocomposites with Enhanced Photocatalytic Activity for Degradation of Tetracycline

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Supporting Information

ABSTRACT: Visible-light-driven C–TiO$_2$ nanocomposites were prepared via a simple calcination and acid etching process. The C–TiO$_2$ nanocomposites were characterized by X-ray photoelectron spectroscopy, Raman spectroscopy, X-ray diffraction, transmission electron microscopy, and high-resolution TEM. The results showed that TiO$_2$ nanoparticles were combined with a porous carbon layer through surface C–O groups, which facilitates the strong interface interaction. The interface combination of nano-TiO$_2$ and carbon material increases the specific surface area of nano-TiO$_2$, widens the range of light response, and improves the efficiency of light-induced electron migration. The visible-light photocatalytic activity of the prepared photocatalyst was evaluated by the decomposition of tetracycline aqueous solution. Compared with that of pure TiO$_2$, the photocatalytic activity of C–TiO$_2$ nanocomposites was significantly improved. Furthermore, a possible photocatalytic mechanism was also tentatively proposed. This work can promote the development of active photocatalysts under solar light for the photodegradation of environmental pollutants.

1. INTRODUCTION

In recent decades, more and more attention has been paid to the widespread use and abuse of antibiotics, which may have adverse effects on human health, agriculture, and planting. In antibiotics, tetracycline (TC) is widely used in human medicine, agriculture, aquaculture, and other fields. However, 70–90% of TC is discharged from the body and ultimately exists in surface water, groundwater, and even drinking water. To solve these problems, several techniques have been developed, such as absorption, photocatalysis, membrane separation, and electrolysis. Compared with the traditional technology, semiconductor-mediated photocatalysis has become a hot spot in the research of antibiotic residue treatment recently because it is a green and efficient technology. For the moment, multiple semiconductors have been researched, including TiO$_2$, SnS$_2$, Bi$_2$O$_3$, ZnO, V$_2$O$_5$, CeO$_2$, and BiPO$_4$. Among various photocatalysts, TiO$_2$ is regarded as one of the most promising materials because of its stability, high activity, nontoxic nature, and biocompatibility. However, its photocatalytic application is still limited due to its wide band gap and high electron–hole recombination rate. Several tactics have been devoted to solve these problems, such as doping, deposition of metals, coupling with narrow band gap semiconductors, or carbonaceous materials as sensitizers. Especially note that carbonaceous materials with sp$^2$-hybridized carbon atoms have been vastly studied due to their tremendous applications in many fields, such as catalyst supports, adsorbents, and electrode materials. Therefore, introduction of carbon reflects a simple strategy, which can reduce the band gap of TiO$_2$ and coincide with the visible-light spectrum, thus enhancing the photoactivity of the obtained materials. Besides, the introduction of carbon can promote the charge transfer from the bulk of the TiO$_2$ structure to the surface area of oxidation reaction and increase the conductivity of TiO$_2$. In addition, compared with other hybrid materials, carbon can be prepared from environmentally friendly raw materials and has the advantages of stability and low cost. Moreover, organic pollutants are easily absorbed into carbon, which is a premise of pollutant decomposition. Up to now, several carbonaceous materials including graphene, carbon nanotubes, and carbon dots have been introduced into TiO$_2$-based composite photocatalysts, which greatly improves their photocatalytic performance. Therefore, TiO$_2$–C hybrid materials with a high specific surface area and high conductivity are expected to become photocatalyst with high activity.

In this study, we demonstrated a facile calcination approach and acid etching method to synthesize porous C–TiO$_2$ nanocomposites using the mixture of TiO$_2$, γ-Fe$_2$O$_3$, and starch as a precursor. Herein, porous carbon was used as a support to disperse TiO$_2$ nanoparticles. In principle, the porous structure can improve the light-harvesting ability and the adsorption...
ability of reactants due to its large specific surface area and multiple scattering effect. TC was chosen as the targeted pollutant to determine the photocatalytic performance of the as-prepared porous C−TiO$_2$ composite catalyst. Compared to that of pure TiO$_2$, porous C−TiO$_2$ hybrid revealed excellent TC degradation efficiencies. Furthermore, the stability of the porous C−TiO$_2$ photocatalyst was investigated and a possible mechanism was proposed.

2. RESULTS AND DISCUSSION
The structures of the pristine TiO$_2$ and C−TiO$_2$-2 samples were analyzed using X-ray diffraction (XRD) spectroscopy, and the results are shown in Figure 1a. All of the samples have similar pattern. The diffraction peaks correspond to the (101), (004), (200), (105), (211), (204), and (116) planes of the tetragonal phase of anatase TiO$_2$ (JCPDS 21-1272), but there are no peaks belonging to rutile phase; the diffraction peaks of carbon are not observed in the complex, which may be due to the low carbon content and relatively low diffraction intensity. The Raman spectra of C−TiO$_2$ nanocomposites (Figure 1b) present the characteristic peaks of both anatase-TiO$_2$ and carbon, among which the peaks at 144 (E$_g^{(1)}$), 393 (B$_1g^{(1)}$), 512 (A$_{1g}$ + B$_{1g}^{(2)}$), and 633 cm$^{-1}$ (E$_g^{(2)}$) were attributed to the typical modes of anatase-TiO$_2$,

and the D-band and G-band of carbon at 1321 and 1583 cm$^{-1}$ shifted a little to 1334 and 1599 cm$^{-1}$ in C−TiO$_2$ nanocomposites due to the interaction between TiO$_2$ and carbon.

In addition, the composition of the C−TiO$_2$-2 and C−γ-Fe$_2$O$_3$/TiO$_2$-2 nanocomposites was studied by energy-dispersive X-ray spectroscopy (EDS) analysis (Figures 1c and S1). The peaks showed that the C−TiO$_2$-2 product was only composed of Ti, O, and C elements.

Figure 1. (a) XRD and (b) Raman patterns of the pristine TiO$_2$, carbon, and C−TiO$_2$-2 nanocomposites. EDS (c) spectrum of C−TiO$_2$-2 nanocomposites.

Figure 2. Typical TEM images of (a) carbon, (b) pristine TiO$_2$, and (c) C−TiO$_2$-2 hybrid. HRTEM image (d) of C−TiO$_2$-2 nanocomposite.
The morphological structure of the samples was examined with transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Figure 2a, carbon has a layered structure and is a thin sheet with irregular morphology. Figure 2b displays the irregular spheres of the TiO\textsubscript{2} particles with diameters in the range of 5–10 nm. The size distribution profile of the TiO\textsubscript{2} particles was described in detail through photon correlation spectroscopy (PCS; Figure S2), and the results confirm that the average distribution profile of the TiO\textsubscript{2} NPs was 6 nm. For the C–TiO\textsubscript{2}-2 nanocomposites (Figure 2c), the TiO\textsubscript{2} nanoparticles are found embedded in the carbon lamellar structure. A typical HRTEM image of C–TiO\textsubscript{2}-2 (Figure 2d) identified a crystal spacing of 0.35 nm, which was assigned to the (101) crystal plane of anatase TiO\textsubscript{2}. In addition, the PCS results in Figure S2 indicate that the average distribution profile of the C–TiO\textsubscript{2}-2 nanocomposites is also around 6 nm, which can be ascribed to the fact that the carbon layer can effectively prevent the agglomeration of TiO\textsubscript{2} at high temperature.\textsuperscript{46}

The full survey spectrum of Figure 3a indicates the presence of titanium (Ti 2p), carbon (C 1s), and oxygen (O 1s) in the C–TiO\textsubscript{2}-2 nanocomposites. In Figure 3b, the Ti 2p spectrum fitted to two peaks at 458.9 and 464.6 eV, which correspond to Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} of TiO\textsubscript{2}.\textsuperscript{47} C 1s fine XPS spectra of C–TiO\textsubscript{2}-2 are shown in Figure 3c. The main C 1s peak for C–TiO\textsubscript{2}-2 was dominated by elemental carbon at 284.5 eV, attributed mainly to extensively delocalized alternant hydrocarbon; the two peaks at 286.2 and 288.6 eV were characteristic of C–O and C\textsuperscript{=}O bonds of carbonate-like species because of oxidized carbon species, respectively.\textsuperscript{48} No peak of the Ti–C bond is found in both Ti 2p and C 1s spectra, which indicates that carbon does not exist as a dopant in TiO\textsubscript{2}.\textsuperscript{49} With respect to the XPS spectra of O 1s in Figure 3d, the O 1s signal was well fitted with three contributions. The four peaks of 530.0, 530.7, and 532.1 eV should be ascribed to Ti = O, C\textsuperscript{=}O and C\textsuperscript{−}OH, respectively.\textsuperscript{50} Valence band (VB)-XPS was obtained to further investigate the property of the band structure, which can probe the total density of state (DOS) distribution in the valence band. Figure S3 shows the valence band XPSs of TiO\textsubscript{2} and C–TiO\textsubscript{2}-2.
The figure indicates that the VB edge of TiO$_2$ occurs at 2.74 eV and that of C$^-\text{TiO}_2-2$ shifts toward negative energy compared with TiO$_2$, which is caused by the contribution of C 2p orbitals.\textsuperscript{51}

In Figure 4a, the N$_2$ adsorption−desorption isotherm of the TiO$_2$ sample exhibits a type IV hysteresis loop according to the IUPAC classifications, which indicates a mesoporous structure of the sample, and the Brunauer−Emmett−Teller (BET) surface area was determined to be 77.9 m$^2$·g$^{-1}$. The pore size distribution of TiO$_2$ calculated by the Barrett−Joyner−Halenda (BJH) method and centered at approximately 28.6 nm (inset of Figure 4a) also confirmed such a microporous structure. The C$^-\text{TiO}_2-2$ nanocomposites exhibited a transitional isotherm from type I to type IV (Figure 4b), which means that micropores and mesopores coexist in the sample.\textsuperscript{52} In the range of $P/P_0 = 0.5−1.0$, H3 type hysteresis loop was observed, which indicated that there were mesopores in the sample. The quantity of N$_2$ adsorbed can be found in the low-pressure region, which further proves that there are abundant micropores, which is attributed to the voids between the deposited TiO$_2$ nanoparticles. The surface area calculated using the BET method of C$^-\text{TiO}_2-2$ was 165.5 m$^2$·g$^{-1}$, which is much higher than that of TiO$_2$ nanoparticles.\textsuperscript{53} As depicted in Figure 5b, PL spectra are measured at room temperature using an excitation wavelength of 325 nm to study the recombination process of photoexcited electrons and holes. Apparently, pristine TiO$_2$ exhibited a high electron−hole recombination intensity, while significant quenching of PL over C$^-\text{TiO}_2-2$ was also observed. The results indicated that the combination of TiO$_2$ and carbon can effectively inhibit the recombination rate of photoinduced electrons and hole pairs, so as to produce more active photocatalytic species and improve the photocatalytic performance. In addition, the electrochemical impedance spectroscopy (EIS) of TiO$_2$ and C$^-\text{TiO}_2-2$ hybrid that is presented as Nyquist plots in Figure S4 attests that the addition of graphite carbon can significantly improve the conductivity of the original TiO$_2$, so as to achieve a rapid interface electron transfer.\textsuperscript{54}

Figure 6a shows the change of the TC concentration with irradiation time in different samples. Before illumination, TC solution was adsorbed on different samples in dark. Obviously, the adsorption capacity of C$^-\text{TiO}_2$ samples is higher than that of the pristine TiO$_2$ sample. Figure 6b shows the change of the photocatalytic activities and (b) kinetics of the as-prepared samples for TC degradation under visible-light irradiation.
pure TiO$_2$, which might be ascribed to the graphitic carbon layer (sp$^2$ bonding) and porous structure of C–TiO$_2$ photocatalysts. The blank experiment demonstrated that the photodegradation of TC could be neglected without photocatalyst. With pure TiO$_2$ as a catalyst, TC concentration decreased gradually after irradiation for 160 min at the rate of 30.4%. After coupling with carbon, the photocatalytic degradation performance of C–TiO$_2$ samples was greatly improved. Under the same reaction conditions, the degradation rate of C–TiO$_2$-2 samples reached 90.8% after irradiation for 160 min. However, with further increase of carbon content in C–TiO$_2$ nanocomposites, the photocatalytic activity of C–TiO$_2$ nanocomposites decreased rapidly, indicating that the appropriate carbon content is of great significance for the optimization of their photocatalytic activity. To obtain a deep insight into the photocatalytic process, the pseudo-first-order reaction kinetics was fitted according to the equation \( \ln(C_t/C_0) = kt \) (Figure 6b), where \( C_0 \) is the initial concentration of the TC solution, \( C \) is the concentration of TC at time \( t \), and the slope \( k \) is the apparent reaction rate constant. The values of the reaction rate constant \( k \) are estimated to be 0.00221 and 0.01258 min$^{-1}$ for pristine TiO$_2$ and C–TiO$_2$-2 nanocomposites, respectively. The rate constant of C–TiO$_2$-2 is up to 5.69-fold higher than that of the bare TiO$_2$. The higher photocatalytic activity of C–TiO$_2$-2 was because its two-dimensional porous carbon layer enhanced the light absorption region, inhibited the recombination rate of photogenerated electrons and holes, and enhanced TC adsorption through the \( \pi-\pi \) stacking.\textsuperscript{55–57} On the other hand, compared to pristine TiO$_2$, C–TiO$_2$-2 nanocomposites showed a lowered \( \zeta \)-potential value at pH = 4.5 (Figure S5), which means a better dispersion of C–TiO$_2$-2 hybrid compared to that of pristine TiO$_2$ nanoparticles.\textsuperscript{38} Cyclic experiments of TC degradation in the presence of C–TiO$_2$-2 nanocomposites were carried out to study the stability and reusability of the photocatalyst. As revealed in Figure 7, after five cycles of operation, the photodegradation efficiency of TC did not decrease significantly, which shows that the C–TiO$_2$-2 photocatalyst has the advantages of high efficiency, reusability, and good stability and has potential practical application value in wastewater treatment.

To elucidate the photodegradation pathway of TC in the presence of C–TiO$_2$-2, the main intermediate products of TC transformation in the photodegradation process were identified by high-performance liquid chromatography–mass spectrometry (HPLC–MS). The mass spectra of TC after reacting for 60 min by C–TiO$_2$-2 are displayed in Figure S6. As shown in Figure S6 and Table S1, TC is completely transformed to seven main photoproducts, which are designated as P1–P7 in the order of retention time. Combining with these detection results and references,\textsuperscript{59–61} degradation and removal process can be divided into three main pathways (Figure 8). The first pathway is the primary degradation by the addition of hydroxyl locating at C$_{11}$–C$_{12}$ and C$_2$–C$_3$ double-bond of TC with the attack of the *OH radicals to generate the intermediate with \( m/z \) 475.3, which is further fragmented to the product P2 (\( m/z \) 396.9) via the deprivation of methyl from the tertiary amine and amide group. Meanwhile, TC was oxidized at position 11 to the corresponding ketone to form the product P3 (\( m/z \) 453.5), and then the amino group at position 1 was bi-demethylated due to the low bond energy of C–N. Subsequently, the dehydroxylation reaction occurred at position 2 and then product P4 (\( m/z \) 417.2) was produced. In addition, the deprotonated product P5 with \( m/z \) of 383.2 was generated via loss of N-diethylmethyl group due to the relatively low bond energy of C–N and the loss of the hydroxyl group. Subsequently, the protonated product P6 with \( m/z \) 340.3 was generated through the detachment of amide group from intermediate of \( m/z \) 383.2. The detachment of water molecule and hydroxyl group involved in the formation of protonated products P7 with \( m/z \) 306.3. Thus, it can be seen that TC is gradually decomposed to produce the corresponding degradation intermediates, which can then be converted into CO$_2$, H$_2$O, and other degradation products.

Based on the above results and discussion, Figure 9 schematically proposes the possible mechanisms of the high photodegradation activity of C–TiO$_2$-2 nanocomposites, including photogenerated electron–hole separation process and free radical formation process. First, the introduction of two-dimensional carbon sheets result in the C–TiO$_2$-2 sample having a larger specific surface area, thus providing a more active reaction center. When the as-prepared C–TiO$_2$-2 nanocomposites are irradiated with visible light, the photogenerated electrons and holes could be prolonged in the transfer process. The separated electrons and holes could be efficiently separated, and the lifetime of the excited electrons and holes could be prolonged in the transfer process. In summary, the significant improvement of the photocatalytic activity of C–TiO$_2$-2 nanocomposites is caused by the improvement of solar energy utilization, the enrichment and adsorption of pollutants, and the subsequent effective separation of photogenerated electron–hole pairs.

3. CONCLUSIONS

In summary, the C–TiO$_2$ nanocomposites were successfully fabricated by a facile calcination approach and acid etching method. The experimental results showed that C–TiO$_2$-2 nanocomposites exhibited superior visible-light photocatalytic activity for the degradation of TC, and the degradation rate was about 5.69 times higher than that of pristine TiO$_2$. The significant improvement of photocatalytic activity is attributed to the increase of specific surface area, the enhancement of light harvesting ability, and the effective separation of photogenerated carriers. In all, the obtained C–TiO$_2$-2 photocatalyst has potential application in solving the problems of worldwide...
environmental pollution and energy crisis by efficiently utilizing solar energy.

4. EXPERIMENTAL SECTION

4.1. Reagents and Chemicals. Titanium dioxide (TiO₂, 5–10 nm), γ-ferric oxide (γ-Fe₂O₃, 20 nm), and tetracycline (TC) were supplied by Aladdin (Shanghai, China) and used without further purification. Starch was obtained from Alibaba.

4.2. Preparation of Photocatalysts. As shown in Figure 10, porous C–TiO₂ composites were fabricated via a facile calcination approach and acid etching method using starch as a carbon source; γ-Fe₂O₃ sphere acts as a graphitization catalyst precursor and a hard template. Typically, 2.0 g of starch was uniformly mixed with 0.2 g of γ-Fe₂O₃ and 4.0 g of TiO₂ by a co-ground method. The resulting powder was then heated at a rate of 3 °C min⁻¹ to reach a temperature of 800 °C and then kept at this temperature for another 2 h in a N₂ atmosphere. The calcined product was washed with hot 3.0 M HCl solution and deionized water for several times to remove the iron species and other metal oxides or salts and dried at 60 °C to get the final C–
TiO₂ nanocomposites. By varying the amounts of starch, the obtained C–TiO₂ samples were denoted as C–TiO₂-1, C–TiO₂-2, C–TiO₂-3, and C–TiO₂-5 with 1.0, 2.0, 3.0, and 5.0 g of starch added, respectively. For comparison, carbon was obtained directly from the carbonization of starch at 800 °C for 2 h.

4.3. Characterization of Photocatalysts. X-ray diffraction (XRD) measurements were performed on a SmartLab XRD spectrometer (Rigaku) with Cu Ka radiation. Then, energy-dispersive X-ray spectroscopy (EDS) was used to analyze the elements of the as-prepared sample. Raman spectra were collected using a DXR Raman microscope (Thermo Fisher Scientific Inc., λex = 532 nm). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a JEM-2100 high-resolution transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurement and XPS valance band (VB) spectra were performed on an ESCALAB 250Xi photoelectron spectroscope (Thermo Fisher Co.) equipped with a standard and monochromatic source (Al Kα). Particle size distribution test and surface ζ-potential of the prepared samples were carried out on a Malvern particle size analyzer (Malvern Zetasizer Nano ZS90). The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2020 (Micromeritics). The analysis of intermediates was performed by a HPLC–MS system (Agilent 1290/6460, Triple Quad MS) equipped with a Zorbax analysis of intermediates was performed by a HPLC measured at 77 K on an ASAP 2020 (Micromeritics). The out on a Malvern particle size analyzer (Malvern Zetasizer Nano ZS90). The nitrogen adsorption and desorption isotherms were measured at 77 K on an ASAP 2020 (Micromeritics). The analysis of intermediates was performed by a HPLC–MS system (Agilent 1290/6460, Triple Quad MS) equipped with a Zorbax XDB-C18 column (5 mm × 150 μm). UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded on a UV–vis spectrometer (UV-3650, Shimadzu) with an integrating sphere attachment. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI920 workstation. The typical photocatalytic activity for degradation of tetracycline under visible-light irradiation. In a typically photocatalytic test, of the photocatalyst was dissolved in TC aqueous solution (10 mg L⁻¹), and then was catalyzed for 0.5 h in the dark to establish an absorption–desorption equilibrium before switching on the lamp. Samples were taken at preselected time intervals using a syringe and filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) syringe filter to remove particles. The quantitative determination of TC was analyzed by a high-performance liquid chromatography (HPLC, Shimadzu LC-20A). After TC photodegradation, the catalysts were filtrated and washed with water. Then, they were added to a photoreactor to be reused in another TC solution to perform the same photodegradation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02411.

EDS spectrum; photon correlation spectroscopy; VB XPS spectra; Nyquist plots; ζ-potential; mass spectra of the TC and intermediates; identified TC and its possible transformation products (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grant No. 21808019), the Natural Science Foundation of Jiangsu Province (Grant Nos. BK20181048, BK20180958, and BK20181476), the Science and Technology Bureau of Changzhou (CJ20190074), the Science Foundation of Jiangsu University of Technology (KYY17001), the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province (18KJB150014), and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX19_0738).

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