Synthesis and characterization of black TiO₂/graphene composites with enhanced photocatalysis

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Abstract

According to the composite design, a series of black TiO₂/graphene composites were synthesized to improve its photocatalytic activity. TiO₂ is generated in situ on the surface of graphene by a facile sol-gel method. The combination of graphene and TiO₂ was beneficial for eliminating the opportunity of photogenerated electron-hole recombination due to the excellent conductivity of graphene. In the subsequent hydrogenation process, the self-doping Ti³⁺ was introduced accompanied by the crystallization of amorphous TiO₂. The narrowed bandgap caused by self-doping Ti³⁺ enhanced the visible light absorption and make the composites appear black. Both of them improved the photocatalytic performance of the synthesized black TiO₂/graphene composites. The band structure of the composite was analyzed by valence band XPS, revealing the reason for the high visible light catalytic performance of the composite. The results proved that the black TiO₂/graphene composites synthesized show attractive potential for applications in environmental and energy issues.

1. Introduction

Titanium dioxide (TiO₂) is regarded as an important photocatalyst because of its good photoelectric properties [1, 2]. Among the four crystal phases of TiO₂, anatase and rutile phases are the most common and have been extensively researched due to their excellent photoactivity [3, 4]. However, their large band gap (rutile at about 3.0 eV and anatase at 3.2 eV) largely limits the activity to the ultraviolet (UV) region of the light. As photocatalysts, they only use less than 5% of the entire solar energy [5, 6]. Moreover, the photogenerated electro-hole pairs in TiO₂ will recombine during the conduction process instead of participating in the photocatalytic reaction. The recombination of electro-hole reduces the quantum efficiency, leading to a weaker photocatalytic efficiency [4]. Therefore, the absorption range of light and recombination of photogenerated electro-hole become the main factors of TiO₂ photocatalysts.

In decades, significant attention has been attracted to improve the photocatalytic activity of TiO₂. For example, through appropriate structural design, synthesis of metal and non-metal element doping and semiconductor composite materials [7–10]. In recent years, carbon nanomaterials have received great attention as composite materials, such as carbon nanotubes, graphene, etc. Especially graphene, because of its excellent electrical conductivity, chemical stability and adsorption capacity, is conducive to the improvement of TiO₂ photocatalytic activity [11, 12]. Many studies indicated that the excellent conductivity of graphene is conducive to the transfer of electrons. Therefore, the combination of TiO₂ and graphene can significantly promote the recombination of photogenerated electron-hole, thereby improving photocatalytic performance [13, 14].

Huang et al. synthesized the TiO₂/graphene composites by a simple solvothermal method. The synthesized composites have excellent photocatalytic performance in degradation of formaldehyde and the effect of chemical bonds in the composites has been revealed [13]. Jung et al. reported a Graphene–

2D mesoporous TiO₂ synthesized via facile hydrothermal process, which showed outstanding degradation of methylene blue, due to the enhanced composite effects of graphene and TiO₂ [14].

Although the TiO₂-graphene composites greatly improve the catalytic performance of TiO₂, this new composite material also has some problems, such as low visible light utilization [15, 16]. In 2011, Chen et al. presented a new method of synthesizing black TiO₂ by hydrogenation to increase solar absorption [17]. Hydrogenation introduced disorder layers outside of the black TiO₂ nanoparticles, dramatically changed the band gap of TiO₂. The black TiO₂ synthesized exhibit a long wavelength absorption and substantial visible light photocatalytic activities. These obviously changed properties make the appropriate integration of black TiO₂ and graphene a promising method to develop the photocatalytic performance. Hence, it is necessary to synthesize and study the black TiO₂/graphene composites.

In this paper, a series of black TiO₂/graphene composites were synthesized by sol-gel method and subsequent hydrogenation process. Amorphous TiO₂ is generated in situ on the surface of graphene by hydrolysis of organic titanium sources. Amorphous TiO₂ precursor was used to synthesize black TiO₂ by surface hydrogenation process. The synthesized photocatalyst had a narrow band gap, which can significantly extend the wavelength of light absorption. And the photocatalyst exhibited excellent photocatalytic performance due to the excellent photogenerated electro-hole separation ability of graphene. Moreover, the influence of graphene on the photocatalytic activity of black TiO₂/graphene composites has been systematically investigated by the degradation of methyl blue.

2. Experimental

2.1. Synthesis of black TiO₂/graphene composites

In typical, the black TiO₂/graphene composites were synthesized by a versatile sol-gel strategy as follows. Tetrabutyl titanate (TBOT) (CP, 98.0%, Sinopharm Group Chemical Reagent Co., Ltd) and graphene (Strem Chemicals, Inc.) served as starting materials. First, a mixture solution of 5 mL TBOT and 250 mL C₂H₅OH (Eth) with different ratios of graphene were prepared. The polyethylene glycol (PEG) was used as surfactant to increase the surface binding between TiO₂ and graphene. Then, the solution prepared was slowly dripped into the stirring solution of 250 mL C₂H₅OH and 250 mL H₂O. In the process, TBOT and the water in the solution occurred hydrolysis and polymerization to form a sol. The overall reaction process is [18, 19]

After reaction for 1 h and precipitation for 3 h, the resulting precipitate was centrifuged and washed 3 times with ethanol. Subsequently, the amorphous TiO₂ graphene composites were obtained by drying at

80°C for 6 h and calcining at 200°C for 2 h in air. The obtained amorphous TiO₂ graphene composites were gradually darkened in color with different graphene contents (1 wt%, 5 wt%, 10 wt%, 15 wt%).

Scheme 1 Schematic diagram showing synthetic procedure of black TiO₂/graphene composites

Finally, the amorphous TiO₂ graphene composites were calcined in H₂ flow at 500°C for 2 h under atmospheric pressure. Then the black TiO₂/graphene composites (denoted as BTG-1, BTG-5, BTG-10, BTG-15 correspond to different graphene content of 1 wt%, 5 wt%, 10 wt%, 15 wt% respectively) were synthesized. The process for synthesizing black TiO₂/graphene composite is shown in Scheme 1.

2.2. Characterization

The morphology, structure and element distribution of the black TiO₂/graphene composites were examined by high-resolution transmission electron microscope (HRTEM, Tecnai G2 20). The crystal structure of the samples was detected by X-ray diffraction (XRD) on Rigaku D/MAX-2400. In order to confirm the chemical compositions and band status of the black TiO₂/graphene composites, XPS spectrum was characterized on AXIS-Ultra DLD-600W. The state of graphene was characterized by Raman spectroscopy with LabRAM HR800 using laser excitation at 532 nm. The Raman spectroscopy scanning range is (100-3000 cm⁻¹). In order to examine the light absorption range of the black TiO₂/graphene composites, UV-Vis absorption spectra were performed on a Shimadzu UV-3600 Plus UV-VIS-NIR Spectrophotometer.

The photocatalytic activity of black TiO₂/graphene composites was determined by using them in the decomposition of the methyl blue (MB). The MB solution of 10 mg/L was prepared to test the visible light catalytic performance of the as-synthesized black TiO₂/graphene composites (BTG). 10 mg of the BTG composites were added to 100ml MB solution, stirred in the dark or 30 min to achieve adsorption/desorption equilibrium. The visible light irradiation of the photocatalysis experiment was from a 300 W halogen tungsten lamp with a cut-off filter ($\lambda > 420$ nm). The temperature of the reaction solution is controlled at 20°C with a water-cooling system. In the photocatalysis experiment, 3 ml of the reaction solution was taken every 10 min, and the catalyst was removed by centrifugation (10000 rpm). The concentrations of residual MB were analyzed by the absorption band maximum (660 nm).

3. Results And Discussion

The XRD patterns of TiO₂/graphene composites before and after hydrogenation process are shown in Fig. 1(A). The XRD patterns of the TiO₂/graphene composites before hydrogenation process show only some diffuse peaks, indicating that the TiO₂/graphene composites before hydrogenation are amorphous [20]. After the hydrogenation process, the peaks occur at 25.28° (101), 37.80° (004), 48.05° (200), 53.89° (105), 55.07° (211), 62.69° (204), 68.93° (116), 70.31° (220), and 75.03° (215) (Fig. 1A(b)), corresponding to the diffractions of anatase TiO₂ (JCPDS 21-1272) [18, 21]. It was indicated that the sample after

surface hydrogenation is crystallized from amorphous to anatase structure, and the average crystal size is approximately 21 nm calculated by Scherrer formula, in agreement with TEM observation.

The structure of black TiO₂/graphene composites can also be characterized by Raman spectra. The Raman spectra of BTG with different graphene contents are shown in Fig. 1(B). The three bands at around 1365 cm⁻¹ (D band), 1580 cm⁻¹ (G band) and 2700 cm⁻¹ (2D band) are corresponding to graphene [22]. For all the BTG with different graphene contents, the Raman peaks occur at around 156 cm⁻¹ (E_{g(1)}), 406 cm⁻¹ (B_{1g(1)}), 523 cm⁻¹ (A_{1g} + B_{1g(2)}), and 646 cm⁻¹ (E_{g(2)}), which match with the characteristic peaks of anatase TiO₂ [23]. Compared with the characteristic peaks of anatase TiO₂, the E_{g(1)} mode shift from 144 cm⁻¹ of bare bulk TiO₂ to 156 cm⁻¹ of BTG synthesized. The shift toward high frequency indicates the ultra-dispersed characteristics of TiO₂ nanoparticles and their combination with graphene [24]. And the disappearance of the graphene 2D band in BTG may be attributed to the composite of graphene and TiO₂ [11]. From the Raman analysis, the characteristic peaks of TiO₂ and graphene appeared in the spectra of BTG, indicating that the black TiO₂/graphene composites were successfully synthesized.

Furthermore, the elemental composition of the black TiO₂/graphene composites was investigated by XPS. In Fig. 2(A), the characteristic peaks of C 1s, Ti 2p, and O 1s are present at 284.6, 457.8, and 529.7 eV respectively. In the Ti 2p XPS spectrum (Fig. 2(B)), the Ti 2p_{3/2} and Ti 2p_{1/2} of TiO₂ are revealed at 457.8 and 463.3 eV. The Ti 2p_{3/2} peak of BTG shifts from 458.6 eV to a lower binding energy corresponds to the presence of a high Ti³⁺ concentration [25-27]. All Ti 2p spectra are symmetrical on the low energy side, indicating that TiO₂ is not doped with carbon [17]. The curve fit of C 1s spectra of BTG is shown in Fig. 2(C). The peak at 284.5 eV is ascribed to the C=C/C-C bond, indicating the presence of graphene. The weak peak at 286.5 confirms the presence of the C-O bond [28]. In addition, there is no Ti-C peak observed in both Fig. 2(B) and (C), which confirms that graphene does not exist as a dopant in the BTG composites. The curve fit of O 1s spectra of BTG is shown in Fig. 2(D). The peak at 529.6 and 532.2 eV are ascribed to Ti-O and C-OH bonds. In both Fig. 2(C) and (D), the appearance of C-O and C-OH bonds indicate the existence of bond between carbon and oxygen atoms in the BTG composites. This phenomenon may be attributed to the oxidation of graphene since TiO₂ is a well-known catalyst.

The morphology, structure and element distribution of the black TiO₂/graphene composites were examined by TEM. The TEM observation in Fig. 3(A) shows that the TiO₂ nanoparticles are well dispersed on the graphene sheets, and 10–50 nm in size.

The selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 3(A). The (101), (004), (200), (204) and (105) diffraction rings are detected in the SAED pattern indicates that TiO₂ in the composites is anatase structure [18]. The SAED result is consistent with the XRD characterization, which indicates that the TiO₂ in the composite is anatase structure with excellent photocatalytic activity. Fig 3(B) shows the HRTEM image. It can be seen that the size of individual TiO₂ nanocrystal was approximately 15 nm in diameter. There was a disordered surface layer surrounding the TiO₂ nanocrystal,

as shown by the dotted red circle in Fig 3(B). The thickness of the disordered layer is about 1 nm, which is consistent with the black TiO₂ reported by Chen et al [17]. The disordered layer surrounding TiO₂ nanocrystal is created by hydrogenation, which causes a significant color change and enhancement of visible light photocatalytic activity. The schematic diagram of sample color change (from blue to black) after hydrogenation is shown in Scheme 1. The inset in Fig 3(B) shows that the interplanar spacing is 3.58 Å, corresponding to the (101) plane of anatase TiO₂. The Energy Dispersive X-ray (EDX) elemental mappings of Ti, C, O taken from the STEM image of Fig 3(C) are given in Fig 3(D-F), respectively. It can be seen from the figures that the Ti and O elements are uniformly aggregated and dispersed on the C element of graphene, which is consistent with the TEM result of Fig. 3 (A). The results further demonstrate the successful assemblies of TiO₂ on graphene in the black TiO₂/graphene composites.

Fig. 4(A) shows the UV-vis diffuse reflectance spectra (DRS) of the black TiO₂/graphene composites synthesized. The presence of graphene significantly improves the visible light absorption of the black TiO₂/graphene composites. The visible light absorption intensity of the black TiO₂/graphene composites is enhanced with increasing graphene content. In order to characterize the band gaps of the black TiO₂/graphene composites, the Kubelka-Munk function $(F(R_{\infty}) \cdot E)^{1/n}$ versus the energy of light ($E = h\nu$) is shown in Fig. 4(B) [29, 30]. For an indirect transition of anatase TiO₂, $n=2$ will give the best linear fit. As the graphene content increases from 1% to 15%, the band gaps are estimated roughly to decrease from 3.05 to 2.94 eV. It is well known that the band gap energy of anatase TiO₂ is 3.2 eV. The band gap around 3 eV of black TiO₂/graphene composites is lower than that of anatase TiO₂, which could be attributed to the self-doping of Ti³⁺. Moreover, the black TiO₂/graphene composites have enhanced light absorption in the range of visible light, which is consistent with the darker sample color with increasing graphene content. The results suggest that both graphene combination and self-doping of Ti³⁺ play a crucial role in the photocatalytic activity of the black TiO₂/graphene composites. The photocatalytic activity of the samples was shown in Fig. 4(C). Fig. 4(C) illustrates the normalized MB concentration in the degradation solution as a function of visible light irradiation time. After a visible light irradiation time of 60 min, 95%, 98%, 99% and 96% MB are decomposed in the presence of the BTG-1, BTG-5, BTG-10 and BTG-15, respectively. A comparative experiment without catalyst during visible light irradiation exhibits only 15% MB decomposition. The photocatalytic process follows first-order kinetics, $c = c_0 \exp(-kt)$, where c_0 and c are the MB concentration before and after visible light irradiation, respectively [31]. The k value in the formula represents the photocatalytic reaction rate. Through fitting calculation, the photocatalytic reaction rates k for BTG-1, BTG-5, BTG-10 and BTG-15 are determined to be 2.88, 3.61, 3.99 and 3.23 h⁻¹, respectively. The BTG-10 exhibits the highest photocatalytic activity. To determine the recyclability of the black TiO₂/graphene composites, the BTG-10 is recycled under several visible light irradiation cycles. As shown in Fig. 4(D), after 5 cycles, the degradation rate of MB still reaches 90% in the presence of the BTG-10, indicating that the catalyst has good stability.

Since BTG-10 has the best catalytic activity in the TiO₂/graphene composites, BTG-10 was selected for valence band (VB) XPS analysis in Fig. 5(A). The VB of BTG-10 is located at 2.68 eV, which is lower than

the commonly used TiO_2 (3.0 eV) [26]. The insets in Fig. 5(A) show the energy band diagrams. According to the energy band model, the conductance band (CB) can be calculated by $\text{CB} = \text{VB} - E_g$, where E_g represents the energy of the band gaps. The E_g of BTG-10 is estimated to be 3.0 eV by Fig. 4(B), so the CB of BTG-10 is calculated as -0.32 eV. The results suggest that the disordered surface layer surrounding the TiO_2 nanocrystal introduced by hydrogenation can upshift both the VB and CB edge of the TiO_2 /graphene composites synthesized. According to the energy band analyses, the VB of the BTG-10 is higher than the $\text{O}_2/\text{H}_2\text{O}$ and CB is H^+/H_2 potential, suggesting that the black TiO_2 /graphene composites synthesized have attractive potential for applications in environmental and energy issues.

The photocatalytic mechanism is also proposed as shown in Fig. 5(B). The disordered surface layer introduced by hydrogenation narrows the band gap of the black TiO_2 /graphene composites, which improves the optical absorption properties [32]. Consequently, the electrons in the VB can easily transition to the CB of TiO_2 under visible light irradiation. It is well known that the graphene which nano-sized black TiO_2 attached to has good electrical conductivity [33]. Therefore, electrons will be transferred to graphene instead of CB, which is conducive to reducing the opportunities of electron-hole recombination and enhancing photocatalytic activity. However, the graphene itself has no photocatalytic activity, and excessive graphene will hinder the absorption of photons by TiO_2 . This hinder effect is the reason why BTG-10 has a higher catalytic activity than BTG-15.

4. Conclusions

A series of black TiO_2 /graphene composites with different graphene contents were successfully synthesized. In the sol-gel process, TiO_2 is generated in situ on the surface of graphene from TBOT as a titanium source. The good conductivity of graphene is beneficial to eliminating the opportunity of photogenerated electron-hole recombination. In the hydrogenation process, self-doping Ti^{3+} is introduced accompanied the crystallization of amorphous TiO_2 . The narrowed bandgap (2.94 ~ 3.05 eV) caused by self-doping Ti^{3+} enhance the visible light absorption. Moreover, the nanostructured black TiO_2 -graphene hybrid materials show enhanced visible light photocatalytic activity in methyl blue degradation. The sample with 10 wt% graphene shows the highest photocatalytic activity and good stability. The incorporation of black TiO_2 caused by hydrogenation and graphene composite expands the light absorption range and reduce the recombination of photogenerated electron-hole, both of which enhances the capacity of photodegrading organic dyes. Therefore, this work is expected to open up a new way for the synthesis of black TiO_2 /graphene composites, and its high photocatalytic activity proves that the black TiO_2 /graphene composites synthesized have attractive potential for applications in environmental and energy issues.

Declarations

Acknowledgement

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Figures

Figure 1

Schematic diagram showing synthetic procedure of black TiO₂/graphene composites

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Figure 2

(A) XRD patterns of TiO₂/graphene composites (a) before and (b) after hydrogenation process. (B) Raman spectra of black TiO₂/graphene composites with different graphene contents.

Figure 2

(A) XRD patterns of TiO_2 /graphene composites (a) before and (b) after hydrogenation process. (B) Raman spectra of black TiO_2 /graphene composites with different graphene contents.

Figure 3

XPS spectra of black TiO₂/graphene composites. (A) Full survey, (B) Ti 2p spectra. (C) C 1s spectra. (D) O 1s spectra.

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XPS spectra of black TiO₂/graphene composites. (A) Full survey, (B) Ti 2p spectra. (C) C 1s spectra. (D) O 1s spectra.

Figure 4

(A) TEM, (B) HRTEM and (C) STEM images of black TiO₂/graphene composites. Elemental mapping of (D) titanium, (E) carbon and (F) oxygen taken from the whole area of (C).

Figure 4

(A) TEM, (B) HRTEM and (C) STEM images of black TiO₂/graphene composites. Elemental mapping of (D) titanium, (E) carbon and (F) oxygen taken from the whole area of (C).

Figure 5

(A) UV-vis diffuse reflectance spectra of black TiO₂/graphene composites, (B) the Kubelka-Munk function versus the energy of light, (C) photocatalytic degradation of methylene blue (MB) under visible light ($\lambda \geq 420$ nm), and (D) cycle test of the samples degradation MB.

Figure 5

(A) UV-vis diffuse reflectance spectra of black TiO₂/graphene composites, (B) the Kubelka-Munk function versus the energy of light, (C) photocatalytic degradation of methylene blue (MB) under visible light ($\lambda \approx 420$ nm), and (D) cycle test of the samples degradation MB.

Figure 6

(A) The valence band XPS spectra of BTG-10, and (B) the proposed photocatalytic mechanism of BTG-10.

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