Enhanced Photocatalytic Activity of Carbon Dots Grafted TiO_2 Nanorods

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***Abstract*—TiO_2, one of the most promising photocatalysts, is widely used in air purification, sewage treatment, water splitting, carbon dioxide reduction, and solar cells. However, TiO_2 can only absorb ultraviolet light, which makes up only a small fraction (< 4%) of the total solar spectrum. Therefore, we successfully prepared carbon dots (CDs) by low-voltage electrolysis of ethanol/sodium hydroxide/water mixture. TEM image shows that the prepared CDs are monodispersed spherical particles with a diameter of 3-5 nm. CDs-grafted TiO_2 nanorods (CDs-TiO_2 nanorods) were prepared by hydrothermal treatment of CDs and TiO_2 nanorod solution at 200 ℃. TGA shows that the content of CDs in CDs-TiO_2 nanorods was about 0.8%. UV-Dis shows that CDs could significantly improve the visible light absorption property of TiO_2 nanorods. With methyl orange as a model pollutant, the photocatalytic activity of CDs-TiO_2 nanorods was 2.17 times higher than that of TiO_2 nanorods under visible light irradiation.**

***Index Terms*—Carbon dots, photocatalytic activity, titanium dioxide, visible light.**

I. Introduction

Titanium dioxide (TiO_2) is considered as one of the best white pigments in the world and is widely used in coating, plastics, paper making, synthetic fibers, cosmetics, and so on. Unlike silica, calcium carbonate, clay, and other materials, TiO_2 has a unique photocatalytic function [1]. Whether in water or in air, the electrons in the valence band of titanium dioxide will be excited to the conduction band under the irradiation of sunlight, especially ultraviolet radiation, producing free electron-hole pairs. Free electron-hole pairs have strong redox ability, which can activate oxygen and water in the air to produce reactive oxygen species and hydroxyl radicals. When pollutants such as benzene, toluene, formaldehyde, bacteria, and viruses are adsorbed on the surface of titanium dioxide, they combine with the reactive oxygen and hydroxyl radicals and decompose into carbon dioxide and water through oxidation-reduction reactions. Therefore, titanium dioxide is one of the most promising photocatalysts at present and is widely used in air purification, sewage treatment, water pyrolysis hydrogen production, carbon dioxide reduction, solar cells, and other fields [2].

However, titanium dioxide can only absorb ultraviolet light, which only accounts for less than 4% of sunlight, seriously inhibiting its photocatalytic activity under sunlight [3]. Therefore, in the recent ten years, people have made great efforts in improving the photocatalytic activity of TiO_2 under visible light irradiation. These efforts include metal and non-metal doping, precious metal deposition, composite with narrow band gap semiconductors (CdS, SnO_2), dye sensitization (chlorophyll, fluorescein), and so on [4]. Carbon doping, combination, and hybridization have been demonstrated as efficient means to achieve visible-light-responding photocatalytic activities of TiO_2. The use of nanostructured carbon, such as nanotubes, fullerene, and graphene, especially, can further enhance photocatalytic activity of TiO_2/C composites. In recent years, carbon dots, a new member of the carbon family with the advantages of non-toxicity and water-solubility, have attracted great interest. Carbon dots have been widely used in chemical sensing, bioimaging, photocatalysis, and electrocatalysis. Many organic compounds can be used to prepare carbon dots, such as graphene oxide, graphite rods, glucose, citric acid, candle ash, polyvinyl alcohol, etc. Some researchers have prepared carbon dots/ TiO_2 composites [5]-[8], such as CDs/TiO_2 nanosheets, CDs/TiO_2 nanotubes, CDs/TiO_2 nanotube arrays, CDs/TiO_2 nanobelts, and CDs/mesoporous TiO_2 by physical blending, impregnation, and electrodeposition. And they found that the CDs/TiO_2 composites are good photocatalysts for degradation of pollutants, solar energy conversion, and hydrogen evolution, because CDs can harvest visible light and inject excited electrons into the conduction band of TiO_2 through the interfacial bonds between CDs and TiO_2. The photocatalytic performance of CDs can be injected into the conduction band of TiO_2, because it absorbs visible light. Therefore, it is very important to strengthen the interfacial interaction between CDs and TiO_2. Strong interaction can accelerate the interfacial electron transfer and improve the photocatalytic activity.

As far as we know, no one has prepared CDs-TiO_2 nanorods composite photocatalyst by high temperature hydrothermal method before until now. Here, we prepared the CDs solution by electrolysis of graphite rods, mixed the CDs solution with TiO_2 nanorods, then arranged the CDs-TiO_2 nanorods composite photocatalyst by high temperature hydrothermal method, and finally characterized the morphology, structure, and catalytic performance of the catalyst.

II. Experiment

A. Materials

Ethanol, sodium hydroxide, and magnesium chloride were all purchased from Beijing Chemical Reagent Co., Ltd, China. TiO_2 nanorods solution (5 wt%) were prepared by referring to the literature [9]. Methyl orange (MO, $(CH_3)_2$-N-C_6H_4-N=N-C_6H_4-SO_3Na), used as the model pollutant, was manufactured by Zhejiang Yongjia Fine Chemical Plant, China. The chemicals listed above were used without further

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purification.

B. Preparation of CDs [10]

95 ml ethanol, 5 g deionized water, and 4 g sodium hydroxide (NaOH) were added into a 150 mL beaker. The solution was mixed equally for 2 minutes, and the obtained solution was colorless and transparent. Two graphite rods were inserted into the mixed solution, and a voltage of 9 was added to the two rods. Observations show that the surface of one of the graphite rods produced large amounts of bubbles. As the experiment went on, the solution gradually changed from colorless to brownish-red. After the reaction was complete, the solution was electrolyzed for five hours, and then 5 g of magnesium chloride was added to the solution. The carbon dots solution was finally obtained by using filter paper to filter out the magnesium hydroxide. The concentration of CDs was approximately 0.3%.

C. Preparation of CDs-TiO_2 Nanorods

10 g of TiO_2 nanorods solution and 55 g of deionized water were added into a 100 mL Teflon autoclave. Then 10 g CDs solution was added dropwise into the autoclave under continuous stirring. The mixture was kept stirring for an hour under room temperature to obtain a homogenous solution. The Teflon autoclave was heated up using muffle roaster with a speed of 3 ℃/min until reaches 200 ℃, then cooled down naturally after 6 hours of reaction. The resulting CDs-TiO_2 nanorods were washed with deionized water and collected by centrifugation. Finally, the CDs-TiO_2 nanorods were dried under 80 ℃ overnight.

D. Characterization

The morphology of the samples was observed by transmission electron microscopy (TEM) The acceleration voltage of TEM (HT7700, Hitachi) was 100 KV. The UV-Vis Diffuse Reflectance spectra were recorded with a UV-Vis spectrophotometer (UV-2600, Shimadzu), the test resolution set to 1 nm, using barium sulfate for baseline correction, scanning range 200-800 nm. The contents of CDs in CDs-TiO_2 nanorods photocatalyst was characterized by thermal gravimetric analysis (TGA, PerkinElmer) under air atmosphere with air flow of 20 mL/min, and about 3 mg of the sample was heated up to 700^{o}C at a heating rate of 20^{o}C/min. Fourier transform infrared spectroscopy (FTIR) was used to analyze the samples. Nicolet Smart Orbit Accessory (Thermo Fisher Science) was used as the reflection accessory of Nicolet Avatar 6700 Fourier transform infrared spectrometer made by Thermal Fisher Company. The wavenumber ranged from 4000 cm-1 to 650 cm-1, the resolution was 4 cm-1, and the scanning time was 32.

E. Photocatalytic Degradation

Methyl orange (MO) was chosen as the target pollutant to evaluate the photocatalytic performance of the new visible light catalyst. The photocatalytic activity of the samples was evaluated from the degradation rate of MO in aqueous solution with an initial concentration of 15 mg/L. 40 mL MO solution and 20 mg TiO_2 were placed in a 50 mL beaker in a typical photodegradation experiment,. Prior to irradiation, the suspension was magnetically stirred (300 r/min) in dark for 2 hours to establish adsorption-desorption equilibrium between dye and photocatalyst. The light source was a 500 W halogen lamp equipped with an ultraviolet cut off filter (λ> 420 nm), and the average visible light intensity measured with a radiometer was 130±10 mW/cm^2. The lamp was put in a cylindrical glass vessel with a recycling water glass jacket to make sure that the mixed solution was kept at room temperature. At regular times, 5 mL suspension was filtered by a 0.22 μm syringe membrane and examined by measuring the absorption at 465 nm using an UV-Vis spectrophotometer. MO degradation efficiency was calculated by the ratio of its concentration (C_t/C_0, C_t, and C_0 can be calculated by the absorbance intensity).

III. Results and Discussions

A. Characterization of CDs

From the TEM photos of CDs solution, a large number of carbon dots were successfully prepared. The carbon dots were well dispersed without agglomeration. The sizes of carbon dots were 3-5 nm, and the size distribution was narrow. TEM image shown in Fig. 1A demonstrates that the prepared CDs are monodispersed spherical particles with a diameter of 3-5 nm. The UV-Vis spectrum of CDs is shown in Fig. 1B; the spectrum of CDs indicates typical absorption peaks at 236 nm and 282 nm, which are identified as aromatic C=C and C=O bonds respectively. These absorption peaks are speculated to be the formation of graphitic structure, carboxyl groups, and conjugated chains. The C=C bond facilitates the transmission of photoexcited electrons, and the COOH group provides the possibility for the hydroxyl reaction between CDs and the surface of TiO_2.

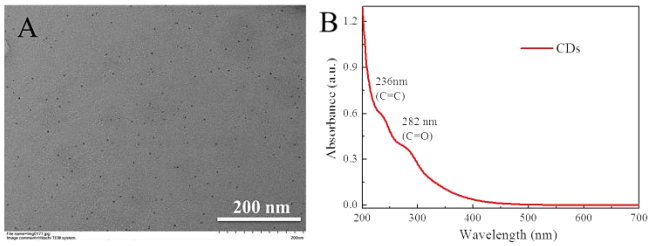

Fig. 1. (A) TEM image of CDs. (B) UV-Vis absorption spectrum of CDs in aqueous solution.

B. Characterization of CDs-TiO_2 Nanorods

Fig. 2 shows the photos of TiO_2 nanorod powder (A) and CDs-TiO_2 nanorod powder (B). It can be seen from the photos that pure TiO_2 nanorods is white and does not absorb visible light, whereas the color of CDs-TiO_2 nanorods is brown, indicating that CDs are grafted on the surface of TiO_2 nanorods and can absorb visible light.

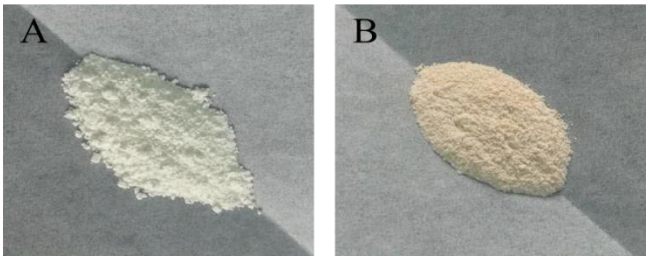

Fig. 2. Photos of TiO_2 nanorods powder (A) and CDs-TiO_2 nanorods powder (B).

Photoabsorption is one of the key factors affecting the photocatalytic performance of photocatalysts. The visible light absorption properties of TiO_2 nanorods and CDs-TiO_2 nanorods were characterized by UV-Dis. As shown in Fig. 3, the absorption range of pure TiO_2 and CDs-TiO_2 nanorods were obvious in the ultraviolet region, indicating that both of them could absorb ultraviolet light. However, Pure TiO_2 has almost no absorption above 400 nm, while the CDs-TiO_2 shows a noticeable absorption in the visible light region ranging from 400 to 800 nm. The marked difference between pure TiO_2 and CDs-TiO_2 nanorods may be attributed to chemical bonding between TiO_2 and CDs with the formation of Ti-O-C bonds. Therefore, CDs play a critical role in the enhanced visible light absorption of the CDs-TiO_2 nanorods.

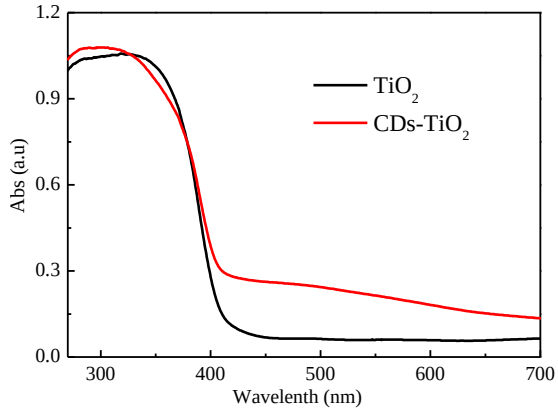

Fig. 3. UV-Vis diffuse reflectance spectra of TiO_2 and CDs-TiO_2 nanorods.

TGA was used to evaluate the content of CDs in CDs-TiO_2 nanorods. As shown in Fig. 4, the weight of TiO_2 decreases slightly with the increase of temperature, which is mainly due to the removal of hydroxyl groups and adsorbed water. The weight of CDs-TiO_2 nanorods tend to be constant when the temperature is over 500 ℃, so the content of CDs was obtained by subtracting the residue weight of pure TiO_2 from the residue weight of CDs-TiO_2 nanorods at 600 ℃; the obtained content of CDs in CDs-TiO_2 nanorods is 0.8%.

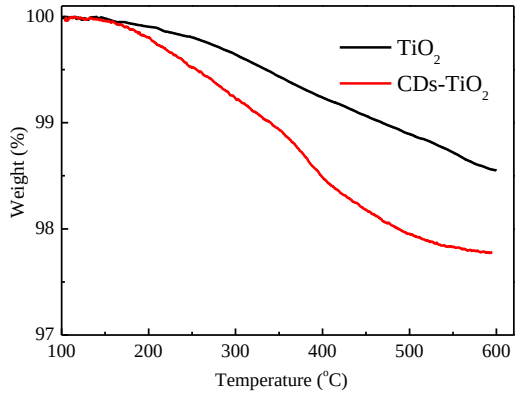

Fig. 4. TGA curves of the TiO_2 and CDs-TiO_2 nanorods (air, 20 °C/min).

TEM was used to observe the distribution of CDs in CDs-TiO_2 nanorods. As shown in Fig. 5A, the prepared TiO_2 nanoparticles were all nanorods with a length of about 50-70 nm and a width of about 8-12 nm. The prepared TiO_2 nanoparticles were slightly agglomerated because of physical adsorption during evaporation of water. The surface of pure TiO_2 nanorods is smooth. However, the TEM image of CDs-TiO_2 nanorods in Fig. 5B reveals that a great number of black dots are attached on the surface of TiO_2 nanorods, with an average size of 4 nm, which is consistent with that of CDs. These results suggest that CDs did not change the shape of TiO_2 nanorods during high temperature and high-pressure reaction and that CDs are chemically grafted onto the surface of TiO_2 nanorods.

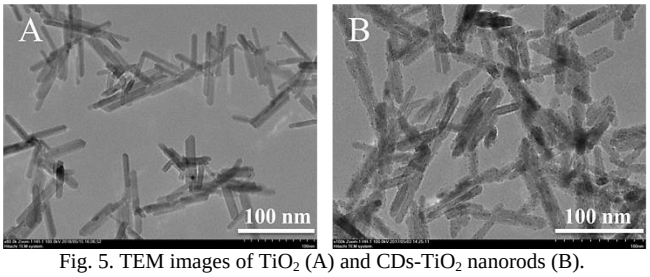

Fig. 5. TEM images of TiO_2 (A) and CDs-TiO_2 nanorods (B).

C. Photocatalytic Degradation

With Methyl orange used as a model pollutant, the photocatalytic activity of TiO_2 nanorods and CDs-TiO_2 nanorods were characterized under visible light irradiation. Fig. 6 shows that the concentration of MO decreased after irradiation, indicating that both TiO_2 nanorods and CDs-TiO_2 nanorods can catalyze the degradation of methyl orange. It is obvious that the photocatalytic activity of CDs-TiO_2 nanorods is higher than that of TiO_2 nanorods. The marked difference between TiO_2 nanorods and CDs-TiO_2 nanorods indicates that CDs can harvest visible light and inject excited electrons into the conduction band of TiO_2, thus improving the photocatalytic activity of TiO_2 nanorods. After 8 hours of photocatalytic reaction, about 12% of methyl orange was degraded by TiO2 nanorods, while about 26% of methyl orange was degraded by CDs-TiO2 nanorods. Under visible light irradiation, the photocatalytic activity of CDs-TiO_2 nanorods was 2.17 times higher than that of TiO_2 nanorods.

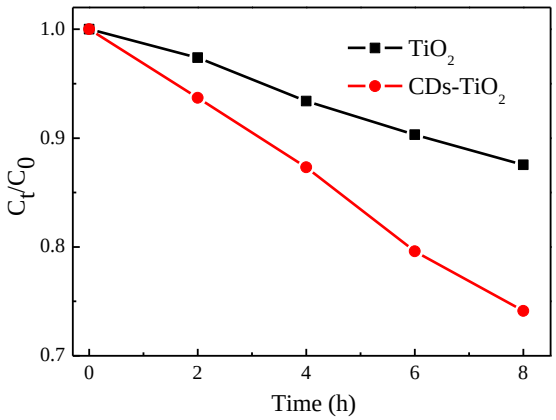

Fig. 6. Photocatalytic degradation of MO solution under visible light irradiation.

IV. Conclusion

In summary, the CDs of about 4 nm were successfully prepared by low-voltage electrolysis of ethanol/sodium hydroxide/water mixture; the method is safe, green, and simple. CDs-TiO_2 nanorods were prepared by hydrothermal method at 200 ℃, and the CDs were successfully grafted onto the surface of TiO_2 nanorods without changing the

shape of nanorods. TGA showed that the content of CDs in CDs-TiO_2 nanorods was about 0.8%. Furthermore, UV-Dis displayed that CDs significantly improved the visible light absorption property of the TiO_2 nanorods. With methyl orange as a model pollutant, the photocatalytic activity of TiO2 nanorods and CDs-TiO_2 nanorods under visible light was characterized. The results showed that CDs significantly improved photocatalytic activity of TiO_2 nanorods under visible light irradiation. The photocatalytic activity of CDs-TiO_2 nanorods was 2.17 times higher than that of TiO_2 nanorods.

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