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论文题目：Immobilization of C@TiO₂ in Calcium alginate hydrogel for photodegradation of organic pollutants

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Immobilization of C@TiO₂ in Calcium alginate hydrogel for photodegradation of organic pollutants

Tianrui Tan, Xiyan You

Abstract

Nano titanium dioxide is a widely used photocatalyst, but there are still two problems with it. On the one hand, nano titanium dioxide can only absorb ultraviolet rays, so the utilization rate of sunlight is relatively low. On the other hand, it is not easy to recycle, which will cause secondary pollution. In response to the above problems, this study prepared polyvinyl alcohol coated nano titanium dioxide by simple solution mixing. By controlling the thermal degradation of polyvinyl alcohol on the surface of nano titanium dioxide into carbon, a carbon coated nano titanium dioxide composite photocatalyst was made. The carbon coating on the surface is about 2.5 nm, and the carbon content is about 3.1%. A supported photocatalyst was prepared by embedding carbon coated nano titanium dioxide in calcium alginate hydrogel. The calcium alginate/carbon coated nano titanium dioxide composite hydrogel has good photocatalytic activity and is easy to recycle.

Keywords: carbon coating; titanium dioxide; hydrogel; visible light photocatalyst

1. Introduction

According to the World Health Organization (WHO), 80% of human diseases are related to water pollution, and more than 800000 people die of diarrhea caused by unsafe water every year[1]. At present, titanium dioxide is regarded as one of the best white pigments. It is broadly utilized in coatings, plastics, papermaking, synthetic fibers and cosmetics. In 1972, Fujishima and Honda discovered that titanium dioxide (TiO_2) can absorb ultraviolet light and decompose water catalytically to produce hydrogen, which has attracted widespread attention[2]. The photocatalysis principle of TiO_2 is shown in Figure 1[3]. When TiO_2 is exposed to sunlight, especially ultraviolet rays, the electrons in the valence band will be triggered and move to the conduction band, no matter in water or in the air, to generate free electrons-hole pairs. Free electron-hole pairs possess strong redox ability, which is able to activate oxygen and water in the air to generate active oxygen and hydroxyl radicals. When benzene, toluene, formaldehyde, bacteria, viruses and other pollutants are adsorbed on the surface of TiO_2 , they will combine with free electrons or holes, causing redox reactions and being decomposed into carbon dioxide and water. At present, nano titanium dioxide are utilized in great scale in air purification, sewage treatment, hydrogen production (by water splitting), CO_2 reduction, and dye-sensitized solar cells[4, 5].

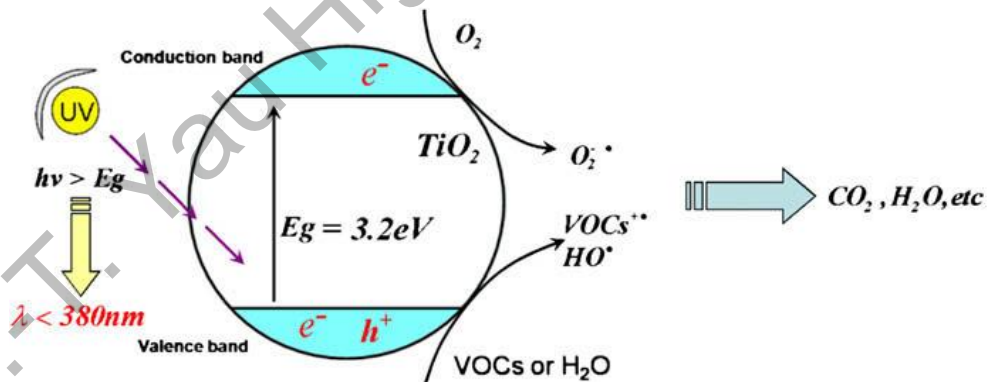


Figure 1 Schematic diagram of TiO_2 catalytic degradation of pollutants under UV irradiation[3]

While using TiO_2 , people discovered that there were two problems with the titanium dioxide photocatalyst. On one hand, because of the relatively large forbidden band width of TiO_2 , about 3.2 eV (Anatase), and the wavelength of light is inversely proportional to

the energy, titanium dioxide can only absorb ultraviolet (UV) below 388nm, while in the sunlight spectrum, the ultraviolet light content is about 4%. Therefore, TiO₂ almost absorbs no visible light, hardly has photocatalytic activity in regions with visible light, and has a poor utilization rate of sunlight[6]. On the other hand, with the continuous reduction of TiO₂ particle size, the specific surface area of TiO₂ increases, Therefore, the TiO₂ used for photocatalysis is all nano TiO₂. However, a problem emerges when using nano TiO₂: the separation and recycle of nano TiO₂ is hard. If it cannot be recycled, the loss of nano TiO₂ particles into the natural environment will pose a potential threat to the ecosystem and human health[7].

In order to improve the visible light absorption performance of TiO₂, a lot of attempts have been made, including doping with a variety of metals and nonmetals, supporting precious metal particles, and coupling with narrow bandgap semiconductors, etc[8]. In recent decades, the grafting of materials containing conjugated structures on the surface of TiO₂ nanoparticles has attracted more and more interest. This is mainly because the conjugated structure can capture visible light and inject excited electrons into the conduction band of TiO₂, thereby improving the photocatalytic activity of TiO₂. Therefore, many materials containing conjugated structures, such as graphene, fullerene, carbon nanotubes, chlorophyll, fluorescein, etc., have been used to improve the visible light catalytic activity of TiO₂[9]. However, scientists have found that only by building a bridge capable of transporting electrons between the conjugated structured material and the TiO₂ can the photocatalytic activity of TiO₂ be greatly improved[10].

In terms of improving the recyclability of nano TiO₂, the most effective method currently is to load or wrap nano TiO₂ particles in a large size solid carrier to prepare a supported nano TiO₂ photocatalyst[11]. Carriers supporting nano TiO₂ can be divided into inorganic carriers and organic carriers. Inorganic carriers mainly include glass beads, ceramics, clay and aluminum foil, etc., and organic carriers mainly include polyethylene terephthalate, polypropylene, cellulose and activated carbon[12]. However, many carriers themselves absorb and block light, which significantly reduces the photocatalytic activity of nano TiO₂.

Therefore, there are still many challenges to develop a cheap and environmentally friendly method for preparing efficient and easy-to-recover TiO₂ composite photocatalysts.

This study proposes a simple, effective, and capable of large-quantities manufacturing method to synthesize carbon coated TiO₂ nanoparticles (C@TiO₂), and then embed the carbon coated nano titania in calcium alginate hydrogel to prepare a supported photocatalyst. The composite photocatalyst has good photocatalytic activity and easy recovery.

2. Experimental

2.1 Materials

Polyvinyl alcohol (PVA, average degree of polymerization 1750±50), sodium alginate (analytical grade), and calcium chloride (analytical grade) were purchased from Sinopharm Reagent Co., Ltd. Nano-TiO₂ (P25, 20% rutile and 80% anatase) with an average particle size of 21nm was purchased from Evonik Industries. Methyl orange (MO) manufactured by Yongjia Fine Chemical Plant in Zhejiang, China was used as a model pollutant. All chemicals were not further purified.

2.2 Synthesis of Carbon Coated Nano Titanium Dioxide (C@TiO₂)

2g PVA was added to 98g deionized water, then the temperature was raised to 95°C, and the mixture was stirred for 1 hour to obtain a clear and transparent PVA solution with a concentration of 2%. 15g nano titanium dioxide and 30g of deionized water was added into a beaker. Then, 40g of the PVA solution mentioned above was added. The mixture was ultrasonically dispersed for 10 minutes, magnetically stirred for 1 hour, then poured into a watch glass and placed in an oven at 80 °C for 10 hours to obtain PVA coated nano titanium dioxide. The PVA coated nano titanium dioxide was put into a muffle furnace, calcined at 230° C for 3 hours, and grounded to obtain brown carbon coated nano titanium dioxide powder.

2.3 Synthesis of Calcium Alginate/ C@TiO₂ (Ca-Alg/C@TiO₂)

0.8g C@TiO₂ was added to 392 g of deionized water. The mixture was ultrasonically dispersed for 10 minutes, then stirred for 2 hours to obtain a brown solution with a concentration of 0.2%. 8 g sodium alginate was added to the C@TiO₂ dispersed solution mentioned above. The mixture was stirred for 1 hour to obtain sodium alginate/C@TiO₂ mixed solution. 16 g anhydrous calcium chloride was added to 384 g of deionized water, and stirred to obtain clear and transparent calcium chloride solution with a concentration of 4%. Sodium alginate/C@TiO₂ mixed solution was drawn by a 5ml medical syringe and

slowly dripped into the stirred calcium chloride solution at a distance of about 15cm. The mixed solution solidified into small pellets immediately after it was dripped into the calcium chloride solution. After 2 hours of cross-linking, the obtained Ca-Alg/C@TiO₂ pellets were rinsed three times with deionized water.

2.4 Photocatalytic Degradation

15mg of methyl orange was added to a 1L volumetric flask. Water was added to the mark. The mixture was then shaken to dissolve to obtain an orange-red methyl orange solution with a concentration of 15mg/L.

50g Ca-Alg/C@TiO₂ pellets was added to a bottle containing 400g methyl orange solution. Then the bottle was placed under sunlight. Every 3 days, samples were taken to test the concentration of the methyl orange solution.

2.5 Characterization

Transmission electron microscope (TEM) and scanning electron microscope (SEM) were used to observe the morphology of the sample. The acceleration voltage of the scanning electron microscope (SU8020, Hitachi) was 15 KV. In order to prepare of the sample of scanning electron microscope, nano titanium dioxide was diluted with alcohol and dropped on the sample stage. After the diluted nano titanium dioxide was dry, gold was sprayed on the surface. Then the sample was ready for observation. In order to prepare the sample of the projection electron microscope sample, nanometer titanium dioxide was diluted with alcohol and dropped on the supporting carbon net. The sample was ready for observation after drying. The Fourier Transform Infrared Spectroscopy (FTIR) analysis of the sample was conducted with the Nicolet Smart Orbit Accessory (Thermo Fisher Scientific) of the Nicolet Avatar 6700 Fourier Transform Infrared Spectrometer of Thermal Fisher Company, the wave number range was 4000~650 cm⁻¹, and the resolution was 4 cm⁻¹. A sample was scanned for 32 times. The thermal weight loss analysis (TGA) under air atmosphere was conducted with the Perkin-Elmer TGA-7 series thermal analysis system, the temperature range was 100°C to 700°C, the heating rate was 20°C/min, and the air flow rate was 20mL/min. The absorbance of the methyl orange solution (MO) solution at the maximum absorption wavelength of 465 nm was measured with an ultraviolet-visible absorption spectrometer (Lovibond, ET99731). The measurement was repeated for three times, and the average value was calculated. The degree of degradation of MO was

described by $C_t/C_0 (=A_t/A_0)$. The C_t/C_0-t curve was plotted.

3. Results and Discussion

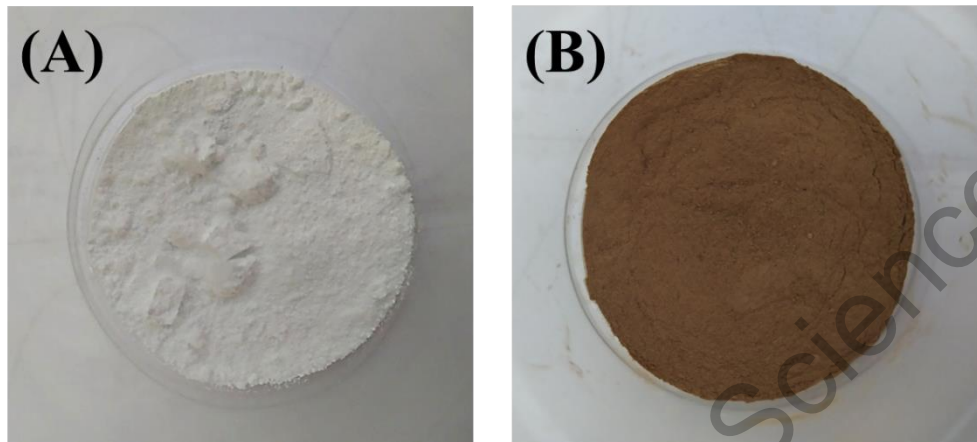


Figure 2 Photos of TiO_2 (A) and C@TiO_2 (B)

Light absorption range is one of the key factors affecting the photocatalytic performance of TiO_2 photocatalyst. As shown in Figure 2 (A), pure nano TiO_2 is white powder, which hardly absorbs visible light, so the photocatalytic activity of pure TiO_2 in the visible light region is very low. The C@TiO_2 is dark brown powder, indicating that the organic polyvinyl alcohol material has undergone thermal degradation on the surface of nano- TiO_2 and formed carbon coated nano TiO_2 . It also shows that the nanoparticles can absorb visible light. Therefore, we tested the light absorption range of nano TiO_2 with Uv-Vis Spectrometer. The results are shown in Figure 3. Pure nano TiO_2 has obvious absorption of ultraviolet light below 400 nm and basically no absorption of visible light above 400 nm, the C@TiO_2 nanoparticles can not only absorb ultraviolet light below 400 nm, but also absorb visible light above 400 nm.

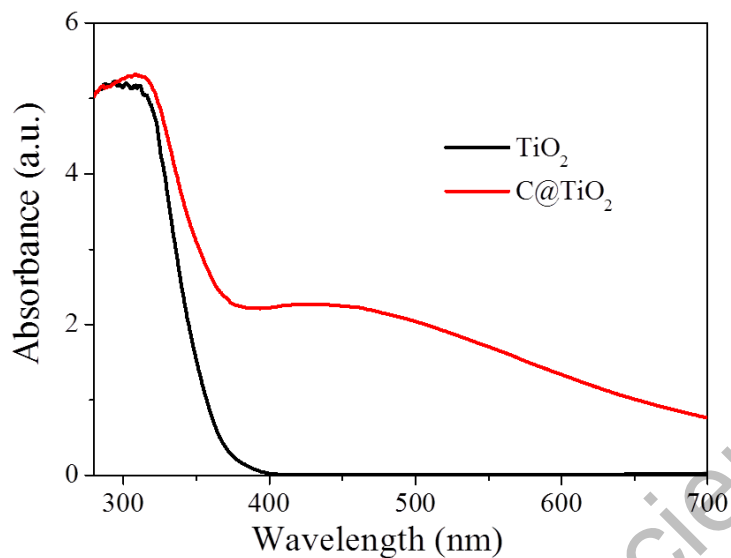


Figure 3 UV-Vis diffuse reflectance spectra of TiO_2 samples

We observed the morphology of nano TiO_2 by scanning electron microscope. The photo in Figure 4 shows that the pure nano TiO_2 particles have good dispersion, the particle size is less than 100nm, and the C@TiO_2 nanoparticles have obvious aggregates, but there are many voids on the surface of the aggregates, indicating that the carbon material slightly adheres the nano TiO_2 particles together. The element scanning function (EDX) of SEM was used to scan C@TiO_2 nanoparticles, as shown in the photo in Figure 5, the distribution of C, O and Ti is basically consistent with the shape of C@TiO_2 nanoparticles, the distribution of in nanoparticles The shape of nanoparticles is basically the same, indicating that the carbon material formed by thermal degradation of polymer is successfully coated on the surface of nano TiO_2 , rather than the simple mixing of carbon and nano TiO_2 .

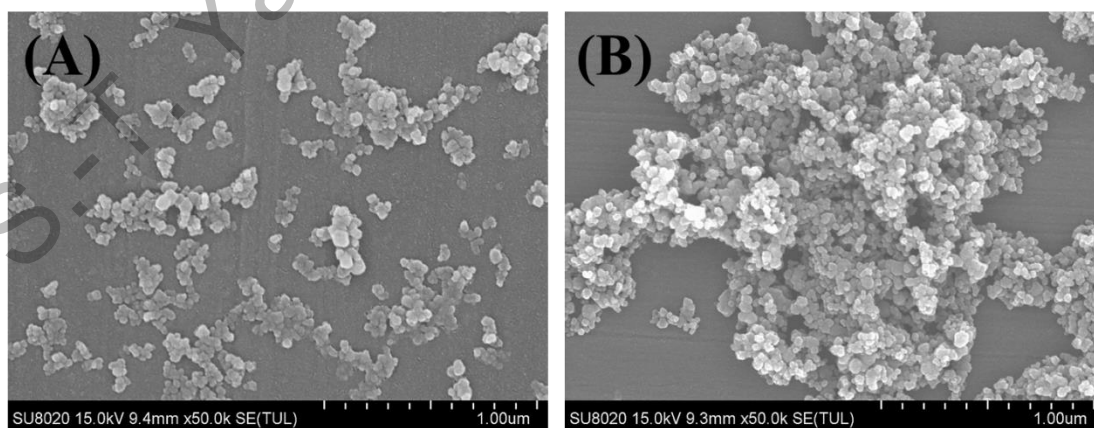


Figure 4 SEM images of TiO_2 (A) and C@TiO_2 (B)

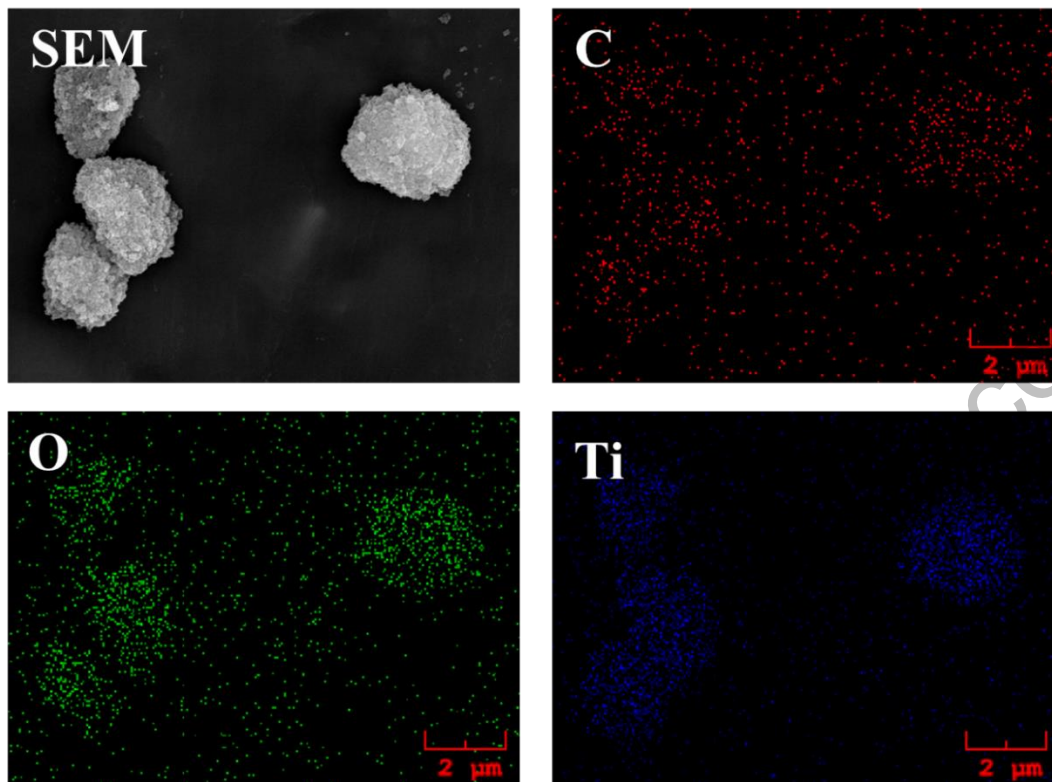


Figure 5 SEM and EDX images of TiO_2 and C@TiO_2

Pure nano TiO_2 and nano C@TiO_2 nanoparticles were further studied by TEM. The photo in Figure 6 show that the surface of pure nano TiO_2 is smooth and the particle size is about 20 nm. However, a fuzzy coating layer can be seen on the surface of C@TiO_2 nanoparticles. The coating layer is evenly distributed and dense. The thickness of the coating layer is about 2.5nm. It can be concluded that the coating layer is a carbon material produced by thermal degradation of polymers, indicating that we have successfully prepared carbon coated nano titanium dioxide nanoparticles.

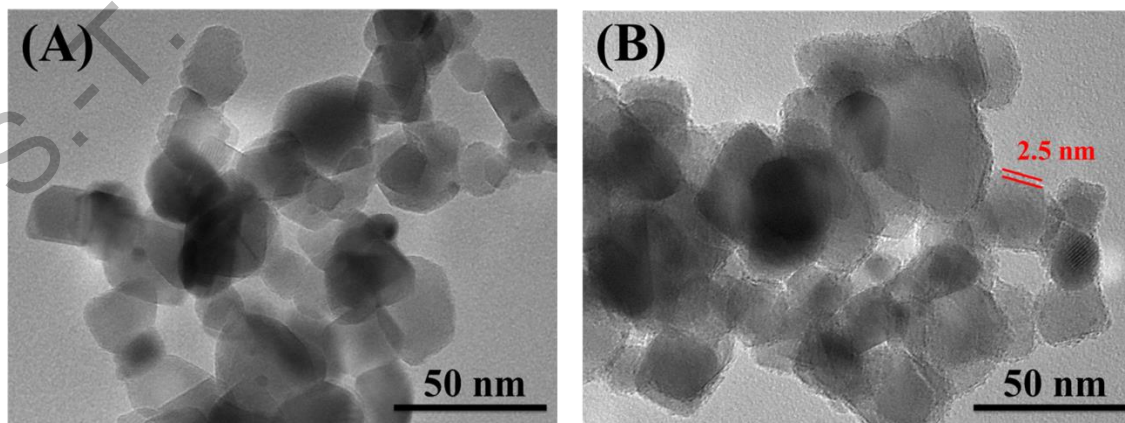


Figure 6 TEM images of TiO₂ (A) and C@TiO₂ (B)

The content of carbon in C@TiO₂ nanoparticles characterized by TGA, which is shown in Figure 7. Nano TiO₂ has good heat resistance, and does not contain organic substances. When heated to 600 °C, there is only 1.3% weight loss. These thermal weightlessness is mainly caused by the removal of adsorbed water on the surface of nano TiO₂. It is worth noting that, there is obvious thermal weight loss of C@TiO₂ nanoparticles at 450 °C, which is mainly caused by the oxidation of carbon materials. The weight of TiO₂ and C@TiO₂ nanoparticles above 500 °C is basically unchanged,

The average weight is basically unchanged above 500 °C, indicating the carbon material on the surface of C@TiO₂ nanoparticles has been completely decomposed. At 600 °C, the weight loss of nano TiO₂ and C@TiO₂ nanoparticles is 1.3% and 4.4% respectively. So, the weight of carbon material coated on the surface of TiO₂ is about 3.1% in C@TiO₂ nanoparticles.

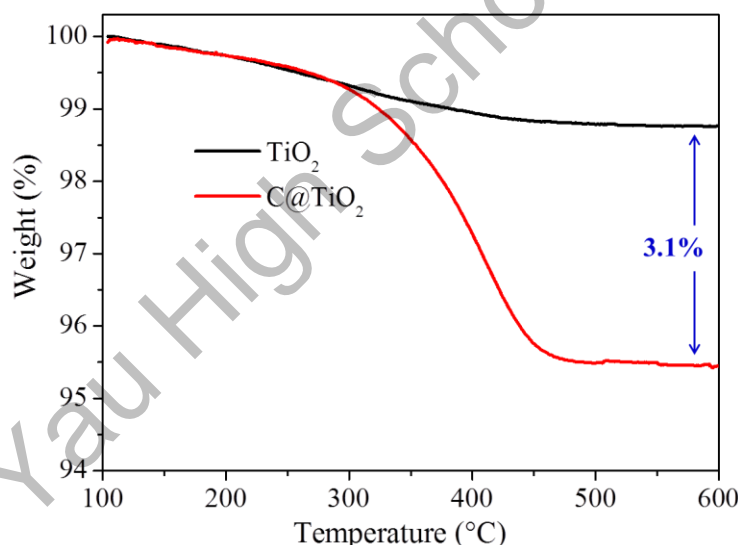


Figure 7 TGA of TiO₂ and C@TiO₂

The Fourier transform infrared spectrometer was used to further characterize the structure of C@TiO₂ nanoparticles. According to the FTIR of nano TiO₂, the absorption peaks at 3270 cm⁻¹ and 1643 cm⁻¹ are attributed to the stretching vibration and bending vibration of OH, indicating that there is adsorbed water on the surface of nano TiO₂, which is consistent with the results of TGA. In C@TiO₂ nanoparticles, the absorption peaks at 3240 cm⁻¹ and 1609 cm⁻¹ are attributed to the absorption of OH, indicating that there is also

adsorbed water on the surface of C@TiO₂ nanoparticles. But in C@TiO₂ nanoparticles, several new absorption peaks have been observed, 2925 cm⁻¹, 1706 cm⁻¹ and 1417 cm⁻¹. These peaks correspond to the stretching vibration of CH₂, C=C double bond stretching vibration and CH₂ bending vibration, indicating that the polymer is degraded into carbon on the surface of nano TiO₂, and formed C=C double bonds, which have been proved to be beneficial to the transmission of electrons[13, 14].

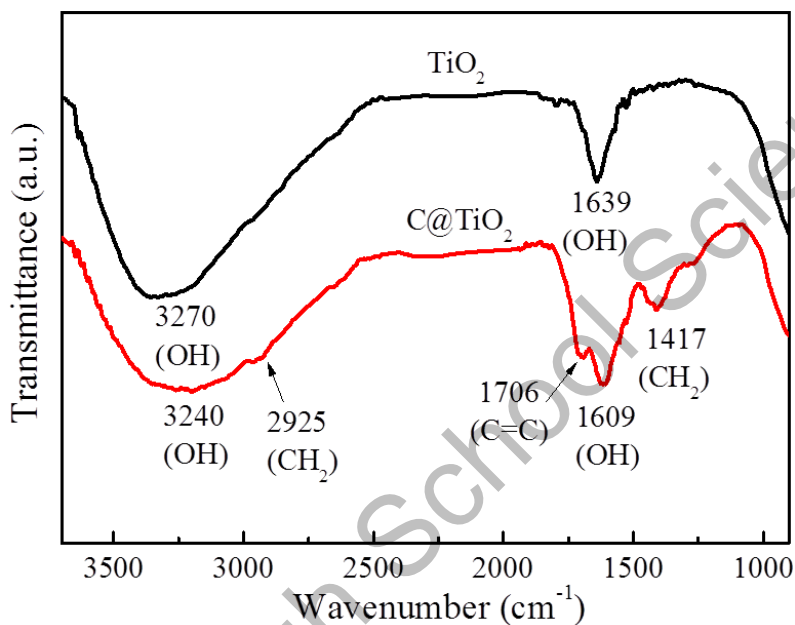


Figure 8 FTIR of TiO₂ and C@TiO₂

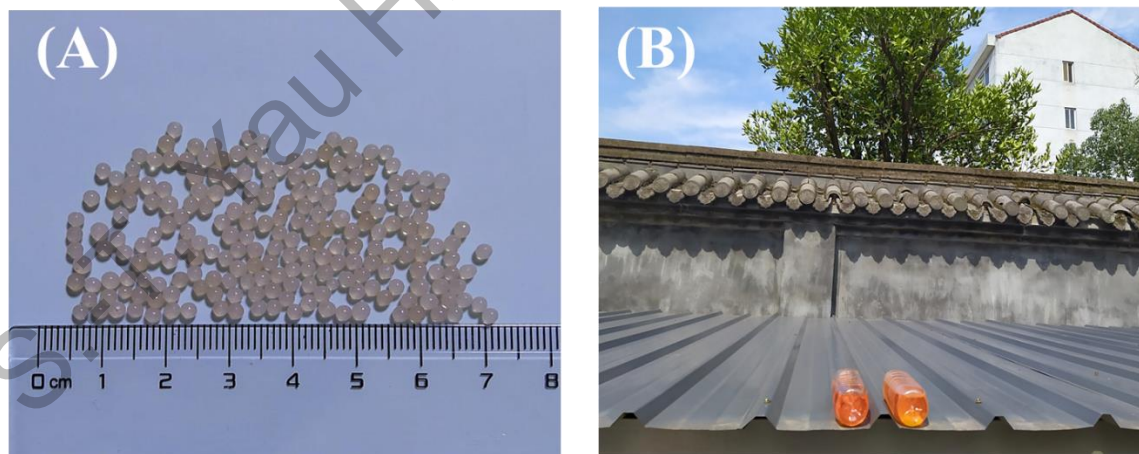


Figure 9 Photos of Ca-Alg/C@TiO₂ hydrogel pellets and photocatalysis under sunlight

Figure 9 shows the Ca-Alg/C@TiO₂ hydrogel pellets that we prepared, the diameter of pellets is about 2mm and color is brown. It shows that C@TiO₂ is more uniformly dispersed in calcium alginate. We mix the Ca-Alg/C@TiO₂ hydrogel pellets with the

methyl orange solution, put them in a transparent bottle, and place them in a place where the sunlight can reach, and take samples every three days to test the concentration of pollutants. The results are shown in Figure 10, the methyl orange solution is orange-red, without the photocatalyst, the concentration of the methyl orange solution is almost unchanged after being irradiated by sunlight for 18 days, merely degraded about 3%. However, under the catalysis of Ca-Alg/C@TiO₂ hydrogel beads, the concentration of methyl orange solution decreased significantly. But as time passed, the decrease rate of the concentration of methyl orange solution slowed down. This is because that the photocatalytic process reaction is a first-order reaction, and as the solubility of the dye decreases, the contact efficiency between the photocatalyst and the pollutants decreases. Under the sunlight, the Ca-Alg/C@TiO₂ composite photocatalyst degraded about 96% of the methyl orange pollutants after 18 days. The color of the solution was really close to colorless and transparent, and the appearance of hydrogel pellets did not change significantly, and the composite photocatalyst was easy to separate from pollutants.

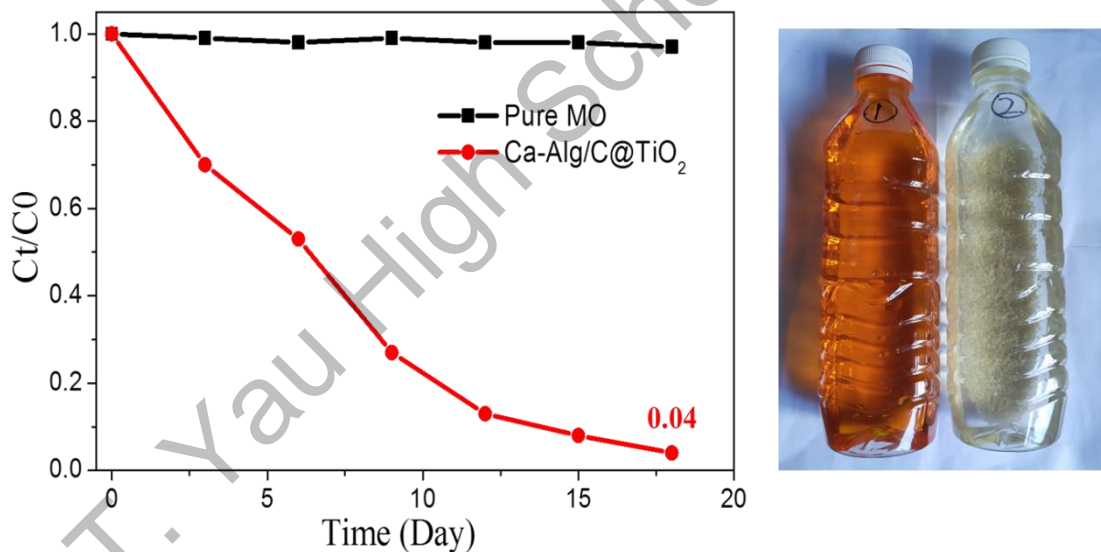


Figure 10 Photocatalytic degradation of Methyl orange solution by Ca-Alg/C@TiO₂ hydrogel pellets

4. Conclusion

Aiming at the problem that nano titanium dioxide cannot absorb visible light and is not easy to recycle, this paper proposes a simple and effective solution. Polyvinyl alcohol coated nano titanium dioxide was prepared by solution mixing, and the coating amount of

polymer was easy to adjust. Then, by controlling the thermal degradation of polyvinyl alcohol on the surface of nano titanium dioxide to carbon, a dark brown carbon coated nano titanium dioxide composite photocatalyst was prepared. The carbon coating layer on the surface of nano titanium dioxide is about 2.5 nm, and the carbon content is about 3.1%. The structure of carbon material made by thermal degradation contains a large number of CH₂ and C=C chemical bonds. By embedding the carbon coated nano titanium dioxide in calcium alginate hydrogel, a supported photocatalyst with a diameter of about 2mm was prepared. This Ca-Alg/C@TiO₂ composite hydrogel pellets have relatively good photocatalytic activity, which catalyzed about 96% of the pollutants under the sunlight in 18 days. In addition, these composite hydrogel pellets are easy to recycle.

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