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Synthesis of peroxo-titanium decorated H-titanate-nanotube-based hierarchical microspheres with enhanced visible-light photocatalytic activity in degradation of Rhodamine B

Yong Qiu\(^a,b\) and Xinjun Li\(^a\)

Peroxo-titanium decorated H-titanate-nanotube-based hierarchical microspheres (PTHM) with large surface area (368 m\(^2\)/g) and mesoporous structure were prepared by an alkaline hydrothermal method in the presence of H\(_2\)O\(_2\) followed by acid wash, which exhibit improved activity in degradation of Rhodamine B under visible light irradiation.

Wastewater discharged by dye production and textile industries has attracted more and more attentions as the dyes in water are highly visible and undesirable even at low concentration\(^ 1\). This kind of wastewater is difficult to treat with conventional bio-degradation methods as these dyes have complex molecular structure\(^ 4\). Photocatalytic oxidation, as one of the advanced oxidation technologies, can produce hydroxyl radicals (\(\cdot\)OH) and O\(_2\)\(_2\) with high oxidizing power that can efficiently degrade organic pollutants. Among various semiconductor oxide photocatalysts, TiO\(_2\) and TiO\(_2\)-based materials are the most widely studied for its high adsorption capacity resulted from the high surface area\(^ 5\). It can work as adsorbent and photocatalyst simultaneously in the removal of dyes under solar light irradiation\(^ 6,7\).

Various titanate nanostructures, such as nanotubes, nanowires, nanofibers and nanoflowers\(^ 10-13\), can be synthesized by simple hydrothermal treatment of TiO\(_2\) or Ti precursor in alkaline solution. However, titanate can only be excited by UV light (only 5% of the solar spectrum) for its large band gap (3.38-3.87 eV)\(^ 14\). So it is necessary to extend the optical response of titanate to visible light. Various strategies have been utilized to improve the visible light activity of titanate, including doping with metal\(^ 15,16\) or nonmetal\(^ 17\),\(^ 18\) elements and coupling with organic dyes, narrow band semiconductors or carbon-based materials\(^ 19-26\). H\(_2\)O\(_2\) is often used to improve the activity of photocatalytic degradation process by releasing \(\cdot\)OH\(^ 27,28\), but it doesn’t show visible light activity. However, H\(_2\)O\(_2\) can react with TiO\(_2\) or titanate to form peroxytitanium, which is yellow in color and shows adsorption in visible light region\(^ 29\). In recent years, it is reported that peroxo-titanium possesses high activity in photocatalytic degradation process. H\(_2\)O\(_2\)-sensitized sulfated TiO\(_2\)\(^ 31\) exhibited excellent performance in degradation of methyl orange under visible light irradiation. The high activity was ascribed to the large amount of acid sites brought by the sulfate ion and absorption in visible light region brought by peroxo-titanium. It is reported that titanium peroxide had high adsorption capacity on cation dyes by the electrostatic adsorption\(^ 32\). It is proposed that Ti-OOH complex releases O\(_2\)\(_2\) in gas phase and •OH in liquid phase to degradation of pollutants\(^ 33\). In addition to improving the activity, H\(_2\)O\(_2\) is also used as precursors of bubble templates to prepare hollow structure and spherical hierarchical structures of TiO\(_2\)\(^ 34,35\) as it can decompose to produce O\(_2\).

Herein, peroxo-titanium decorated H-titanate-nanotubes-based hierarchical microspheres (PTHM) were prepared via a hydrothermal reaction with the addition of H\(_2\)O\(_2\) solution followed by acid wash. Briefly, 5 mL of tetrabutyl titanate and 5 mL of H\(_2\)O\(_2\) solution (30%) were added into 50 mL of NaOH aqueous solution (10 M). After stirred at room temperature for 15 min, this white sticky suspension was transferred to a Teflon-lined autoclave and heated at 140 °C for 24 h. The white hydrothermal product turned to light yellow after washed thoroughly with deionized water. The product turned from light yellow to yellow when dispersed in 0.1 M HCl solution. After bathed in 0.1 M HCl solution for 12 h, the yellow precipitate was washed thoroughly by deionized water until the solution conductivity was less than 5 µs/cm and finally dried at 60 °C for 12 h. The dried yellow sample was named as PTHM. White H-titanate (WT) without addition of H\(_2\)O\(_2\) was also prepared for comparison.

Fig.1 (a), (b) and (c) exhibit the SEM images of PTHM. It can be seen that PTHM are urchin-like hierarchical microspheres with a diameter of 3-5 µm. These microspheres are composed of bundles nanotubes, as shown in Fig. 1 (d). The spaces between the adjacent nanotubes can introduce incident light and target molecular into the inner space of microspheres, which are beneficial for the photocatalytic activity\(^ 37\). The SEM images of WT were exhibited in Fig. 1 (e, f). It can be seen that WT are composed by irregular aggregates with a diameter in the range of 0.6-0.8 µm. The morphology of WT is quite different from that of PTHM. It can be concluded that H\(_2\)O\(_2\) plays an important role in the formation of PTHM. Fig. 2 shows the N\(_2\) adsorption-desorption isotherms of PTHM, which could be assigned as type IV isotherms with H3-type hysteresis loops, indicating the presence of mesopores. Mesoporous
TiO₂ has been paid much attention for its high surface-to-volume ratio and more active sites. The pore size distribution of PTHM, as shown by the inset image, exhibits that PTHM have small mesopores (3.8 nm) and large mesopores (above 30 nm). The small mesopores may correspond to the pores inside the nanotubes and large mesopores can be attributed to the voids in the aggregation of the nanotubes. The specific surface area and pore volumes of PTHM are 368 m²/g and 0.85 cm³/g, respectively.

Fig. 3 shows the XRD patterns of PTHM and WT, which are almost the same. The peaks in the XRD pattern of PTHM and WT located at 2θ values of 24.3° and 48.5° can be ascribed to the (102) and (020) facet of H₂Ti₃O₇, while the peak located at 27.7° belongs to the (130) facet of lepidocrocite titanate. It can be concluded that addition of H₂O₂ has no impact on the crystalline structure of titanate. The FT-IR spectra of PTHM and WT are shown in Fig. 4. There are no obvious differences in FT-IR spectra between PTHM and WT. All the samples exhibit the strong absorptions at 3600~2500 cm⁻¹, which correspond to the surface adsorbed water and the hydroxyl groups. The bands in the range 450~700 cm⁻¹ are related to the different types of Ti-O-Ti vibrations. There is no obvious characteristic peak of peroxo-titanium shown up in Fig. 4, which may be limited by the detection resolution of IR. However, the existence of peroxo group can be verified by XPS spectra. Fig. 5 shows the O1s XPS spectra of WT and PTHM. WT has two peaks located at 530.1 and 531.7 eV, which can be assigned to Ti-O and Ti-OH. While in the case of PTHM, there are three peaks located at 530.3, 531.8 and 533.1 eV, which can be assigned to Ti-OH and peroxo groups.

Fig. 6 shows the optical images and UV-Vis absorption spectrum of PTHM and WT. WT with white color only shows adsorption in UV light region for its large band gap. However, PTHM is yellow in color and shows adsorption from UV to visible light region (~520 nm), which is attributed to the presence of peroxo-titanium.

Here, a possible mechanism for the formation of PTHM is proposed: tetrabutyl titanate hydrolyzed to white Ti(OH)₄ after it was added into NaOH solution (10 M). H₂O₂ is stable in high pH value solution. Ti(OH)₄ reacted with NaOH and H₂O₂ to produce [Ti(H₂O₂)₂(OH)₆]₄⁻(OH)₆ complex. The titanate aggregated together to grow up and assembled into a microspherical shape with the assistant of O₂ bubbles produced from part of H₂O₂. The other H₂O₂ reacted with titanate to form peroxo-titanium. Excess Na⁺ was adsorbed by the peroxo group to balance the negative charge. After
The photocatalytic activity of PTHM and WT was investigated by degradation of RhB under visible light irradiation, as shown in Fig. 7. The absorbance change of RhB solution under visible light irradiation over PTHM is displayed in Fig. 7 (a). The characteristic absorption peak of RhB at 553 nm greatly decreased and exhibited markedly blue shift under visible light irradiation, indicating the fast degradation of RhB. Results of photocatalytic degradation of RhB over PTHM and WT under visible light irradiation are displayed in Fig. 7 (b). RhB is stable under visible light irradiation without photocatalyst, which can eliminate the self-degradation effect of RhB from the degradation results. WT is pure H-titanate without decoration of peroxo-titanium and shows no adsorption in visible light region. 8% of RhB is degraded over WT under visible light irradiation for 25 min. So the photosensitization effect of RhB exists in the degradation process. However, about 95% of RhB is degraded over PTHM after 25 min under visible light irradiation. The contribution of photosensitization effect on the degradation of RhB over PTHM is relatively limited. The result demonstrates that peroxo-titanium greatly enhances the visible light activity of H-titanate nanotubes.

Different scavengers can be used to investigate the main active oxidative species for degradation of dyes \(^{47}\). The results of degradation of RhB over PTHM in the presence of isopropanol (IPA, scavenger for hydroxyl radicals), benzoquinone (BQ, scavenger for superoxide radicals), ammonium oxalate (AO, scavenger for holes) under visible light irradiation were exhibited in Fig. 7 (c). The addition of BQ and AO both remarkably decreased the degradation rate of RhB compared with no scavenger, however, the addition of IPA nearly has no effect on the degradation rate of RhB, which means superoxide radicals and holes were the main active oxidative species. The result of repeated degradation of RhB over PTHM was shown in Fig. 7 (d). The visible light photocatalytic activity of PTHM gradually decline from the first run to the third run. However, the activity of used PTHM can be regenerated by treatment with \(\text{H}_2\text{O}_2\) solution. As the amount of peroxo-titanium on the surface of PTHM is difficult to control, the activity of the regenerated sample is higher than that of original sample. The result indicates that peroxo-titanium not only serves as visible light absorbing sensitizers and brings the visible light activity, but also participates in the degradation process.

The high visible-light-induced photocatalytic activity of PTHM could be attributed to the following reasons. Firstly, large amount of superoxide radicals and holes can be generated from peroxo-titanium in PTHM suspension under visible light irradiation, which can effectively degrade of RhB. Besides that, titanium peroxide has been reported that it has
In summary, peroxo-titanium decorated H-titanate-nanotubes based hierarchical microspheres (PTHM) were prepared via a hydrothermal method with the addition of H₂O₂ follow by acid wash. H₂O₂ played an important role in the formation of urchin-like hierarchical microspheres with diameter in the range of 3–5 µm. The yellow peroxo-titanium was formed in the acid wash process, which expanded the optical response of H-titanate to visible light region and led to the enhanced visible light activity in degradation of RhB by releasing large amount of superoxide radicals and holes.

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Notes and references

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Graphic Abstract

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Peroxo-titanium decorated H-titanate nanotubes hierarchical microspheres were prepared by a hydrothermal method, which exhibited enhanced visible-light activity.