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Synthesis and photocatalytic activity of sepiolite supported nano-TiO₂ composites prepared by a mild solid-state sintering process

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Abstract. Supported nano-TiO₂ photocatalysts play an important role in water environment restoration because of their potential application to photocatalytic degradation of organic contaminants in waste water. With sepiolite as the support, the nano-TiO₂/sepiolite composite photocatalysts were synthesized by an easily operated and mild solid-state sintering process. The microstructure and photocatalytic property of the sepiolite supported nano-TiO₂ composites were characterized and analyzed by X-ray diffraction spectroscopy, UV-Visible spectroscopy and fluorescence spectroscopy. In addition, the influences of calcination temperature and load ratios on the photocatalytic activity of sepiolite supported nano-TiO₂ composites were studied. The results indicated that appropriate ratios of sepiolite supports to nano-TiO₂ contributed to uniform dispersion of nanoparticles, and enhanced the absorption ability within the UV-Vis range, and consequently increased the photocatalytic activity of the composites. Under the preparation conditions of 90 wt. % TiO₂ loading and calcinated at 400 °C, a maximum in photocatalytic activity of nano-TiO₂ sepiolite composite was obtained.

1. Introduction

Owing to stable photochemical performance, high activity, and non-toxicity, nano-TiO₂ has good prospects in the photocatalytic degradation of organic pollutants in water [1-3]. However, its practical



application is limited by the difficult separation and recycling in water. Supported and immobilized nano-TiO₂ on a high surface area carrier is an effective method to solve the problem [4-5]. Currently, the porous structure materials are considered as favorable load carrier of nano-TiO₂, which is beneficial for the effective utilization of photocatalytic activity of nano-TiO₂. As a kind of hydrous magnesium-rich silicate mineral with chain structure, sepiolite has the largest surface area in non-metallic minerals (up to about 900 m²/g), the most unique pore structure, and the strongest adsorptive capacity of clay minerals, as well as stable chemical property, rich resource and low cost. Thus, sepiolite is a good carrier candidate for supporting nano-TiO₂.

In the past few years, many different approaches of preparing mineral supported nano-TiO₂ composites have been developed, including: sol-gel method, settling method, cross-coupling method, powder sintering method and so on [6-9]. Powder sintering or a solid diffusion method can build strong binding force between each phase because of the thermal diffusion effect. However, synthesis of sepiolite supported nano-TiO₂ composites with this method is rarely reported.

In this paper, sepiolite supported nano-TiO₂ composites were synthesized by an easily operated and mild solid-state sintering process as high performance photocatalysts. The influences of calcination temperature and load ratios on the photocatalytic activity of sepiolite supported nano-TiO₂ composites were studied, which provided a theoretical basis for its application in degradation of organic contaminants in waste water.

2. Materials and methods

The main raw materials were: sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O, SiO₂ content about 50 wt.%, MgO content about 21 wt.%); nano-TiO₂ particles P25 (Degussa, Germany, TiO₂ content > 98 wt.%); ethanol (AR); NaOH (AR); terephthalic acid (AR); distilled water. At first, nano-TiO₂ particles and different weight of sepiolite powder were mixed and wet milled for 30 min and calcinated at a certain temperature for 6 h. After cooling off to room temperature slowly, the samples were grinded until the particle size was well-distributed. A series of sepiolite supported nano-TiO₂ composites of different load ratios were obtained. According to TiO₂ weight percentage, these materials were respectively marked as 40%T/S (TiO₂/sepiolite), 70%T/S, 80%T/S, 90%T/S, 95%T/S. The percentages involved in this paper are all mass ones.

Micro-structural observations and light absorption characteristic analysis were carried out with an X-ray diffractometer (XRD, Bruker D8 Advanced, German) and a UV-Visible spectrophotometer (UV-Vis, Shimadzu UV-2550, Japan). The •OH concentration produced during photocatalytic reaction could effectively characterize the photocatalytic activity of photocatalysts. According to the capture effect of terephthalic acid on •OH, the as-produced hydroxylate 2-hydroxyterephthalic acid (TAOH) could transmit unique signals near the spectral peak of the fluorescence at 426 nm, and thereby indirectly indicated •OH concentration formed in the solution. In this experiment, •OH relative concentration generated in a 90 min reaction time was used to characterize photocatalytic activity of composite photocatalytic materials.

3. Results and discussion

3.1. Effect of preparation conditions on the structure of sepiolite supported nano-TiO₂ composites.

Figure 1 (a) shows XRD spectra of 70%T/S composites prepared at different calcination temperatures. While the calcination temperature increases from 300 °C to 400 °C, the ratio of peak intensities of characteristic peaks of anatase phase at $2\theta = 25.3^\circ$ and rutile phase at $2\theta = 27.4^\circ, 54.5^\circ$ increased slightly, indicating that crystalline phase of anatase TiO₂ is more intact. As the calcination temperature rises, the ratio of peak intensities of characteristic peaks of anatase phase and rutile phase decreased, indicating that the anatase to rutile phase transformation gradually occurs in the composites. Generally, anatase is considered more active than rutile in photocatalysis, so the calcination temperature at 400 °C is preferred for preparation of the composite photocatalysts. Figure 1 (b) gives XRD spectra of T/S composites with different load ratios (wt. %) calcinated at 400 °C. There was no apparent change in TiO₂ characteristic peak position and FWHM, which proved the uniform dispersion of nanoparticles on the sepiolite carrier. With loading content of TiO₂ increases, anatase diffraction peak intensity gradually increased, while the peak intensity of sepiolite decreased.

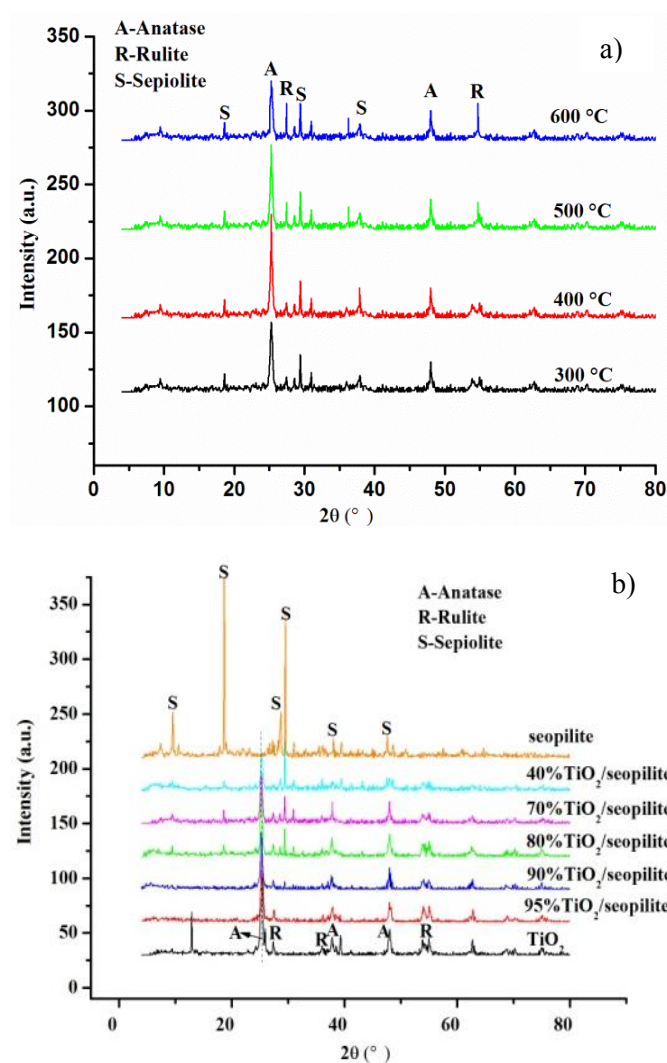


Figure 1. X-ray diffraction spectra (XRD) of (a) 70%T/S composite samples obtained from different calcination temperatures and (b) T/S composite samples with different load ratios (wt. %) calcinated at 400 °C.

3.2. Photocatalytic property of sepiolite supported nano-TiO₂ composites

UV-Visible light diffuse reflectance spectra (DRS) of T/S composites with different load ratios are shown in figure 2. In general, compared with pure TiO₂, visible light (390~780 nm) absorption ability of the composites are all enhanced, which is induced by relatively strong visible light absorption ability of sepiolite. That is to say, the composites of sepiolite and nano-TiO₂ can improve the visible light utilization for photocatalysis. Furthermore, 40%T/S composites have the strongest visible light absorption intensity, 90%T/S composites take second place. However, the UV light (200~380 nm) absorption intensity of 40%T/S composites are apparently depressed, which might be caused by UV-shielding effect of high content sepiolite. Thus, in accordance with the utilization efficiency of both ultraviolet and visible light for these photocatalysts, 90% T/S composites represent better photocatalytic response ability in UV-Vis range, which is more beneficial for the photocatalytic activity.

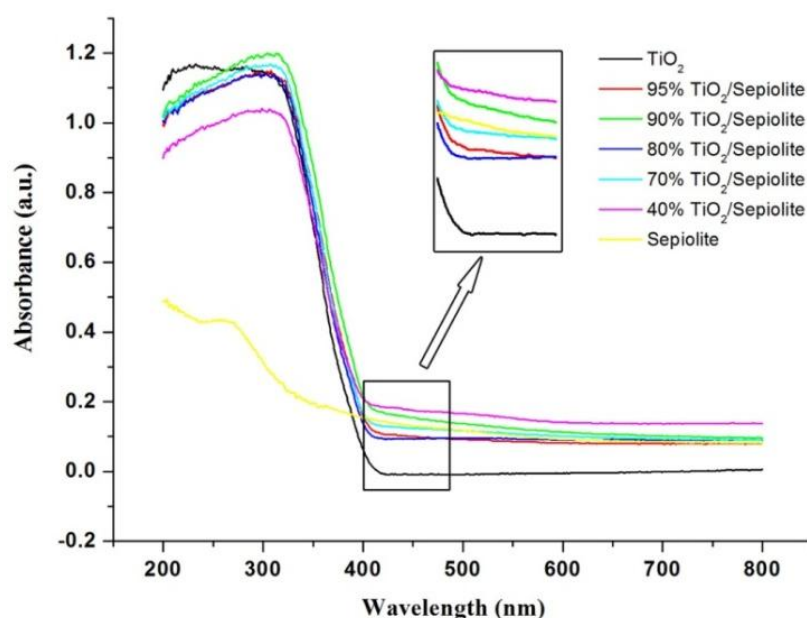


Figure 2. Diffuse reflectance spectra (DRS) of raw TiO₂, sepiolite and T/S composite samples with different load ratios (wt. %).

Figure 3 shows time dependences of fluorescence intensity at 426 nm for T/S composites in terephthalic acid solution irradiated by UV-visible light. The “intensity-time” slopes k_{I-T} of the composites could be used to estimate the generation speed of $\bullet\text{OH}$ in the solution. The greater the k_{I-T} is, the higher the generation speed of $\bullet\text{OH}$ is, and then the stronger the photocatalytic activity. As shown in figure 3(a), the curve slope k_{I-T} for the composites increases first and then decreases with the increment of loading content of TiO₂. The k_{I-T} for 90%T/S composites is the highest one, which implies the optimal photocatalytic activity. It should be attributed to the uniform dispersion of nanoparticles and favorable photocatalytic response ability in UV-Vis range, proved in figure 1(b) and figure 2. Excessive TiO₂ load on sepiolite would result in nanoparticle accumulation and blocking in sepiolite pores, which hinders improvement on the photocatalytic activity on the contrary. In addition, as shown in figure 3(b), the curve slope k_{I-T} for 90% T/S composite prepared by different calcination temperatures increases

first and then decreases with the rise of the temperature. The photocatalytic activity for the composites calcinated at 400 °C is preferred, which is consistent with the results shown in figure 1(a).

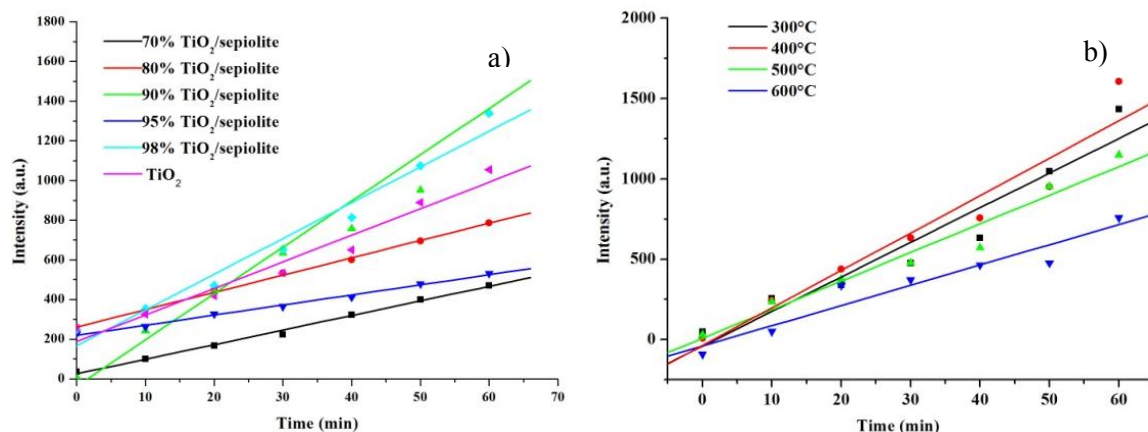


Figure 3. Time dependences of fluorescence intensity at 426 nm for T/S composites in terephthalic acid solution irradiated by UV-visible light: (a) T/S composites with different load ratios calcinated at 400°C; (b) 90% T/S composites prepared by different calcination temperatures.

4. Conclusions

Sepiolite supported nano-TiO₂ composites were synthesized by an easily operated and mild solid-state sintering process. The existence of sepiolite carrier could significantly contribute to uniform dispersion of nanoparticles, enhance their photocatalytic response ability in UV-Vis range, and subsequently improve photocatalytic activity of the composites. The photocatalytic activity of the composites was influenced by the preparation conditions including load ratios and calcination temperature. 90% T/S composites prepared at 400°C were preferred to achieve optimal photocatalytic activity.

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