One-step microwave-assisted synthesis of mesoporous TiO_2 hollow spheres and their photocatatalytic performance

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Abstract: Mesoporous anatase TiO_2 sub-microspheres were fabricated using one step template-free method under microwave irradiation. The morphology and microstructure of the obtained materials were characterized by Field Emission Scanning Electron Microscope (FESEM) and High Resolution Transmission Electron Microscope (HRTEM). Our results show the hollow spherical structure with rough surface was obtained within 2 hours. The structure of the obtained material was mainly influenced by the ratio of ethanol and water in the solution. When the ratio was adjusted to 1, the obtained photocatalyst exhibited the highest activity among the samples with other ratios. One step microwave-assisted synthesis method supplies a new approach for designing powerful mesoporous spherical catalysts.

Keywords: anatase, mesoporous, microwave, microsphere

1. Introduction

In this study, we fabricated hollow anatase TiO_2 microspheres using one step template-free method under microwave irradiation. One step template-free method is a kind of solvothermal method with Ostwald ripening process. In the reaction system, TiF_4 was dissolved water and form HF.HF can control TiO_2 crystallization. H_2O can hydrolyze Ti ion into TiO_2. Between the reaction continuous interactions, we will get hollow anatase TiO_2 microspheres. Heating with microwave can reduce the reaction time, decrease reaction temperature, and reduce the difficulty of preparation, enhance the preparation efficiency. The mesoporous hollow structure improves surface area and enhances the photocatalytic efficiency.

2. Experimental

In this study we used microwave reactor to synthesize mesoporous anatase TiO_2 sub-microspheres material by using one step template-free method. One step microwave synthesis reaction procedure including: Mixed ethanol and water in specific ratio, added into TiF_4 with stirring to form a colorless transparent solution in a flask. The solution was transferred to autoclave with Teflon linear and heated at 140 °C for several hours. Then, it was cooled to room temperature, and the product was separated by centrifugation. Finally, the sample was dried at 70 ˚C in air for 6h. The resulting sample was labeled as TMS X-Y-Z (TMS X-Y-Z，X= hour；Y-Z= ratio of ethanol and water). The appearance and microstructure of the products were characterized using a Field Emission Scanning Electron Microscope (FE-SEM，JEOL JSM-6500) and High Resolution Transmission Electron Microscope (HRTEM ，JEOL JEM-2100).In photocatalytic activity experiments, 0.05g of sample was added into 500mL of paratecemol solution (50 mg/L) and stirred for 1 hour under shade conditions. Then, the solution was irradiated using UV light, sampled to detect the concentration of paratecemol periodically by HPLC (High Pressure Liquid Chromatography).

3. Results and discussion

In this study, we synthesized of mesoporous anatase TiO_2 sub-microspheres using one step microwave synthesis method. The morphology and microstructure of mesoporous anatase TiO_2 sub-microspheres was showed by Field Emission Scanning Electron Microscope and High Resolution Transmission Electron Microscope.

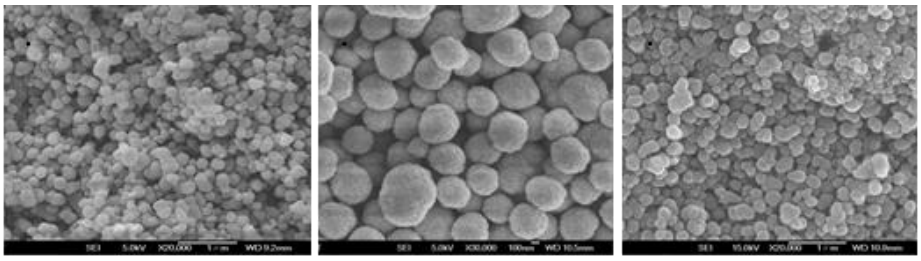

Fig.1 SEM images of (a) TMS 1-7-7, (b) TMS 2-7-7, and (c) TMS 3-7-7.

From SEM images in Fig.1, the spherical structure is obvious, diameter about 200nm. The morphology of material surface is rough. In the first 1 hour, the size of the obtained spheres is uneven, and then extended to 2 or 3 hours, the same sizes obtained. It indicates the reaction had been finished within 2 hours. Fig.2 is the TEM images of TMS 2-9-5, TMS 2-7-7 and TMS 2-5-9. This HRTEM image shows structure of material was influenced by ratio of ethanol and water. High moisture content is more hollowed then lower one.

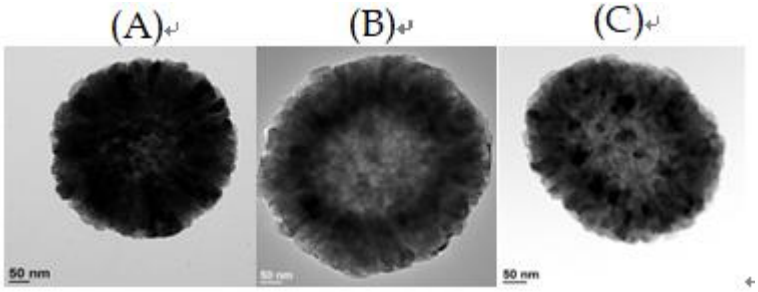

Fig.2 HRTEM images of Mesoporous anatase TiO_2 sub-microspheres; (A) TMS 2-9-5; (B) TMS 2-7-7; (C) TMS 2-5-9.

Photocatalytic degradation experimental was working in the UV light reactor. The solution was irradiated using UV light, sampled to detect the concentration of paratecemol by HPLC periodically. We compared degradation efficiency of different reaction condition in Fig.3(a) (b)and (c). TMS 2-7-7 had degraded paratecemol completely within 210 minutes. It indicates our material was not only prepared in short period of time but also high photocatalytic activity, it can degrade organic pollutants fast in environment.

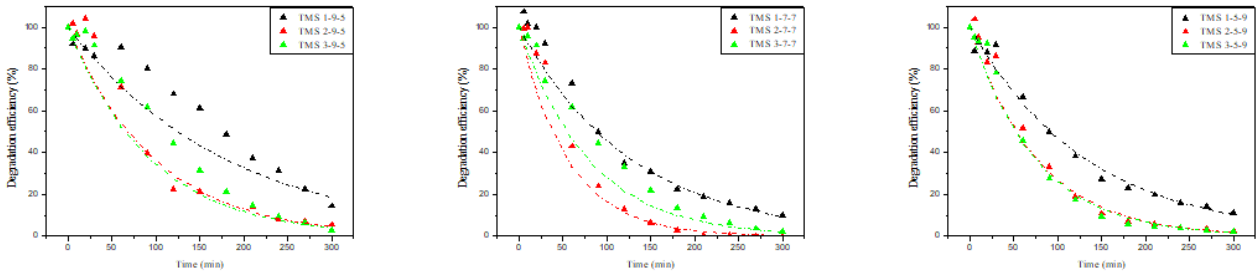

Fig.3 Photocatalytic activity of (a)TMS X-9-5(X=1, 2, 3), (b) TMS X-7-7(X=1, 2, 3), and (c) TMS X-5-9(X=1, 2, 3)

4. Conclusions

In this study, we report a novel and simple approach for the synthesis of Au doped Ti^{3+}/TiO_2 hierarchical microspheres by hydrothermal method. Through a serial measurements and analysis, the sample shows high absorption of visible light because of a new energy level from Ti^{3+} ions and surface plasmon resonances from Au nanoparticles. The highest H_2 production rate was 1806 mL/h for sample which contains 0.5 wt% of Au concentration, which demonstrated five times better than pristine TiO_2.

References

1. Shuqin Shang, Xiuling Jiao, and Dairong Chen, "Template-Free Fabrication of TiO_2 Hollow Spheres and Their Photocatalytic Properties ", ACS Appl. Mater. Interfaces, Vol.4, pp. 860-865 (2012).