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Hydrothermal Synthesis of ZnO/SnO_2 Nanoparticles with High Photocatalytic Activity

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***Abstract*—**The paper reports the preparation and photocatalytic activity of ZnO/SnO_2 and SnO_2 nanoparticles. These nanoparticles were synthesized by hydrothermal method. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Their grain sizes are about 50-100 nm. The photocatalytic activities of these materials were investigated for congo red removal from aqueous solution under UV light irradiation. It was shown that the use of ZnO/SnO_2 as photocatalyst have better photocatalytic activity for degradation of congo red than SnO_2 or TiO_2 (anatase, particle size: 30nm) alone.

***Keywords*—**ZnO/SnO_2 nanoparticle, hydrothermal, photocatalysis

I. Introduction

In recent years, heterogenous photocatalysis has received increasing attention for environmental applications such as air purification, water disinfection, hazardous remediation and water purification [1-3]. However, the high photocatalytic degradation of semiconductors, such as TiO_2 and ZnO has attracted extensive attention of many researchers [4, 5]. In such semiconductors, photogenerated carriers (electrons and holes) could tunnel to a reaction medium and participate in chemical reactions. The high degree of recombination of these carriers decreased greatly their photocatalytic efficiency. Clearly, a wider separation of the electron and the holes increases the efficiency of photocatalyst [6]. Fortunately, utilize of coupled oxide semiconductors could increase the charge separation and extend the energy range of photooxidation. By far, many research groups have carried out the photocatalitic activity experiments of various coupled semiconductors [7-10]. However, the preparation of the coupled ZnO/SnO_2 often carried out by co-preparation method [11,12]. In this research, we synthesize ZnO/SnO_2 nanoparticles by hydrothermal method. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Also, the photocatalytic activities were evaluated using congo red as a model organic compounds.

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II. Experimental

ZnO/SnO_2 nanoparticles were synthesized by hydrothermal method. In typical experiments, 0.05 g of ZnO (zincite >99.9 Wt% rdh) and 1 g of Na_2SO_4 salt were added to 40 ml of distilled water. Then, 0.25 g of $SnCl_2$. $2H_2O$ (Merck >97 %) was added the above mixture. To acidify the above solid-solution mixture, 1 ml of 4 M HNO_3 solution was used. The mixture was then transferred to a Teflon-lined stainless steel autoclave and placed inside an oil batch at 120°C for two days. After the reactions, the oil batch cooled naturally at room temperature, the solid products were separated from the liquid phase via centrifugation and washed with deionized water and pure ethanol. Then, the final products were dried in vacuum desiccators at room temperature overnight for material characterization. Also, SnO_2 nanoparticles were synthesized with the same method without using ZnO.

III. Results

Fig. 1a and 1b showed the SEM images of the as-synthesized SnO_2 and ZnO/SnO_2 respectively, indicating products consist of nanoparticles structures. Statistical analysis of different SEM images showed that the average diameter of these nanoparticles was in the range of 50 -100 nm.

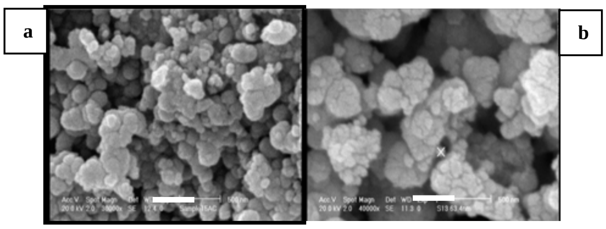

Fig. 1 (a) SEM image of SnO_2 (b) ZnO/SnO_2 nanoparticles prepared by hydrothermal

The structure and crystalline state of the powders were characterized by X-ray diffraction. Fig. 2a and 2b showed a representative XRD pattern of the ZnO/SnO_2 and SnO_2 nanoparticles respectively. All the diffraction lines are assigned to tetragonal rutile crystalline phases of tin oxide which is consistent with the standard data file 21-1445. No characteristic peaks of impurities, such as Zinc oxide or other tin oxides, were observed.

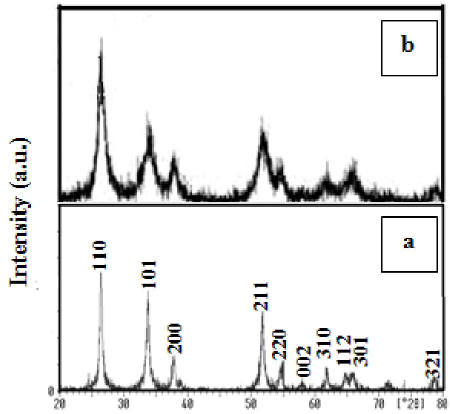

Fig..2 XRD patterns of a) ZnO/SnO_2 nanoparticles b) SnO_2 nanoparticles

The time-dependent UV-Vis Spectra of congo red during the irradiation are demonstrated in Fig. 3. It can be seen that the maximum absorbance of 497nm almost disappear after irradiation for100 min.

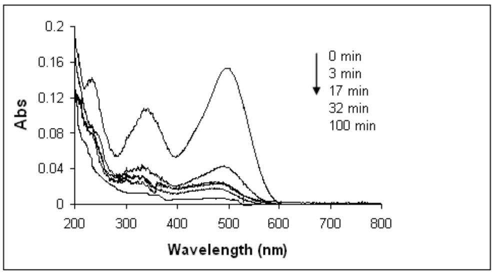

Fig..3 Absorbance spectral changes of congo red solution in the presence of ZnO/SnO_2

Fig. 4 shows comparison of the activities of ZnO/SnO_2, SnO_2 and TiO_2 at λ = 497nm. The experimental results showed that the ZnO/SnO_2 had high photocatalytic activity and its photocatalytic efficiency was higher than the pure SnO_2 and anatase TiO_2.

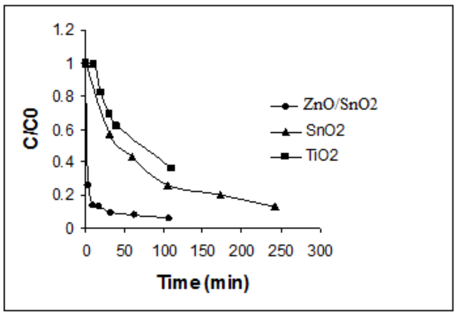

Fig. 4 Comparison of the activities of ZnO/SnO_2, SnO_2 and TiO_2 at λ = 497nm, Condition: amount of catalyst= 0.05 g/l

A mechanistic scheme of the charge separation and photocatalytic reaction for ZnO/SnO_2 photocatalyst is shown in Fig. 5

This scheme shows the conduction band (CB) position of SnO_2 is lower than that of ZnO, so that the former can act as a sink for the photogenerated electrons in the coupled oxides [13, 14]. Since the holes move in the opposite direction from the electrons, the photogenerated holes in SnO_2 might be trapped within the ZnO particle, making charge separation more efficient; then the recombination of electrons and holes in ZnO/SnO_2 is greatly suppressed. This is reason that the nanometer ZnO/SnO_2 possessed both higher photocatalytic oxidation and reduction activities than those of single TiO_2 or SnO_2.

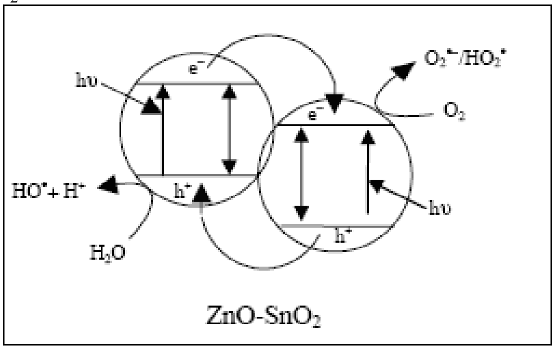

Fig. 5 A diagram illustrating the principle of charge separation and photocatalytic activity

IV. Conclusion

In the present experiment, we synthesize ZnO/SnO_2 and SnO_2 nanoparticles via hydrothermal method as a photocatalyst. The products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Also, the photocatalytic activities were evaluated using congo red as a model organic compounds. The experimental results showed that the ZnO/SnO_2 had high photocatalytic activity and its photocatalytic efficiency was higher than the pure SnO_2 and anatase TiO_2.

Acknowledgment

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