Enhanced Photocatalytic Activity of Polyvinylpyrrolidone Assisted Microwave Hydrothermal Grown Tin Oxide Photocatalysts

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Abstract
Pure and well mono-dispersed SnO2 nanoparticles were synthesized by a microwave assisted hydrothermal method, where polyvinylpyrrolidone (PVP) was used as a surfactant and SnCl2·2H2O as tin source. The structure and surface morphology of as-obtained products were well characterized by X-ray diffraction, scanning electron microscope and UV-Vis diffuse reflectance spectroscopy. The results show that the particle size of SnO2 nanoparticles is about 200-300 nm and there are many small prisms grown on SnO2 nanoparticles surface. The morphologies of the samples were notably affected by the amount of PVP. When the amount of PVP was increased from 1.2 g to 4.8 g, the particle size increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased. The UV absorption edges of the obtained samples show a little red move and the band gap increased at first and then decreased.

Keywords: SnO2; Nanoparticles; PVP; Photocatalytic; Microwave hydrothermal

Introduction
Tin oxide (SnO2), as one of the most important N-type semiconductor materials with a wide band gap (about 3.6 eV at 300K) [1], has been used in many areas, such as gas sensors [2], solar cells [3,4], transparent electrodes [5], photocatalytic [6,7], lithium ion batteries [8,9], light-emitting materials [10,11] and superconductors [12]. And there are many research on preparing SnO2 nanoparticles with different morphologies, including sol-gel method [13,14], hydrothermal method [15,16], microemulsion method [17,18], electrochemical deposition [19], chemical vapor deposition [20], chemical precipitation method [21,22], flame synthesis method [23] and so on.

The morphology and structure of nanomaterials directly affect the physical and chemical properties. Hence, the synthesis of shape-controlled and well monodispersed SnO2 nanomaterials has become a hot research in recent years [24,25]. Surfactant modification can effectively control the aggregation of nanopowder to control the size of SnO2 particles, such as PVP, PEG, SDS and so on. Especially, because of the template and protective effect of PVP, not only can prepare monodisperse nanoparticles to enhance the stability of nanoparticles but also control the geometrical morphologies of SnO2 particles [26]. Xia Y group dissolved metal salts in the polyl (such as ethylene glycol, etc.), using PVP as a dispersant and controlling the different concentrations and reaction temperatures to obtain monodispersed noble metal nanoparticles with a variety of morphologies [27,28].

Herein, monodispersed SnO2 nanoparticles with different morphology were prepared by a microwave hydrothermal route, where polyvinylpyrrolidone (PVP) was used as surfactant, SnCl2·2H2O and NaOH as raw materials. We changed the concentrations of PVP to discuss the effect on the morphologies of the samples and tried to propose the possible growth mechanism of SnO2 nanoparticles. The photocatalytic activities of the as-synthesized SnO2 nanoparticles were evaluated by the degradation of rhodamine B (RhB) under UV-light illumination.

Experimental
Preparation
All chemicals used in this work were analytical-grade reagents without further purification. In a typical preparation procedure: 1.353 g of SnCl2·2H2O was dissolved into 40 mL distilled water under continuous magnetic stirring to form white slurry. Then 1.44 g of NaOH and 5 mL of 30% H2O2 were slowly added to the above mixture. After stirring for 10 minutes, a certain amount of polyvinylpyrrolidone (PVP) (MW 40,000) was introduced. When PVP was completely dissolved by magnetic stirring, the obtained solution was transferred into 100 mL teflon autoclaves, which was treated in a MDS-8 microwave hydrothermal system (manufactured by Shanghai Sino Microwave Chemistry Technology Co. Ltd) at 180°C for 60 min and allowed to cool to room temperature naturally. The resulting white powder was collected by centrifugation, washed several times with absolute ethanol and distilled water. The final products were dried in vacuum at 60°C for 12 h for further characterization.

Characterization
The as-synthesized SnO2 nanoparticles were characterized by X-ray powder diffraction (XRD, D/Max-2200) using Cu Kα radiation with λ=1.5418 Å to verify crystal phase. The morphologies of the samples were observed by using a high-resolution field emission environmental scanning electron microscope (JSM-6700). All the images were obtained under high vacuum mode without sputter coating. UV absorption spectrum was measured on a UV/Vis/NIR spectrophotometer (LAMBDA-950) in the wavelength range of 200-800 nm.
Photocatalytic activity measurement

The photocatalytic activity of as-synthesized SnO\(_2\) nanoparticles was evaluated in terms of the degradation of 5 mg/L Rhodamine B (RhB) in a BL-GHX-V multifunctional photocatalytic reactor (Shanghai Bilon Experiment Equipment Co. Ltd., Shanghai, China). The volume of the reaction solution was 30 mL, into which 30 mg of photocatalyst was added in a quartz tube and stirred in the dark for 30 min to establish an adsorption-desorption equilibrium. The solution was dispersed by sonication for 10 min, and then transferred to test tubes. Irradiation was provided by a medium-pressure mercury lamp (500 W), and the reaction temperature was kept 25°C. Magnetic stirring was being carried out during the photocatalytic testing. The whole system including the mercury lamp and reactant suspension solution was maintained at room temperature by a flow of cooling water. Certain volume of the RhB suspension solutions was withdrawn at a sequence of time intervals. After desired time intervals of irradiation, the photocatalysts were unloaded and centrifuged at 10,000 rpm for 5 min to separate the supernatant liquid from the photocatalysts. The supernatant liquid was collected and analyzed by recording the characteristic absorption of Rhodamine B (554 nm) based on the Beer-Lambert Law using an UV-Vis spectrophotometer (LAMBDA-950).

Results and Discussion

XRD and SEM analysis

The XRD patterns of the obtained products with different amount of PVP are shown in figure 1. All the diffraction peaks of the XRD pattern are in accordance with the tetragonal rutile SnO\(_2\) with \(a=4.742\ \text{Å}\) and \(c=3.182\ \text{Å}\) (JCPDS No. 41-1445). No impurity diffraction peaks are observed, indicating the high purity of the final products. The pattern of obtained products with 1.2 g PVP is relatively weak compared with other products, indicating low crystallinity. The patterns become sharper and stronger with the amount of PVP increasing from 1.2 to 3.6 g, which indicates higher crystallinity. However, when the amount of PVP is up to 4.8 g, the diffraction peaks are broadened and weakened, due to the relative size-quantization effect of nanomaterials. When the amount of PVP is more than 1.2 g, the intensity of diffraction peak of (110) planes is higher than that of (101) planes. When the concentration of PVP is larger, PVP can be fully adsorbed or wrapped in (110) planes of SnO\(_2\), decreasing the growth rate of (110) planes. According to the Scherrer equation, \(D=\frac{K\lambda}{\beta\cos\theta}\), the average crystallite grain sizes of SnO\(_2\) calculated from the main diffraction peak are about 17.3, 20.3, 21.6 and 18.8 nm, respectively. For comparison, we have done the experiment without PVP addition according to the experimental procedure as described above, but we got yellow gelatinous substance rather than white precipitation. It demonstrates that the template and protective effect of PVP can induce SnO\(_2\) crystal nucleuses to grow up to generate stable SnO\(_2\) particles.

Scanning electron microscopy (SEM) images of the as-obtained products with different amount of PVP are shown in figure 2. As can be seen from figure 2a, the sample is spherical, and the diameters about 0.2-1 μm are clearly observed. Higher magnification SEM image (Figure 2b) demonstrates the detailed structural information of the as-prepared sample with 1.2 g PVP. Figure 2b shows that the spheres are the accumulation of small particles and seriously conglomerated. When the amount of PVP is up to 2.4 g, a number of SnO\(_2\) flower-like spheres with the diameters about 1-3 μm appear (Figure 2c). A high-magnification SEM image (Figure 2d) indicates that many small prisms are observed on the surface of flower-like spheres, and there are fewer conglomerations. There are also a few of slags on the surface, which can attribute to uncompleted formation.
process of the sphere or self-assemble. When 3.6 g PVP is introduced, the diameters become smaller and many irregular particles also can be seen in figures 2e and 2f while the dispersion of the sample is better. When the amount of PVP is up to 4.8 g, the morphology of the product is clearly shown in figures 2g and 2h. The product with irregular shape is homogeneous and the particle size significantly decreases to 200-300 nm, and there are also many small prisms grown on the surface of SnO₂ particles. This is because the crystal nucleuses of SnO₂ are adsorbed by more PVP molecules with the increasing amount of PVP, reducing the growth rate of SnO₂ grains. In addition, the solution viscosity is obviously increased with the amount of PVP increasing, which affects the diffusion of nanoparticles. These reveal that the morphology of SnO₂ nanopowders is strongly influenced by the amount of PVP. The morphology of the samples becomes regular when the amount of PVP is less than 2.4 g and the particle size is larger, while too much PVP molecules can make the morphology irregular and the particle size small.

Uv-vis analysis

The absorption characteristic of the semiconductor photocatalyst is determined by the electronic and band structure, which is also closely related to the activity of photocatalyst. Figure 3 shows the UV-Vis absorption spectra of the obtained samples with different amount of PVP. Their optical band gaps are basically the same, but some differences also exist. The fundamental absorption edges of SnO₂ are located at the UV region, which are 351, 355, 358, 362 nm with 1.2, 2.4, 3.6 g, 4.8 g PVP, respectively, as shown in figure 3 inset curves. The absorbance of the samples gradually increases and the UV absorption edges show a little red move with the amount of PVP increasing. The band gaps of the samples can be roughly calculated based on their UV absorption edge using the formula $E_g = \frac{1240}{\lambda} \text{ (eV)}$ ($\lambda$: absorption edge wavelength), which are 3.33, 3.49, 3.46, 3.43 eV, respectively.

Evaluation of photocatalytic activities

The photocatalytic activities of the obtained SnO₂ products were evaluated by photocatalytic degradation of the RhB solution at room temperature under UV irradiation. The kinetics of these reactions could be monitored by UV-Vis spectroscopy measured at different irradiation times, as shown in figure 4a-d. The original RhB solutions show a strong absorbance at around 554 nm. After 30 min adsorption-desorption equilibrium in the dark, the absorbance decreases initially, indicating adsorption of the dye. About 8%, 9%, 17%, 19% of RhB molecules are adsorbed on the surfaces of the prepared SnO₂ catalysts with 1.2 g, 2.4 g, 3.6 g, and 4.8 g PVP, respectively. The absorbance of RhB gradually decreases and the maximum absorbance shows obviously blue shift as prolonging the UV light irradiation time. After irradiated for 60 min, the photodegradation efficiency of these samples are 64%, 80%, 95% and 99%, respectively. It clearly demonstrates that the as-synthesized SnO₂ photocatalysts have an excellent photocatalytic activity of RhB. The color of RhB solutions faded after the reaction, indicating that the chromophore group of RhB molecule was destroyed with medium-pressure Hg lamp irradiation. De-ethylation reaction took place during the degradation process of RhB, which lead to a hypsochromic shift of the maximum absorbance.

Additional experiment in the absence of photocatalyst was carried out as well. From these experiments, the variation in the concentrations of the RhB solutions is plotted against the irradiation time (Figure 5). RhB almost doesn’t decompose without photocatalyst under UV light irradiation, and RhB content is still about 97% after being irradiated for 60 min. However, in the presence of the prepared SnO₂ with 4.8 g PVP as the catalyst, the photodegradation efficiency for the RhB solution is nearly 100% after 60 min irradiation. It can be noted that a trend of the photocatalytic activity is in the order: d>c>b>a. On the studies of photocatalytic reaction mechanism, most people think that photocatalytic activity is affected by many factors, such as the crystal structure, particle size, specific surface area, calcination temperature, the morphology of the catalyst and so on. The well monodispersed SnO₂ nanoparticles with small size were obtained when the amount of PVP was 4.8 g, which increased the adsorbance of the dye to improve the photocatalytic activity. This is in accordance with the calculated adsorbance of the dye from figure 4. As can be seen from figure 3, the UV absorption edges of the obtained samples with the increasing amount of PVP show a little red move, which will cause the light absorption range of samples expanded. And the decrease in the band gaps will cause the reduction of the excitation energy requirement of the catalyst, which will lead to more electron-hole pairs formed under UV irradiation to improve the photocatalytic activity.

Study on growth mechanism

In the reaction process, SnCl₂·2H₂O may considered as SnCl₂ when it was added to water. At first, Sn²⁺ and OH⁻ in the system may make a homogeneous precipitation reaction to form Sn(OH)₂ precipitation under alkaline condition. H₂O₂ was introduced after the NaOH added, so that Sn(OH)₂ could be completely transferred to Sn(OH)₃Sn(OH)₃ had dehydration condensation and crystallization reactions during hydrothermal treatment process, finally formed SnO₂ nanocrystals. On the basis of our experiment results and observations, relevant possible chemical reactions can be proposed as follows:

$$\text{SnCl}_2\cdot 2\text{H}_2\text{O} \rightarrow \text{Sn(OH)}_2\downarrow + 2\text{NaCl} \quad (1)$$

$$\text{Sn(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Sn(OH)}_3\downarrow \quad (2)$$

$$\text{Sn(OH)}_3 \rightarrow \text{SnO(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} \quad (3)$$

PVP is a water-soluble surfactant produced from the polymerization of N-vinyl pyrrolidone (NVP), using K to represent average molecular weight. In this work, we used PVPK30 of which the average molecular weight is 40000. When the concentration of PVP is low, the surface of the particles cannot be completely covered by PVP molecule so that the particles easily agglomerate under the combined


doi: http://dx.doi.org/10.4172/2324-8777.1000103
effect of thermal motion and the Brownian motion. When the amount of PVP is more than 2.4 g, the concentration of PVP exceeds the critical micelle concentration, which leads to the aggregation of PVP molecules. Then PVP forms micelles, finally forming small ball template where the SnO$_2$ crystal nucleuses will deposit to form the SnO$_2$ flower-like spheres during microwave hydrothermal process. When the PVP amount is up to 3.6 g, there are fewer and smaller spheres in the sample and many irregular particles are also observed. This is due to strong protective effect of PVP, which hinder the formation of spheres by limiting the nanocrystals movement and assembled process. The uniform and well monodispersed SnO$_2$ nanoparticles with narrow size distribution were obtained when the amount of PVP was upto 4.8 g. This is because SnO$_2$ crystal nucleuses can be adsorbed by more PVP molecules and the solution viscosity is obviously increased, which affect the growth rate of SnO$_2$ grains, as discussed previously in SEM analysis. When the amount of PVP is larger, PVP can be fully adsorbed or wrapped in (110) plane of SnO$_2$, reducing the growth rate of (110) planes to prevent the agglomeration of nanoparticles. Thereby, we can get nanostructures with different shapes by controlling the growth rate of different crystal faces [29,30]. In addition, PVP polymer chain can enhance steric hindrance and electrostatic repulsion to expand the distance between the particles, which weakens the van der Waals force, so that the direct collision and agglomeration of the particles are reduced to inhibit the growth of particles [31].

**Conclusions**

In summary, uniform and well monodispersed SnO$_2$ nanoparticles with particle size of 200–300 nm were successfully synthesized using PVP-K30 as surfactant via microwave hydrothermal process. The amount of PVP has significant influences on the morphology and size of SnO$_2$ nanopowders. The UV absorption edges of the obtained samples show a little red move and the band gaps is gradually decreased with the increasing amount of PVP, and the samples also exhibit excellent photocatalytic activity. The template and protective effect of PVP not only can control the morphology of nanomaterials...
but also efficiently prevent the agglomeration of nanoparticles.

Acknowledgments

This work was financially supported by the Specialized Research Fund for the Doctoral Program of Higher Education (No. 2006125110001), and the Postgraduate Innovation Fund of Shaanxi University of Science and Technology.

References