Large amounts of SnO$_2$ nanospheres are successfully synthesized through a simple and effective hydrothermal method. The as-synthesized products consist of numerous small SnO$_2$ nanocrystals with an average diameter of 40 nm. The as-prepared SnO$_2$ nanospheres are further used as the photocatalysts for photodegrading several organic dyes (methylene blue, methyl orange, Congo red, and rhodamine B) under UV light irradiation. The photocatalytic results show that the as-synthesized SnO$_2$ nanospheres possess high photocatalytic activities. Compared with the degradation rates of other dyes, that of methylene blue reaches 98.5% by 30 min irradiation. It reveals that the as-prepared product might be potential candidate in wastewater purification.

1. Introduction

Nowadays, with quick development of the industry and the improvement of people’s life, environmental pollution has become one of the most serious problems [1–3]. Therefore, it is urgent to find effective solutions for these issues. The photocatalytic technique possesses fast and complete decomposition advantage when the pollutants are degraded by the oxidation of photocatalytic process [4, 5]. Among them, semiconductor oxide nanomaterials as the photocatalysts present many advantages compared with traditional oxidants. They can completely degrade the contaminants with sunlight or UV radiation at room temperature and do not cause any secondary pollution [6]. These oxide nanomaterials include TiO$_2$ [7–9], ZnO [10–12], SnO$_2$ [13–15], and Fe$_2$O$_3$ [16–19].

SnO$_2$ is an important n-type semiconductor material with excellent chemical and physical performances. As an effective photocatalyst, SnO$_2$ nanostructures can photodegrade organic pollutants to other nontoxic small molecules by UV irradiation process. The size and morphology of the nanomaterials have significant effects on their properties [20–22]. So far, researchers have prepared various morphologies of SnO$_2$ nanostructures, such as nanospheres, nanocubes, nanoflowers, nanowires, and nanodendrites. In this work, we report on the synthesis of large scale SnO$_2$ nanospheres using a one-pot hydrothermal method and investigate their photocatalytic properties under UV light irradiation.

2. Experimental Details

In a typical synthesis, the experimental procedures are described as follows: Na$_2$SnO$_3$ and C$_6$H$_{12}$O$_6$ with a molar ratio of 1:4 (7.5 mmol and 30 mmol) were added to 50 mL deionized water by stirring for 2 h to form a stable and clear solution at room temperature. Then the above mixture was transferred to a 100 mL Teflon lined stainless steel autoclave and heated at 160°C for 3 h. Then it was naturally cooled to room temperature. The brown precipitates were collected by centrifuging at 4000 rpm and then washed for three times with deionized water and ethanol and dried at 80°C.
Finally, the as-prepared precursors were calcined at 500°C for 5 h.

The morphology and microstructure of the as-prepared product were characterized by using scanning electron microscopy (SEM, Hitachi-4800) and transmission electron microscopy (TEM, JEOL-2010). To examine the crystal structure of the products, the as-prepared sample was investigated by using X-ray diffraction (XRD, Rigaku Dmax-rB, CuKa radiation, λ = 0.1542 nm, 40 kV, 100 mA). The efficiency of the photocatalytic degradation was analyzed by monitoring dye decolorization at the maximum absorption wavelength using a UV/Vis Spectrometer (Shimadzu UV-2550).

The photocatalytic activities of the as-synthesized products for the degradation of four dyes aqueous solution were evaluated. 0.1 g of SnO₂ nanospheres was dissolved in 200 mL organic dyes (20 mg L⁻¹). The mixtures were continuously stirred for 1 h in the dark to ensure adsorption/desorption equilibrium. And then the solution was exposed to UV irradiation using a 500 W mercury lamp. For evaluating their photocatalytic activities, the dye samples were collected at regular intervals to measure the dye-degradation using UV-vis spectroscopy. Subsequently, SnO₂ photocatalysts were separated from the dye solution by centrifugation, washed with ethanol and water, and calcined at 500°C for reuse in the next run.

3. Results and Discussion

Figure 1(a) shows that the as-synthesized sample possesses a sphere-like shape. The average diameter of the nanosphere is 40 nm and their surfaces are very rough and consist of many small particles, as shown in Figure 1(b). TEM characterization was further conducted. Figure 1(c) shows a typical TEM image of a single nanosphere. One can find the nanosphere is formed by the aggregation of several smaller nanoparticles. Figure 1(d) shows the measured lattice fringes from HRTEM image are 0.264 and 0.334 nm, respectively, which are consistent with the (110) and (101) planes of tetragonal rutile SnO₂ phase. The SAED pattern in the inset in Figure 1(d) reveals the as-synthesized nanospheres are polycrystalline.

Crystal structures of the as-prepared SnO₂ product are characterized by XRD, as shown in Figure 2(a). All of the diffraction peaks can be straightforwardly indexed to tetragonal rutile SnO₂ phase which are in accordance with
the standard PDF card (JCPDS: 36-1451). No peaks of other phases were detected in the as-synthesized products, revealing high purity of the as-prepared SnO$_2$ nanospheres. All the strong and sharp diffraction peaks mean high crystallinity of the as-synthesized products and the broad diffraction peaks might be ascribed to small grain sizes.

In order to further study specific surface area and pore diameter distribution of SnO$_2$ nanospheres, the sample is characterized by nitrogen adsorption/desorption measurements. Figure 2(b) is the nitrogen adsorption/desorption isotherm, revealing a typical IV isotherm with a typical H$_3$ type hysteresis loop. Pore diameter distribution curve in the inset of Figure 2(b) shows that the as-synthesized product possesses mesoporous structure and the pore diameter is 5 nm. BET surface area of the product is 48.39 m$^2$ g$^{-1}$.

To investigate potential applications in wastewater purification of the as-synthesized products, photocatalytic degradation experiments of SnO$_2$ nanospheres for methylene blue, rhodamine B, methyl orange, and Congo red aqueous solution under a mercury lamp of 500 W irradiation were carried out, respectively. The adsorption spectra of these organic dyes are shown in Figure 3. It is found that main absorption peaks of these dyes are almost completely diminished by irradiation. Figure 3(a) shows the adsorption spectra of methylene blue solution at different time intervals. The color of the solution almost completely disappears when irradiation time reaches 30 min, corresponding to a photocatalytic degradation rate of 98.5%. Figure 3(b) indicates rhodamine B degradation rate of 96.5% with 70 min irradiation under the same photocatalytic experimental condition. Figure 3(c) represents the adsorption spectra of methyl orange dye with SnO$_2$ nanospheres. After 40 min irradiation, it was observed that the main absorption peak decreases to 97.6%. The adsorption spectra of Congo red solution is shown in Figure 3(d). The intensity of the characteristic adsorption peak of Congo red diminishes gradually with the extension of the exposure time. After 35 min of irradiation, the decomposing rate reaches 98.4%. The photocatalytic results indicate that the as-synthesized SnO$_2$ nanospheres exhibit excellent photocatalytic activity toward these organic dyes under UV light irradiation, and each dye solution is almost fully decomposed. In order to illustrate which dye is highly selective to SnO$_2$ nanospheres, the tests are done to compare the degradation efficiency of different dyes with the same degradation time. Figure 4(a) shows that SnO$_2$ nanospheres possess highest degradation rate to methylene blue at 30 min irradiation. To investigate the stability and reusability of the photocatalyst, the recycle experiment for methylene blue was performed. Figure 4(b) shows that there is no significant change even after five cycles. The concentration changes of these dyes are calculated as follows:

$$I = \frac{C}{C_0} \times 100\%.$$  

(1)

$C_0$ represents the initial concentration of these organic dyes. $C$ is the real time concentration under UV light. $C/C_0$ can be used to evaluate the photocatalytic efficiency derived from the concentration changes of these dyes.
4. Conclusion

In summary, large scale SnO$_2$ nanospheres are successfully synthesized via a simple hydrothermal method. The as-synthesized product consists of numerous small SnO$_2$ nanocrystals with an average diameter of 40 nm. Photocatalytic experiments show that SnO$_2$ nanospheres can degrade several organic dyes quickly, revealing excellent photocatalytic performance. The as-prepared photocatalysts might have a potential application in water purification.
**Figure 4:** Degradation of SnO$_2$ nanospheres photocatalyst for dye. (a) Degradation rate curve for different dye molecules. (b) Recycling test of SnO$_2$ nanospheres photocatalyst for MB dye.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

**Acknowledgments**

This work was supported by Starting Fund from Shenyang University of Technology.

**References**


