Synthesis of Hierarchical SnO2 Microflowers Assembled by Nanosheets and Their Enhanced Photocatalytic Properties

Jing Wang1,2, Hui-qing Fan1,* and Hua-wa Yu2

1State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi’an 710072, China
2School of Science, Xi’an Polytechnic University, Xi’an 710048, China

Hierarchical SnO2 microflowers assembled by aggregative sheets have been successfully synthesized via a facile one-pot hydrothermal method. The crystal structure and optical properties of the product were investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy-dispersive spectroscopy (EDS), transmission electron microscopy (TEM), selected area electron diffraction (SEAD), Raman spectroscopy, UV-vis absorption and photoluminescence (PL) spectroscopies. By utilizing the SnO2 microflowers as a photocatalyst, improved photocatalytic degradation was observed towards rhodamine B (RhB) dye under UV light illumination. The improved photocatalytic activity may be attributed to their unique morphology and surface defects. [doi:10.2320/matertrans.M2015287]

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1. Introduction

Tin oxide (SnO2) is an n-type oxide and wide band gap (3.6 eV) semiconductor.1 Its high optical transparency, electrical conductivity, and chemical stability make it a very attractive material for solar cells, photocatalysis, and gas sensing applications.2-4 In the application of photocatalyst, SnO2 can generate electron-hole pairs under UV light irradiation, which promotes the formation of powerful oxidizing agents on the surface that favors the decomposition of organic compounds and pollutants. However, the photocatalytic activity of SnO2 is also affected by the fast recombination of the photogenerated electron-hole pairs which reduces the efficiency of the photocatalytic processes. In order to increase the charge separation of the photogenerated electron-hole pairs, doping or coupling SnO2 with other semiconductors, such as Zn-doped SnO2,5 ZnO/ SnO2,6 SnO2/Fe2O3,7 have been investigated extensively. Whereas, SnO2 single crystal as a photocatalyst was rarely reported due to its low photocatalytic properties. Photocatalytic reactions mainly take place on the surface of the catalyst, a nanoscale material with high specific surface area is believed to improve the photocatalytic performance. Moreover, when the size of the photocatalyst reaches the nanoscale, the probability of recombination of photogenerated electron–hole pairs diminishes owing to their fast arrival at reaction sites on the surface.8 Some studies9-11 showed that pure SnO2 nanomaterials with high surface area exhibited much higher photocatalytic activity than that of conventional TiO2 (P25). Therefore, the nanoscale SnO2 structures with high specific surface area may overcome the obstacles of SnO2 application in photocatalysis alone. 3D hierarchical structures are also helpful to improve the photocatalytic performance, because of their efficient light harvesting, high organic dye or pollutant adsorption, and unique hierarchical characteristics.12,13 Most of the reported 3D hierarchical SnO2 structures are based on 0D (nanoparticles into hollow/porous structures) and 1D (nanorod arrays) building blocks. However, there are few reports on the photocatalytic properties of SnO2 hierarchical structures with 2D building blocks. In the study, the simple one-pot hydrothermal strategy is employed to fabricate a 3D hierarchical SnO2 microflowers assembled by nanosheets. The prepared SnO2 sample are characterized by different techniques and the application in the photodegradation of rhodamine B (RhB) under UV-light has been investigated. As expected, the result showed as-prepared SnO2 microflowers can be used as a photocatalyst alone.

2. Experimental Procedure

Stannous chloride dihydrate (SnCl2·2H2O), cetyltrimethyl ammonium bromide (CTAB) were purchased from Tianjin Kernel Chemical Corporation, China. Sodium hydroxide (NaOH) and commercial SnO2 were purchased from Sinopharm Chemical Reagent Co. Ltd., China. The above chemical reagents were analytical grade, without further purification.

In a typical procedure, 1 mmol of SnCl2·H2O and 0.1 mmol CTAB were dissolved in 40 mL of deionized water. Then 4 mmol NaOH was dropped into the above solution and followed by 30 min stir. After that, the mixed solution was harvested after centrifugation and dried at 60°C for 12 h.

The product was characterized by a X-ray diffractometer SmartLab using Cu-Kα radiation (λ = 0.15406 nm), field emission scanning electron microscopy (FE-SEM, Zeiss Supra 55 operated at 15 kV), transmission electron microscopy (TEM, JEM-3010, Questar, New Hope, operated at 300 kV), Raman spectroscopy (inVia, Renishaw, excited by 785 nm), UV-vis absorption (PerkinElmer, Lambda 950) and photoluminescence (PL, HORIBA fluoromax-4, excited by 300 nm) spectroscopies. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using a surface area analyzer (Micromeritics, Gemini VII 2390).

The photocatalytic performance of the product was evaluated by photocatalytic degradation of RhB under UV
light irradiation. 0.1 g of the as-prepared SnO\textsubscript{2} product was dispersed in 100 ml of a 10 mg/L RhB solution followed by stirring in the dark for 30 min to establish absorption equilibrium. Then, the suspension was irradiated by UV light (300 W mercury lamp) under continuous magnetic stirring. At given time intervals, 5 mL reaction suspension was centrifuged and characterized using a UV–Vis spectrophotometer (UV-2450, SHIMADZU).

3. Results and Discussions

Figure 1 illustrates the typical XRD pattern of as-prepared product. All the diffraction peaks can be well indexed to the tetragonal rutile SnO\textsubscript{2} structure (JCPDS Card no. 41-1445, \(a = 0.4738\) nm, \(b = 0.3187\) nm). No other diffraction peaks of impurities are detected, which indicates that the product is a pure SnO\textsubscript{2} phase. The relatively sharp diffraction peaks suggest that the SnO\textsubscript{2} phase synthesized in this work is highly crystalline. The average crystallite sizes of the SnO\textsubscript{2} microflowers and commercial SnO\textsubscript{2} were calculated to be about 17 nm and 66 nm, respectively, using the Scherrer formula\textsuperscript{14) \[ d = \frac{k\lambda}{B\cos\theta}, \] where \(d\) is the mean crystallite size of the powder, \(\lambda\) is the wavelength of Cu-K\(\alpha\) equal to 0.15406 nm, \(B\) is the full width at half-maximum (FWHM) intensity of the (110) peak in radian, \(\theta\) is Bragg’s diffraction angle and \(k\) is a constant usually equal to 0.9.

Figure 2(a) shows a low magnification SEM image of SnO\textsubscript{2} microflowers. It can be observed that these microflowers are constructed with numerous sheets, arranging perpendicularly and pointing out from the center. In the high magnification SEM image (Fig. 2(b)), the surface of sheets is rough and many tiny nanoparticles enwrapped on. Additionally, the edge thickness of sheets was measured about 19 nm. On the basis of the above results, the as-prepared microflowers can be generally classified as hierarchical structures. In the EDS spectrum of the SnO\textsubscript{2} microflowers (Fig. 2(c)), the peaks of O and Sn are obviously observed. The peak of C is result from the conductive adhesive. It indicates that the as-prepared SnO\textsubscript{2} microflowers are pure SnO\textsubscript{2}. Figure 2(d) shows the SEM image of commercial SnO\textsubscript{2}, which consisted of irregular nanoparticles with different sizes. A typical TEM image is shown in Fig. 2(e). In this picture, the size and shape are similar to these of the SEM observations. By means of HRTEM image (Fig. 2(d)), the space of the crystallographic planes is about 0.34 and 0.26 nm, which corresponds to (110) and (200) facets, respectively. The sharp reflection spots observed in the selected-area electron diffraction (SAED) pattern (the inset of Fig. 2(d)) indicate that the individual sheet is single crystalline.

Figure 3 shows the Raman spectrum of as-prepared SnO\textsubscript{2} microflowers. According to group theory,\textsuperscript{15) a single SnO\textsubscript{2} crystal with tetragonal rutile structure shows four Raman active modes, \(A\textsubscript{1g}, B\textsubscript{1g}, B\textsubscript{2g}\) and \(E\textsubscript{g}\). The \(A\textsubscript{1g}\) and \(B\textsubscript{2g}\) modes are nondegenerate and vibrate in the plane perpendicular to the c-axis, while the doubly degenerated \(E\textsubscript{g}\) mode vibrates in the direction of the c-axis. The Raman peaks at 617 and 474 cm\textsuperscript{-1} can be attributed to the vibration modes \(A\textsubscript{1g}\) and \(E\textsubscript{g}\), respectively, whereas the \(B\textsubscript{2g}\) mode (757 cm\textsuperscript{-1}) is too weak to be observed. These Raman bands further confirm that as-prepared SnO\textsubscript{2} microflowers actually possess a tetragonal rutile structure. In addition to these classical vibration modes, four additional Raman scattering peaks at 231, 279, 329 and 685 cm\textsuperscript{-1}, which are not found in Raman spectrum of bulk SnO\textsubscript{2} crystals, can be observed in as-prepared SnO\textsubscript{2} microflowers. These additional Raman peaks were usually reported in nanoscaled SnO\textsubscript{2} with small grain size\textsuperscript{16-19)} and may be explained as follows. In the nanocrystalline SnO\textsubscript{2} based system, as the surface properties are sensitive not only to the grain size and their distributions but also to the oxygen vacancies and local disorder, there may be a possibility of the appearance of new modes in the Raman spectrum.\textsuperscript{20) The UV-vis absorption spectrum of SnO\textsubscript{2} microflowers is shown in Fig. 4. It is observed that there exist a strong
absorption peak around 324 nm. The band gap $E_g$ of the product was determined by using the Tauc equation $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where $\alpha$, $h\nu$, $E_g$, and $A$ are the absorption coefficient, light frequency, band gap energy, and a constant, respectively. The band gap energy ($E_g$) of SnO$_2$ microflowers can be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy ($\nu$). The estimated band gap was 3.1 eV, which was lower than the value of bulk SnO$_2$ crystals (3.6 eV).

The PL spectra for hierarchical SnO$_2$ microflowers and commercial SnO$_2$ are depicted in Fig. 5(a). Several visible emission bands are observed for as-prepared SnO$_2$ microflowers, which include a weak violet emission at 421 nm (2.95 eV), a weak blue emission at 450 nm (2.76 eV), a blue emission at 482 nm (2.58 eV) and a weak green emission at 563 nm (2.20 eV). In contrast, the emissions in the visible region of commercial SnO$_2$ are weak. Because the energy gap of the SnO$_2$ microflowers is 3.1 eV, the violet emission at 421 nm maybe originate from the near band edge (NBE) emission of SnO$_2$. In NBE emission, the donor level lies just a little below the valence band and electron in conduction band. The other due to the formation of a VO$^{++}$ luminescent center in the SnO$_2$ nanocrystal, as shown in Fig. 5(b). Oxygen vacancy center can trap an electron, leading to formation of a Vo$^+$ state. The surface trapped hole in the valence band recombines with an electron in the deep trap (Vo$^+$) to form a Vo$^{++}$ center. Then recombination of a Vo$^{++}$ center with an electron in the conduction band gives rise to trap emission in visible light. For SnO$_2$ nanostructure, O$^{2-}$ is usually stable with several cationic surrounding in crystal lattices. However, it is different on the surface of crystal that, the stability of O$^{2-}$ decreases rapidly as a result of the discontinuity of surface lattice. Therefore, a lot of O$^{2-}$ ions can escape from the host lattice, leading to formation of oxygen vacancies (defects) on the surface and subsequently result in the visible luminescence. Form the PL spectra, the intensity of the as-prepared SnO$_2$ microflowers is much stronger than that of commercial SnO$_2$, indicating more defects such as oxygen vacancies in the as-prepared SnO$_2$ microflowers.

The photocatalytic performance of the product was evaluated by photocatalytic degradation of RhB under UV light irradiation. The plots of the photocatalytic degradation percentage versus irradiation time are shown in Fig. 6(a). $C_0$ and $C$ are the initial concentration after the equilibrium adsorption and the reaction concentration of RhB, respectively. It can be seen that the degradation of RhB hardly occurs in the absence of SnO$_2$. As for hierarchical SnO$_2$ microflowers, its photocatalytic rate to RhB dye reaches 99% after 120 min. However, for the commercial SnO$_2$, the photocatalytic rate is 28% at the same time interval. In order to evaluate the photostability, the cyclic photodegradation of RhB over the as-prepared SnO$_2$ microflowers was also examined. As shown in Fig. 6(b), after three cycles, the as-prepared SnO$_2$ microflowers still maintained a similar photocatalytic efficiency to the decomposition of RhB, suggesting their reusability and stability.

To answer the question of the cause of SnO$_2$ in photocatalytic activity, it is important to understand the mechanism of semiconductor photocatalysis. The mechanism can be given as followings:

\begin{align}
SnO_2 + h\nu &\rightarrow SnO_2(h^+ + e^-) \\
h^+ + H_2O &\rightarrow OH^+ + H^+ \\
h^+ + OH^- &\rightarrow OH^+ \\
e^- + O_2 &\rightarrow O_2^{2-} \\
O_2^{2-} + e^- + 2H_2O &\rightarrow 2OH^+ + 2OH^- \\
OH^+ + RhB &\rightarrow CO_2 + H_2O + NO_3^- + NH_4^+ 
\end{align}
If the absorbed energy was larger than the band gap, valance band electrons will transit to the conduction band and produce electron–hole pairs on the surface (eq. 1)). Holes can move to the surface where there are electron acceptors like hydroxyl groups (OH⁻) and H₂O that will absorb on the SnO₂ surface. These reactions result in the formation of OH⁻ radicals (eqs. 2)–(3)). Electrons on the surface of SnO₂ can also act to reduce any electron acceptors, usually dissolved oxygen on the SnO₂ surface (eq. 4)). This also results in the formation of OH⁻ radicals (eq. 5)). The OH⁻ radical is an extremely strong, non-selective oxidant (E₀ = +3.06 V) which can oxidize organic compounds and are favorable for the RhB degradation (eq. 6)). However, if the photogenerated electron–hole pairs are recombined, the photocatalytic activity will be decreased or eliminated.31,32 Defects in SnO₂ crystal, such as oxygen vacancies, will help to create sub-bands inside the structure. These defects serve as the centers to capture the photo-induced electrons and thus the electron–hole recombination could be effectively inhibited.9 Based on the visible emission peaks observed in the PL spectrum, it is concluded that there are many surface oxygen defects in as-prepared SnO₂ microflowers, which could greatly enhance the photocatalytic activity. Moreover, the specific surface area of as-prepared SnO₂ microflowers was determined by the BET method using a surface area analyzer and found to be 26.515 m²/g, which is much higher than that of the commercial SnO₂ (3.481 m²/g). The large exposed surface not only decrease steric hindrance for the diffusion of reactants33 but also provides highly surface sites, where OH⁻ radicals could be generated and reacted with RhB molecule. Another factor improves the photocatalytic performance may be attributed to its unique structure. The hierarchical structure possesses good light-scattering properties, which can provide more efficient light harvesting.34 Furthermore, with the ultrathin 2D nanosheets, the diffuse time of the photo-generated electrons and holes from bulk of SnO₂ to the surface become short, decreasing their complex probability and the quantity of electrons and holes arrive at the surface are inevitably enhanced.35

4. Conclusion

In summary, hierarchical SnO₂ microflowers assembled by sheets have been successfully synthesized via a facile one-pot hydrothermal method. The structure, morphology, optical properties, photocatalytic performance of as-prepared SnO₂ microflowers were investigated in detail. The experimental results demonstrated that the SnO₂ microflowers had higher photocatalytic activity than that of commercial SnO₂ for degradation of RhB under UV light irradiation, which can be attributed to their large surface defects as well as their unique structure. The recycling test demonstrated that degradation rate of as-prepared SnO₂ microflowers was quite stable and as no obvious decrease in the activity for three cycles, indicating their potential application in waste water treatment.

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