**Research Article**

**Synthesis, Characterization, and Photocatalytic Activity of Zn-Doped SnO$_2$/Zn$_2$SnO$_4$ Coupled Nanocomposites**

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Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites were prepared via a two-step hydrothermal synthesis method. The as-prepared samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), UV-vis diffuse reflection spectroscopy, and adsorption-desorption isotherms. The results of FESEM and TEM showed that the as-prepared Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites are composed of numerous nanoparticles with the size ranging from 20 nm to 50 nm. The specific surface area of the as-prepared Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposite is estimated to be 71.53 m$^2$/g by the Brunauer-Emmett-Teller (BET) method. The photocatalytic activity was evaluated by the degradation of methylene blue (MB), and the resulting showed that Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites exhibited excellent photocatalytic activity due to their higher specific surface area and surface charge carrier transfer.

1. **Introduction**

Since the discovery of photoelectrochemical water splitting using TiO$_2$ electrodes [1], the investigation of the development of oxide semiconductor photocatalysts used for the degradation of environmental organic pollutants has attracted considerable attention for the past two decades [2–8]. Recently, Zn$_2$SnO$_4$ is considered to be a promising photocatalyst due to its high electron mobility, high electrical conductivity, and favorable stability in acidic and basic solutions [9–13]. It is reported that Zn$_2$SnO$_4$ nanostructures were used to decompose organic pollutants under UV light irradiation in previous studies [11, 12]. Ai et al. proposed a hydrothermal route to synthesize Zn$_2$SnO$_4$ microcubes and the photocatalytic activity of Zn$_2$SnO$_4$ microcubes was evaluated by the degradation of NO and HCHO under UV-light irradiation [11]. Tian et al. prepared Zn$_2$SnO$_4$ and Zn$_2$SnO$_3$ nanostructures by the combined strategy of laser ablation and hydrothermal treatment, and the results showed that Zn$_2$SnO$_3$ was active and effective for the degradation of methyl orange [12]. However, the fast recombination rate of the photogenerated electron/hole pairs of Zn$_2$SnO$_4$ prohibits the desirable photocatalytic activity. It is generally accepted that the technique of coupled oxides with different band gap widths is an effective approach to enhance the photocatalytic activity by increasing the separation of recombination rate of the photogenerated electron/hole pairs and extending the energy range of the photoexcitation [14–17]. Zn$_2$SnO$_4$ and SnO$_2$ have been investigated for the degradation of organic pollutants [11, 12, 18–21], and they have available matched band gap widths for coupled composites [18, 19]. Additionally, the photocatalytic activity of SnO$_2$ can be enhanced by the zinc dopant ions incorporation into the lattice [20, 21]. Additionally, there are few reports on the synthesis and photocatalytic activity of Zn-doped SnO$_2$/Zn$_2$SnO$_4$.

Herein, we reported a two-step hydrothermal synthesis route for the preparation of Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites. The photocatalytic activity of the samples was evaluated by the degradation of MB, and the degradation process of MB was investigated in detail. To the best of
our knowledge, this is the first time to report the preparation and photocatalytic activity of Zn-doped SnO₂/Zn₂SnO₄ nanocomposites.

2. Experimental Details

2.1. Preparation of Zn-Doped SnO₂. The preparation of Zn-doped SnO₂ was also described in our previous studies [21]. All the reagents were analytically pure, purchased from Shanghai chemical industrial company, and used as received. In a typical procedure, 24 mmol NaOH was dissolved in 80 mL of mixed solvents containing 60% water and 40% ethanol. 3.43 mmol SnCl₂·5H₂O was added to the mixed solution under rigorous stirring. After constant stirring for 30 min, 0.57 mmol Zn(NO₃)₂·6H₂O was introduced into the mixed solution. After another 30 min of stirring, the obtained precursor was transferred into a 100 mL Teflon-lined stainless steel autoclave, and was put into an electric oven. The autoclave was maintained at 180°C for 20 h and cooled naturally to room temperature. The products were centrifuged and washed with distilled water and ethanol for several times, followed by drying in a vacuum oven at 60°C for 12 h.

2.2. Preparation of Zn-Doped SnO₂/Zn₂SnO₄. In a typical procedure, 2 mmol tin (IV) chloride pentahydrate (SnCl₂·5H₂O) and 4 mmol zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) were dissolved in 20 mL mixed solvents of water and ethanol (volume ratio of 4:1) to form two transparent solutions, respectively. The above solutions were mixed together under magnetic stirring. A certain amount of the as-prepared Zn-doped SnO₂ was added into the mixed solution (Zn-doped SnO₂/Zn₂SnO₄ = 15 wt%). Then, 16 mmol sodium hydroxide (NaOH) was dissolved in 40 mL mixed solvents of water and ethanol (volume ratio of 4:1) to make a clear solution. In the next step, the NaOH solution was slowly dropped into the above mixed solution under magnetic stirring, and then the above solution was mixed by a magnetic stirrer for 1 h. The obtained white suspension was transferred to Teflon-lined stainless steel autoclave with 100 mL capacity and heated at the temperature of 200°C for 15 h. After the autoclave had cooled naturally to room temperature, the final precipitates were centrifuged and washed with distilled water and ethanol, respectively, followed by drying under vacuum at 60°C for 12 h. Additionally, pure Zn₂SnO₄ was also obtained via a similar hydrothermal synthesis route without adding Zn-doped SnO₂.

2.3. Characterization. XRD pattern was carried out on a Rigaku ultima III diffractometer meter equipped with Cu Kα radiation (λ = 0.15406 nm). FESEM images were taken using a Hitachi S-4800 field emission scanning electron microscope. TEM images were recorded on a JEM-2100 transmission electron microscope. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Quantachrome NOVA 2000e sorption analyzer after samples were vacuum-dried at 473 K overnight. UV-vis diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (UV2500, Shimadzu). The photoluminescence (PL) spectra were measured using a Hitachi F-4600 fluorescence spectrophotometer.

2.4. Photocatalytic Experiments. The photocatalytic activity was evaluated by the decolorization of MB aqueous solution. As reported in our previous work [21, 22], 20 mL MB aqueous solution with a concentration of 1.0 × 10⁻⁵ M was added into the dish with 0.1 g prepared catalyst. A UV lamp (15 W, 365 nm) was used as light source to trigger the photocatalytic reaction. After irradiating for a certain time, the reacted solution was filtrated to measure the concentration variation of MB by recording the variation of the intensity of absorption peak centered at 664 nm using UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). Consulting the literatures [23–25], the photodegradation efficiency of MB was evaluated by C/C₀, where C is concentration of the MB solution at reaction time t and C₀ is the adsorption/desorption equilibrium concentration of MB (at reaction time 0).

3. Results and Discussion

3.1. Phase and Morphology. XRD patterns of Zn-doped SnO₂, Zn₂SnO₄, and Zn-doped SnO₂/Zn₂SnO₄ nanocomposites are shown in Figure 1, respectively. From Figure 1, it can be found that the diffraction peaks in the pattern of Zn-doped SnO₂ are assigned to the tetragonal rutile structure of SnO₂ with lattice parameters comparable to the standard values (JCPDS, number 77-0451). Meanwhile, the characteristic peaks of Zn₂SnO₄ including (110), (220), (311), (222), (400), (422), (511), and (440) are in good accordance with the standard card of cubic Zn₂SnO₄ (JCPDS number 74-2184). For Zn-doped SnO₂/Zn₂SnO₄ nanocomposites, additional characteristic peaks with 2θ values of 26.36° and 33.86° appeared, which could be indexed to the (110) and (101)
Figure 2: FESEM and TEM images of the Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites: (a) the panoramic FESEM image; (b) the high magnification FESEM image; and (c) TEM image.

![Figure 2: FESEM and TEM images of the Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites](image)

Figure 3: Nitrogen adsorption-desorption isotherm with its corresponding pore size distribution in the inset of the Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites.

3.2. BET Surface Area and Pore Volume. The specific surface area and pore structure of the as-prepared Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites were investigated by nitrogen adsorption-desorption isotherm. Figure 3 shows the nitrogen adsorption-desorption isotherm with its pore size distribution in the inset. It is clear that the as-prepared Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites exhibit the type IV isotherm with type H3 hysteresis loop for the relative pressure $P/P_0$ in the range of 0.6–1 according to Brunauer-Deming-Deming-Teller (BDDT) classification [15, 26], revealing the characteristic of mesoporous materials and the presence of mesopores (2–50 nm) [27]. The specific surface area estimated by Brunauer-Emmett-Teller method is $71.53 \text{ m}^2/\text{g}$. Furthermore, the observed hysteresis loop approaches $P/P_0 = 1$ indicating the presence of macropores (>50 nm) [27], which is in good agreement with the result of the corresponding pore size distribution of the sample in the inset of Figure 3. Additionally, the above macropores might result from the gaps between Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanoparticles.

crystal planes of SnO\textsubscript{2}. No other impurities peaks are found in Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites, suggesting that the nanocomposites have a two-phase composition: Zn\textsubscript{2}SnO\textsubscript{4} and Zn-doped SnO\textsubscript{2}.

Figure 2 shows the FESEM and TEM images of Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites prepared via a two-step hydrothermal synthesis method. As seen in the typical FESEM image at low magnification (Figure 2(a)), the as-prepared Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites are composed of monodispersed and uniform nanoparticles. Figure 2(b) is the FESEM image at high magnification, which shows that the surfaces of the as-prepared Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites are rough. Furthermore, it is clearly observed that the size of the nanoparticles ranges from 25 nm to 50 nm from Figure 2(c), suggesting that the Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanocomposites might have larger surface area.

Additionally, the above macropores might result from the gaps between Zn-doped SnO\textsubscript{2}/Zn\textsubscript{2}SnO\textsubscript{4} nanoparticles.
3.3. UV-vis and PL Spectra. Figure 4 shows UV-vis absorbance spectra of pure Zn$_2$SnO$_4$ and Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites. The band gaps of pure Zn$_2$SnO$_4$ and Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites are estimated at 3.58 eV and 3.60 eV, respectively. The band gap of Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites is slightly higher than that of pure Zn$_2$SnO$_4$, which may be attributed to the synergistic effect of Zn-doped SnO$_2$ coupled with Zn$_2$SnO$_4$ homogeneous nanocomposites [28, 29].

To investigate the separation capacity of photogenerated carrier in nanocomposites, PL spectra of pure Zn$_2$SnO$_4$ and Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites were measured and the results are given in Figure 5. Two asymmetric peaks centered at 410 nm and 472 nm are observed from Figure 5, whereas the band to band emission peak (~360 nm) is not found in the curve. Consulting the literature [30, 31], the two peaks can be attributed to oxygen vacancies or surface states. It is also clear from Figure 5 that Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites exhibited lower emission intensity than that of pure Zn$_2$SnO$_4$ in the range of 400 nm and 500 nm. The above results reveal that the recombination of the photogenerated carriers in the composites decreased and a synergistic effect occurred between Zn-doped SnO$_2$ and Zn$_2$SnO$_4$ that favored the electron transfer [28, 29].

3.4. Photocatalytic Activity. Figure 6 presents the variations of adsorption spectra of aqueous MB in the presence of pure Zn$_2$SnO$_4$, Zn-doped SnO$_2$, and Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites under ultraviolet irradiation with the wavelength 365 nm. As seen in Figure 6(a), the intensity of the characteristic adsorption peak of MB at around 663 nm decreased with the irradiation time in the degradation process. Meanwhile, the color of the suspension faded away gradually with the irradiation time prolonging in the experiment. The characteristic adsorption peak disappeared, suggesting that the MB aqueous solution was degraded completely when the irradiation time reached 120 min. Figure 6(b) shows the photocatalytic performance of different photocatalysts with otherwise identical conditions under ultraviolet irradiation with the wavelength 365 nm. Blank test (MB without any catalyst) exhibited little photolysis. Meanwhile, the decrease of MB with Zn$_2$SnO$_4$ in the dark was similar to that of the blank test, which demonstrated that the adsorption of MB on the as-prepared photocatalysts was negligible after the adsorption-desorption equilibrium was reached. Additionally, the photocatalytic activities of pure Zn$_2$SnO$_4$ and Zn-doped SnO$_2$ were also performed to demonstrate the photocatalytic activity of Zn-doped SnO$_2$/Zn$_2$SnO$_4$. It is clear from Figure 6(b) that the Zn-doped SnO$_2$/Zn$_2$SnO$_4$ exhibited higher photocatalytic activities than that of pure Zn$_2$SnO$_4$ and pure Zn-doped SnO$_2$. Concerning the catalyst of pure Zn$_2$SnO$_4$, the complete degradation of MB was achieved when the irradiation time was 180 min.

It is well known that the augment of specific surface area and band gap is helpful for the improvement of photocatalytic activity [32–34]. In this experiment, pure Zn$_2$SnO$_4$ and Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites obtained via a similar hydrothermal synthesis route have similar specific surface area. Meanwhile, combined with the analysis of the UV-vis spectra, the value of the band gap of pure Zn$_2$SnO$_4$ is very close to that of Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites. Consequently, it can be inferred that surface area and band gap would have little effect on the photocatalytic performance of the above two catalysts. Based on the analysis, the enhanced photocatalytic activity can be explained as follows. The band gaps of Zn$_2$SnO$_4$ and Zn-doped SnO$_2$ have matched band potentials of coupling semiconductor. On the basis of the energy diagram reported in previous literature [10, 17–19], a proposed energy band structure diagram of the nanocomposites was elucidated schematically in Figure 7. Under UV light irradiation, Zn-doped SnO$_2$ and Zn$_2$SnO$_4$ would be excited simultaneously and generated electron-hole pairs.
Figure 6: (a) The variations of adsorption spectra of aqueous MB in the presence of Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites at different periods of time under ultraviolet irradiation; (b) the comparisons of photocatalytic degradation activity of different photocatalysts, including pure Zn$_2$SnO$_4$, pure Zn-doped SnO$_2$, and 15% Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites.

Figure 7: Schematic diagram for the illustration of the energy band structure and photogenerated electron hole pair separation in the Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites [10, 17–19].

pairs. As observed in Figure 7, the photogenerated electrons transfer occurred from CB of Zn-doped SnO$_2$ to the CB of Zn$_2$SnO$_4$ through the interface, whereas the photo-generated holes transfer occurred from VB of Zn$_2$SnO$_4$ to the VB of Zn-doped SnO$_2$ conversely, which led to the efficient separation of the photogenerated electrons and holes. Thus, the recombination rate of photoinduced charge carriers was suppressed significantly, which is also in good agreement with the result of PL spectra. Furthermore, the efficient charge separation could prolong the life time of the charge carriers and enhance the efficiency of the interfacial charge transfer to adsorbed substrates and then account for the higher photocatalytic activity of Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites. Additionally, it is noteworthy to be mentioned that the introduction of zinc ions is beneficial for the enhanced photocatalytic activity of the nanocomposites.

4. Conclusions

In summary, Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites were successfully prepared via a two-step hydrothermal synthesis route. The as-prepared nanocomposites are composed of numerous nanoparticles with the size ranging from 20 nm to 50 nm with higher specific surface area. The investigation of the photocatalytic activity indicated that the as-prepared Zn-doped SnO$_2$/Zn$_2$SnO$_4$ nanocomposites exhibit enhanced photocatalytic activities in the degradation of MB under UV light irradiation compared with that of pure Zn$_2$SnO$_4$, which is ascribed to the effective separation of photoinduced electron hole pairs.

Conflict of Interests

The authors declared that they do not have a direct financial relation with the commercial identities mentioned in this paper that might lead to any conflict of interests for any of the authors.

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