



Enhancing the visible-light photoresponse of SnO and SnO₂ through the heterostructure formation using one-step hydrothermal route

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ABSTRACT

The effort to enhance the visible-light photoresponse of SnO₂ and SnO has been designed by the heterostructure formation of tin oxide. The formation was conducted by controlling the oxidation state of precursor through adjusting the precursor acidity. The result shows that the transformation route as a function of precursor initial pH involve the formation of intermediate phase began by SnO₂ to SnO₂/Sn₃O₄ to SnO/Sn₃O₄, and finally SnO. The characterization indicated that Sn₃O₄ played the important role in enhancing the visible light response of both SnO₂ and SnO in the heterostructure formation.

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1. Introduction

SnO₂ and SnO are reported as the most studied tin oxide and have been widely applied in several application [1,2]. SnO₂ has been attracting a great deal of research interest as photocatalyst application owing to its excellent photocatalytic activity in UV light region [3], while SnO has gained less attention because of its weak photoresponse [4]. The photoresponse properties played the role to determine the proper wavelength to activate the catalyst [5]. Furthermore, the current development of tin oxide have been shifted to design the visible-light activated material which has been reported to have higher photocatalytic performance compared to UV light activated tin oxide and offer lower energy activation to excite the electron during the material activation [6]. Several efforts have been made to enhance the visible-light response of semiconductor [7]. Among the efforts, the heterostructure formation has been a promising approach as it is not only enhance the visible-light photoresponse but also increase the lifespan of photo-generated carrier resulting in higher photocatalytic performance [8]. Xia (2014) proved that the interfacial charge transfer as a resulting of band alignment in heterostructure semiconductor of SnO/Sn₃O₄ and SnO₂/Sn₃O₄ improves the photocatalytic activity compared to the intrinsic semiconductor.

Many studies have been reported to synthesize the heterostructure semiconductors [7]. However, most of fabrication methods require two step formation and have difficulties in controlling the morphology and phase of semiconductor [9]. Based on our previous experiment [10], the facile preparation of heterostructure could be achieved by controlling the oxidation state of tin oxide. Each semiconductor has specific acidity formation associated to the hydrolysis precursors. Moreover, the formation of heterostructure Sn₃O₄ potentially enhance the visible-light response due to its narrow bandgap. Therefore, the proper preparation technique is still a major challenge to trap the specific condition for synthesizing heterostructure tin oxide. Herein in this present paper, we synthesized heterostructure tin oxide and discussed its transformation route as a function of precursor acidity.

2. Experimental

0.900 g of SnCl₂·2H₂O (E-Merck) was dissolved into a mixture of distilled water and absolute ethanol (2:1 in volume). The suspended-solution was transferred into a Teflon-line stainless steel autoclave and hydrothermally annealed at 150 °C with a heating rate of 50 °C min⁻¹ for 12 h. The final product was collected by centrifugator in 10.000 rpm, and washed with distilled water several times and ethanol. All obtained product was dried at 70 °C for 24 h and characterized. In order to study the transformation as a function of precursor initial pH, the procedures were

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repeated by changing the pH of mixture solution to 2.5, 3, and 4. All the as-prepared semiconductor is characterized using X-Ray Diffractometer (Bruker D8 Advance with Cu K α , $\lambda = 0.15406$ nm), Scanning Electron Microscope (Nova NanoSEM 450, FEI), and UV–Vis Diffuse Reflectances Spectrophotometry (Shimadzu UV–2600 Series).

3. Results and discussion

The diffraction patterns of as-prepared semiconductor at varying precursor initial pH are shown in Fig. 1. At pH 2 (control), most of the diffraction peaks correspond to tetragonal SnO₂ phase reflections with lattice constant $a = b = 4.7382$ Å and $c = 3.1871$ Å related to JCPDS No. 41-1445. The small number peaks of Sn₃O₄ (JCPDS No. 16.0737) were also observed, indicating the simultaneous existence of triclinic Sn₃O₄ phase. By increasing the initial pH to 2.5, most of the XRD spectra of SnO₂ phase transforms into triclinic Sn₃O₄ with a small composition of tetragonal SnO₂ peak observed. In literature [6], the pH 2 and 3 were critical pH for synthesizing mixed-valent Sn₃O₄ through the hydrothermal method which in accordance with this work result where SnO₂ and Sn₃O₄ start to be formed at pH 2 and at pH range of 2–2.5, respectively. The weak Sn₃O₄ peak was still observed at pH 3, indicating most of Sn₃O₄ continuously transform to SnO through the reduction process. When the initial precursor pH was increased to 4, the product were completely transformed into pure romarchite tetragonal SnO at pH 4 which was confirmed by fitting the SnO peaks (JCPDS No. 06.0395). The formation of different phase as the function of initial precursor pH proved that the precursor initial pH plays an important role to determine the oxidation state of tin oxide correlated with hydrolysis of precursor solution [11,12]. It is interesting that the transformation route of SnO₂ to SnO in this study involves the formation of intermediate oxidation state of Sn₃O₄ began by forming heterostructure SnO₂/Sn₃O₄ to SnO/Sn₃O₄, and finally SnO in which several works reported the direct transformation of SnO₂ to SnO without forming any intermediate oxidation state [13,14]. Thus, the existence of Sn₃O₄ during the transformation of SnO₂ provides the opportunity to enhance the visible-light response of SnO₂ and SnO.

SEM images and UV–Vis spectrophotometer were also used to confirm the transformation of as-prepared tin oxide. Fig. 2A demonstrates that the semiconductor synthesized at pH 2 possesses a sphere-like shape with 50–100 nm of average diameter.

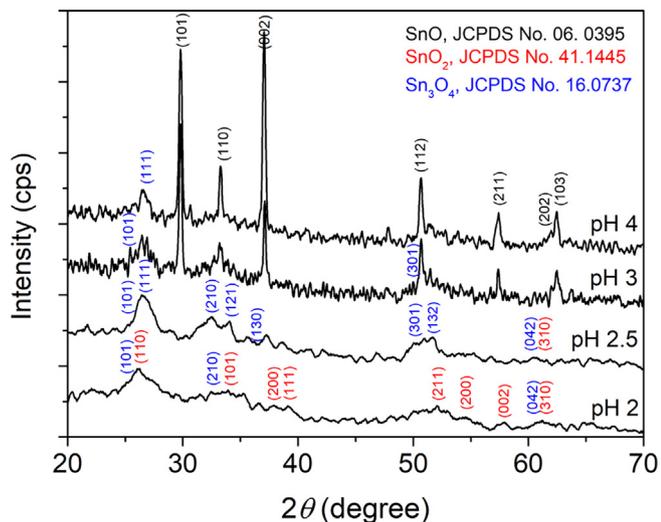


Fig. 1. XRD patterns of as-prepared tin oxide at varying precursor initial pH.

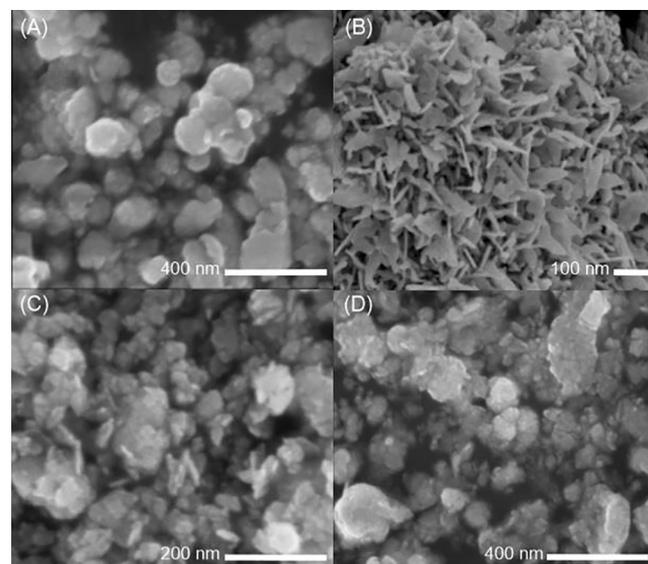


Fig. 2. SEM images of as-prepared semiconductor at pH (A) 2, (B) 2.5, (C) 3, and (D) 4.

The surface morphology has a rough surface and consists of many small particles. There is no clearly flower-like structure which refers to Sn₃O₄ structure at pH 2 indicating that most of the morphology at pH 2 refers the morphology of SnO₂ [15]. Furthermore, at pH 2.5, the surface morphology converts to prickly sheets shape due to the transformation of SnO₂ to Sn₃O₄ with varying thickness of 10–20 nm (Fig. 2B). Increasing pH to 3 initiate the agglomeration of prickly sheets structure and continuously assembles to form microsheet shape morphology at pH 4 (Fig. 2C and D) which is reported as the morphology of SnO [16]. Additional analysis using Energy dispersive x-ray spectroscopy (EDS) confirmed that all the prepared catalysis are consisted only by Tin (Sn) and Oxygen (O) (Fig. 1S).

The results of UV–vis spectrophotometer equipped with diffuse reflectance analysis are shown in Fig. 3, and demonstrate that tin oxide synthesized at pH 2, 2.5, and 3 have visible-light response and the one synthesized at pH 2.5 has the highest photoresponse. The presence of mixed-valent Sn₃O₄ in the heterostructure formation with SnO and SnO₂ enhance the visible-light response of these intrinsic semiconductor which the intensity was affected by the amount of Sn₃O₄. It can be seen that semiconductor synthesized at pH 3 has the smallest visible-light photoresponse due to consisting small amount of Sn₃O₄. However, at 4, all the SnO₂ and Sn₃O₄ completely transform to SnO which has weak or no photoresponse in visible wavelength and has small photoresponse in the UV wavelength that is found to be negligible [17].

The photoresponses properties data are supported by calculating their bandgap energy through utilizing Tauc plot equation [18,19]. Fig. 3B and C show the two slopes formation in semiconductors synthesized at pH 2, 2.5, and 3 confirmed the heterostructure formation. Furthermore, the bandgap calculation of SnO₂ and Sn₃O₄ consisted in tin oxide prepared at pH 2 are calculated as 3.297 eV and 2.886 eV, respectively. However, the bandgap values of SnO₂ and Sn₃O₄ increase to 3.160 eV and 2.725 eV by increasing the pH to 2.5. It is most likely because the composition of SnO₂ and Sn₃O₄ was different between both catalysts. Based on XRD pattern, tin oxide synthesized at pH 2 has SnO₂ as main compound which has wide bandgap while tin oxide synthesized at pH 2.5 has Sn₃O₄ as main compound resulting the narrow bandgap. The increasing pH to 3 slightly decrease the bandgap energy to 1.462 eV and 3.218 eV for SnO and Sn₃O₄, respectively, and com-

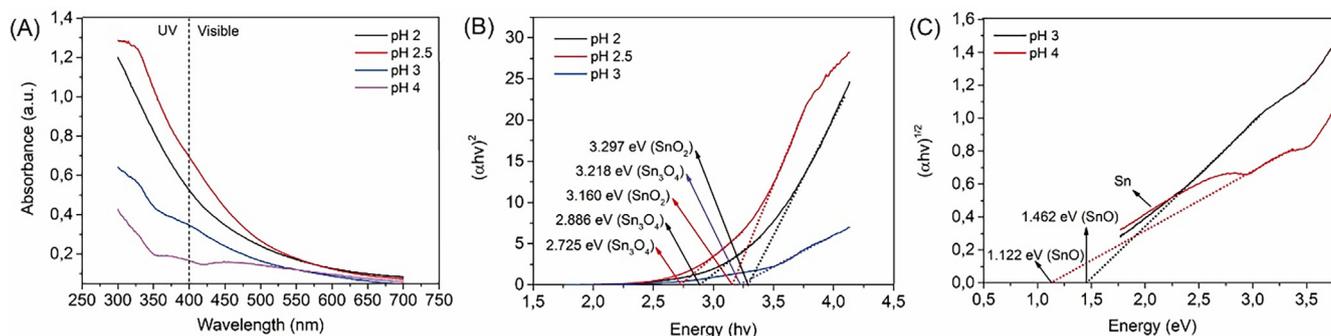


Fig. 3. (A) UV-Visible absorption spectra of as-prepared semiconductor. (B and C) Calculated-direct bandgap, and indirect bandgap of synthesized-catalysts.

pletely decrease to 1.122 eV by increasing pH to 4 which is in agreement with the reported bandgap value of SnO [20]. Above all, the result shows that the calculated bandgap is correlated with the photoresponse of as-prepared tin oxide in which the presence of Sn₃O₄ forms the relatively narrow bandgap of semiconductor which could effectively harvest the visible-light photon energy.

4. Conclusion

The heterostructure formation has successfully enhanced the visible-light response of SnO and SnO₂ by the presences of Sn₃O₄. The initial precursor pH plays the role to determine the oxidation state of tin oxide in the heterostructure formation. The proper acidity in the Sn₃O₄ formation generates the visible-light response in which the improper acidity form the no visible-light photoreponse. We conclude that studying the transformation approach could be used to find the best condition in the heterostructure formation of high efficient visible-light semiconductor.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2018.11.169>.

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