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Hydrothermal Synthesis and Characterization of Flower-like SnO_2-Zn_2SnO_4 Nanocomposites†

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Flower-like SnO_2-Zn_2SnO_4 nanocomposites were prepared *via* a simple hydrothermal process. X-ray diffraction patterns show that as-prepared sample is the composite of SnO_2 and Zn_2SnO_4. Transmission electronmicroscopy characterizations confirm that the morphologies of SnO_2 and Zn_2SnO_4 nanocomposites are "flower". Photoluminescence measurement of the SnO_2-Zn_2SnO_4 nanocomposites reveals a stable purple emission band centered at *ca.* 440 nm. The influences of the hydrothermal temperature and time, the molar ratio of Zn^{2+} and Sn^{4+} and the concentrations of NaOH have been studied. The possible growth mechanisms of flower-like nanocomposites and the possible reaction process were discussed.

Key Words: Flower-like, Hydrothermal synthesis, SnO_2-Zn_2SnO_4, Nanocomposites.

INTRODUCTION

Recently wide band-gap semiconductor materials have been studied extensively due to excellent optical, electrical, chemical properties and high thermal stability[1-3]. As important semiconductor materials, SnO_2, ZnO, Zn_2SnO_4 and their composites have been proved to have potential applications in many fields, such as gas sensors, glass electrodes, secondary lithium batteries, solar cells, transistors and catalysts[4-6]. In the past several years, low-dimensional structure of SnO_2, ZnO and Zn_2SnO_4 nanocrystals, such as nanoparticles, nanorods, nanobelts, nanowhiskers and nanowires, have also been studied due to special optoelectronic properties and potential applications[7-10]. Many researchers have devoted lots of strategies, such as thermal oxidation method, sol-gel method, template-assisted synthesis, hydrothermal method and other methods, to prepare low-dimensional structure of SnO_2, ZnO and Zn_2SnO_4 nanocrystals[7-13]. However the fabrication of SnO_2-Zn_2SnO_4 nanocomposites with low-dimensional structures is still a challenge.

In this paper, we successfully prepared flower-like SnO_2-Zn_2SnO_4 nanocomposites by a simple hydrothermal process without using surfactant as template. The photoluminescence spectrum of the nanocomposites reveals that a purple emission band centered at *ca.* 440 nm. To the best of our knowledge, flower-like SnO_2-Zn_2SnO_4 nanocomposites have never been reported before. The influences of hydrothermal temperature and time, the concentrations of NaOH and the molar ratio of Sn^{4+} and Zn^{2+} were studied. The possible growth mechanism of flower-like structure and the possible reaction process were also discussed.

EXPERIMENTAL

Sample preparation: Flower-like SnO_2-Zn_2SnO_4 nanocomposites were prepared using the hydrothermal method. All the analytical chemical components were purchased from Shanghai Chemical Reagent Company and used without further purification. $SnCl_4\cdot5H_2O$ and $ZnCl_2$ were used as the starting materials and NaOH as the precipitant. $SnCl_4\cdot5H_2O$ and $ZnCl_2$ in a molar ratio of 7:3. Experimental details were as follows: firstly, $SnCl_4\cdot5H_2O$ (3.5 mmol) and NaOH (24 mmol) were dissolved in a minimum amount of deionized water, respectively. Secondly, $SnCl_4$ solution was slowly dropped into NaOH solution under magnetically stirring and a transparent solution was attained. Thirdly, $ZnCl_2$ solution was added dropwise to the vigorously stirred solution, white slurry was obtained and continuously stirred for 0.5 h. Lastly, the white slurry was transferred into a 60 mL Teflon-lined stainless autoclave up to 80 % of the total volume. The autoclave was sealed and maintained in a furnace at 200 ºC for 36 h and then passively cooled down to room temperature. The obtained white precipitate was filtered off, washed several times in distilled water and absolute ethanol and dried under air at 60 ºC

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for 6 h. The other samples obtained at different conditions were also prepared by the same procedure.

Sample characterization: Transmission electron microscopy images were taken by a Hitachi H-800 transmission electron microscope. X-ray diffraction patterns of the samples were measured by using a Japan Rigaku D/max 2200PC diffractermeter with CuK_α radiation (λ = 0.15406 nm) and graphite monochromator. The photoluminescence spectrum was recorded by applying a Hitachi (850) fluorescence spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of the as-prepared sample (Sn^{4+}/Zn^{2+} = 7/3, molar ratio) obtained at 200 ºC for 36 h. The X-ray diffraction peaks in Fig. 1 fit well the tetragonal rutile structure of SnO_2 and the cubic structure of Zn_2SnO_4, according to the JCPDS file No. 41-1445 and the JCPDS file No. 24-1470. No other crystalline phase was detected in the X-ray diffraction patterns. That means the sample is a compound of SnO_2 and Zn_2SnO_4.

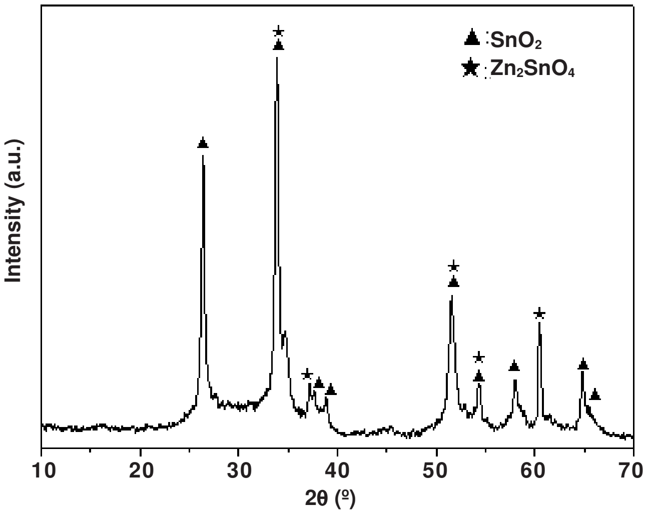

Fig. 1. XRD pattern of the as-prepared sample (Sn^{4+}/Zn^{2+} = 7/3, molar ratio) obtained at 200 ºC for 36 h

In order to study the influences of reaction conditions, such as the molar ratio of Sn^{4+} and Zn^{2+}, the reaction temperature and time, the concentrations of NaOH, other samples at different conditions were also prepared. We noticed that the molar ratio of Sn^{4+} and Zn^{2+} was an important condition of the preparation. With the decrease of the ratio of the Sn^{4+} and Zn^{2+}, the other crystal phase could be detected. When the ratio of Sn^{4+} and Zn^{2+} equals 10/1, the sample is Zn^{2+}-doped SnO_2. Fig. 2a shows the XRD patterns of sample prepared with Sn^{4+}/Zn^{2+} = 10/1. From the XRD patterns in Fig. 2a only SnO_2 phase can be found. While the ratio of Sn^{4+} and Zn^{2+} equals 3/7, the ZnO phase could be found. Fig. 2b shows the XRD patterns of sample prepared with Sn^{4+}/Zn^{2+} = 7/3. From the XRD patterns we notice that the sample is mainly composed of ZnO and Zn_2SnO_4.

The hydrothermal temperature and time was also studied. When the temperature became low and the time was too short, the $Zn[Sn(OH)_6]$ phase was detected. Fig. 2c shows the XRD patterns of sample (Sn^{4+}/Zn^{2+} = 7/3) obtained at 160 ºC for 12 h. From the XRD peaks we can observe that the sample is a compound of $ZnSn(OH)_6$ and SnO_2. It means that the temperature increasing and the time prolonging can help the formation of SnO_2 and Zn_2SnO_4 compound.

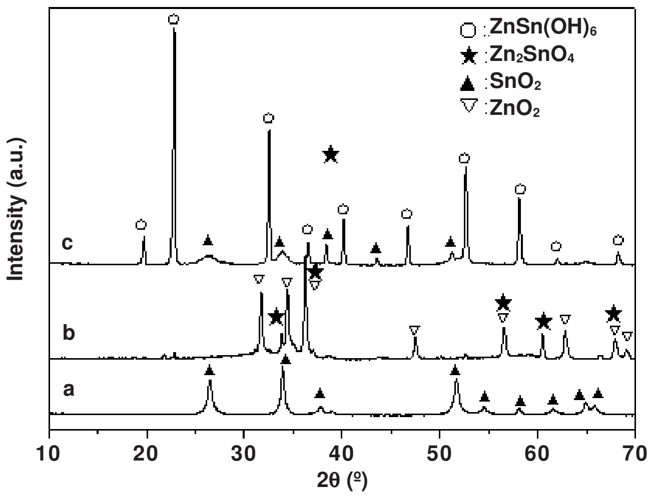

Fig. 2. XRD patterns of the as-prepared sample obtained at different hydrothermal conditions

Furthermore, the influences of the concentrations of NaOH have also been investigated. We found that the concentrations of NaOH played a key role during the process of sample preparation. With the concentration of NaOH increasing, $ZnSn(OH)_6$ phase could be detected in the samples. Moreover, we noticed that no white slurry was found before the hydrothermal process and no precipitates were attained after the hydrothermal growth when the concentration of NaOH was too high.

Fig. 3a presents the whole morphologies of the sample (Sn^{4+}/Zn^{2+} = 7/3) attained at 200 ºC for 36 h. Fig. 3b shows the part morphologies of the same sample. From the images in Fig. 3a, the morphologies of sample seem to be "urchin" and some shorts nanorods are on the surface of urchin. Through observing the part images of the sample in the Fig. 3b, the morphologies may be better described as "flower". The scale of one flower is *ca.* 500 nm and the flowers are composed of many nanorods. The width of nanorods is *ca.* 20 nm and the length is *ca.* 300 nm. We also notice that the flower-like patterns in Fig. 3b are nanorods radiating from the center and these naonorods construct sphere flowers.

About the formation of flower-like SnO_2-Zn_2SnO_4 nanocomposites, we argued that zinc ions act as an important role during the growth process. As we know, ZnO crystal is a polar crystal and SnO_2 crystal is a nonpolar crystal. Lots of researches have approved that ZnO could easily develop the low-dimensional structure nanocrystals during hydrothermal process even if without template assisting. However, the low-dimensional structure SnO_2 nanocrystals are difficult to be attained without template assisting during the hydrothermal process. Therefore, it is presumed that the formation of low-dimensional structure nanocrystals depends on their crystalline nature mainly. When some quantities of zinc ions were introduced the hydrothermal process, SnO_2 nanocrystals will have some polarity due to the producing of ZnO and Zn_2SnO_4. During the hydrothermal process, some quantities of ZnO or Zn_2SnO_4 nanocrystals in the SnO_2 nanocrsyatals can guide SnO_2 nanocrystals growth along (101) orientation and form nanorods. The growth mechanism of flower-like SnO_2-Zn_2SnO_4 nanocomposites is similar to that of larger ZnO crystals[14]. So we think that zinc ions act as a template during the growth process of flower-like nanocrystals.

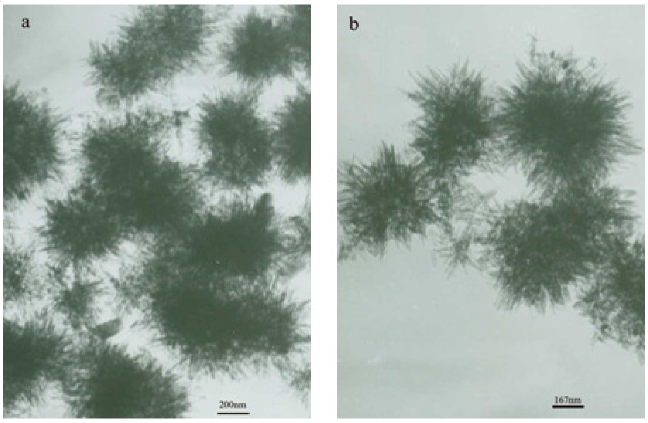

Fig. 3. TEM images of the sample ($Sn^{4+}/Zn^{2+} = 7/3$, molar ratio) attained at 200 ºC for 36 h. (a) the whole morphologies of the sample, (b) the part morphologies of the sample

The photoluminescence spectrum of the flower-like SnO_2-Zn_2SnO_4 nanocomposites was measured at room temperature, (Fig. 4). It reveals a stable and broad purple emission band centered at 440 nm with the excited wavelength of 360 nm. This is different with many SnO_2, ZnO and Zn_2SnO_4 nanocrystals as reported in previous articles. In the previous investigations of semiconductor nanoparticles, the photoluminescence mechanisms have always been attributed to excitatonic luminescence or trapped luminescence. In our study, we hold that the purple emission of flower-like SnO_2-Zn_2SnO_4 nanocompounds mainly arises from the effect of the oxygen vacancies. The unique morphologies of the flower-like SnO_2-Zn_2SnO_4 nanocomposites with high specific surface and high aspect ratio may favour the existence of large quantities of oxygen vacancies. These oxygen vacancies would induce new energy levels in the band gap and contribute to the purple emission of flower-like SnO_2-Zn_2SnO_4 nanocompounds.

We give a possible reaction mechanism according to the experimental and the analytical results, the reaction may be described as follows:

$$Sn^{4+} + 6OH^- \leftrightarrow Sn(OH)_6^{2-} \quad (1)$$

$$Zn^{2+} + Sn(OH)_6^{2-} \leftrightarrow Zn[Sn(OH)_6]\downarrow \quad (2)$$

$$2Zn[Sn(OH)_6] + Sn(OH)_6^{2-} \leftrightarrow Zn_2SnO_4\text{-}2SnO_2 + 2OH^- + 8H_2O + \Delta H \quad (3)$$

We can see that the influences of different conditions from the reaction equation. When the concentration of NaOH is high $Zn[Sn(OH)_6]$ phase will exist within the products because the reaction (3) is restrained with increasing concentrations of NaOH. When the concentrations of NaOH was too high, Zn^{2+} will develop $Zn(OH)_4^{2-}$ phase and Sn^{4+} will form $Sn(OH)_6^{2-}$ phase for reacting with OH^-, which can restrain the formation of $Zn[Sn(OH)_6]$ phase. It can be confirmed by the experimental results that no precipitates can be found when the concentration of NaOH was too high. We found the feasible acidity condition was pH-12. With the ratio of Zn^{2+} increasing, ZnO phase will develop due to the $Zn(OH)_4^{2-}$ phase reacting with $Zn[Sn(OH)_6]$. When the temperature is too low and the time is too short, the reaction (3) will become difficult.

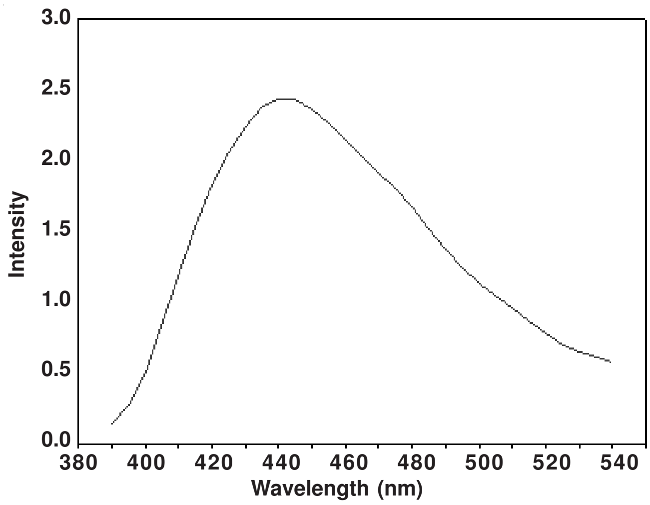

Fig. 4. Photoluminescence spectrum of sample was measured with the excited wavelength of 360 nm at room temperature. It reveals a stable and broad purple emission band centered at 440 nm

Conclusion

Flower-like SnO_2-Zn_2SnO_4 nanocomposites have been synthesized firstly *via* a hydrothermal process. The concentrations of NaOH, the molar ratio of Sn^{4+} and Zn^{2+}, the reaction temperature and time are the important factors for the synthesis of the samples. Photoluminescence measurement of SnO_2-Zn_2SnO_4 nanocomposites shows a purple emission band centered at 440 nm. The possible explanation of luminescence is due to the existence of large quantities of oxygen vacancies.

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