Research Article

Structure and Property Investigation of Composite ZnO/SnO₂ Nanocrystalline Particles after High-Pressure Treatment

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Composite ZnO/SnO₂ nanocrystalline particles (ZnO/SnO₂) were synthesized by sol-gel method and with treatment of high pressure at 6 GPa. The crystallinity and the particle size of the prepared samples were analyzed by X-ray diffraction (XRD) spectroscopy. The results indicated that all the samples had the good crystallinity, and the particle size of ZnO and ZnO/SnO₂ decreased after high-pressure treatment. The infrared (IR) spectra showed that the distance of crystal lattice was shortened after high-pressure treatment, and the size distribution became more uneven after SnO₂ doping. With the high-resolution transmission electron microscope (HRTEM), we got some morphology information and evidence to support the IR and XRD analysis results. The results of ultraviolet-visible absorption (UV-Vis) spectra showed that ZnO/SnO₂ might improve the photocatalytic property of the samples after high-pressure treatment.

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1. INTRODUCTION

People gradually realize that pollutants in water should be removed urgently. There are two common techniques to treat such wastewater: one is adsorption and the other is chemical coagulation. However, these methods merely transfer pollutants from the liquid to the solid phase causing secondary pollution and requiring further treatment.

On the other hand, as a new technique the photocatalytic method can be conveniently applied toward the degradation of pollutants such as dye, without causing secondary pollution. Photogenerated carriers (electrons and holes) in a semiconductor particle can tunnel to a reaction medium and can participate in chemical reactions. Photocatalysis depends on the energy of the electron-hole pairs and the extent of their separation. While TiO₂ is widely employed as a photocatalyst, composite material may be more suitable than TiO₂ attributing to different band gap which can effectively reduce the recombination of electron-hole pairs [1]. High-pressure treatment is a new attempt to improve photocatalytic property which may change particle structure and excite particle quantum effect to induce decrease of the recombination of electron-hole pairs.

ZnO/SnO₂ is a kind of excellent photocatalyst [2]. Many experiments proved that simple ZnO/SnO₂ mixture system

[3, 4] and complex system (e.g., SnO₂ gel/ZnO system [5], Zn₂SnO₄(ZnSnO₃) nanocrystal [6, 7]) both have very good effect. However, their structure and properties after high-pressure treatment were not reported so far. In this study, ZnO/SnO₂ was prepared by sol-gel method, using zinc acetate dihydrate, oxalic acid, and stannous chloride as raw materials. Then, samples were treated under high pressure at 6 GPa.

2. EXPERIMENTAL

2.1. Preparation of ZnO/SnO₂

ZnO/SnO₂ was prepared by the following method. Oxalic acid ((COOH)₂·2H₂O) solution and stannous chloride(SnCl₂·2H₂O) solution were prepared with absolute ethyl alcohol as the solvent. The stannous chloride solution was slowly added to the oxalic acid solution with stirring. Then, zinc acetate dihydrate solution was slowly added to the mixture solution (with the molar ratio of ZnO : SnO₂ = 100 : 3). The resultant solution was aged for 2 hours to obtain the required sol. The sol was heated at 75°C for 12 hours to produce the gel which should be dried over for at least one day, followed by annealing in air at 500°C for 2

hours and cooling to room temperature at last. Pure ZnO was also prepared by a similar method [8].

2.2. High-pressure procedure

Cubic anvil press was used as high-pressure equipment which can generate a pressure up to 6 GPa. The samples were assembled in a cube block, and the assembly steps were as follows [9]. At first, powder was processed into a rotund piece using low-pressure molding which was then put into the carbon pipe center with the sodium chloride (NaCl) piece filled in. At last, assembled pipe was put into pyrophyllite block center and also was covered with pyrophyllite. Figure 1 shows the overall assembled cube block.

Assembled sample was put into the center of the cubic anvil press, boosted for 2 minutes, kept pressure for 30 minutes, decompressed for 3 minutes, and then was taken out.

2.3. Characterization of assynthesized samples

The mean crystallite size, d , was measured from the XRD (D/MAX-YB, RIGAKU) peaks at a scanning rate of $15^\circ/\text{min}$ based on Scherrer's equation:

$$d = \frac{0.89\lambda}{\beta \cos\theta}, \quad (1)$$

where λ is the wavelength of the X-rays, θ is the diffraction angle, and β is the full width at half maximum.

IR spectra (60SXB, Nexus) were also used to characterize the samples, and the crystal morphology and micromechanism of the asprepared powder were characterized by HRTEM (JEM-2100F, JEOL Corporation). Absorption spectra were recorded with a spectrophotometer (UV-Vis Spectrophotometer 754PC, Shanghai Spectrophotometer Instruments Co, LTD). The band gap energy was calculated by the following equation:

$$\lambda_g = \frac{1240}{E_g}, \quad (2)$$

where λ_g is the wavelength of the characteristic absorption peak value; E_g is the band gap energy.

3. RESULTS AND DISCUSSION

3.1. XRD spectra analysis

Figure 2 shows the XRD spectra of different samples: pure ZnO, pure ZnO after high-pressure procedure, ZnO/SnO₂, and ZnO/SnO₂ after high-pressure procedure. The Sn peaks were not observed in the spectra because the concentration of Sn was too low. The diffraction peaks were in good agreement with those given in the standard data (PCPDF, 79-0207) for ZnO and showed a good crystallinity. This means that asprepared materials had crystallized in a hexagonal wurtzite ZnO (see Table 1).

As shown in Figure 2, the peak width of pure ZnO/6G and ZnO(SnO₂)/6G is obviously wider than that of ZnO and

FIGURE 1: sketch diagram of assembled cube block (1) pyrophyllite, (2) carbon pipe, (3) NaCl piece, and (4) sample piece.

FIGURE 2: X-ray diffraction spectra of pure ZnO, pure ZnO after high pressure, ZnO/SnO₂, and ZnO/SnO₂ after high-pressure procedure.

ZnO(SnO₂) because of high-pressure effect. For the mean crystallite size, d is in inverse proportion to the full width at half maximum β ($d = 0.89\lambda/(\beta \cos\theta)$), indicating that the high-pressure procedure can cause the initial grain size to decrease. Table 2 lists the calculation results of the average particle size of the samples. About the reason for the particle size decreasing, there are two possibilities. One is that the high pressure can smash the particles and the other is that the high pressure can make the crystallite more dense by grain squeeze.

The peak intensity of pure ZnO and ZnO/SnO₂ also changed after high-pressure procedure, which reveals that the high pressure may affect the orientation of the samples, but this part needs further in-depth study.

3.2. IR spectra analysis

Figure 3 shows the IR spectra of different samples. From the figure, it can be seen that peaks occur around wavenumber 400 cm^{-1} and 500 cm^{-1} which are due to stretching mode of ZnO. After high-pressure treatment, the characteristic peak of ZnO moved from wavenumber 438 cm^{-1} to 451 cm^{-1} , and

TABLE 1: the XRD parameters of (h k l), and d -value of standard wurtzite phase ZnO and samples.

(h k l)	Int-f	PCPDF79-0207 d (nm)	ZnO d (nm)	ZnO/6G d (nm)	ZnO/SnO ₂ d (nm)	ZnO/SnO ₂ /6G d (nm)
(1 0 0)	570	0.28204	0.28220	0.28272	0.28220	0.28203
(0 0 2)	416	0.26062	0.26107	0.26151	0.26092	0.26078
(1 0 1)	999	0.24806	0.24820	0.24860	0.24820	0.24793
(1 0 2)	210	0.19141	0.19140	0.19163	0.19140	0.19133
(1 1 0)	291	0.16284	0.16268	0.16284	0.16268	0.16263
(1 0 3)	251	0.14793	0.14784	0.14801	0.14788	0.14835
(1 1 2)	203	0.13810	0.13796	0.13803	0.14082	0.14052

TABLE 2: Average particle size of different sample.

Sample	ZnO	ZnO/6G	ZnO(SnO ₂)	ZnO(SnO ₂)/6G
Size	17.22	16.20	19.68	14.50

FIGURE 3: IR spectra of pure ZnO, pure ZnO after high-pressure procedure, ZnO/SnO₂ and ZnO/SnO₂ after high-pressure procedure.

the characteristic peak of ZnO/SnO₂ moved from wavenumber 441 cm⁻¹ to 453 cm⁻¹. It was said that the characteristic peaks of both pure ZnO and ZnO/SnO₂ showed blue shift after high-pressure treatment. It was also noticed that the characteristic peak width of ZnO/6G is broader than that of ZnO, and the peak width of ZnO(SnO₂) and ZnO(SnO₂)/6G is wider than that of ZnO and ZnO/6G.

There are a few reasons to explain the above two phenomena. Peaks occurred with blue shift indicate that high pressure may improve the samples crystallinity and shorten the distance of crystal lattice, which causes enhancing of the field effect of crystal and increasing of the band vibration frequency. In this theory, we exclude the assumption that the decrease of particle size is caused by smashing effect. On the peaks width, it may be caused by interfacial effect and size distribution effect. After high-pressure treatment, the particle interface defects increased, and the size distribution was more disordered. The characteristic peaks of ZnO(SnO₂) and ZnO(SnO₂)/6G are wider than those of ZnO and ZnO/6G, respectively, because of interfacial effect and size distribution effect.

3.3. Morphology and micromechanism

From the HRTEM image of ZnO (a), it can be seen that the particles show a homogeneous size of 18 nm, consistent with the XRD results (17.22 nm). Figure 4(b) shows the good crystallinity of ZnO, also consistent with the XRD results.

Compared with ZnO images, there was some difference in ZnO/6G images (Figures 4(c) and 4(d)). Deformation area near the crystal grain boundary is obvious in Figures 4(c) and 4(d). Maybe it was caused by squeezing between crystals. From Figure 4(c), it can be seen that the crystal lattice was distorted by the grain squeeze below, while the area in Figure 4(d) was distorted by the grain squeeze above, which reveals that deformation always occurs around crystalline exterior. So, it can be supposed that the decrease of particle size was caused partially by particle squeeze.

Figures 5(a) and 5(b) show the ZnO/SnO₂ morphology and microstructure. In Figure 5(a), the big particles are ZnO which are about 20 nm, while SnO₂ particles are much smaller about several nanometers. The ZnO particles were surrounded by SnO₂ particles. So, this microstructure could improve photocatalytic properties [1]. Because of uneven size, the characteristic peak of ZnO/SnO₂ in IR spectra was wider than that of pure ZnO.

In Figures 5(c) and 5(d), the deformation areas of ZnO/SnO₂ particles were obvious. Compared with pure ZnO after high-pressure treatment, the deformation area of ZnO/SnO₂ was more complicated. Probably, the particle size of ZnO/SnO₂ was more uneven than that of pure ZnO, and the grain squeeze was more complicated. Moreover, the particle gap was smaller than that of pure ZnO, indicating a greater degree of compression, which was in agreement with the XRD result (Table 2).

3.4. UV-Vis spectra and band gap energy

The UV-Vis spectra of the samples are displayed in Figure 6. The top absorption peak of both ZnO and ZnO/SnO₂ occurs at the wavelength of 380 nm (3.26 eV). The band gap energy of ZnO/SnO₂ was little changed after doping SnO₂ particles, and the intrinsic absorption peak of SnO₂ did not appear, which may be due to the reunion phenomenon of the SnO₂ particles. For the composite structure, the UV absorption strength of ZnO/SnO₂ was higher than that of ZnO. After high-pressure treatment, the characteristic absorption peak values of ZnO and ZnO/SnO₂ increased

FIGURE 4: HRTEM images of different samples. (a) ZnO morphology image, (b) ZnO crystal lattice image, (c) ZnO/6G crystal lattice image, (d) ZnO/6G crystal lattice image.

FIGURE 5: HRTEM image of different samples. (a) ZnO/SnO₂ morphology image, (b) ZnO/SnO₂ crystal lattice image, (c) ZnO (SnO₂)/6G crystal lattice image, and (d) ZnO (SnO₂)/6G crystal lattice image.

FIGURE 6: UV-Vis absorption spectra of pure ZnO, pure ZnO after high-pressure procedure, ZnO/SnO₂, and ZnO/SnO₂ after high-pressure procedure.

with obvious blue shift, which are at wavelength of 368 nm (3.37 eV) and 366 nm (3.39 eV), respectively. It revealed that after high-pressure procedure, the band gap energy of ZnO and ZnO/SnO₂ increased so that it can decrease the recombination of electron-hole pairs effectively. For the

inverse relationship between the recombination efficiency of electron-hole pairs and the photocatalytic property, it can be inferred that after high-pressure procedure ZnO/SnO₂ has some benefits for photocatalytic property.

4. CONCLUSION

In this work, the ZnO/SnO₂ powders were synthesized by sol-gel method and treated by high-pressure procedure. The X-ray diffraction (XRD) spectra of the samples showed that the nanocrystals had good crystallinity, and the size decreased after high-pressure treatment. The infrared (IR) spectra showed that the distance of crystal lattice was shortened after high-pressure treatment, and the size distribution became more uneven after doping. Through high-resolution transmission electron microscope (HRTEM), some morphology information and evidence support to IR spectroscopic analysis results were obtained. The UV-Vis spectra of the samples showed that ZnO/SnO₂ has some benefits for photocatalytic property after high-pressure procedure.

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