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The Effect of PVP Addition and Heat-treatment Duration on Zinc Oxide Nanoparticles

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Abstract: ZnO nanoparticles were prepared by hydrothermal method different size ZnO nanoparticles were obtained by changing the quantity of PVP which was added to optimize the particle size. The effectiveness of PVP on the particle size has been studied. ZnO nano sheets and ZnO nanorods were prepared by heat-treated of ZnO nano particles for different durations. TEM, XRD and SEM were used to investigate the particles size, particles shapes and the transformation process. We found that by adding more PVP we can get smaller size and good dispersion ZnO nanoparticles and the heat-treatment duration affected the shape which resultant from the aggregation of nanoparticles. A completely transformation from $Zn(OH)_2$ face to ZnO face process has been shown.

Key words: Nanopaericles, nanosheets, nanorods, hydrothermal synthesis, X-Ray diffraction, crystal morphology

INTRODUCTION

Zinc oxide is an n-type semiconductor and it has a large band gap [3.3-3.6 ev], also ZnO shows both photoconductivity and photocatalystic activity (Kash you *et al*., 2005; Gordillo and Coldron, 2001). ZnO nanoparticles show size dependent electronic and optical properties which are known as quantum size effects (Zhang and Li, 2003). For the above reasons zinc oxide seems to be an important and interesting material (Kash you *et al*., 2005; Gordillo and Coldron, 2001), specially in photovoltaic applications, where it has been improved to be very effective as transparent contact in $CulnSO_2$ and $CU(Ln,GA)SO_2$ solar cells (Gordillo and Coldron, 2001). In order to obtain high quality zinc oxide powder with fine size, a narrow size distribution and special morphology. Various techniques have been used to synthesis zinc oxide nanoparticles including hydrothermal method (Ming Yang *et al*., 2006; Li *et al*., 1999) precipitation (Rodriguez *et al*., 2001) sol-gel (Dinghua *et al*., 1998) micro emulation (Zou *et al*., 1999) spray pyrolysis (EL Shal *et al*., 1995; Spanhel and Anderson, 1991) laser vaporization condensation (Samy *et al*., 1995). The precipitation method has been widely used industrially, commonly, but it need heat processing which consume more energy. During the heat processing the particles are subjected to aggregate together and this leads to broader particle size distribution. Colloid solutions of ZnO with particle size smaller than 10 nm can be obtained (Kang and Park, 1997) but the organic solvent must be used. The favored deposition techniques is sputtering RF from ZnO:Al target because this technology was established and produces a highly-quality films (Gupta and Am, 1990; Rodriguez *et al*., 2001) meeting the standard requirements for transparent conductor has been deposited at higher rates by relative sputtering method (Kang *et al*., 2005).

In this study ZnO nanoparticles of different particle size was prepared by hydrothermal method first and then converted into ZnO nanosheets and ZnO nanorods shapes subsequently after it has been heat-treated for different durations.

MATERIALS AND METHODS

ZnO nanoparticles were prepared by hydrothermal method as follow 13 g from $ZnCl_2$ dissolved in water then a solution contained 8 g NaOH added while the stirring was going on. The resultant solution kept on stirring for 8 h. After that it washed with distill water 6 times, the obtained precipitations dissolved in water, then PVP was added, in the first sample the PVP weight: $ZnCl_2$ weight was 1:1, 1:2 in the second sample and 1:5 in third one. After adding PVP stir the solution to get a homogenous liquid which was put in autoclave and heat-treated at 160°C for 8 h and let it cooled to the room temperature. The obtained ZnO nanoparticles precipitations were washed to get rid of PVP. ZnO nanosheets and ZnO nanorods were prepared by heat-treatment of the above obtained ZnO nano particles. After ZnO nanoparticles

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were put outside the autoclave directly stirred for three hours and divided into two solutions, one was heated for three addition hours at 160°C in the autoclave to get ZnO nanosheets and the other solution heated in the same conditions for 6 h to get ZnO nanorods. Transmission electron microscopy [TEM] was used to investigate the morphology and the dispersion of ZnO nanoparticles, X-ray diffraction [XRD] measurements were performed by a BrukerD8 Advance diffractometer with Cu K α radiation. The morphology of the samples was also studied by JSM6700F scanning electron microscope [SEM] operated at an accelerating voltage of 5 KV. The experiments have been done in the Department of Physics, (Nanomaterials Center) Central China Normal University in October 2005.

RESULTS AND DISCUSSION

ZnO nanoparticles was obtained according to the following reactions

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$
$$2Zn(OH)_2 \longrightarrow 2ZnO + 2H_2O$$

Figure 1 shows TEM images of ZnO nanoparticles in different sizes, Fig. 1A contains particles of average diameter about 18 nm and in Fig. 1B particles have an average diameter of about 21 nm, while in Fig. 1C the particles have an average diameter of about 38 nm. Hence, we can say that the particles diameter appeared a reverse proportion to the quantity of PVP, which shows strong evidence that by adding more PVP small particle size can be obtained. This can be due to that PVP can form a shell surrounding the particles to prevent them from being large in size by means of aggregation. Also the donation double bond of both oxygen and nitrogen in the polar group of one PVP molecule may occupy the orbitals of the metal ions, the formation of coordinate bond between PVP and metal ions such as Ag+ and Zn+2 has been reported. Here we believe that Zn+2 can coordinate with PVP, which result in the decrease of Zn+2 concentrations. The higher PVP concentration leads to the lower Zn+2 concentrations. And it is supposed that more PVP present, the lower crystal growth and aggregation rate occur so smaller crystal size in definite growth time obtained (Fanfei *et al*., 2005).

Also the growth of nuclei is a factor of determining the crystal size, it assumed that while growing, the nucleation sites formed in the initial stage will be arranged simultaneously and therefore, secondary nucleation happens, which leads to nucleation sites reducing. PVP serves as an agent of restraining secondary nucleation.

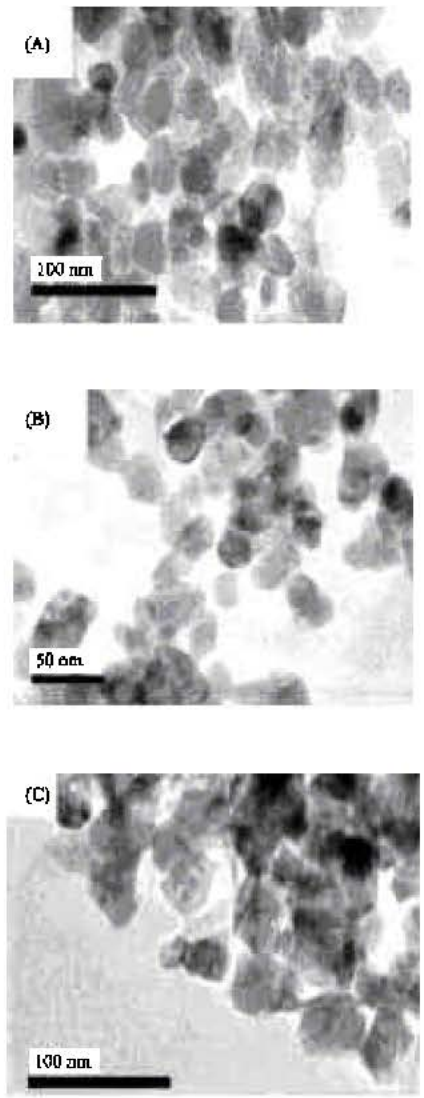

Fig. 1: TEM images of ZnO nanoparticles, (A) ZnO prepared by adding 13 g PVP, (B) ZnO prepared by adding 6.5 g PVP, (C) ZnO prepared by adding 2.6 g PVP

Therefore under higher concentration of PVP secondary nucleation was lower, so the crystal size is small (Li *et al*., 1999). To get more pure ZnO nanoparticles this involve to remove PVP from the specimen by washing or heating, but heating increases the particle size by the means of aggregation. Figure 2 shows SEM images of ZnO, Fig. 2A shows nanoparticles of about 18 nanometers in diameter, Fig. 2B indicates nanosheets of about 160 nm in diameters whereas in Fig. 2C an abundant of nanorods have diameters ranging from 80 to 100 nm and several micrometers in length. The nanosheets and nanorods

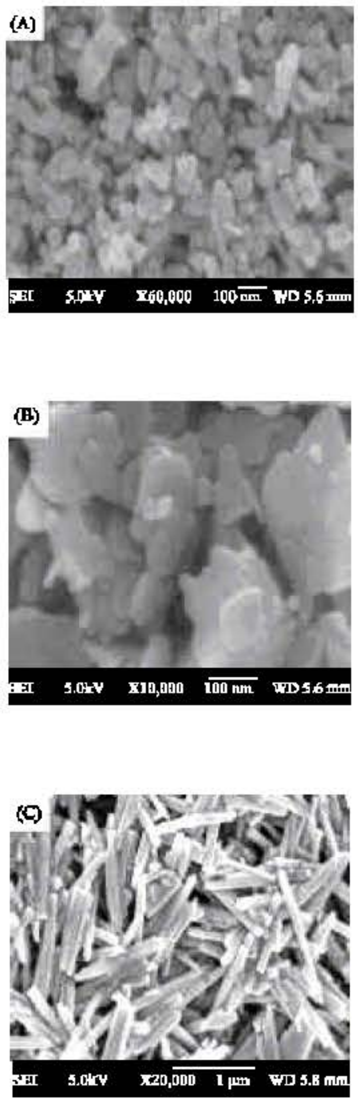

Fig. 2: SEM image (A) ZnO nanoparticles prepared by heat-treatment of $Zn(OH)_2$ (B)ZnO nanosheets prepared by heat-treatment of ZnO nanoparticles for 3 h (C) SEM image of ZnO nanorods prepared by heat-treatment of ZnO nanoparticles for 6 h

were yield by the heat-treatment of ZnO nanoparticles for different durations; appearance of these two shapes is due to the nanoparticles aggregation and assembling in one-dimensional order (Xiangdong *et al*., 2005). ZnO nanoparticles which heated for three hours agglomerated forming sheets shape and one that heated for six hours formed the nanorods shape.

Figure 3 shows x-ray diffraction pattern of ZnO prepared by hydrothermal method. From this pattern we see that the sample contained no impurities, all peaks appeared are ZnO, which means $Zn(OH)_2$ phase was transformed to ZnO completely after the heating process.

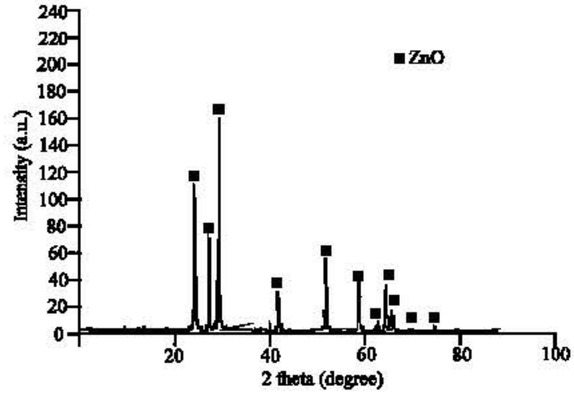

Fig. 3: X-ray diffraction pattern of ZnO prepared by hydrothermal method

CONCLUSIONS

ZnO particles of different size can be prepared by hydrothermal method from $ZnCl_2$ solution and NaOH solution by adding different quantity of PVP, the particle size decreases with the increase of PVP quantity. The ZnO particles were formed by aggregating several single crystals along a certain direction. ZnO nanosheets and nano rods shapes can be obtained by addition heat-treatment of ZnO solution for different durations, the appearance of those shapes was due to the one dimensional aggregation of ZnO nano particles after heating process.

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