The preparation and characterization of ZnO ultrafine particles

Liqiang Jing a,*, Zili Xu b, Jing Shang b, Xiaojun Sun a, Weimin Cai a, Haichen Guo b

a Department of Environmental Science and Engineering, Harbin Institute of Technology, Post Box 760, Harbin 150001, People’s Republic of China
b Department of Environmental Science and Engineering, Jilin University, Changchun 130023, People’s Republic of China

Received 6 April 2001; received in revised form 29 August 2001

Abstract

In this paper, ZnO ultrafine particles (UFPs) were prepared by the thermal decomposition method of the precursor, zinc carbonate hydroxide. The structure and properties of the as-prepared ZnO UFPs were studied using TEM, XRD, BET, SPS, ESR, Raman, XPS and UV–Vis absorption spectroscopy. It was found that the prepared ZnO UFPs exhibited obvious quantum size effect and surface effect. In addition, there were many active species on the surface of ZnO UFPs such as oxygen deficiencies and hydroxyls, both of which can improve the photocatalytic activities of ZnO UFPs. © 2002 Published by Elsevier Science B.V.

Keywords: ZnO; Ultrafine particles; Quantum size effects; Oxygen deficiencies; Surface effects

1. Introduction

When semiconductors are prepared in the form of ultrafine particles (UFPs), they experience great changes of properties, such as light absorption threshold shift to the blue and large increase of surface area. These changes were shown for CdS [1,2], ZnS [3] and TiO2 [4]. The changes are due to charge carrier confinement resulting in the increase of the band gap energy. Zinc oxide is a standard material in semiconductor electrochemistry and photochemistry, and also in conventional catalysis [5,6]. Therefore, ZnO UFPs have been attracting researchers’ interest for a long time, and the applications and preparations of ZnO UFPs have been in the focus in the past 20 years [7,8]. It is usually used as a photocatalyst in the field of environment to purify and degrade pollutants, especially under the condition of light radiation [9,10]. However, these reported methods are relatively expensive and it is not easy to accumulate samples. In this paper, we report a new, easy and relatively inexpensive method. ZnO UFPs were prepared by calcining the precursor, Zn5(CO3)2(OH)6, at different temperatures. In addition, their characteristics, such as particle size, structure and surface state and composition were also investigated, which can give useful information about the applications of ZnO UFPs, such as photocatalytic activities. Therefore, this paper is of interest in various fields of research related to semiconductors.

2. The preparation of ZnO UFPs

2.1. The preparation of precursor

After 40.0 ml of 0.5 mol/l NaOH solution was slowly added dropwise into 100.0 ml of 0.1 mol/l ZnSO4 solution under vigorous stirring in order to produce the Zn(OH)2 precipitate, an appropriate amount of NH4HCO3 powder was added into it. After stirring for 30 min, a semi-transparent zinc carbonate hydroxide colloid was obtained. After 30 min, the colloid was filtered with G3 filter under reduced pressure and dried at 80 °C. Thus, the precursor of a small crystallite of Zn5(CO3)2(OH)6 was formed. It was intentional to retain some Na+ and SO42- ions in order to inhibit the growth of the ZnO crystallite during calcining.
2.2. The formation of ZnO UFPs

The precursor was calcined at 320, 430 and 550 °C for 1 h to obtain the samples. Then, they were filtered with G4 filter under reduced pressure after they were washed and rinsed with distilled water and absolute alcohol for three or four times. After the filtration they were dried at 70 °C, thus affording the pure phase ZnO UFPs calcined at different temperatures.

3. The characterization of ZnO UFPs

3.1. The particle size and structure of ZnO UFPs

The particle size and morphology of the ZnO UFPs were measured with a Hitachi H-8100 transmission electron microscope (TEM). The TEM photomicrographs showed that the ZnO UFPs were very small global grains with a narrow size range. The average particle sizes of the ZnO UFPs calcined at 320, 430 and 550 °C were about 12, 18 and 25 nm, respectively, which demonstrated that the average particle sizes increased as the calcining temperature increased.

The crystallite structure of the ZnO UFPs and a commercial ZnO sample (200 nm) were tested by means of a D/MAX-rA powder diffractometer with a nickel-filtered Cu Kα source, as shown in Fig. 1. The ZnO UFPs and the commercial ZnO sample were proved to be pure phase and to be of a wurtzite structure attached to the hexagonal system. In addition, the crystallite size $D$ of the UFPs can be estimated from the width of the lines in the X-ray diffraction spectrum with the aid of the Scherer formula:

$$ D = \frac{K \lambda}{\beta \cos \theta}, $$

where $\lambda$ is the wavelength of the X-ray used, $\beta$ is the width of the line at the half-maximum intensity, and $K$ is a constant [11]. The estimated values of $D$ of the ZnO UFPs calcined at 320, 430 and 550 °C were 12.1, 17.9 and 25.3 nm, respectively. Besides, the distribution figure of particle size was obtained using the testing technique of the small angle X-ray scattering, as shown in Fig. 2. It showed that the crystallite size $D$ and the average particle size were in good agreement with the result of particle size of the ZnO UFPs measured by the electron microscope.

Fig. 1 shows the X-ray diffraction patterns of the ZnO UFPs calcined at 320, 430 and 550 °C and a commercial ZnO sample. It should be noted that the ZnO UFPs have a wider and lower diffraction spectrum than the commercial ZnO sample. The UFPs are meso-morphous, and the crystallite size of the UFPs has only one or several orders of magnitude difference from that of the atom or molecule. Because of its very small crystallite size, the UFP cannot be seen as an ideal crystal with innumerable crystal faces; hence, the diffraction spectra of the UFPs become wider and lower [4]. In addition, it also demonstrates that the ZnO UFPs calcined at lower temperatures contained some non-crystals and had smaller crystallite size.

3.2. The surface effect of ZnO UFPs

Using a specific computer program based on the XRD data of ZnO particles [12], their unit cell volumes and second strain root-mean-square values (SS) were obtained, as shown in Table 1. It was found that the ZnO UFPs had a smaller unit cell volume than the commercial ZnO sample.
3.3. The surface area of ZnO UFPs

The surface areas were measured by N$_2$ adsorption with a MIKE ASAP-2010 adsorption apparatus. The surface areas of the ZnO UFPs baked at 320, 430 and 550 °C were 47.3, 35.5 and 22.6 m$^2$/g, respectively, indicating that the surface area decreased as the calcining temperature increased. In general, it is favorable in common heterogeneous catalysis to have a large surface area. So it is supposed that the ZnO UFPs calcined at lower temperature can have a higher catalytic activity.

3.4. The quantum size effect of ZnO UFPs

The Raman spectrum (measured in a Bruker RFS-100 FT Raman spectrophotometer, as shown in Fig. 3), the surface photovoltage spectrum (measured in the Department of Chemistry, Jilin University, as shown in Fig. 4) and the ultraviolet–visible absorption spectrum (measured in a PE Lambda20 Spectrometer) of the ZnO UFPs showed a large deviation from that of the commercial ZnO sample. It is commonly observed that commercial ZnO sample. From the SS data, the malposition extent of the ZnO UFP surface atom was greater than that of the commercial ZnO surface atom, indicating that it is easy for the UFP to produce unit cell distortion and surface atom malposition, which were attributed to the quantum size effect and surface effect [13].

<table>
<thead>
<tr>
<th>ZnO UFPs (size, nm)</th>
<th>Binding energy of two kinds of oxygen (eV)</th>
<th>The percent of that oxygen to total oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (12 nm)</td>
<td>530.164, 531.448</td>
<td>32.30, 67.70</td>
</tr>
<tr>
<td>b (18 nm)</td>
<td>530.122, 531.659</td>
<td>41.19, 58.81</td>
</tr>
<tr>
<td>c (25 nm)</td>
<td>530.339, 531.787</td>
<td>48.68, 51.32</td>
</tr>
</tbody>
</table>
the optical absorption threshold shifts to the blue with decrease of particle size, which is often attributed to quantum size effect [14,15].

The surface photovoltage spectrum (SPS) is also a kind of spectrum. Its signal is produced on the basis of light absorption, and it can reflect the properties such as the transfer and lifetime of the photoinduced charge carrier at the excited state. The surface photovoltage originates from the photoinduced charge transfer between the surface (surface space charge region) and the main body (neutral region) of the semiconductor materials. The intensity of SPS response mainly depends on the change of the net charge on the materials’ surface [16]. Fig. 4 shows the SPS of a commercial ZnO sample and the ZnO UFPs calcined at 320, 430 and 550 °C. It can be seen that the intensity of the SPS responses of the ZnO UFPs decreased as the particle size decreased. It had been found that the light-induced electrons and holes are very easy to be trapped on the particle surface because the UFPs are smaller in diameter. Therefore, the results of the UFPs are different from those of the usual powder photocatalyst, i.e. the weaker the surface photovoltage signal, the higher the photocatalytic activity [17].

3.5. The surface composition and structure of ZnO UFPs

The surface composition of the ZnO UFPs was examined by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB MKII spectrometer). The X-ray source emitted Al Kα radiation (1436.8 eV). For all of the binding energy spectra of Zn and O obtained, the pressure was maintained at 6.3 × 10⁻⁵ Pa. Binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV).

According to the different characterizing binding energies of different elements on the surface of materials, we can examine the element composition on the surface of the material. It was found that there were three kinds of elements, carbon, zinc and oxygen, on the surface of the ZnO UFPs. The XPS for Zn₂p and O₁s of the ZnO UFPs baked at 320, 430 and 550 °C had similar patterns. So, we might take the sample of the ZnO UFP baked at 320 °C as a model, whose XPS for O₁s and Zn₂p are shown in Figs. 5 and 6, respectively. From Fig. 5, it can be seen that the O₁s XPS was asymmetric (the right side is wider than that of the left), indicating that at least two kinds of oxygen species were present in the near surface region. The peak at about 530 eV is due to the ZnO crystal lattice oxygen, while the peak at about 532 eV is due to chemisorbed oxygen [18]. The comparison of oxygen binding energies of metal oxide and that of metal hydroxide shows the latter is higher than the former [19]. So, it was speculated that the chemisorbed oxygen was the contribution of the surface hydroxyl. The XPS for Zn₂p was sharp (Fig. 6), demonstrating that there was only Zn²⁺.

In addition, we can complete the relative quantitative analysis using the XPS peak area data of different elements and their own elemental sensitivity factor according to the equation: \( n(E1)/n(E2) = [A(E1)/S(E1)]/ [A(E2)/S(E2)] \), where \( n \) is the number of the element, \( E \) is the element, and \( S \) is the elemental sensitivity factor. The relative XPS data of O₁s and Zn₂p of the ZnO UFPs baked at different temperatures were obtained and are shown in Tables 2 and 3, respectively.

It was found that the peak positions of binding energy of two kinds of oxygen species on different UFP surfaces did not change by much. Also, the percentage of the crystal lattice oxygen to total oxygen increased and that of the hydroxyl oxygen to total oxygen decreased as the calcining temperature increased (Table 2). But the atom ratio of Zn to total oxygen did not change by much (Table 3), that is, the surface hydroxyl amount of the ZnO UFPs decreased as the calcining temperature increased. Some researchers had reported that the surface hydroxyl was an active species and the surface composition and structure of ZnO UFPs

<table>
<thead>
<tr>
<th>ZnO UFPs (size, nm)</th>
<th>Binding energy of Zn (eV)</th>
<th>The atom ratio of Zn to crystal lattice oxygen</th>
<th>The atom ratio of Zn to total oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (12 nm)</td>
<td>1021.9</td>
<td>2.42</td>
<td>0.781</td>
</tr>
<tr>
<td>b (18 nm)</td>
<td>1021.6</td>
<td>2.02</td>
<td>0.832</td>
</tr>
<tr>
<td>c (25 nm)</td>
<td>1021.8</td>
<td>1.60</td>
<td>0.780</td>
</tr>
</tbody>
</table>
played an important role in semiconductor photocatalysis [20,21]. So, it can be predicted that the photocatalytic activities of the ZnO UFPs would decrease as the calcining temperature increased.

Besides, the atom ratio of Zn to crystal lattice oxygen on the surface of the ZnO UFPs calcined at 320, 430 and 550 °C all were much more than 1.0, while that of Zn to crystal lattice oxygen on the surface of the commercial ZnO sample is 1.0 or a little more according to theory. So, it could be demonstrated that there were many oxygen deficiencies on the UFP surface, as could be proved by the electron paramagnetic resonance spectrometry of ZnO UFPs, as shown in Fig. 7. Thus, there were many vacancies and unsaturated chemobonds that could combine with other atoms or groups easily, indicating that the catalytic activities of the ZnO UFPs would decrease as the calcining temperature increased.

The electron paramagnetic resonance spectrometry (EPR) is an effective method for investigating the electron spin state and the structure of the surface of nanosized crystallites. The common or the commercial ZnO is antimagnetic, as can be proved from theory or from experiments; that is, the commercial ZnO does not have the EPR signal. But the ZnO UFPs showed a strong and stable EPR signal with a g factor of 2.0106 at room temperature, which was in agreement with the EPR signal with a reported g factor of 2.0109 [22,23]. The EPR signal resulted from the O$^{2−}$ deficiencies on the ZnO UFP surface which can capture and restrict the electrons so that the paramagnetic resonance sources with $S=1/2$ were produced, exhibiting the stable EPR signal. The relative EPR intensity of the ZnO UFPs calcined at 320, 430, 550 and 700 °C (38 nm) were 14.49, 9.06, 3.99 and 1.0, respectively, demonstrating that the relative EPR intensity of the ZnO UFPs rapidly decreased as the calcining temperature increased, which corresponds to the XPS results. So, the recombinations of the light-induced electron(s) (e$^{−}$) and hole(s) (h$^{+}$) could be restrained now that the O$^{2−}$ deficiencies on the ZnO UFPs surface can capture and restrict the electrons.

3.6. The characterization of photocatalytic activity of the ZnO UFPs

Applying the three kinds of ZnO UFPs and a commercial ZnO sample to the photocatalytic reaction system of heptane or SO$_2$ (4000 ppm, balance nitrogen), oxygen (20% oxygen, balance nitrogen) and ultrapure nitrogen (99.99%), as shown in Fig. 8, it can be seen that on increasing the treatment temperature from 320 to 550 °C the degradation process is retarded, in agreement with the statements discussed above, indicating that the photocatalytic activities are mainly influenced by the properties of the ZnO particle. When the particle diameter decreases, the chances of recombination for photoinduced electron–hole pairs decrease because of their arrival at the reaction site of the surface is faster [24]. The surface oxygen deficiencies can act as the capturer of the light-induced electrons so as to effectively restrain the recombination of electrons and holes, while the surface hydroxyl groups can act as the centers of photocatalytic reactions [25]. The hole (h$^{+}$) attacks the surface hydroxyl and yields a surface-bound OH radical, an active species. So, the photocatalytic activity of the ZnO UFPs increases as the particle size decreases.

4. Conclusions

The ZnO UFPs prepared by the new method had a wurtzite structure attached to a hexagonal system; their properties were also studied using TEM, XRD, BET, SPS, ESR, Raman, XPS and UV–Vis absorption spectra. The results indicated that the prepared ZnO UFPs presented obvious quantum size effect and surface effect, also that the ZnO UFPs have decreased particle size and increased contents of surface oxygen deficien-
cies and hydroxyl active species as the calcining temperature decreased. Besides, the photocatalytic activities are mainly influenced by the properties of the ZnO particle, especially surface characteristics like the contents of surface oxygen deficiencies and hydroxyl active species proved to be essential to the photocatalytic reaction.

Acknowledgements

This work was supported by the National Nature Science Foundation of China.

References