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Chemical Engineering Journal 139 (2008) 642–648

Chemical Engineering Journal

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Synthesis and surface hydrophobic functionalization of ZnO nanocrystals via a facile one-step solution method

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Received 19 October 2007; received in revised form 15 January 2008; accepted 17 January 2008

Abstract

One-dimensional hydrophobic ZnO nanocrystals were successfully prepared via a one-step process through a direct precipitation reaction in aqueous solutions of $ZnSO_4$ and NaOH with self-prepared octadecyl dihydrogen phosphate ($C_{18}H_{37}OPO_3H_2$, ODP) as a surface functionalizing reagent. Scanning electron microscope (SEM) and X-ray diffraction (XRD) results showed that the obtained ZnO particles were one-dimensional (1D) with hexagonal crystal structure. Measurements of relative contact angle and active ratio indicated that the obtained 1D ZnO nanocrystals were hydrophobic. The results of Fourier transform infrared spectroscopy (FT-IR) spectrum and X-ray photoelectron spectroscopy (XPS) clearly showed the formation of interfacial chemical bonds between ZnO and ODP. Furthermore, from the results of TGA test, it was confirmed that a certain amount of organic components existed in the 1D ZnO nanocrystals. These results suggested that the formed organics were bonded onto the surface of 1D ZnO nanocrystals during the reaction process, besides, the organics resulted in the perfect compatibility of obtained ODP functionalized ZnO particles with common organic reagents like ethanol, cyclohexane, and acetone. The influences of ODP on the size of the obtained ZnO particles and the mechanism of surface hydrophobic functionalization by ODP were presented.

Keywords: ZnO; 1D nanocrystals; Surface hydrophobic functionalization; Octadecyl dihydrogen phosphate

1. Introduction

Semiconductor nanocrystals have attracted a great deal of attention for both fundamental size-dependent optoelectronic properties and wide range of applications. ZnO, as one of the II–VI compound semiconductors, is a versatile material and has achieved applications in photocatalysts [1], solar cells [2], chemical sensors [3], piezoelectric transducers [4], transparent electrodes [5], electroluminescent devices [6] and ultraviolet laser diodes [7].

Since the application of ZnO nanorods as optoelectronic nanodevices was reported [8], many efforts have been focused on the synthesis and properties study of one-dimensional (1D) nanocrystals [9,10]. Besides, 1D ZnO nanocrystals are usually necessary to be dispersed in a lipophilic matrix to study the properties of them. For example, ZnO nanorods should be dispersed in acetaldehyde to estimate their ability to the photocatalytic decomposition of the organic compounds [11]. However, pure ZnO particles are hydrophilic and they are difficult to be immersed in a lipophilic matrix. Hence, it becomes very urgent to investigate the synthesis and surface hydrophobic functionalization of 1D ZnO nanocrystals. So far, many researchers had paid lots of efforts on the strategies of the synthesis of hydrophobic ZnO particles mostly based on the two-step synthesis method. For example, Hong et al. [12] realized the surface functionalization by a two-step method: (1) preparation of ZnO particles by calcinations of the precursor (precipitates of zinc acetate and ammonium carbonate) at 450 °C for 3 h; (2) surface hydrophobic functionalization of the obtained ZnO particles by capping with oleic acid. Wu et al. [13] also reported the synthesis and surface hydrophobic functionalization of ZnO particles through a two-step colloidal process, by using 3-aminopropyl trimethoxysilane, tetraethyl orthosilicate, mercaptosuccinic acid, 3-mercaptopropyl trimethoxysilane and polyvinylpyrrolidone as functionalizing reagents. The mentioned methods used in the above two examples were effective to prepare particles with distinct morphology, and conduct surface hydrophobic functionalization with certain organic agent. The morphology changing of the particles derived from the addition of organic reagents was also avoided and ZnO particles

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doi:10.1016/j.cej.2008.01.027

could keep the original crystal shape as 1D nanocrystals. But a two-step synthesis must include two processes named synthesizing the particles and then coating the particles. So, washing and re-dispersing the particles between the two processes were inevitable. Therefore, the two-step process would not be facile compared with the one-step synthesis.

The one-step solution synthesis would attract more interests, which combined the preparation and surface hydrophobic functionalization directly in mild condition. However, during solution synthesis procedure, the functionalizing reagents, which were indispensable to fabricate hydrophobic ZnO particles by the chemical process, would critically influence the morphology of ZnO particles, and various morphologies of ZnO like flowers, towers were always obtained [14]. So it was a more difficult thing for the one-step preparation to fulfill the surface hydrophobic functionalization of ZnO particles together with the 1D growth.

In our previous work, we reported the preparation and surface hydrophobic functionalization of ZnO particles by a precipitation transformation of $Zn_5(OH)_6(CO_3)_2$ into ZnO in the presence of sodium oleate [15]. Here, we used our self-prepared octadecyl dihydrogen phosphate ($C_{18}H_{37}OPO_3H_2$, ODP) as a functionalizing reagent to produce surface functionalized 1D ZnO nanocrystals through a direct precipitation reaction in aqueous solutions of $ZnSO_4$ and NaOH via a one-step process. The synthesis and surface hydrophobic functionalization of 1D ZnO nanocrystals were finished at the same time. The active group of ODP could associate with Zn^{2+} by interfacial recognition of molecules. Furthermore, the ODP could not only induce the nucleation of 1D ZnO nanocrystals but also change the surface property of ZnO from hydrophilic to hydrophobic. The obtained ODP functionalised 1D ZnO nanocrystals showed perfect compatibility with common organic reagents, such as ethanol, cyclohexane, and acetone, which could broaden the use of conventional ZnO in organic systems. The effect of ODP on the preparation of 1D ZnO nanocrystals was investigated and the mechanism of surface hydrophobic functionalization was also presented in detail.

2. Experimental

2.1. Materials

Zinc sulfate ($ZnSO_4$) was adopted as the source material for zinc species. Sodium hydroxide (NaOH) was employed as the precipitators for the formation of ZnO particles. Octadecyl dihydrogen phosphate ($C_{18}H_{37}OPO_3H_2$, ODP) synthesized in our lab was chosen as the functionalizing reagent. All chemicals purchased from Beijing Chemicals Co. Ltd. were of analytical grade and used as received. Distilled water was used throughout.

2.2. Preparation of the functionalizing reagent

P_2O_5 was added into H_3PO_4 solution (the H_3PO_4 concentration is about 85%) under constant stirring at 50 °C for 1 h. Then octadecyl alcohol ($C_{18}H_{37}OH$) was introduced into the system with the protection of N_2. After increasing the temperature to 80 °C, the esterification reaction processed and was maintained for 4 h. Finally the resulting suspension octadecyl dihydrogen phosphate ($C_{18}H_{37}OPO_3H_2$) was obtained.

2.3. Preparation and surface hydrophobic functionalization of ZnO particles

In this work, ZnO particles were fabricated by a direct precipitation reaction in aqueous solutions of $ZnSO_4$ and NaOH, to follow the growth habit of ZnO from $Zn(OH)_4{}^{2-}$ to ZnO particles. In a typical synthesis, a 50 mL $ZnSO_4$ solution with a concentration of 1 M mixed with a certain amount of ODP was set in a three-necked flask and vigorously stirred at 90 °C. Then 50 mL NaOH solution with a concentration of 2 M was added. The weight ratio of ODP/ZnO, R, is varied in a range from 0.0 to 3.5 wt.% with the interval of 0.5 wt.%. The solution was stirred for another 1 h. Subsequently, the resulting slurry was filtered and washed several times to remove the excessive ions by distilled water (90 °C) and ethanol. Finally, the functionalized ZnO particles were obtained after being dried in an oven at 60 °C for 20 h. Four samples obtained at 90 °C and with 0.0, 1.0, 1.5 and 2.5 wt.% of ODP were denoted as ZnO-A, -B, -C and -D, respectively. Two other temperatures, 50 and 70 °C, were also chosen to the synthesis of ODP functionalized ZnO particles. For the comparison, these three control experiments were performed at 90, 70 and 50 °C in the absence of ODP, so three kinds of non-functionalized ZnO samples were obtained.

2.4. Characterization

The crystalline structures of the obtained ZnO powders were examined by X-ray powder diffraction (XRD) with Cu Kα ($\lambda = 1.54056$ Å) radiation on a SHIMADZU-6000 X-ray diffractometer. The dimension and morphology of ZnO samples were investigated by scanning electron microscopy from a JEOL JSM-6700F electron microscope. Water contact angle characterization of ZnO samples was carried out through a FT Ǻ200 (USA) contact angle analyzer. Fourier transform infrared (FT-IR, Nicolet Bruker FT 5DX) was also used to investigate the component and chemical bonding. XPS measurements were carried out in a Vacuum Generators ESCALab MK II instrument (VG Co., UK). And the spectra of Zn 2p and O 1s lines were recorded. All recorded lines were calibrated to the C1s line at 284.6 eV. Thermogravimetric analysis (TGA) was measured in air on SDTA851e thermoanalyzer at the heating rate of 20 °C/min from 50 to 600 °C.

3. Results and discussion

3.1. Surface property of ZnO particles

In order to study the surface characteristics, non-functionalized and ODP functionalized ZnO particles were analyzed with measurements of floating test. The floating test was used to measure the ratio of the floated product to the overall weight of the sample after they were mixed in water and

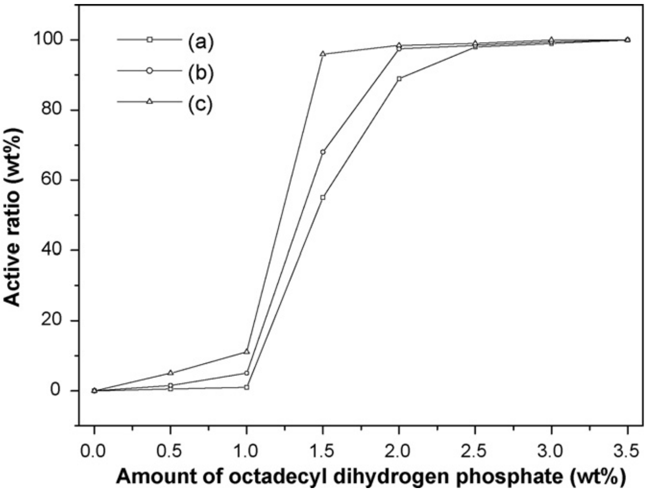

Fig. 1. Influence of the amount of octadecyl dihydrogen phosphate (ODP) on active ratios of the obtained ZnO samples produced at 50 °C (a), 70 °C (b) and 90 °C (c), respectively.

stirred vigorously. The ratio above was called the active ratio. Both the weight ratio of ODP/ZnO (*R*) and the reaction temperature could influence the active ratio of the ZnO particles. Three plots of the active ratio versus the amount of ODP used to functionalize ZnO samples at 50 °C (a), 70 °C (b) and 90 °C (c) were shown in Fig. 1. Without the addition of ODP, the obtained ZnO particles were hydrophilic, and the active ratios were 0.0%. From the three plots, it could be seen that the active ratios increased slowly with *R* increasing from 0.0 to 1.0 wt.%, and became sharply with *R* being 1.5 and 2.0 wt.%. When *R* was 2.5 wt.%, the active ratios of three samples obtained at 50, 70 and 90 °C were all above 98.0%, and the active ratio of the sample synthesized at 90 °C was 99.9%. From the three plots, it could also been seen that when *R* was below 2.5 wt.%, the active ratio of the sample obtained at 90 °C had the highest active ratio. For example, when *R* was 1.50 wt.%, the active ratios of three samples obtained at 90, 70 and 50 °C were 96.0% (c), 68.0% (b) and 55.0% (a), respectively. Therefore, it could be concluded that the amount of ODP was a crucial parameter to surface hydrophobic functionalization. In conclusion, a high reaction temperature (90 °C) was more beneficial to surface hydrophobic functionalization, and the optimal amount of ODP was 2.5 wt.% to make the surface of ZnO hydrophobic. The floating fact might demonstrate that the hydrophobic organic molecules had been probably bonded onto the surfaces of the obtained functionalized ZnO particles. Because the hydrophobic property of functionalized ZnO particles were maintained even being washed by hot water and ethanol.

A functionalized ZnO sample obtained at 90 °C with 2.5 wt.% of ODP (ZnO-D) was further analyzed by relative contact angles to study the surface property. Non-functionalized ZnO sample obtained at 90 °C (ZnO-A) was also measured as a contrast sample, as shown in Fig. 2a. In order to do the contact angle tests, ZnO powders were firstly pressed into compact slices with a pressure of about 20 Pa. And the volume of the water droplet was fixed as 5.0 μL with a diameter of about 2.0 mm. When the water droplet dropped onto the surface of the thin ZnO-A slice (Fig. 2a), no stable drop shape formed, and water droplet was imbibed in the slice, which indicated that the non-functionalized ZnO-A sample was hydrophilic and the relative contact angle was nearly 0°. In contrast, stable drop shape formed on the surface of the ODP functionalized ZnO-D slice and the relative contact angle was about 109° which indicated that the transformation of the surface property from hydrophilic to hydrophobic was realized. The two different relative contact angle results proved that the surface of obtained hydrophobic ZnO particles was capped by organic molecules.

To study the interfacial compatibility between the obtained ODP functionalized ZnO particles and organic reagents, three types of common organic reagents were chosen, including ethanol, cyclohexane, and acetone. Fig. 3a–d shows the pictures of ODP functionalized ZnO-D particles in distilled water and these three kinds of organic reagents (ethanol, cyclohexane, and acetone) at room temperature. From Fig. 3a, phase separation phenomenon was obviously detected that no functionalized ZnO-A particles were dispersed in distilled water. While in Fig. 3b–d, the ODP functionalized ZnO-D particles were uniformly dispersed in these organic reagents and showed perfect compatibility with them. Therefore, the ODP functionalized ZnO particles could be expected to be applied in those systems where these three kinds of solvents were used, to study the special properties of them.

3.2. Structural and morphological characteristics

Fig. 4 shows the calculated X-ray diffraction pattern of ZnO (a, JCPDS 36-1451) and the X-ray diffraction pattern of ODP functionalized ZnO-D sample. As can be seen in Fig. 4b, all these X-ray diffraction peaks could be indexed as the hexagonal ZnO, the same as the values in the standard card (Fig. 4a). By the functionalization of ODP, the (0 0 2) peak of ZnO became stronger relative to its corresponding (1 0 0) peak. Zhang et al.

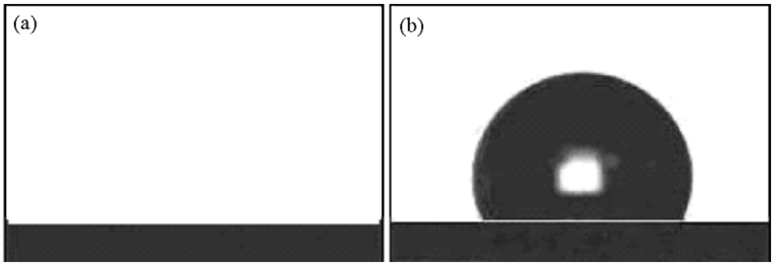

Fig. 2. Water contact angles of the two ZnO samples: (a) non-functionalized ZnO-A and (b) octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D.

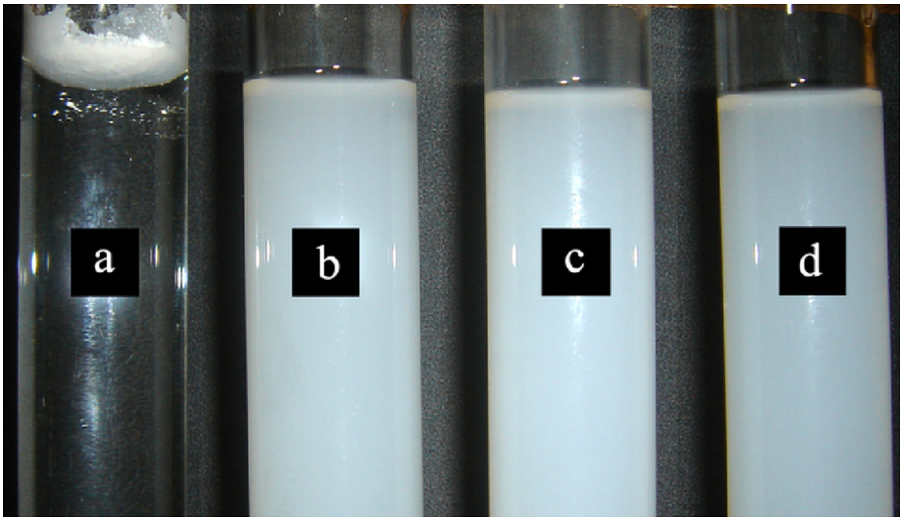

Fig. 3. Pictures of octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D particles in distilled water (a), ethanol (b), cyclohexane (c), and acetone (d).

had reported that this phenomenon could reveal the ⟨0 0 0 1⟩-oriented growth of ZnO particles [16].

ZnO-A and ODP functionalized ZnO-B, -C and -D samples were chosen as representatives to study the effects of surface functionalization on the morphology and the size of obtained ZnO particles. Furthermore, in order to keep the original morphology and size of the obtained ZnO sample, we did not use ultrasonic to treat the ZnO particles before the SEM tests. According to Fig. 5a, the non-functionalized ZnO-A particles had a wide particle size distribution of 100–700 nm and the average length of the sample was about 400 nm. When 1.0 wt.% of ODP was added in the preparation, the length of the obtained functionalized ZnO-B particles was about 200–300 nm in a narrow range (Fig. 5b). By increasing the amount of ODP to 1.5 wt.%, the length of the obtained functionalized ZnO-C decreased to 100–250 nm (Fig. 5c). By further increasing the amount of ODP to 2.5 wt.%, the obtained functionalized ZnO-D particles were uniform with an average length of about 180 nm (Fig. 5d), which was much smaller than that of the non-functionalized ZnO-A particles shown in Fig. 5a. Clearly, ODP played an important role in the formation of the small and 1D ZnO nanocrystals. It was reported that 1D ZnO nanocrystals could be used in the promising application of optoelectronic nanodevices [8]. Regarding all above results, it was clear that ODP could alternate the surface property of ZnO particles from hydrophilic to hydrophobic without changing the 1D morphology.

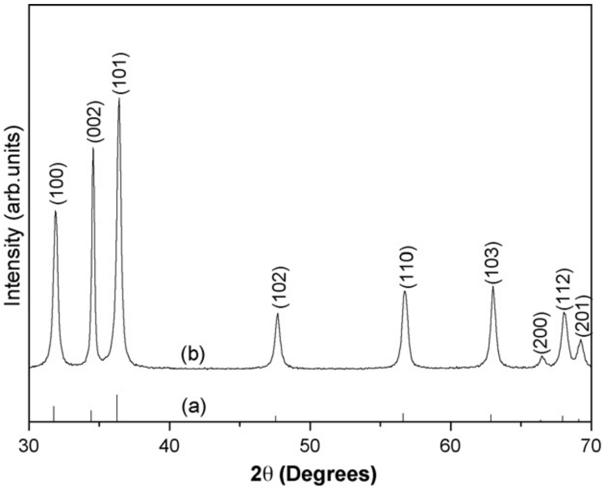

Fig. 4. Calculated X-ray diffraction pattern of ZnO (a) and the X-ray diffraction pattern of octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D sample (b).

3.3. Mechanism

In order to study the mechanism of the functionalization process, the Fourier transform infrared (FT-IR) spectra of the obtained ZnO powders were examined. Fig. 6 shows the FT-IR spectra of non-functionalized ZnO-A (a), ODP functionalized ZnO-D (b) and surface functionalization reagent ODP (c). The peak area of the particles nucleated in the absence of ODP was chosen as the standard for comparison. The FT-IR absorption band at 401 cm^{-1} (Fig. 6a) was the characteristic absorb peak of ZnO, which was the same as that of curve b shown in this region. The absorption peak of ODP occurred around 2916, 2847 cm^{-1} ($\nu(\text{CH}_2)$), 1472 cm^{-1} ($\delta(\text{CH}_2)$) and 715 cm^{-1} ($\nu(\text{PC})$) were consistent with the appearance of the alkyl groups from the ODP. The appearance of the peaks at 2916 and 2847 cm^{-1} in curve b confirmed the presence of ODP in the functionalized 1D ZnO nanocrystals.

Non-functionalized ZnO-A and ODP functionalized ZnO-D were measured by XPS to identify the mechanism of the successful conversion of hydrophilicity to hydrophobicity and the state of ODP in the functionalized 1D ZnO nanocrystals. Binding energies (EB) were referenced to the C 1s energy at 284.6 eV. Fig. 7(a1 and b1) shows the Zn 2p and O 1s core level spectra of non-functionalized ZnO-A. The binding energy of the Zn 2p3 component was recorded to be 1020.9 eV and O 1s is 531.4 eV. The Zn 2p and O 1s core level spectra of 2.50 wt.% of ODP func-

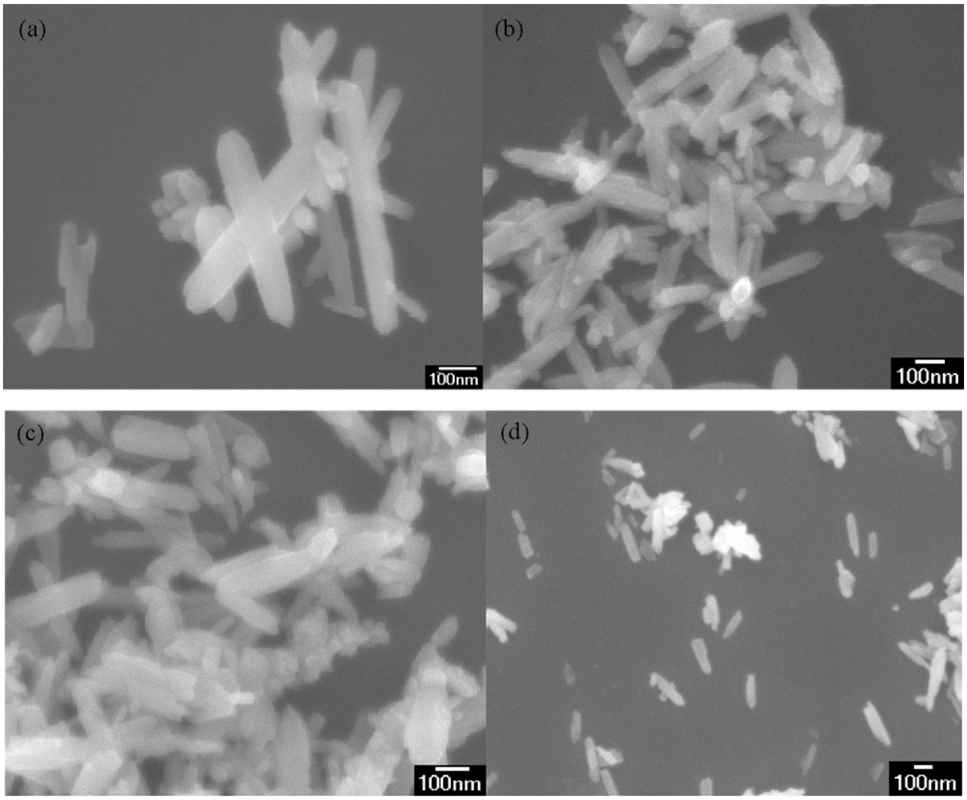

Fig. 5. SEM images of non-functionalized ZnO-A (a) and octadecyl dihydrogen phosphate (ODP) functionalized ZnO samples: ZnO-B (b), ZnO-C (c) and ZnO-D (d).

tionalized ZnO-D were shown in Fig. 7(a2 and b2), from which it was known that the binding energy of the Zn 2p3 component was recorded to be 1020.0 eV and the O 1s was 530.6 eV. The change of Zn 2p3 and the shift of O 1s could demonstrate that the alkyl chains were successfully bonded onto the surface of ZnO, because the non-functionalized and functionalized samples were synthesized almost with the same conditions but the addition of ODP. We have also calculated C/Zn atomic ratio by the result of XPS according to the below formula:

$$C_x/Zn_y = (A_c/S_c)/(A_{Zn}/S_{Zn}),$$

$$A\text{—peak area } (A_c = 9916,\ A_{Zn} = 77486),$$

$$S\text{—sensitivity factor } (S_c = 0.25,\ S_{Zn} = 4.8).$$

And the atomic ratio was about 2.46, from which the surface coverage was calculated as 12.02% (C was considered all from ODP). The appearance of the organics on the surface of obtained

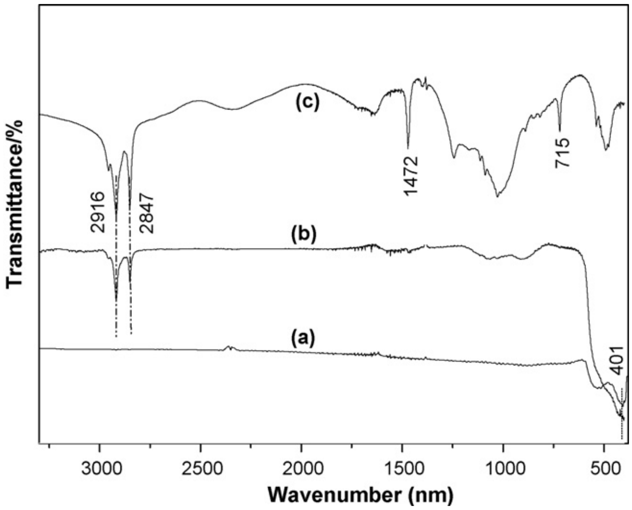

Fig. 6. FT-IR spectra of non-functionalized ZnO-A (a), octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D (b) and functionalization reagent ODP (c).

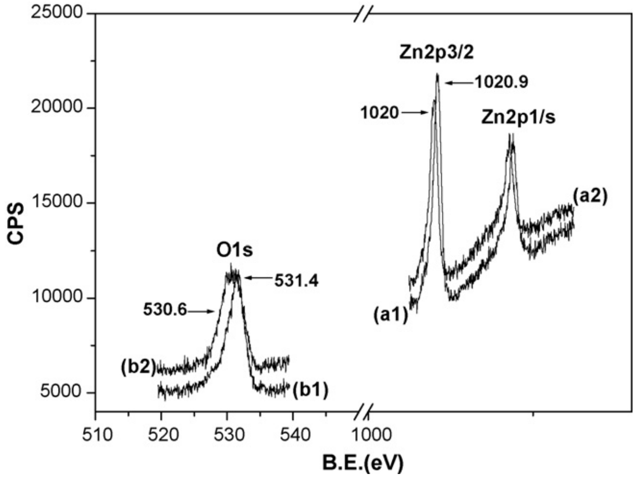

Fig. 7. XPS spectra of the Zn 2p (a1) and O 1s (b1) core levels recorded from non-functionalized ZnO-A and Zn 2p (a2), O 1s (b2) from octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D.

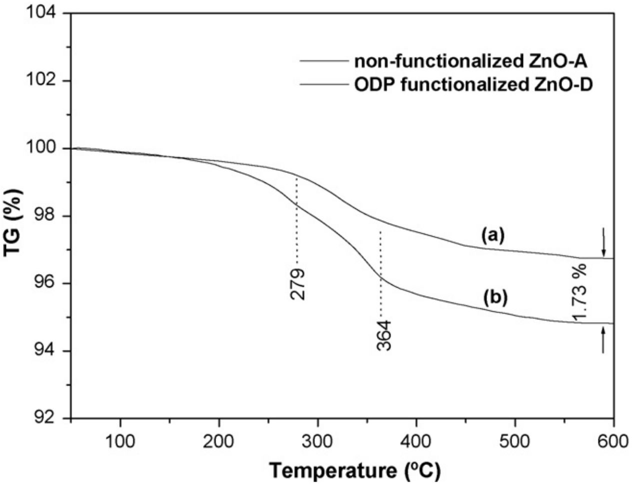

Fig. 8. TGA curves of non-functionalized ZnO-A (a) and octadecyl dihydrogen phosphate (ODP) functionalized ZnO-D (b).

ZnO might also encourage the nucleation and prevent the 1D growth of ZnO particles with smaller length.

The ODP molecules deposited on the surfaces of ZnO might be in the form of insoluble salts according to previous work [17,18]. It was very hard for ODP molecules to form a compact layer because of steric hindrance between them. However, when the amount of the insoluble salts reached to a degree, the obtained ZnO particles would show hydrophobicity. TGA test was taken to prove the above conclusion that a certain amount of organic molecules was built on the surface of 1D ZnO nanocrystals. The TGA curves of non-functionalized ZnO-A (Fig. 8a) and ODP functionalized ZnO-D samples (Fig. 8b) obtained at 90 °C were shown. For non-functionalized ZnO-A, there was a weight loss of 3.43 wt.% when the sample was heated from 50 to 600 °C, which was due to the removal of physically adsorbed water, chemically adsorbed water and the decomposition of hydroxide groups. The hydrophobic ZnO-D sample had a total weight loss of 5.16 wt.%, when the temperature changed from 50 to 600 °C. Some differences were detected between curves (a) and (b) in the temperature range of 279–364 °C, which might be caused by desorption of the octadecyl phosphate in the functionalized ZnO-D sample. Compared with curve a, the total weight losses of the hydrophobic ZnO-D sample shown in curve b indicated that the grafting amount of ODP were 1.73 wt.%, which might be the monolayered amount of ODP for ZnO particles to be hydrophobic. The amount of ODP calculated by TGA was less than that was added in the preparation process. This might be mainly due to that the reaction ratio of ODP was less than 100%.

In summary, in the presence of functionalizing reagent ODP, Zn^{2+} could be bonded to the negatively charged ODP and resulted in the nucleation of ZnO particles, and ODP prevented the 1D growth, so 1D ZnO nanocrystals with smaller length were obtained. Furthermore, ODP also changed the surface property of ZnO from hydrophilic to hydrophobic. Kuo and Mikkelsen had reported that the complexes of phosphate could deposit on the surfaces of calcite particles [17]. So it was concluded that organic phosphate could also sedimentate on the surfaces of 1D ZnO nanocrystals by chemical reaction. Besides, the presence of chemical bond between ZnO and ODP had been proved by the result of XPS test (Fig. 7). According to these results shown in Figs. 6–8 and our previous work [18], it could be implied that the organics bonded on the surface of ZnO could be zinc alkyl phosphate.

4. Conclusion

One-dimensional hydrophobic ZnO nanocrystals were successfully produced by using $ZnSO_4$, NaOH as raw materials, and the self-prepared octadecyl dihydrogen phosphate (ODP) as a functionalizing agent. ODP used in direct precipitation process, played a dual role of surface functionalization and the maintenance of 1D morphology of ZnO. XRD analysis indicated that the product was of hexagonal structure. SEM analyses showed that ODP regulated the size of ZnO particles, and uniform and hydrophobic 1D ZnO nanocrystals with an average size of about 180 nm were successfully obtained. FT-IR, XPS and TGA analyses indicated that a certain amount of organics was formed onto the surfaces of ZnO particles. The organics could be alkyl zinc phosphate and significantly changed the surface properties of ZnO particles from hydrophilic to hydrophobic. And the hydrophobic property of functionalized ZnO particles could be maintained even being washed by hot water and ethanol. Measurements of active ratio and relative contact angle indicated that ZnO samples were hydrophobic, which showed perfect compatibility with common organic reagents like ethanol, cyclohexane and acetone and could broaden the use of conventional ZnO in organic systems. In a word, it is a simple way to prepare 1D ZnO nanocrystals with a hydrophobic surface during an in situ preparation.

Acknowledgement

This work was supported by The Natural Science Foundation of Jilin Province under grant number 20020336.

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