Research Article

Understanding the Factors That Control the Formation and Morphology of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ through Hydrothermal Route

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The influence of the choice of ethanol-water volume ratio, concentration of zinc salt, and ZnO buffer layer on the formation and morphology of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ grown from the hydrothermal route was systematically discussed. Experimental results suggested that $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ upright-standing plates were obtained by limiting ethanol-water volume ratio. The concentration of zinc salt was crucial for getting phase-pure $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The presence of ZnO buffer layer could lead to the that chemical composition of product grown on the substrate was totally different from the product grown in the solution. Possible formation mechanism of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was also studied. Raman spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ displays a complex behavior with four modes, which can be assigned to the vibrational modes of Zn-H-O, Zn-O, H₂O-nitrate, and nitrate. Porously ZnO rectangle sheets were obtained by thermal treatment of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets.

1. Introduction

As a family of lamellar compounds, layered basic zinc salts have attracted increasing attention on account of their specific structure and potential applications for ion exchange, catalysts, absorption, complex organic-inorganic hybrid, and drug delivery agent materials [1–3]. According to the classification of Louër et al., the structure of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (LBZN) belongs to type IIb [4]. One-quarter of the octahedrally coordinated zinc atoms are removed from the layer and positioned at the bottom and top of the empty octahedral, with tetrahedral coordination. Three vertices of such tetrahedral coordination are found to be occupied by hydroxide groups belonging to the octahedral sheet, while the fourth, pointed to the interlayer space, is occupied by a water

molecule. NO_3^- groups are located between the layers and they are not directly coordinated with the zinc atoms [3, 5]. Compared to other ions such as SO_4^{2-} and CO_3^{2-} groups, NO_3^- groups have a bigger volume/charge rate, which facilitate ionic exchange reactions [6, 7]. Furthermore, porous materials could be massively obtained by thermal treatment or other methods [8–11], and these ZnO porous structures obtained by thermal treatment of different layered basic zinc salts are very different from any other nanostructured ZnO [12, 13], which are expected to apply in photoelectrochemical fields including chemical sensors, photocatalysts, and solar cells. For example, the dye-sensitized solar cells fabricated by porous ZnO nanosheets from the pyrolysis of layered hydroxide zinc carbonate have a conversion efficiency of 3.9% [14].

Numerous efforts have been employed in synthesizing $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ nano- or microstructures [15, 16]. Among them, the practical requirements for material synthesis are guaranteeing the easier formation of phase pure $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and morphology control. The hydrothermal method featuring low temperature, simplicity and large-scale production is of special interest in the synthesis of nano- or microstructures [17]. Therefore, in order to synthesize phase pure $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with regular architectures through the hydrothermal route, it is very useful and important to understand the factors that control the formation and morphology of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

In the present work, we reported on the influence of the choice of ethanol-water volume ratio, concentration of zinc salt, and ZnO buffer layer on the formation and morphology of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ through the hydrothermal route at 80°C . $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ upright-standing plates were obtained by limiting ethanol-water volume ratio. The concentration of zinc salt was crucial for getting pure-phase $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The presence of ZnO buffer layer could lead to that the chemical composition of product grown on the substrate was totally different from the solution. Possible formation mechanism of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was also studied. Raman spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ displays a complex behavior with four modes, which can be assigned to the vibrational modes of Zn–H–O, Zn–O, H_2O -nitrate, and nitrate. Porously ZnO rectangle sheets were obtained by thermal treatment of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets.

2. Experimental Details

Before the hydrothermal synthesis, a uniform ZnO buffer layer was deposited on a $2\text{ cm} \times 2\text{ cm}$ substrate (Si or glass) by thermally decomposing zinc acetate at 350°C [18]. Then, analytically pure $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 mmol) and hexamethylenetetramine (HMTA) (1 mmol) were added into an autoclave of 50 mL capacity. The autoclave was filled with ethanol-water mixture at different volume ratio up to 80% of the total volume. After stirring for 5 minutes, a substrate with or without ZnO buffer layer was transferred into the autoclave which was then sealed and maintained at 80°C for 12 h. Finally, the autoclave was cooled to ambient temperature, the obtained precipitates and substrate were collected, washed with deionized water, and dried at 60°C in air before characterization. In addition, part of the dried precipitates was annealed at 500°C for 20 minutes.

The as-synthesized products were characterized by X-ray powder diffraction (XRD; Rigaku D/Max-2550), field emission scanning electron microscopy (FE-SEM; Hitachi S-4800). The Raman spectra were recorded on LABRAM-1 B confocal laser micro-Raman spectrometer with 532 nm radiations at room temperature. The PL spectra were measured under continuous-wave (cw) 325 nm He–Cd laser excitation, using a 1800 line/mm single grating monochromator and a photomultiplier.

3. Results and Discussion

3.1. The Function of Ethanol. To explore the function of ethanol, the ethanol-water volume ratio was adjusted from 3:1 to 2:1, 1:1, 0.5:1, 0:1, and 1:0, keeping other reaction condition identical. Figure 1(a) is typical FE-SEM image of as-prepared products grown in solution as the ethanol- H_2O volume ratio of 3:1. It reveals that large amounts of well-defined rectangle sheets with length ranging from 10 to $45\text{ }\mu\text{m}$ and width ranging from 5 to $40\text{ }\mu\text{m}$ are formed in the solution. The thickness of side face is about $2.2\text{ }\mu\text{m}$ without laminated feature (see insets of Figure 1(a)). Figure 1(b) is typical FE-SEM image of as-prepared products grown on the substrate coated with a ZnO buffer layer, showing many upright-standing plates are formed. No laminated feature can be observed on the surface of these plates (see insets of Figure 1(b)). This kind of nearly upright-standing structure breaks the thermodynamic restriction and might be ascribed to hydrophobic properties of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and the substrate [14, 19]. Figure 1(c) is typical FE-SEM image of as-prepared products grown on a plain substrate, where the nearly upright-standing plates are also observed. However, compared to plates grown on the substrate with ZnO buffer layer, laminated feature is observed (see insets of Figure 1(c)). Figures 1(d) and 1(e) are typical XRD patterns of as-prepared precipitates collected from the solution and as-prepared products grown on the substrate with or without the ZnO buffer layer, respectively. All the samples exhibit two strong peaks at $2\theta = 9.08$ and 18.20° , which are indexed to diffraction of the (200) and (400) planes, respectively, of the monoclinic $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ phase with cell constants $a = 19.48\text{ }\text{\AA}$, $b = 6.238\text{ }\text{\AA}$ and $c = 5.517\text{ }\text{\AA}$ (JCPDS no. 72-0627), suggesting all the samples have a preferential growth direction along the (200) orientation. No impurities are detected, indicating the products are highly phase pure. When ethanol-water volume ratio was changed to 2:1, as-prepared precipitates formed in solution were also $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets. However, the size distribution of these sheets was large (not shown). Figures 2(a) and 2(b) are XRD patterns of as-prepared products grown in the solution and grown on the substrate coated with a ZnO buffer layer as the ethanol-water volume ratio of 1:1, respectively. All diffraction peaks of as-prepared products grown on the substrate are indexed to hexagonal ZnO (JCPDS no. 36-1451), at the same time as-prepared products grown in the solution are $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Figure 2(e) is typical FE-SEM image of the ZnO film grown on the substrate coated with a ZnO buffer layer (corresponding to Figure 2(b)), in which the grains with an in-plane size ranging from 100 to 300 nm are formed. The ZnO film consists of closely connected particles and the average thickness of the film is about $1.1\text{ }\mu\text{m}$ (see inset of Figure 2(e)). Figures 2(c) and 2(d) are the XRD patterns of as-prepared products grown in the solution and grown on the substrate coated with a ZnO buffer layer as the ethanol- H_2O volume ratio of 0.5:1. Both as-prepared products are pure-phase ZnO. Figure 2(f) is typical FE-SEM image of the ZnO film grown on the substrate coated with a ZnO buffer layer (corresponding to Figure 2(d)), in which the column-sheet composite structure

FIGURE 1: FE-SEM images of (a) as-prepared precipitates collected from the solution; (b) the products grown on the ZnO buffer layer; (c) products grown on a plain substrate as the ethanol-water volume ratio of 3 : 1. XRD patterns of (d) as-prepared precipitates collected from the solution; (e) products grown on a substrate with or without a ZnO buffer layer as the ethanol-water volume ratio of 3 : 1. Si substrate is labeled with asterisk (*).

is formed. The thickness of composite structure is about $1.8\ \mu\text{m}$ (see inset of Figure 2(f)). Figures 3(a) and 3(b) are the XRD patterns of as-prepared products grown in the solution and grown on the substrate coated with a ZnO buffer layer as the ethanol- H_2O volume ratio of 0 : 1. Both as-prepared products are pure-phase ZnO. Moreover, the strong intensity of the (002) diffraction peak located at about $2\theta = 34.5^\circ$ confirms that the product grown on the substrate has a preferential growth direction along the c -axis orientation. Figure 3(e) is typical FE-SEM image of the ZnO film grown on the substrate coated with a ZnO buffer layer (corresponding to Figure 3(b)), in which the grains with an in-plane size from 200 to 400 nm are formed. The thickness of columnar structure is about $3.4\ \mu\text{m}$ (see inset of Figure 3(e)). Figures 3(c) and 3(d) are the XRD patterns of as-prepared products grown in the solution and grown on the substrate as the ethanol- H_2O volume ratio of 1 : 0. Both as-prepared products are pure-phase $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

Figure 3(f) is typical FE-SEM image of the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ spheres grown on the substrate (corresponding to Figure 3(d)), in which spheres are composed of many sheets. The diameter of each sphere is about $45\ \mu\text{m}$ (see inset of Figure 3(f)).

According to above results, we found that the formation of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ strongly depends on the composition of ethanol. When ethanol- H_2O volume ratios were 3 : 1, 2 : 1 and 1 : 1, the as-prepared precipitates collected from solution were $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ microsized rectangle sheets. When ethanol-water volume ratio was changed to 0.5 : 1, 0 : 1, and 1 : 0, as-prepared precipitates formed in solution were ZnO twinning structures, ZnO sea urchins, and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ particles composed of small sheets, respectively (not shown). Generally, HMTA acts as a weak base which slowly hydrolyzes into formaldehyde and ammonia with increasing temperature [20]. Then ammonia would react with water to form ammonium hydroxide and generate

FIGURE 2: XRD patterns of (a) as-prepared precipitates collected from the solution; (b) products grown on a ZnO buffer layer as the ethanol-water volume ratio of 1:1; (c) as-prepared precipitates collected from the solution; (d) products grown on a ZnO buffer layer as the ethanol-water volume ratio of 0.5:1. FE-SEM images of (e) products grown on a ZnO buffer layer as the ethanol-water volume ratio of 1:1; (f) FE-SEM image of products grown on ZnO buffer layer as the ethanol-water volume ratio of 0.5:1. Si substrate is labeled with asterisk (*).

FIGURE 3: XRD patterns of (a) as-prepared precipitates collected from the solution; (b) products grown on ZnO buffer layer as the ethanol-water volume ratio of 0 : 1; (c) as-prepared precipitates collected from the solution; (d) products grown on a substrate as the ethanol-water volume ratio of 1 : 0. FE-SEM images of (e) products grown on ZnO buffer layer as the ethanol-water volume ratio of 0 : 1; (f) FE-SEM image of products grown on a substrate as the ethanol-water volume ratio of 1 : 0.

FIGURE 4: (a) XRD pattern of as-prepared samples collected from the solution when the concentration of zinc salt was lowered to one-third; (b) room temperature Raman spectrum of the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets.

OH^- ions, which can complex with Zn^{2+} to form hydroxyl species, including $\text{Zn}(\text{OH})^+(\text{aq})$, $\text{Zn}(\text{OH})_2(\text{aq})$, $\text{Zn}(\text{OH})_2(\text{s})$, $\text{Zn}(\text{OH})_3^-(\text{aq})$, and $\text{Zn}(\text{OH})_4^{2-}(\text{aq})$ [21]. Solid ZnO nuclei are formed and continue to grow by dehydration of these hydroxyl species and the whole process occurring in the solution can be described as follows [20, 21]:

However, when enough ethanol molecules were introduced into the precursor solution, a new structural form of zinc ligand ($[\text{Zn}(\text{C}_2\text{H}_5\text{OH})_{4-n}(\text{OH})_n]^{2-n}$) might be formed, which would create a new Zn-ligand balance between $\text{Zn}(\text{OH})_m^{m-2}$ ($m=0,1,2,3,4$) and $[\text{Zn}(\text{C}_2\text{H}_5\text{OH})_{4-n}(\text{OH})_n]^{2-n}$. Their balances might be as follows:

Ghoshal et al. obtained ZnO nanocrystals along with a few nanorods in the precursor comprising of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sodium hydrate, and mixed solvent of water and ethanol. The process described by (4) took place due to a much higher OH^- concentration ($\text{pH} \sim 13.6$) and $\text{Zn}(\text{OH})_m^{m-2}$ was the majority, resulting in formation of ZnO nanocrystals [22]. However, in this work, the sodium hydrate was replaced by HMTA, which effectively lowered the OH^- concentration. Therefore, the progress described by (5) would take advantage. The growth unit might be no more $\text{Zn}(\text{OH})_m^{m-2}$ but $[\text{Zn}(\text{C}_2\text{H}_5\text{OH})_{4-n}(\text{OH})_n]^{2-n}$. Finally, $[\text{Zn}(\text{C}_2\text{H}_5\text{OH})_{4-n}(\text{OH})_n]^{2-n}$ would transfer into

$\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rather than ZnO through the following reaction:

3.2. The Function of Zinc Salt. The solution viscosity can be elevated by using relatively high concentration of zinc salt, which causes halfway transfer of the nutrients and impedes the dehydration of zinc ligands. If the reaction solution is water, viscosity brought by more zinc salts has no obvious influence on the growth process owing to the high dielectric constant of water (78.5). However, compared to water, the dielectric constant of ethanol (24.3) is much lower, which implies that the viscosity brought by more zinc salts has apparent effect. To affirm this assumption, the amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was changed from 3 mmol to 2 mmol, 1 mmol, and 4 mmol, keeping other reaction condition identical, respectively. Figure 3(a) is the XRD patterns of as-prepared products grown in the solution as the amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1 mmol. It reveals that as-prepared products have two different phases, which are hexagonal ZnO and monoclinic $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, respectively. Because the viscosity was lowered, the nutrients can transfer in the whole system easily. Then, the dehydration of zinc ligands might tend to occur, causing (4) and (5) taking place at the same time. Finally, as-prepared products with two different phases were obtained. When the amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were equal to or greater than 2 mmol, as-prepared products with pure $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ phase were obtained (see Figure 1(a)). According to above results, although the introduction of ethanol could facilitate the formation of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, enough zinc salt was also important to get phase pure $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

FIGURE 5: (a) XRD pattern of ZnO microsized rectangle sheets; (b) SEM image of ZnO microsized rectangle sheets; (c) room temperature Raman spectrum of ZnO microsized rectangle sheets; (d) room temperature PL spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ microsized rectangle sheets; (e) room temperature PL spectrum of ZnO microsized rectangle sheets.

3.3. The Function of ZnO Buffer Layer. As mentioned above, when the ethanol-water volume ratio was 1:1, keeping other reaction condition identical, the as-prepared products grown on the substrate coated with a ZnO buffer layer were ZnO thin film (see Figures 2(a) and 2(e)), whereas $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ plates with laminated feature were formed on the plain substrate (see Figure 1(c)). When the ethanol-water volume ratio was 3:1, keeping other reaction condition identical, the as-prepared products grown on the substrate coated with a ZnO buffer layer were $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ plates without laminated feature (see Figures 1(b) and 1(e)), whereas $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ plates with laminated feature were formed on the plain substrate (see Figures 1(c) and 1(e)). These results indicated that the ZnO buffer layer not only had great effect on the morphology of as-prepared product but also determined the phase in certain condition. For the case of the ethanol-water volume ratio of 1:1, the differences in preferred crystal structure of the as-prepared product on the different substrates might be attributed to the disparities in the number of possible nucleation sites and the lattice match for ZnO [23]. For the case of ethanol-water volume ratio of 3:1, more ethanol molecules might promote the formation of $[\text{Zn}(\text{C}_2\text{H}_5\text{OH})_{4-n}(\text{OH})_n]^{2-n}$, which would transfer into $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rather than ZnO. Although the as-prepared product grown on the substrate coated with a ZnO buffer layer was also $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, the difference from the morphology of as-prepared product grown on the plain substrate was still observed. Because the lattice mismatch between the (001) face of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and the (001) face of ZnO is about 6% [23], the intervals between sheets in $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ plates formed on substrate coated with ZnO buffer layer might be narrower than plain substrate. This compact structure might experience sufficient Oswald ripening period, forming the complete architecture without the laminated structure (see Figure 1(b)).

3.4. Raman Spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. As mentioned above, for $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, one-quarter of the octahedrally coordinated zinc atoms are removed from the layer and positioned at the bottom and top of the empty octahedral, with tetrahedral coordination. Three vertices of such tetrahedral coordination are found to be occupied by hydroxide groups belonging to the octahedral sheet, while the fourth, pointed to the interlayer space, is occupied by a water molecule. NO_3^- groups are located between the layers and they are not directly coordinated with the zinc atoms [3, 5]. Therefore, Raman spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets displays a complex behavior with four modes, which can be assigned to the vibrational modes of Zn-H-O, Zn-O, H_2O -nitrate, and nitrate.

Figure 4(b) is typical Raman spectrum of the as-prepared $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets. There are ten peaks at 333, 401, 440, 532, 709, 730, 885, 1055, 1335, and 1359 cm^{-1} . The peaks at 709, 730, 1055, 1335, and 1359 cm^{-1} can be assigned to the vibration of nitrate ion [24–26]. The peak at 885 cm^{-1} is ascribed to Zn-O-H bond [27]. The peaks at 333, 401, and 440 cm^{-1} are attributed to the

stretching of Zn-O modes [28, 29]. The peak at 532 cm^{-1} may be related to the OH-O units formed as a result of the interaction between water and the NO_3^- . The situation is similar to the case of hydrotalcite structure [30].

3.5. Fabricating Porous ZnO Rectangle Sheets. The unusual precursor and its decomposition process induce ZnO with different morphologies. Figure 5(a) is XRD patterns of as-prepared products after thermal treatment of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets. All diffraction peaks are indexed as hexagonal ZnO, which reveals that $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets had been completely transformed into ZnO through decomposition process. Figure 5(b) is the corresponding FE-SEM image, which presents that porous ZnO micro-sized rectangle sheets can be obtained by thermal treatment of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets. Porously ZnO micro-sized rectangle sheet consists of a large number of small particles with the average diameter of 40 nm (see inset of Figure 5(b)). Obviously, the dehydration of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheet at high temperature generated small pores. Figure 5(c) is room temperature Raman spectrum of porous ZnO rectangle sheets, which shows typically vibrating properties of ZnO [31, 32]. Figure 5(d) is representative PL spectra of as-prepared $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized rectangle sheets, in which no obvious peaks related to ZnO can be found, which suggests the $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ sample is phase pure. Figure 5(e) is PL spectrum of porously ZnO micro-sized rectangle sheets. There are five obvious emission peaks locating at the wavelength of ~380, ~456, ~550, ~600, and ~660 nm, which are attributed to the recombination between electrons in the conduction band and holes in the valence band, the transitions of excited electrons from the level of interstitial zinc to the valence band, the ionized oxygen vacancy, the interstitial oxygen, and defect complexes, respectively [33–35].

4. Conclusion

In summary, the influence of the choice of ethanol-water volume ratio, concentration of zinc salt, and ZnO buffer layer on the formation and morphology of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ grown from the hydrothermal route at 80°C was systematically discussed. $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ rectangle sheets and $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ upright-standing plates were obtained by limiting ethanol-water volume ratio. The concentration of zinc salt is crucial for getting pure phase $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The presence of ZnO buffer layer could lead to the that chemical composition of product grown on the substrate was totally different from the solution. The possible formation mechanism of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was also studied on the basis of understanding these factors. Raman spectrum of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ displays a complex behavior with four modes, which can be assigned to the vibrational modes of Zn-H-O, Zn-O, H_2O -nitrate, and nitrate. Porously ZnO rectangle sheets were obtained by thermal treatment of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ micro-sized

rectangle sheets, which could be expected to apply in photoelectrochemical fields including chemical sensors, photocatalysts, and solar cells.

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