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Shape and size-controlled fabrication of ZnO nanostructures using novel templates

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A simple wet chemical method was developed to control the size and shape of the Zinc oxide (ZnO) nanostructures in the presence of new, efficient, and low-cost templates like ameline, sorbitol, and polyethylene glycol (PEG, $M_w = 200$) at low temperature within a few minutes. Nanorods and nanoparticles have been achieved through applying these templates and tuning other growth parameters. The products were characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The effect of the growth parameters such as template, Zn^{2+} source/Template ratio, pH, reaction time, and temperature on the growth and morphology of ZnO nanostructures have been investigated in detail. The results revealed that template has an important effect on the morphology and size of the ZnO nanostructures. Also, reaction time is believed to be a key factor because it can change the quality of nano ZnO produced by this method. By tuning these parameters nanorods, nano particle/rod, nano porous structures have been achieved.

Keywords: ZnO; ameline; PEG; sorbitol; nanostructures

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1. Introduction

Zinc oxide (ZnO) is an important semiconductor material with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, which should ensure excitonic survival well above room temperature [1,2]. Because of the excellent chemical and thermal stability of ZnO semiconductor and its specific optoelectronic [3–5], a broad range of applications, ranging from microwave dielectric [6], light emitting diodes [7,8], optical switches [9,10], solar cells [11–13], human skin protection [14] to gas sensors [15] have been reported. ZnO nanocrystals with various shapes including one-dimensional (1D) (rod [13,16–24], tube [25,26], fibre [27], wire [18,24,27–31], and needle [16,21,28,29]); two-dimensional (2D) (sheet [30], hexagon [32,33], layer [34,35], and film [32,35,36]); and multi-dimensional (flower [16,17,19,25]), have been fabricated.

The synthesis of 1D ZnO nanostructures has attracted considerable interest because of their promising and fascinating applications in optics [37], optoelectronic [2], catalysis [27],

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chemical absorbers [32,38], thermoelectricity, and piezoelectricity [4,39]. ZnO nanostructures have been fabricated by chemical vapour deposition (CVD) [33,36,40], thermal evaporation [29,41], molecular beam epitaxy (MBE) [42,43], and a high-temperature vapour transport process [28] using high temperature and\or special equipments. But above methods require high temperature or accurate gas concentration, flow rate, or scarce raw materials or complex process, and so on. So it is important to develop a simple, low temperature and short time method for the synthesis of ZnO nanocrystals in large scales. Compared with above synthesis methods, the wet chemical approach is relatively popular since it is easy, low cost, and environmentally friendly.

During experiments, we discovered a simple, facile, and efficient approach to synthesising size and shape controlled ZnO nanocrystals through tuning the growth parameters such as the type of materials used as template, Zn^{2+} source/template ratio, reaction time, and temperature, and also pH. Various controlled morphologies of ZnO nanostructures were obtained at low temperature using $Zn(NO_3) \cdot 6H_2O$ in the presence of special new templates (sorbitol and ameline) for the first time which are environmentally friendly with low cost, making the process more economic for scaling up. Furthermore, this approach can be easily applied in various fields due to its large-scale and short time production.

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2. Experimental procedure

An appropriate amount of $Zn\ (NO_3) \cdot 6H_2O$ was dissolved in 500 mL distilled water in order to form 0.3 M solution (Solution A). Different quantities of template (PEG ($M_w = 200$), sorbitol and ameline) was added separately to an amount of $NH_3 \cdot H_2O$ and well blended by stirring for 5 min. The result solution was added drop wise to solution A at room temperature under constant stirring. The final mixture was heated to reach to the reaction temperature of 60, 70, and 80°C and kept for few minutes. Experiments were carried out in different molar ratios of Zn^{2+} source/template including 0.4, 0.9, and 2 while the pH value was adjusted in 10.5 during the reaction time. As the reaction completed the resulted white solid products were centrifuged, washed with distilled water and ethanol to remove the ions possibly remaining in the final products, and finally dried at 60°C. To study the effect of other growth parameters on morphology and size of the nanostructures, reaction time was tuned during the synthesis for desired size and morphology of nanostructures that can be used for different applications.

The as-prepared products were characterised and analyzed using scanning electron microscopy (SEM) (Philips, XL30), X-ray diffraction (XRD) (Philips, PW 1840, lump $3UK\alpha = 1.5\,\text{Å}$). The morphology and dimension of the products were observed by transmission electron microscopy (TEM, Philips 200 kV).

3. Results and discussion

3.1. *Effect of template*

Table 1 depicts the experimental conditions studied to achieve a controllable growth of ZnO nanostructures by finding the most effective parameters. Different morphologies of ZnO nanostructures were obtained through the influence of template. These templates were PEG200, sorbitol, and ameline examined in the similar experimental conditions.

Table 1. Experimental conditions and shape of the ZnO nanostructures fabricated by template assisted wet chemical process.

Set	Template	Zn^{2+}source/ template	Temperature (°C)	Reaction time(min)	PH	Morphology
1	PEG200, Ameline, Sorbitol	2	70	10	10.5	R[a] S-Rc S[b]
2	PEG200	0.4, 0.9, 2	70	10	10.5	R, R, R
3	PEG200	2	60, 70, 85	10	10.5	R-S, R, S
4	PEG200	2	70	10, 15	10.5	R, R-S
5	PEG200	2	70	10	9, 10.5, 12	R-S, R, S

[a]R: Rod- like.
[b]S: Spherical.
[c]R- S: Mixed structure of rods and spherical nanoparticles.

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It is also worth nothing that applying these new different materials specially sorbitol and ameline decreases the cost of product.

The surface morphology of ZnO nanostructures was evaluated by SEM and TEM. The results indicate that the variation of template can greatly alter the morphology of ZnO nanomaterials. Figure 1 shows the SEM and TEM images of the ZnO nanorods/nanoparticles by using different templates. From the images, it can be seen that by using PEG200 as a template, ZnO nanorods with diameter of 64 nm and 280 nm lengths were obtained (Figure 1(a)). In our experiments, the formation of ZnO nanostructures may be due to the creation of nuclei by the addition of template firstly. This is evidenced by the fact that no white precipitate in the reactive system appeared without the addition of template. In the case of PEG200, it first was absorbed on the surface of ZnO nuclei and the growth kinetic of the growing ZnO cell is modified. In other words, PEG200 played a crucial role in the formation of nuclei and in directing the growth of the crystals [16]. The further characterisation of the sample is performed by TEM. From the TEM image (Figure 1(a)), the ZnO nanorods with diameter of 42 nm and length of 283 nm are seen (Figure 1(b)). This result is in agreement with the studies performed by Hou et al. [16] but they constructed 1D nano needles using PEG400 as a template. However, the result of this work was much more successful in comparison to the result of Zhang et al. [17] which had the advantage of PEG200 as template in order to produce micro rod-like materials. In this work the obtained rod-like nano materials are significantly thinner than those produced in micro meter scale diameter.

When sorbitol was used as a template, a different morphology was obtained according to Figure 1(c). By using ameline as a template, both ZnO nanorods and nanoparticles grow as shown in Figure 1(d). Ameline is applied as a new, low cost and environmentally friendly template which successfully produced nano ZnO materials for the first time in this work. So, this crucial parameter will be the subject of a more detailed analysis in future publications.

The XRD patterns of the products are as shown in Figure 2. As shown in the figure, all the diffraction peaks in the pattern could be indexed to the wurtzite structure of ZnO (JCPDS 36-1451, $a = 3.24982$ Å and $C = 5.20661$ Å).

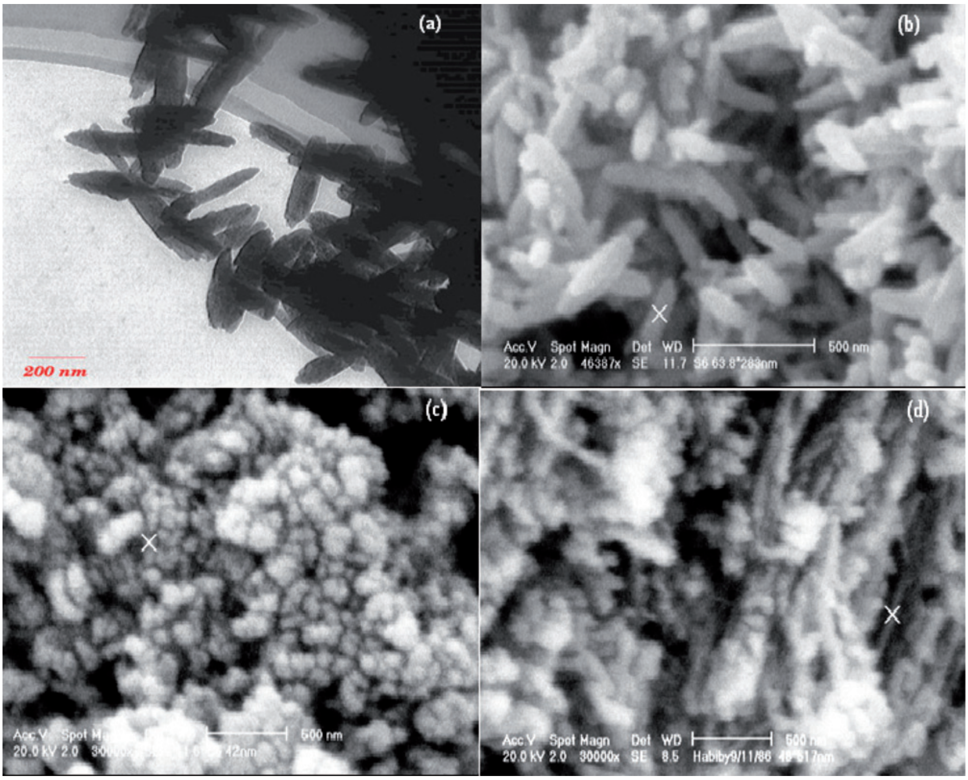

Figure 1. The SEM and TEM images of samples synthesised using (a) (TEM), (b) (SEM) PEG200, (c) (SEM) Sorbitol, and (d) (SEM) Ameline as template. (Zn^{2+} source/template ratio = 2, $T = 70°C$, Reaction time = 10 min, pH = 10.5).

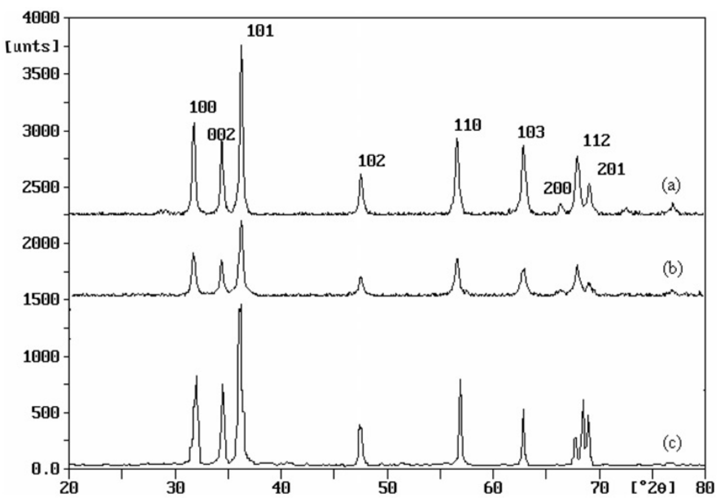

Figure 2. X-Ray diffraction patterns of the samples synthesised using (a) PEG200, (b) Sorbitol, and (c) Ameline as a template (Zn^{2+} source/template ratio = 2, $T = 70°C$, reaction time = 10 min, pH = 10.5).

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3.2. *Effect of Zn^{2+} source/template ratio*

In order to investigate controllable growth of nano ZnO, different Zn^{2+} source/template ratios were used, employing PEG200 as a template. The ratios were 0.4, 0.9, and 2, respectively. The SEM results showed that the nanorod morphology has grown uniformly through tuning the ratio (Figure 3). Furthermore, the images reveal that when the Zn^{2+} source/template ratio increased from 0.4 to 2 the rods gradually became larger and their length has enlarged from 175 to 283 nm. Also the diameter increased from 42 to 64 nm; therefore the ratio of Zn^{2+} source/template is the main parameter to control individually the size of nanorods. This parameter has been investigated by Hou et al. [16] by using PEG400 and resulted in a different outcome. The morphology of nano materials altered from rod-like to flower-like and had no effect on the size of rods as the ratio increased. This difference may be due to the effect of template type applied to study ratio parameter. The crucial effect of template type on the synthesis of nano products has been discussed in the other part previously. In addition, Zhang et al. [17] obtained a change in morphology of materials as a result of different ratios. This is also because of a dissimilar type of template, pH and of the method of synthesis that they applied to study this parameter.

3.3. *Effect of reaction parameters*

3.3.1. *Effect of temperature*

The SEM images of products, studying the effect of temperature, are shown in Figure 4(a). According to this figure, the morphology of the products alters significantly with

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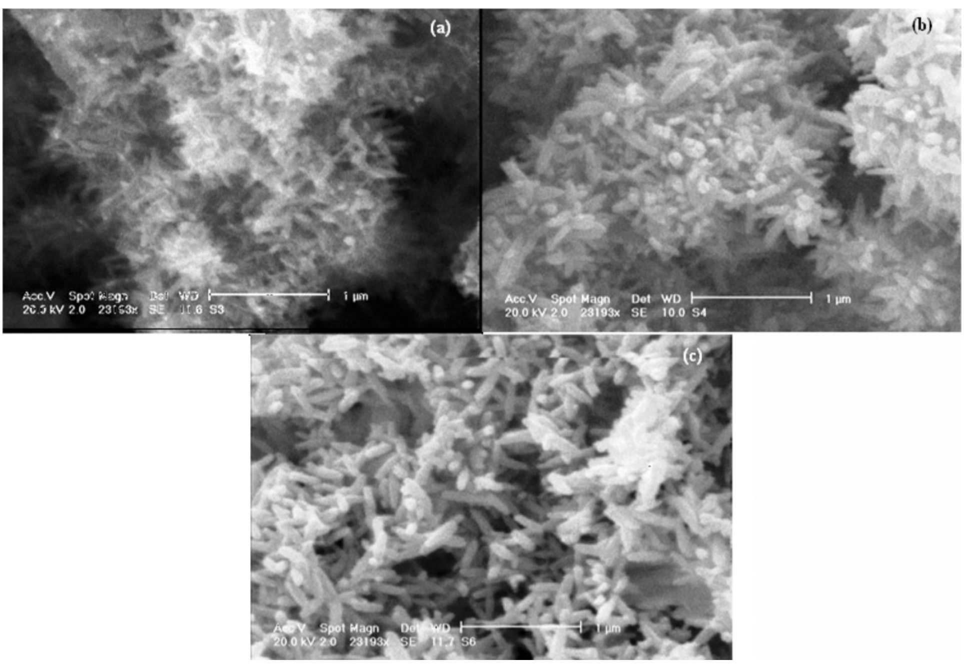

Figure 3. The SEM images of samples synthesised at Zn^{2+} source/template ratio of (a) 0.4, (b) 0.9, and (c) 2 (Template = PEG200, $T = 70°C$, pH = 10.5, Reaction time = 10 min).

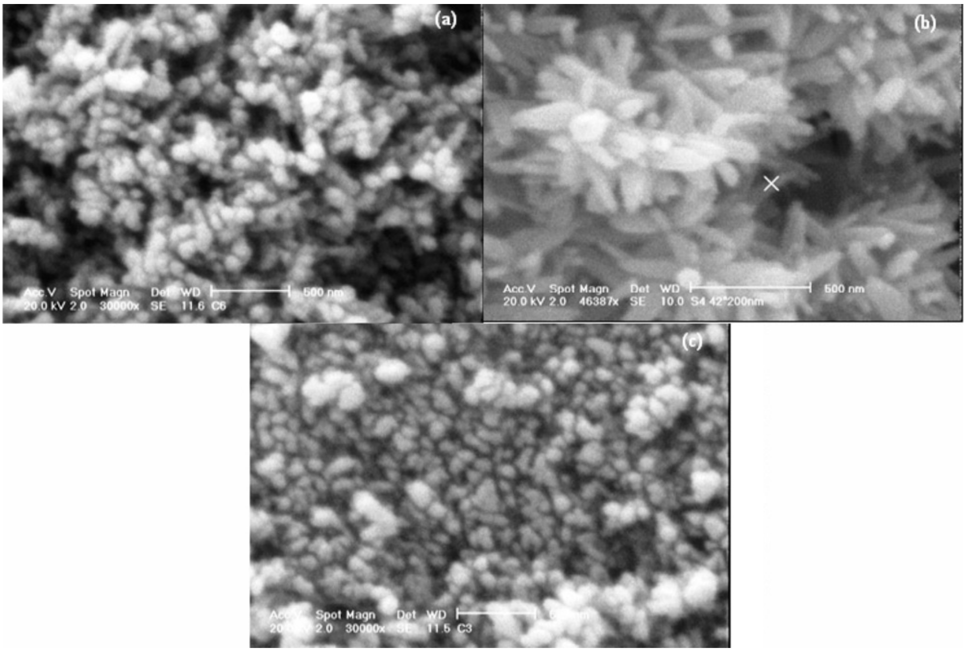

Figure 4. The SEM images of samples synthesised at reaction temperature of (a) 60°C, (b) 70°C, and (c) 85°C. (Template = PEG200, Zn^{2+} source/template ratio = 2, Reaction time = 10 min, pH = 10.5).

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increasing synthesis temperature. At 60°C, a mixed morphology of ZnO nanorod/nanoparticle has formed. When the reaction temperature increased, the rods became thicker and shorter; in contrast, when the reaction was performed at a higher temperature (85°C), the morphology inclined to nanoporous structure. In order to verify the temperature effect on morphology, the possible reactions in an aqueous solution [44] can be expressed as follows:

$$\begin{aligned}
&NH_3 + H_2O \leftrightarrow NH_3 \cdot H_2O \leftrightarrow NH^{4+} + HO^-\\
&Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+}\\
&Zn(NH_3)_4^{+2} + 2OH^- \leftrightarrow ZnO + 4NH_3 + H_2O\\
&Zn^{2+} + 4OH^- \leftrightarrow Zn(OH)_4^{2-}\\
&Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^-.
\end{aligned}$$

It can be seen that ZnO nuclei are obtained by the dehydration of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$. In the presence of PEG200, units of $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ are easily adsorbed by the atom O in the C–O–C chain, so that $Zn(OH)_4^{2-}$ or $Zn(NH_3)_4^{2+}$ can be transformed into ZnO crystalline particles and grown on active sites around the surface of ZnO nuclei. When the reaction temperature is low (60°C), the production rate of NH_3 is slow and more Zn^{2+} are transformed into ZnO nuclei in the function of hydroxyl. Thus more ZnO nuclei with active sites aggregate spontaneously, which provides both rod-like and particle nanostructures. When the synthesis temperature rises to 70°C, Zn^{2+} with NH_3

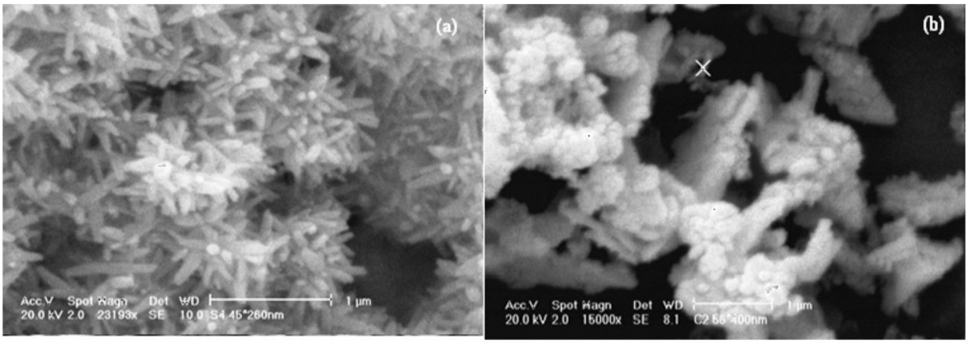

Figure 5. The SEM images of samples synthesised at reaction time of (a) 10 min and (b) 15 min. (Template = PEG200, Zn^{2+} source/template ratio = 2, $T = 70°C$, pH = 10.5).

producing more $Zn(NH_3)_4^{2+}$ in the reaction system, this decreases the rate of the formation of ZnO nuclei in comparison to when temperature is 60°C. Slow formation of ZnO nuclei reduces the chance for the formation of both particle and nanorods. When the rate of growth matches the rate of formation of ZnO nuclei, single nanorod structures are fabricated at 70°C. Hence, when it reaches 85°C, the morphology of products varies from rod-like to nanoporous structure.

On the basis of the experimental results mentioned above, it is noticeable that the reaction temperature has a major impact on the performance of ZnO nano particle production. In the range of 60–85°C the morphology changes from nano particle to single nano rods and finally to porous materials. The observed behavior is in direct agreement with results reported by Grabowska [29] when using silicon substrate [20] and in contrast with results stated by Wei [18], where longer rods were observed at higher temperature which may be the result of difference in type of template, pH, method of synthesis and all methods of preparation and drying of the product.

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3.3.2. *Effect of reaction time*

The effect of time was studied from 10 to 15 min and results are shown in Figure 5. As seen in the figure, when the reaction was performed in extended times of 15 min, unexpectedly an alternation of morphology happened and the rod-like nanomaterials disappeared. This undesirable result indicates that for achieving nanomaterial structures, a short reaction time in the wet chemical method is demanded. Also, adjusting the reaction time can be the key parameter to achieve a special morphology of nanomaterials. The effect of reaction time has been investigated by the other scientists too and they found a noticeable influence of this parameter on the morphology, depending on the condition of experiments [14,17,25,35]. One of the novel characteristics of this work is gaining ZnO nanomaterials in shorter time.

3.4. *The effect of pH value*

In order to investigate how impressive the morphology of products can be influenced by pH value, a series of experiments performed in the temperature of 70°C for 10 min in

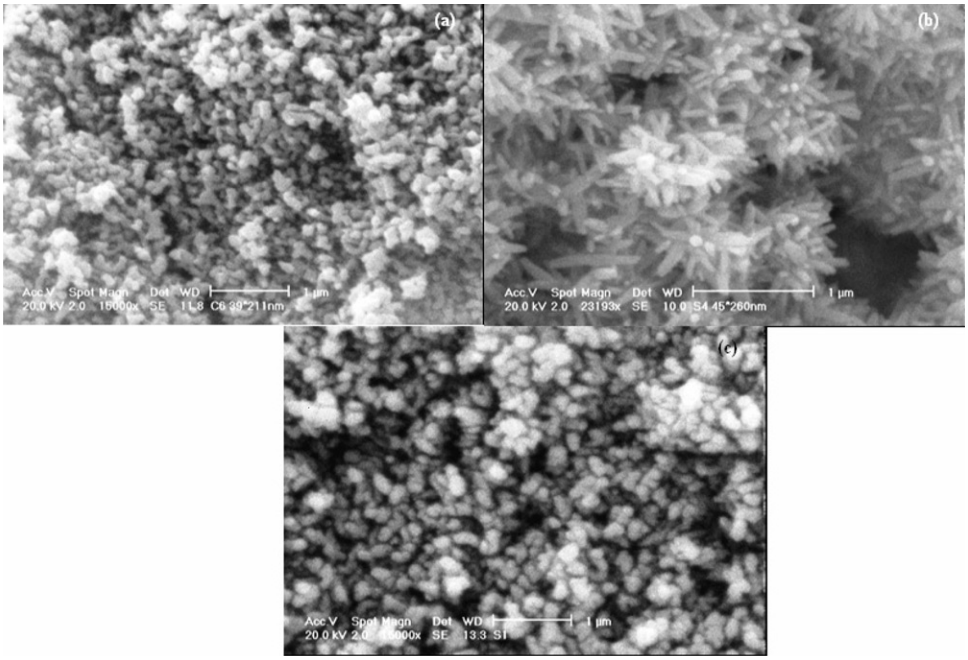

Figure 6. The SEM images of samples synthesised at pH values of (a) 9, (b) 10.5, and (c) 12. (Template = PEG200, Zn^{2+} source/template ratio = 2, $T = 70°C$, Reaction time = 10 min).

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condition that the Zn^{2+} source/template ratio was 2. The pH values were changed from 9 to 12. The results are shown in Figure 6.

Compared with sample (b) (rod-like, pH = 10.5), the growth of rods was not complete enough in sample (a) (pH = 9). As a result nanostructural morphology has exhibited in sample (a) under pH value of 9.

The reasonable mechanism of formation of ZnO under different pH is given [44].

When concentration of ammonia in system is low (pH = 9), more $Zn(NH_3)_4^{2+}$ are easily transformed to ZnO in the function of weak OH^-. Thus abundant ZnO nuclei are formed in initial stages, which conduct the morphology to nanostructural product. When the concentration of ammonia is higher (pH = 10.5), the quantity of OH^- is larger in comparison with the one under pH = 9, which is advantageous for $Zn(NH_3)_4^{2+}$ to form ZnO nuclei. So, more nanorods can be seen in sample (a).

However, in higher pH value of 12 the morphology disobeyed from this mechanism and changed to spherical nanoparticles. Hence tuning the pH value, a variety of morphologies can be achieved. Recently, micro ZnO materials have been achieved by other scientific groups which shows the crucial influence of this parameter on the morphology of the products too [11,45].

4. Conclusion

Highly crystallised, size and shape controlled morphologies of ZnO nanostructures like nanorods and nanoporouses were successfully synthesised under the assistance of ameline, sorbitol, and PEG200 as the template. This process offers even convenient and economical advantages of being environmental friendly by using special, new templates while scaling up is easy and not time consuming. The experimental results indicate that the morphology of ZnO nanostructures was effectively influenced by the type of template. Furthermore, applying these new materials specially sorbitol and ameline for the first time which are new, low-cost chemicals is one of the outstanding originalities put in this work to achieve size and shape-controlled nano ZnO structures which were more economic.

In addition, other growth parameters exhibited a capability to change considerably the morphology of products as we expected. The size of nanorods in the product was found to be significantly influenced by the Zn^{2+} source/template ratio. Nanorods of smaller diameter can be formed at lower ratios. Large rods were obtained at higher ratios. Moreover, reaction time is believed to be a key factor because it can greatly change the quality of nano ZnO. By adjusting those parameters nanorods, nano particle/rod, nano porous structures have been achieved.

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