Growth of well-defined ZnO microparticles with additives from aqueous solution

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Abstract

By heating $Zn(OH)_2$ precursor in aqueous solution to reflux temperature (101 °C), ZnO microparticles with a diversity of well-defined morphologies, including rod-like, nut-like, and rice-like samples, have been successfully synthesized. The shape of the crystallite depends critically on the additive added in the reaction solution. To further understand the effect of the additive on the formation process of ZnO crystallite, scanning electron microscopy analyses of the solid product and concentration measurements of zinc ion remaining in the solution have been made at regular intervals throughout the reaction with and without the addition of sodium dodecyl sulfate (SDS) and triethanolamine (TEA). Results show that SDS and TEA added in the solution remarkably lower the formation rate of ZnO crystallite.

1. Introduction

Controlling the size and morphology is a matter of considerable importance for the manufacture of microcrystalline powders, as for many applications both the size and shape of the particles determine the usefulness of the product [1]. Zinc oxide is a very interesting multifunctional material, which is extensively used in medicine, pigments, ceramics, rubber additives, varistors, and optical devices [2–6]. In addition, due to its wide direct-band gap of 3.37 eV and high exciton binding energy of 60 meV, ZnO has potential uses as light-emitting diodes, field-effect transistors, and ultraviolet nanolasers [7–9]. Recently, room-temperature UV property of ZnO has been reported [10–12], highlighting the prospects of corresponding research interests in the fabrication of ZnO-based candidate materials, whose effectiveness depends to a great extent on the size and shape of the constituent particles, which are normally in the micron range.

Various chemical and physical processes, such as conventional sputter deposition technique [13], spray pyrolysis [14], sol–gel reaction [15], and microemulsions growth [11] can be used to synthesize ZnO particles. Over the past few years, chemical vapor deposition [16,17], thermal evaporation [12,18], and hydrothermal process [19–22] have been the three major methods to prepare nano- or microscaled ZnO particles in various sizes and morphologies. In addition to these methods, a simple solution route, by thermal treatment of the reactant in solutions [1,23–25], has become a promising option for large-scale production of ZnO microcrystals owing to its simple, fast, and less expensive virtues.

In this paper, we describe a simple aqueous solution route to synthesize ZnO microcrystals with well-defined morphologies. The method studied here uses aqueous solutions with high concentrations of zinc nitrate and sodium hydroxide, so that large quantities of the oxide

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can readily be produced in high yield directly from the solutions, while dispensing with further calcination. Moreover, ZnO microparticles with new morphologies such as nut-like, especially rice-like, have been obtained with the assistance of sodium dodecyl sulfate (SDS) and triethanolamine (TEA). However, systematic studies on the morphological modulation of ZnO with additive in aqueous solution are still inadequate. Therefore, it seems necessary to study the relationship between additive and ZnO morphologies for exploring an effective and simple route to control the morphology of ZnO for practical applications.

2. Experimental

Hexahydrate zinc nitrate $(Zn(NO_3)_2 \cdot 6H_2O)$, sodium hydroxide (NaOH), SDS, TEA purchased from Tianjin Chemical Reagent Company, are analytical-grade reagents (the purity is 99%), and are used as received without further purification. The solvent used for the reaction system is distilled water.

The zinc oxide particles were prepared as follows: sodium hydroxide (2 M, 48 mL) was dropped with stirring into aqueous zinc nitrate (1 M, 20 mL) in a 250 mL beaker. Then certain volume of distilled water was added into the mixture to get a 100 mL milky solution (pH~9), which was subsequently transferred to a 250 mL round-bottomed flask. When the additive was employed in the reaction, SDS (0.1 M, 10 mL) or TEA (1 M, 10 mL) was dropped into the milky solution prior to the transferring. After a while, the above reaction mixture was heated with stirring to reflux temperature (101 °C, after ca. 50–55 min) and holding the temperature constant for a given time period. The hot solution was cooled to room temperature and then filtered. White powders were collected and dried in air to constant weight.

The growth patterns of ZnO crystal were studied by removing samples at regular intervals using a pipette and then centrifugalizing through a centrifugal filter. The filtrate taken from the reaction at various stages was buffered at pH 10 using an ammonia–ammonium chloride buffer solution and the concentration of Zn^{2+} ion was measured by using the EDTA chelate titration method. The morphologies of the solid sampled at corresponding time were observed by scanning electron microscopy (SEM, Hitachi S-570). The crystal structure of the final product was also characterized by X-ray powder diffraction (XRD, Bruker-AXS D8 ADVANCE X-ray diffractometer) with a CuKα radiation ($\lambda = 0.154178$ nm).

3. Results and discussion

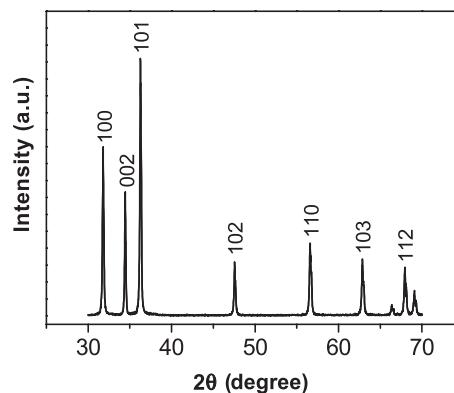All obtained ZnO samples are of wurtzite structure (hexagonal phase, space group $P6_3mc$). Fig. 1 shows the

Fig. 1. XRD patterns of the obtained ZnO microparticles.

XRD pattern of rod-like ZnO powders obtained by heating aqueous solutions containing $Zn(OH)_2$ precursor for 4 h. All the diffraction peaks are well assigned to hexagonal-phase ZnO reported in JCPDS card (No. 36-1451). No characteristic peaks of impurities, such as $Zn(NO_3)_2$, $Zn(OH)_2$, and other compounds are observed, indicating the high purity of the obtained products.

The general morphologies of the obtained ZnO crystals are characterized by SEM shown in Fig. 2. Heating $Zn(OH)_2$ precursor in H_2O solvent at 101 °C for 4 h gives rod-like ZnO crystals, with diameters ranging from 400 to 500 nm and average length of about 3.6 μm (aspect ratio ~8:1) as shown in Fig. 2a. When 0.01 M of SDS is added into the reaction solution (keep the other conditions identical), nut-like ZnO crystals with twin structure are obtained as shown in Fig. 2b. The diameter of the hexagonal cross-section ranges from 1.2 to 1.5 μm, and aspect ratio is a little smaller than 1:1. As shown in Fig. 2c, a new morphology, well-defined rice-like of ZnO, appears attributed to replacing 0.1 M of TEA by 0.01 M of SDS in the reaction solution. The diameters of the particles are similar to those nut-like, while the aspect ratio is slightly larger than 1:1.

It can be concluded from the SEM images shown in Fig. 2 that the additives of SDS and TEA produce a significant effect on the morphology of the obtained ZnO crystals. It has long been known that trace concentrations of certain additives can have profound effects on crystal growth rate and habit. But up to now, there has not yet been an adequate mechanism to account for the behavior. With regard to the effect of the additive on morphology, the adsorption mechanism seems to be more reasonable. In the early 1960s, Michaels et al. [26] reported the modification of growth rate and habit of adipic acid crystal with surfactants from solution. In our reaction system, it is suggested that SDS or TEA adsorbs to some extent on a crystal
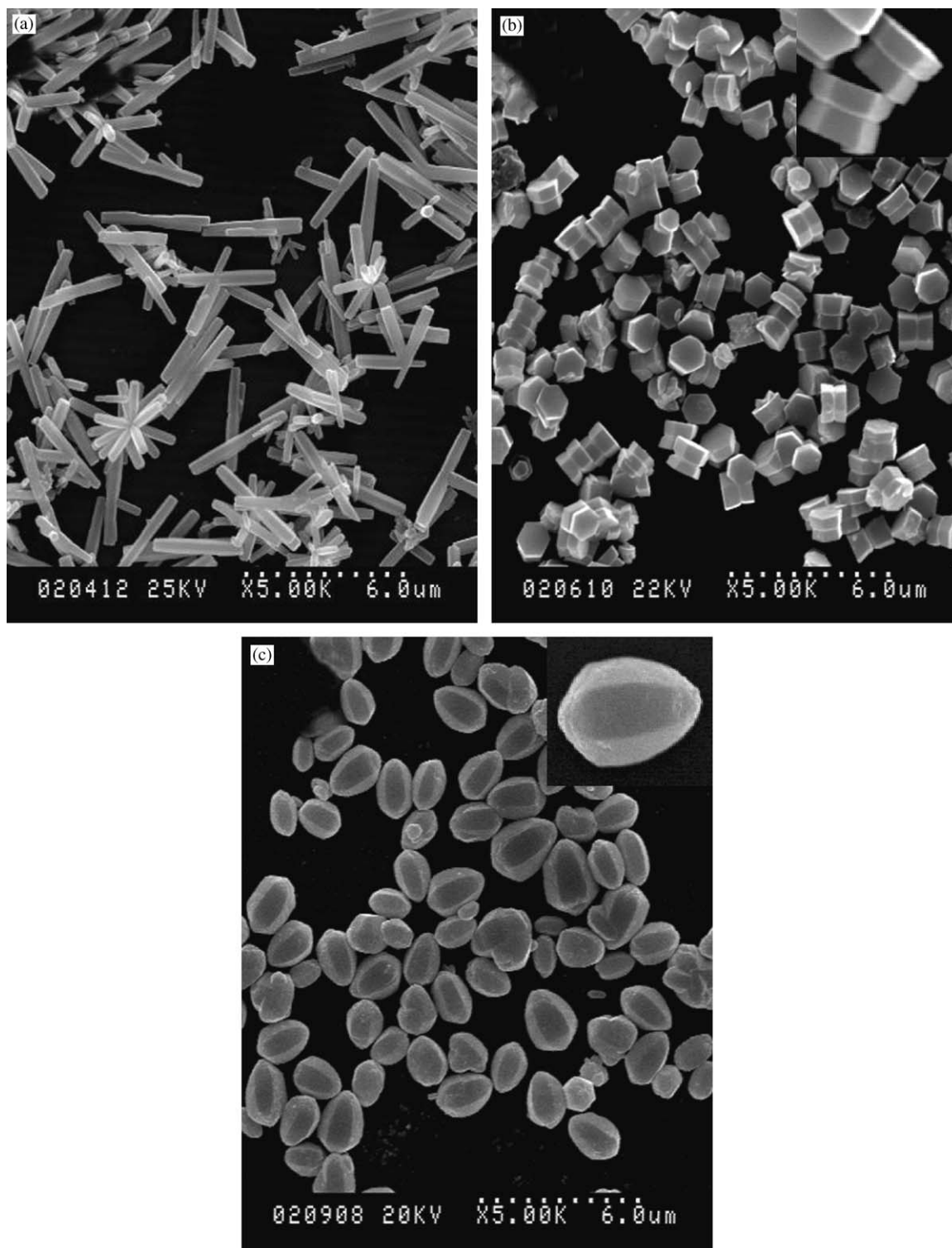
Fig. 2. SEM images of ZnO microparticles prepared with different additives: (a) no additive; (b) with 0.01 M SDS; and (c) with 0.1 M TEA.

surface of ZnO and thus inhibits the growth along the c-axis. ZnO crystal is a polar crystal whose positive polar plane (0001) is rich in Zn and negative polar plane (000$\bar{1}$) is rich in O. In the solution process, the growth rate of each plane is different as following:

$$V(0001) > V(\bar{1}01\bar{1}) > V(\bar{1}010) > V(\bar{1}011) > V(000\bar{1}) \quad [23].$$

It is well known that SDS is a typical anionic surfactant; however, it is scarcely known that SDS is also characterized by a gemini surfactant, which can be described as two individual surfactant molecules
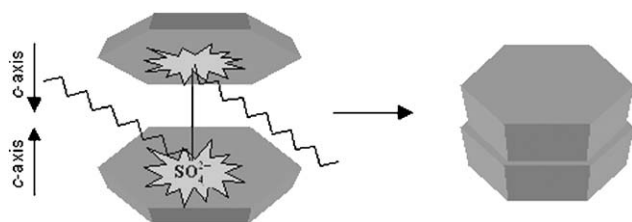
Fig. 3. The mode of SDS modifying the habit of ZnO crystal.

connected by a bridge, according to the recent report on surfactants [27]. Consequently, the structure of the geminal SDS consists of two active anionic radicals (SO_4^{2-}), joined at opposite ends of the structure, due to the spatial symmetry. Each of the geminal SDS can simultaneously adsorb two ZnO nuclei on the (0 0 0 1) face due to the Coulomb force action, thus, sticking the two (0 0 0 1) faces together by acting as an adhesive. As a result, the growth along the c-axis is greatly retarded and growth can only occur on the (0 0 0 $\bar{1}$) face with the slowest growth rate and the side faces, and nut-like ZnO with twin-structure is formed. The mode of SDS modifying the habit of ZnO is shown in Fig. 3. Moreover, it is suggested that another factor, defective growth, may also contribute to the formation of twinned ZnO crystals. As to TEA, the adsorption mechanism is probably more complicated. According to the resulting rice-like shape, the growth along the c-axis is also retarded; however, some additional facets appear other than the regular hexagonal one, indicating that the adsorption that occurs on a certain face of ZnO nuclei is not as uniform as SDS is. Thus, it is still an open question to answer.

To further understand the effect of SDS and TEA on the formation process of ZnO, experiments with and without the additive were carried out at the same conditions. At the same time, morphologies of solid samples, concentrations of zinc remaining in the solution were determined, respectively, at various growth stages. A detailed discussion is as follows:

3.1. Without additive

Fig. 4 shows the SEM images of solid samples at different growth stages without the additive. It was observed that during the initial 35 min of heating time, only plate-like structures were present (Fig. 4a). It must be stated that the plate-like structures are not genuine $Zn(OH)_2$ because several characteristic peaks of ZnO are identifiable in the XRD patterns. After 40 min heating (ca 97 °C), a part of rod-like ZnO, with mean diameter of 260 nm and average length of 2.3 μm appeared, among the plate-like structures, which decreased in size (Fig. 4b). When heating time was prolonged to 50 min (reflux temperature, 101 °C), the rod-like ZnO increased in size,

while the plate-like structures became even smaller (Fig. 4c). When heating time was extended up to 80 min, plate-like structures disappeared, and the solid was composed solely of rod-like ZnO, with little change in morphology and size (Fig. 2a), compared to that with heating time of 50 min. We can therefore suggest that such a rapid transformation may take place by dissolution–reprecipitation mechanism.

After the solid sample had been removed from the reaction mixture, the filtrate was analyzed by EDTA titration (Fig. 5a). On examining the curve, it is evident that concentration of Zn^{2+} in the solution increases rapidly $(7.8 \times 10^{-5}$–0.028 M) during the first 50 min heating, and after 80 min heating, the concentration of Zn^{2+} in the solution levels off at approximately 0.036 M. This result correlates well with the observed changes in SEM images, as it appears that while the dissolution of the initial precipitate (plate-like structures) takes place, the concentration of Zn^{2+} increases rapidly. When the reaction creates an equilibrium of dissolution–precipitation of ZnO, the change in $[Zn^{2+}]$ is almost zero. This also identifies the dissolution–reprecipitation mechanism.

3.2. With additive

When 0.01 M SDS or 0.1 M TEA is present in the reaction mixture, the changes in particle size at different stages are similar to those without the additive, except for the time when the solid is composed solely of ZnO (see ESI). It is 200 min for SDS, and 110 min for TEA. Both are more than for that without the additive (80 min). This also correlates with the curves of concentration of Zn^{2+} in solution-dependent time (Fig. 5). In particular in Fig. 5b, the time needed for reaching the equilibrium of dissolution–precipitation is substantially prolonged. Moreover, the curve with TEA (Fig. 5c) is very different from others, in that Zn^{2+} ions in solution have been kept in existence at a considerably low concentration $(10^{-4}$–10^{-5} M) throughout the reaction, which may be attributed to the strong complexion of TEA with Zn^{2+} ions. Perhaps it is another important factor leading to the rice-like samples. In general, the formation of ZnO is to some extent retarded by the addition of SDS and TEA. This presumably results from the greatly retarded growth of (0 0 0 1) face of ZnO, which originally has the fastest growth rate vide supra.

4. Conclusions

ZnO microcrystals with a diversity of well-defined morphologies, such as rod-like, nut-like, and rice-like samples, have been successfully synthesized by a simple solution approach. The formation process of ZnO was studied by SEM analyses and concentration measure-
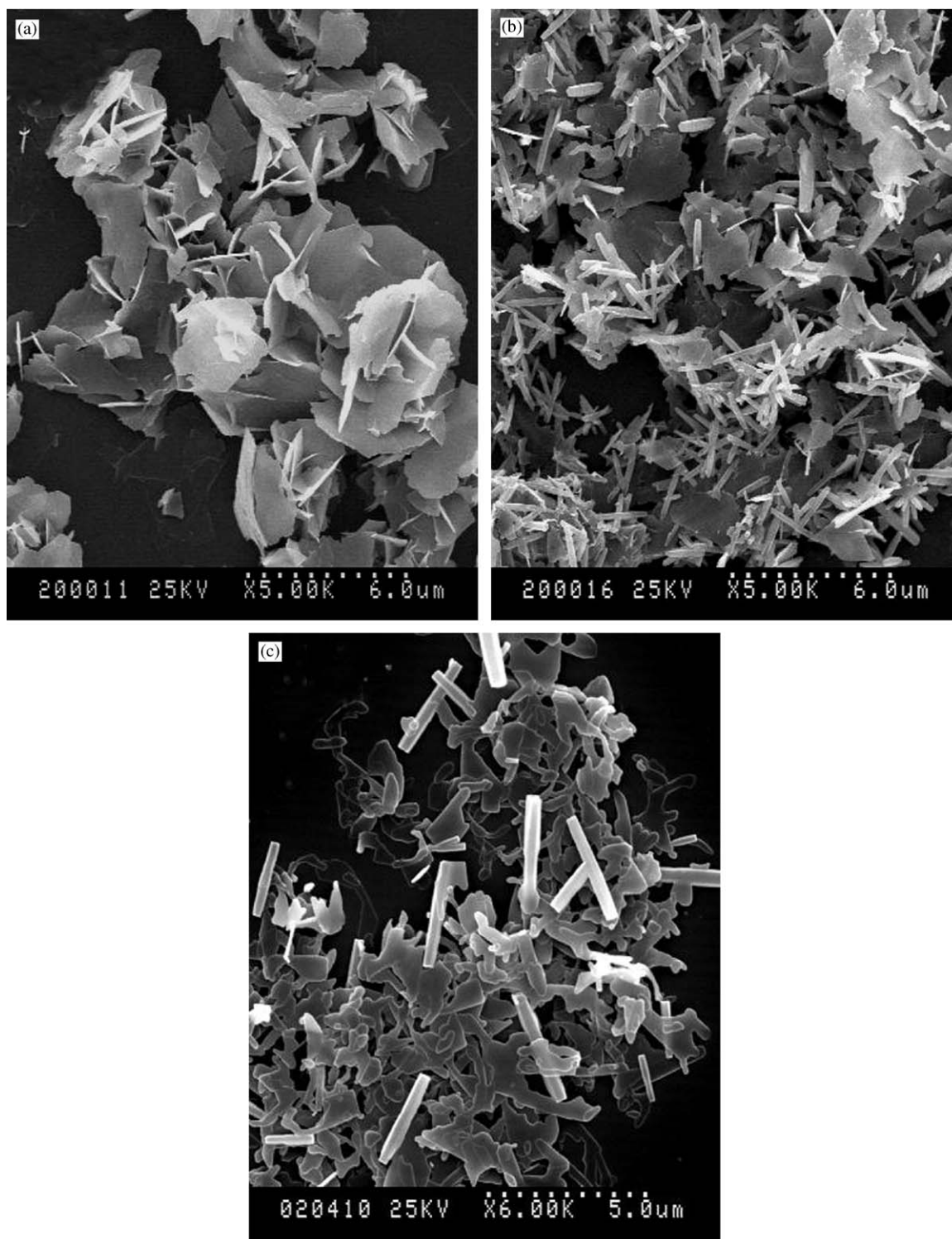
Fig. 4. Growth of rod-like ZnO crystals prepared without additive by heating for (a) 0–35 min; (b) 40 min; and (c) 50 min.

ments of Zn^{2+} in solution throughout the reaction. Based on the experimental results, we suggest that the transformation may take place by a dissolution–reprecipitation mechanism. The effects of additives on the formation were also investigated. It is found that the additives of SDS and TEA remarkably affect not only the particle shape but also the formation rate of ZnO.
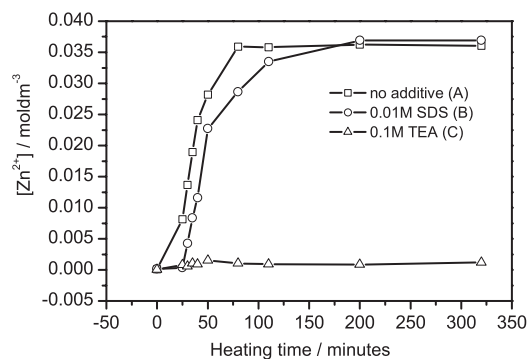
Fig. 5. $[Zn^{2+}]$ in solution at various times during the reaction.

References

[1] R.A. McBride, J.M. Kelly, D.E. McCormack, J. Mater. Chem. 13 (2003) 1196.

[2] W.-L. Lee, R.-L. Yong, Appl. Phys. Lett. 69 (1996) 526.

[3] K.G. Hendrikse, W.J. Mcgill, J. Reedijk, P.J. Nieuwenhuizen, J. Appl. Polym. Sci. 78 (2000) 2290.

[4] K.G. Hendrikse, W.J. Mcgill, J. Appl. Polym. Sci. 78 (2000) 2302.

[5] D.E. McCormack, P. O'Brien, R. Ramesh, J. Mater. Chem. 13 (2003) 2586.

[6] J. Zhang, L.D. Sun, J.L. Yin, H.L. Su, C.S. Liao, C.H. Yan, Chem. Mater. 14 (2002) 4172.

[7] B.J. Jin, S.H. Bae, S.Y. Lee, S. Im, Mater. Sci. Eng. B 71 (2000) 301.

[8] S.-W. Chung, J.-Y. Yu, J.R. Heath, Appl. Phys. Lett. 76 (2000) 2068.

[9] Y. Wu, H. Yan, M. Huang, B. Messer, J.H. Song, P. Yang, Chem. Eur. J. 8 (2002) 1260.

[10] M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Webber, R. Russo, P. Yang, Science 292 (2001) 1897.

[11] L. Guo, Y.L. Ji, H.B. Xu, P. Simon, Z.Y. Wu, J. Am. Chem. Soc. 124 (2002) 14864.

[12] Y.G. Wang, C. Yuen, S.P. Lau, S.F. Yu, B.K. Tay, Chem. Phys. Lett. 377 (2003) 329.

[13] W.-T. Chiou, W.-Y. Wu, J.-M. Ting, Diamond Relat. Mater. 12 (2003) 1841.

[14] O. Milosevic, D. Uskokovic, Mater. Sci. Eng. A 168 (1993) 249.

[15] C.-H. Hung, W.-T. Whang, Mater. Chem. Phys. 82 (2003) 705.

[16] S.C. Lyu, Y. Zhang, H. Ruh, H.-J. Lee, H.-W. Shim, E.-K. Suh, C.J. Lee, Chem. Phys. Lett. 363 (2002) 134.

[17] J.-J. Wu, S.-C. Liu, J. Phys. Chem. B 106 (2002) 9546.

[18] J.Q. Hu, X.L. Ma, Z.Y. Xie, N.B. Wong, C.S. Lee, S.T. Lee, Chem. Phys. Lett. 344 (2001) 97.

[19] Q. Tang, W.J. Zhou, J.M. Shen, W. Zhang, L.F. Kong, Y.T. Qian, Chem. Commun. 6 (2004) 712.

[20] B. Liu, H.C. Zeng, J. Am. Chem. Soc. 125 (2003) 4430.

[21] J.M. Wang, L. Gao, J. Crystal Growth 262 (2004) 290.

[22] H. Zhang, D.R. Yang, Y.J. Ji, X.Y. Ma, J. Xu, D.L. Que, J. Phys. Chem. B 108 (2004) 3955.

[23] N. Uekawa, R. Yamashita, Y.J. Wu, K. Kakegawa, Phys. Chem. Chem. Phys. 6 (2004) 442.

[24] Z. Wang, X.F. Qian, J. Yin, Z.K. Zhu, Langmuir 20 (2004) 3441.

[25] Z. Wang, X.F. Qian, J. Yin, Z.K. Zhu, J. Solid State Chem. 177 (2004) 2148.

[26] A.S. Michaels, F.W. Tausch, J. Phys. Chem. 65 (1961) 1730.

[27] J.X. Xiao, Z.G. Zhao, Application Principle of Surfactant, first ed, Chemical Industry Press, Beijing, 2003.