

六角形氧化锌超晶格粒子的控制制备

王晓娟 张宪玺 马长勤* 张建华 朱庆增 姜建壮*
(山东大学化学系, 济南 250100)

本文通过蒸发微乳液体系中的溶剂得到了六角形的氧化锌亚微米粒子, 其具有超晶格结构。所得产物用红外(FT-IR)和透射电镜(TEM)进行了表征, 并进行了热重分析(TGA)。通过监测反应过程, 研究了该粒子的形成机制。实验观察到约 7nm 的纳米氧化锌粒子聚集成亚微米的球形超晶格粒子, 该球形粒子随溶剂蒸发进行了自组装, 并由于界面相互作用转换成六角形的超晶格粒子。

关键词: 氧化锌 控制制备 超晶格 形成机制
分类号: 614.24*1

The Controlled Preparation of ZnO Superlattice Particles with Hexagonal Shape

WANG Xiao-Juan ZHANG Xian-Xi MA Chang-Qin*
ZHANG Jian-Hua ZHU Qing-Zeng JIANG Jian-Zhuang*
(Department of Chemistry, Shandong University, Jinan 250100)

The submicron ZnO superlattice particles with hexagonal morphology were prepared through vaporizing solvents in microemulsion. The products were analyzed using FT-IR, TEM and TGA techniques. The formation mechanism is investigated by monitoring the reaction process using TEM techniques. In our experiment, initially, the submicron superlattice particles with spherical shape are created through nanoparticles about 7nm aggregating via hydrogen bonds instead of through the direct growth process of small particles. With vaporizing solvent, these spherical particles self-assemble due to hydrophobic interaction between surfactant molecules. Meanwhile, because the surfactant on the surface of superlattice particles strengthens the interfacial interaction, the spherical particles evolve into the hexagonal ones.

Keywords: ZnO controlled preparation superlattice formation mechanism

0 Introduction

As we know, if semiconductor material is sufficiently small, the bulk energy level scheme is not valid to be used to explain the conducting properties of corresponding semiconductor material. The bulk energy

level scheme of certain material does not only depend upon the size but also on the shape of the crystallite as well as the nature of the material^[1]. Therefore, there are many great changes in physical and chemical properties for such small crystallite less than 100nm

收稿日期: 2002-08-16。收修改稿日期: 2002-11-04。

国家自然科学基金资助项目(No. 20171028), 国家科学技术部("973"计划, 2001CB6105-04, 2001CB6105-06)及山东省自然科学基金资助项目(No. Z99B03)。

* 通讯联系人。E-mail: jzjiang@sdu.edu.cn

第一作者: 王晓娟, 女, 27 岁; 研究方向: 纳米材料。

and consequently a great interest has been focused on the control of material morphology, size, monodispersity and also on the self-assembly for the small crystallite in recent years^[2~4]. For instance, various shapes of the semiconductor ultrafine particles have been fabricated. Some properties and formation mechanism or kinetics have been proposed^[5~9]. ZnO is an important multifunctional material with a wide bandgap (3.37 eV), large exciton binding energy (60 meV) and positive dielectric constant ($\epsilon_0 = 8.75$, $\epsilon_\infty = 3.75$), which has been widely applied in many fields such as solar cells, gas sensors, surface acoustic wave (SAW) devices, transparent conductive oxide, varistors, and so on. Recently, it has been reported that the realization of quantum confinement is likely to further enhance the excitonic and biexcitonic binding energies of zinc oxide with further increasing oscillator strengths and could lead to the fabrication of low threshold, ultrafast excitonic devices capable of operating in the UV range^[10]. Furthermore, room-temperature UV lasing in ZnO nanowire arrays has been demonstrated^[11]. Obviously, ZnO semiconductor nanomaterials would have a great impact on the modern life.

In this work, the submicron ZnO superlattice particles with perfect hexagonal shape were prepared via vaporizing solvent in microemulsion consisting of water, n-pentanol, toluene and sodium dodecyl sulfonate. The formation mechanism of ZnO superlattice particles is also investigated. It is noteworthy that nanosized ZnO particles with hexagonal shape have been reported^[12], but the present work is the first paper dealing with the controlled preparation of submicron ZnO superlattice particles with perfect hexagonal shape to the best of our knowledge. Moreover, in the present microemulsion system, although a large amount of surfactant and cosurfactant are present, the shapes of ZnO particles are not determined by the structure of system but by interfacial interaction between particles. Because the fabricated ZnO superlattice particles are modified by salts of dodecyl sulfonate, which is a kind of useful antistatic agent, it is expected that the ZnO superlattice particles have antistatic properties. In ad-

dition, because ZnO superlattice particles can be broken into small nanoparticles less than 10 nm in absolute ethanol, it will provide a new method for storing tiny nanoparticles.

1 Experimental Section

1.1 Preparation and Characterization of Zinc Oxide with Hexagonal Shape

0.025 mol zinc acetate dihydrate $\text{Zn}(\text{OAc}) \cdot 2\text{H}_2\text{O}$ was added to 70 mL pentanol. The mixture was heated and refluxed in three-neck flask under stirring. When the solution became translucent, 10 mL deionized water was added and the solution got to be transparent. Then 23 mL toluene and 0.025 mol sodium dodecyl sulfonate were added to this mixture. This mixed solution was refluxed at 94°C to form transparent microemulsion of water in oil. The present microemulsion became cloudy gradually with refluxing. About 5 minutes later after the microemulsion began to be cloudy, 2.4 mL of ammonia (25~28%) was injected by injector whose needle was submerged in the solution. And then, part of solvents was removed through the refluxing condenser (200 mm) by stopping the cooling water till the boiling point of this mixed solution changed to 110°C after 15 h. In succession, the solution was just kept refluxing at 110°C for 3 h by connecting the cooling water of the condenser. After stopping heating and stirring, the system cooled down naturally and stood for 12 h. The superstratum was removed by decanting and the precipitate at the bottom of flask was washed for four times with deionized water and four times with absolute ethanol before drying under vacuum. The sample obtained was divided into two portions. One of which, (a), is directly applied for characterization by means of FT-IR (Bio-Rad FTS 165 spectrometer), TEM (JEM-1200EX from JEOL, absolute ethanol as dispersant, copper grid covered with formvar film) techniques and the second part, (b), was immersed in absolute ethanol for two weeks before being analyzed also by TEM method.

1.2 Investigation of Mechanism

(1) A small amount of the ZnO sample from part

(a) was heated from room temperature to 700°C at the constant rate of $10^{\circ}\text{C} \cdot \text{min}^{-1}$ under a stream of nitrogen gas for thermal analysis (Rheometric Scientific TGA-1500), and the change of weight was measured and recorded continuously.

(2) Part of sample also from portion (a) was heated to 200°C and 450°C in tube furnace under nitrogen flow at the constant rate of $10^{\circ}\text{C} \cdot \text{min}^{-1}$, respectively. After being cooled down naturally to room temperature, the products were characterized by infrared spectra.

(3) In order to investigate the formation mechanism of ZnO superlattice particles, the reaction process was monitored by using transmission electron microscope (TEM). From the point that the solution became cloudy to 110°C, a small amount of sample in reaction system was extracted in different intervals of time for characterization using TEM (JEM-100CX II from JEOL, copper grid is covered with polyvinyl formal film).

2 Result and Discussion

Perfect hexagonal submicron particles of ZnO were found by TEM from portion (a). Their assembly was shown in Fig. 1. The FT-IR spectrum confirms that the samples are zinc oxide modified by surfactant. Selected area electronic diffraction (SAED) analysis shows that the single crystal pattern belongs to hexagonal crystal system, which was given in the inset of Fig. 1. A particular result was obtained from the sample of portion (b): Small nanoparticles in the size of about 7nm are separated out of the hexagonal body as shown by the TEM micrograph in Fig. 2. This seems to suggest that small nanoparticles about 7nm are combined via hydrogen bonds to build ZnO submicron particles. When the sample is immersed in absolute ethanol, the hydroxyl groups will be replaced by ethoxy groups^[9]. Therefore, the hydrogen bonds between ZnO nanoparticles in the submicron particles were destroyed which results in the decreased interaction among ZnO nanoparticles. As a result, a large number of nanoparticles were separated out and could be observed clearly

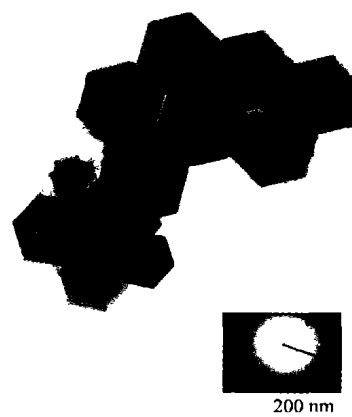


Fig. 1 TEM micrograph showing that nearly perfect hexagonal submicron particles of ZnO are assembled, the size of particles distributed mostly in 200 ~ 300nm; inset showing the electronic diffraction pattern of hexagonal particle which present a single crystal pattern belonging to a hexagonal crystal system



Fig. 2 TEM micrograph showing that the nanoparticles about 7nm separate out of hexagonal body after the sample is immersed in absolute ethanol for two weeks

in the submicron ZnO particles immersed in the absolute ethanol. This seems to indicate that these submicron particles have superlattice structure created via hydrogen bonds among the ZnO nanoparticles.

In order to expound the results above-mentioned, at first the TGA and FT-IR technology was applied. The thermal analysis diagram is exhibited in Fig. 3. The sample weight was observed to begin to decrease markedly for the first time at 130°C and to begin to decrease sharply for the second time at 320°C. The

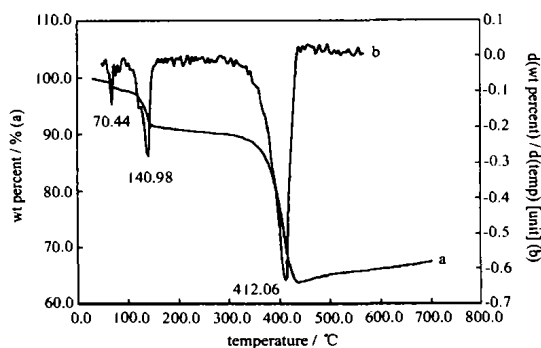


Fig. 3 Results of thermogravimetry

The sample was heated at a constant rate of $10^{\circ}\text{C} \cdot \text{min}^{-1}$ from room temperature to 700°C under nitrogen flow

weight loss of about 6 ~ 7% of the initial weight of the sample observed at temperatures lower than 160°C is considered to be due to the evaporation of loosely bound organic materials remained in the sample, which do not chemically adsorbed to the surfaces of ZnO particles^[13]. Comparing IR spectra of the unheated sample and the heated sample, the typical changes of absorbance was described in Fig. 4: Curve (a) showing the infrared absorbance of unheated sample; curve (b) showing that of the sample heated to 200°C ; curve (c) showing that of the sample heated to 450°C . It can be observed that the absorption bands appearing at 1165 (vs), 1082 (w), and 1202cm^{-1} (vs) for the unheated sample (curve a) have disappeared, the shoulder absorption at 1224cm^{-1} has also disappeared and the

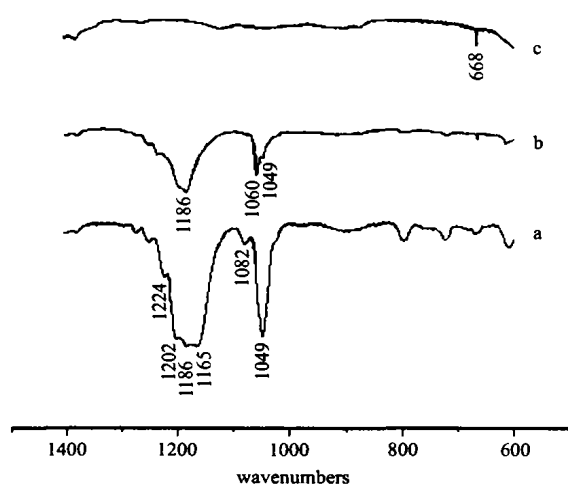


Fig. 4 Infrared spectra of fired and unfired samples
(a) unfired sample; (b) 200°C ; (c) 450°C

strong and sharp absorption at 1049cm^{-1} has turned into a shoulder absorption after the sample was heated to 200°C (curve b), meanwhile, a new peak emerged at 1060cm^{-1} . According to the characteristic IR absorptions of sodium dodecyl sulfonate at 1174cm^{-1} (very strong $-\text{SO}_2-$ asymmetric stretching vibration), 1045cm^{-1} (strong $-\text{SO}_2-$ symmetric stretching vibration), and 1205cm^{-1} ^[14], the absorptions described above and observed for the unheated sample are considered to be related to the dodecyl sulfonic groups which are not chemically adsorbed on the surface of ZnO particles. However, the band at 1165cm^{-1} could be assigned to the $-\text{SO}_2-$ asymmetric stretching vibration and the absorption at 1049cm^{-1} could be assigned to the $-\text{SO}_2-$ symmetric stretching vibration. Obviously, these bands have a shift in comparison with those of sodium dodecyl sulfonate, which might be attributed to the change occurring at the dodecyl sulfonic groups after adsorbed by the ZnO particles. It is easy to understand that the vibrations of $-\text{SO}_2-$ group will be influenced by the positively charged Zn atom on the surface of ZnO particles when the dodecyl sulfonic groups are in adsorbed state. In particular, the appearance of absorption at 1082cm^{-1} seems to support this point because some dodecyl sulfonic salts such as silver and lead also show absorption at the same position in their IR spectra^[14].

The second weight loss, 27% of the initial weight, beginning at about 320°C , is considered to result from the loss of dodecyl sulfonate that are chemically bonded to the zinc atom on the surface of submicron ZnO particles. In the IR spectra, the absorbance at 1186cm^{-1} has no change after being heated to 200°C (curve b), which is assigned to $-\text{SO}_2-$ asymmetric stretching vibration for zinc dodecyl sulfonate. In turn, the band emerged at 1060cm^{-1} after heated to 200°C is assigned to the $-\text{SO}_2-$ symmetric stretching vibration of zinc dodecyl sulfonate. The higher frequencies of these vibration modes compared with those in sodium dodecyl sulfonate may be attributed partly to the partial covalent bond between Zn and O, which results in the increase in the double-bond character of

-SO₂- and thus leads to the blue-shift of these vibration modes^[15]. On curve (c), after the sample was heated to 450°C, all these absorptions have vanished, indicating that zinc dodecyl sulfonate created through chemical bonding between dodecyl sulfonic group and zinc atom of the ZnO particle has been decomposed completely. In addition, it has been found that the weight of sample does not lose anymore after 430°C. In reverse, an increase in weight was observed. This reveals that the special surface area increases and nitrogen gas is adsorbed continuously due to the formation of nanoparticles after heating over 430°C. In fact, it has been verified by TEM characterization that the submicron particles are broken up into nanoparticles in the size of less than 50nm after fired at 500°C for 2h as shown in Fig. 5.

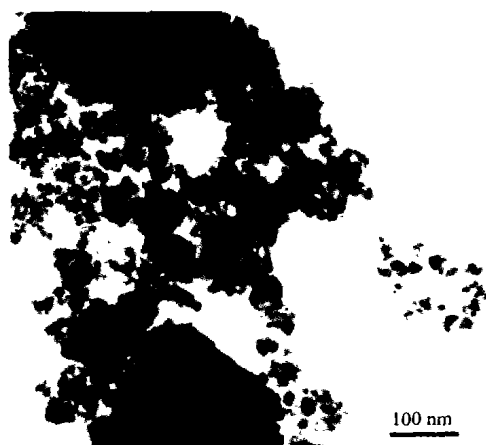


Fig. 5 TEM micrograph showing that the hexagonal particles fission into nanoparticles which sizes are less than 50nm after fired at 500°C for 2h

Secondly, the formation process for submicron particles has been monitored by TEM technique and the micrographs are shown in Figs. 6 to 11. At the point that the microemulsion just became cloudy, a small amount of sample was extracted immediately from the reaction system for TEM characterization. As can be seen from Fig. 6, some thin-films observed under low magnifying power were found to present a porous network structure that contained nanoparticles and nanoclusters with the sizes less than 10nm, under high magnifying power. Meanwhile, selected area electronic diffraction (SAED) method was also applied and both

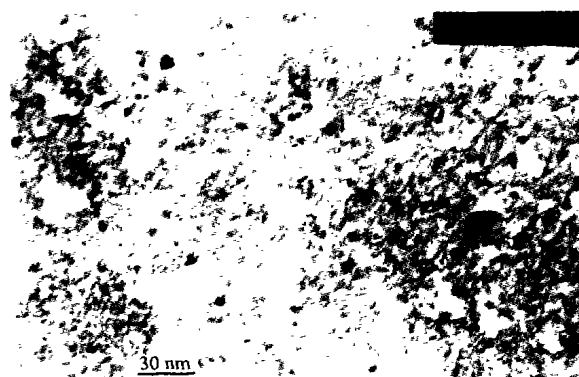


Fig. 6 TEM micrograph showing that large numbers of nanoparticles with various sizes less than 10nm appear when the solution just begin to be cloudy to structure a network

single crystal and polycrystalline patterns were observed in this sample. It is interesting to point out that during the SAED study, the diffraction rings or spots, characteristic patterns of the polycrystals or single crystals, became thinner and thinner along with time and finally disappeared. It is probably due to such a fact that the tiny clusters of ZnO occurring in the solution are very easy to be destroyed by electronic beam. After 5min, the mixed solution became cloudier and a large number of nanoparticles have been formed at this stage, most of which were in the size of about 5 ~ 10nm as observed in the network as displayed in the TEM micrograph, Fig. 7. When ammonia was injected into the solution, aggregation of these 5 ~ 10nm nanoparticles took place. This was reflected by the appearance of network shrinking around some certain centers and the resulting shrinkages of network under TEM as shown in Fig. 8.

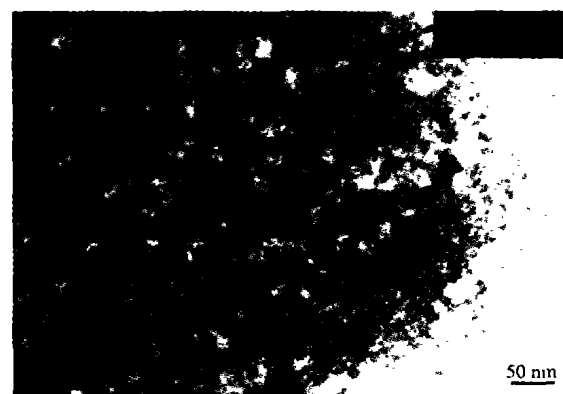


Fig. 7 TEM micrograph showing that the nanoparticles less than 10nm have occurred densely when solution becomes cloudier about 5min later

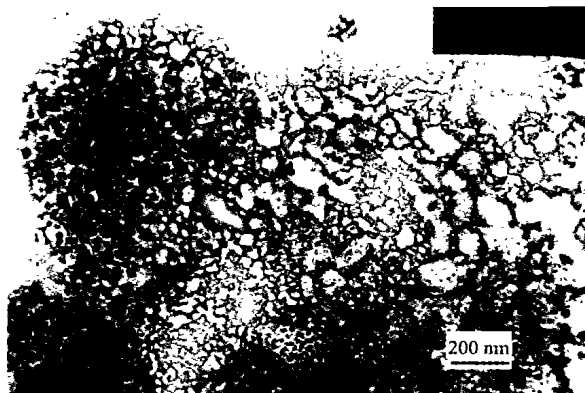


Fig. 8 TEM micrograph showing that nanoparticles aggregate like shrinkage of network about half an hour later after the ammonia is added

Furthermore, it was found that some aggregation started to occur around a hollow hole, as shown in Fig. 9. Additionally, about half an hour later after ammonia was injected, most aggregates formed to take the spherical shape in submicron dimension. However, a small part of aggregates took the approximate hexagonal shape, as shown in Fig. 10. The reason that aggregates with hexagonal shape occurs after addition of ammonia will be discussed in the following section. With compacting and crystallizing, the aggregates show the appearance as crystallized particle with spherical shape. By vaporizing the solvent, the submicron ZnO spherical particles were inclined to self-assemble and turn into the particles with hexagonal shape at about 109°C.

In view of all the above-mentioned facts, we now try to propose a formation mechanism of ZnO submicron particles with hexagonal shape. At the temperature of 94°C, the mutual solubility of *n*-pentanol and water

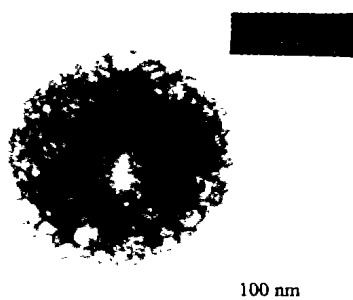


Fig. 9 TEM micrograph showing that large numbers of nanoparticles aggregate and become compact around a hole



Fig. 10 TEM micrograph showing submicron particles consisting of nanoparticles with transitional shape between hexagon and sphere during the course of agglomerating

gets increased. As a result, both surfactant and zinc acetate have a large solubility in oil phase and in water phase because of the existence of alcohol. Moreover, due to the dehydrating properties of alcohol^[16], a large number of ZnO nanoclusters can be created in water and oil phase. On the surface of nanoclusters, surfactant molecules can be chemisorbed in the form of $\text{Zn}(\text{OSO}_2\text{C}_{12}\text{H}_{25})$. This induces such a result that a large number of nanoclusters are inclined to be extracted into the oil phase to create the porous network, Fig. 6, and “water pool” is unable to play the role as template and microreactor at all. Along with continuous heating, the initially formed small nanoclusters in the oil phase become denser and denser and finally aggregate into larger nanoparticles with the size of 5 ~ 10 nm, Fig. 7. Meanwhile, most of surfactant molecules chemisorbed on the surface of nanoclusters were squeezed out onto the surface of nanoparticles because the atoms or molecules on the surface of nanoclusters are considered in the liquid state^[17]. After ammonia was injected, surfactant molecules on the surface of nanoparticles and nanoclusters tend to be substituted by hydroxy groups. Therefore, nanoparticles and nanoclusters start to agglomerate closely via hydrogen bonds. Meanwhile, as mentioned above, there are few nanoparticles inside the “water pool”, which, however, are full of ammonia after the ammonia injection and could act as the aggregating center of nanoparticles because the hydroxy group source is supplied. Since nanoparticles with hy-

droxy groups induced by the ammonia injection can get into small “water pools” from outside, which are in the majority and easy to be filled up instantly, leading to the formation of large amount of solid aggregates. However, for large “water pools” which are in the minority, aggregates have been formed and compacted into spherical shape before the pools are filled with nanoparticles. This is the reason that few aggregates with a hollow hole in center can be obtained. The process of nanoparticles infiltrating into “water pool” from outside can be observed clearly in Fig. 9. As a result, hollow particles with a hole can be obtained in the target product as shown in Fig. 11. Besides, the size of nanoparticles formed before the addition of ammonia, 5 ~ 10 nm, is similar to that of those obtained by immersing the hexagonal body in absolute ethanol for two weeks. This suggests that part of the surfactant molecules remained on the surface of nanoparticles prevent the dehydration of hydroxy groups between ZnO nanoparticles. Therefore, it leads to large numbers of hydroxy groups remaining in the process of aggregating. With the compacting and crystallizing of spherical aggregates, the crystallized particles occurred with superstructure, which was built by nanoparticle-blocks via hydrogen bond interaction among hydroxy groups. Finally, with the solvent vaporization, the spherical superlattice particles were transformed into the hexagonal ones. In this experiment, when the sample extracted from the reaction system at about 103°C was characterized by TEM, a transitional shape from sphere to polygon was found, the TEM micrograph shown in

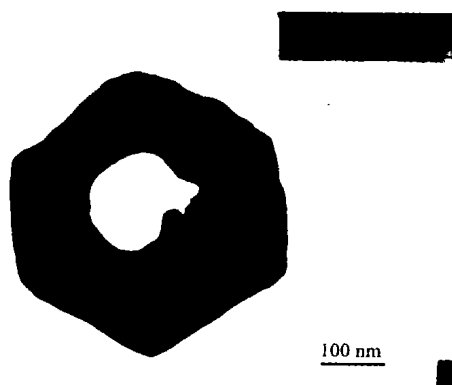


Fig. 11 TEM micrograph showing a hexagonal particle with a hole in center occurs in final product

Fig. 12. Obviously, the hexagonal shape of superlattice particles has occurred at the temperature of 103°C along with a close array in two dimensions. In Fig. 12, most of particles give the shape of hexagon besides two particles lying on the edge of array, which absolutely are not spherical, whose edges adjacent with other particles were found to be flattened, marked with arrow in Fig. 12, to form a transitional shape from sphere to polygon. Herein, it is considered that interfacial factor plays the important role in determining the shape of superlattice particle. As far as we know, in some cases of crystallization, the crystals are prone to decrease the curvature of solid-solid interface between crystals in order to decrease interfacial energy, which results in the change in the shape of particles. Theoretically the 120° intersection angle between interfaces is preferred in two dimensions under certain conditions^[18]. Therefore hexagonal shape is prior to others for superlattice particles. Actually, as mentioned above, in the process of nanoparticles aggregating, small amount of aggregates neighboring with each other also show the interfacial effect due to the same reason, as shown in Fig. 10, while most of them isolated from each other, give the spherical shape. In our experiment, although the spherical aggregates have crystallized into superlattice particles, their surfaces still have good fluidity



Fig. 12 TEM micrograph showing the assembly of submicron particle is created in the process of preparation and interfacial factor have an effect on the shape of particles; when the edges of particles are neighboring with those of others, the edges are prone to be flattened; whereas the isolated edges still keep arc. The arrows point to the flattened edge

which would arouse a metamorphosis in response to some actions. Because the surface of superlattice particles was modified by surfactant molecules, the interaction between hydrophobic groups is considered to contribute to the metamorphosis. In other words, while the concentrations of surfactant and particles were increasing with vaporizing solvent, the possibilities increased for collision and for self-assembly of particles via hydrophobic interaction^[19], which created more and more solid-solid interfaces. Due to the interaction between hydrophobic groups on interfaces, the interfacial interaction was strengthened. In consequence, in order to decrease the interfacial energy, the interfacial curvature has to be decreased to stabilize the system^[20]. Then the spherical shape evolved into the hexagonal one.

3 Conclusion

In this paper, the controlled preparation of sub-micron ZnO superlattice particles with hexagonal shape has been described and their formation mechanism has been proposed. At the beginning, the ZnO superlattice particles with spherical shape are created through the aggregating process of nanoparticles via hydrogen bonds instead of through the direct growth process of small particles. With vaporizing solvent, the self-assembly of superlattice particles was obtained due to hydrophobic interaction among surfactant molecules. Meanwhile, because the surfactant strengthened the interfacial interaction between particles, which gave rise to the decrease of interfacial curvature, the spherical particles evolved into the hexagonal ones.

References

- [1] Brus L. E. *J. Chem. Phys.*, **1984**, **80**, 4403.
- [2] Matifevic E. *Chem. Mater.*, **1993**, **5**, 412.
- [3] Pileni M. P. *Langmuir*, **1997**, **13**, 3266.
- [4] Puentes V. F., Krishnan K. M., Alivisatos A. P. *Science*, **2001**, **291**, 2115.
- [5] Peng X., Manna L., Yang W., Wickham J., Scher E., Kadavanich A., Alivisatos A. P. *Nature*, **2000**, **404**, 59.
- [6] Murray C. B., Norris D. J., Bawendi M. G. *J. Am. Chem. Soc.*, **1993**, **115**, 8706.
- [7] Pinna N., Weiss K., Urban J., Pileni Marie-Paule, *Adv. Mater.*, **2001**, **13**, 261.
- [8] Peng X., Wickham J., Alivisatos A. P. *J. Am. Chem. Soc.*, **1998**, **120**, 5343.
- [9] Rodriguez-Paez J. E., Caballero A. C., Villegas M., Moure C., Duran P., Fernandez J. F. *J. Eur. Ceram. Soc.*, **2001**, **21**, 925.
- [10] Chen Y., Bagnall D., Yao T. *Mater. Sci. and Eng.*, **2000**, **B75**, 190.
- [11] Huang M. H., Mao S., Feick H., Yan H., Wu Y., Kind H., Weber E., Russo R., Yang P. *Science*, **2001**, **292**, 1897.
- [12] LIU Xue-Ning, YANG Zhi-Zhong *Wuli Huaxue Xuebao*, **2000**, **16**, 746.
- [13] Sakohara S., Tikanen L. D., Anderson M. A. *J. Phys. Chem.*, **1992**, **96**, 11086.
- [14] Nersasian A., Johnson P. R. *J. Appl. Poly. Sci.*, **1965**, **9**, 1653.
- [15] Robinson E. A. *Can. J. Chem.*, **1961**, **39**, 247.
- [16] Koch U., Fojtik A., Weller H., Henglein A. *Chem. Phys. Letters*, **1985**, **122**, 507.
- [17] Gasser U., Weeks E. R., Schofield A., Pusey P. N., Weitz D. A. *Science*, **2001**, **292**, 258.
- [18] PAN Jin-Sheng, TONG Jian-Min, TIAN Min-Bo *Elements of Material Science*, Beijing: Tsinghua University Press, **1998**.
- [19] Li M., Schnablegger H., Mann S. *Nature*, **1999**, **402**, 393.
- [20] Alfredsson V., Keung M., Monnier A., Stucky G. D., Unger K. K., Schüth F. *J. Chem. Soc., Chem. Commun.*, **1994**, 921.