

Fabrication of hierarchical β -Co(OH)₂ microspheres via hydrothermal process

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Abstract. Hierarchical β -Co(OH)₂ microspheres with 20–50 μm diameter assembled from nanoplate building blocks were successfully fabricated via a hydrothermal process in the presence of a cation surfactant cetyltrimethylammonium bromide (CTAB). The products are characterized in detail by multiform techniques: X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis. The effect of CTAB and pH value on the β -Co(OH)₂ morphology was also investigated. When pH value is maintained at 9, an appropriate added amount of CTAB (3 g) is the crucial prerequisite for the formation of this interesting morphology. In this experiment, pH value of the solution and the cation surfactant CTAB together results in the formation of hierarchical β -Co(OH)₂ microsphere structures assembled from nanoplates.

Keywords. β -Co(OH)₂; microstructure; electron microscopy; hierarchical.

1. Introduction

The crystallography, shape, and size of the material greatly influence their optical, electronic, and other properties (Kuang *et al* 2009). Recently, scientists have paid more and more attention to the organization of complex microarchitectures, especially hierarchical architectures which are assembled by nanostructured building blocks such as zero dimension (quantum dots or nanoparticles), one dimension (nanorod, nanowire, or nanoribbon), or two dimension (nanosheet or nanoplate) (Lao *et al* 2002; Cölfen and Mann 2003; Shi *et al* 2003; Kanaras *et al* 2005; Zhang *et al* 2005; Song *et al* 2007a; Li *et al* 2009). To date, many self-assembly processes driven by chemical or physical principles have been developed to organize hierarchical structures. For example, 3D aperiodic hierarchical porous graphitic carbon materials have been synthesized and used for electrode materials in electrochemical capacitors (ECs) with good performances (Wang *et al* 2008), ZnO hollow spheres have been successfully prepared (Chen and Gao 2008), Se nanostructures with sea urchin shapes were synthesized by a sodium dodecyl sulfate-assisted hydrothermal process (Fan *et al* 2009), Ni(OH)₂ with three-dimensional nanostructures were prepared in a water-in-oil reverse micelle/microemulsion system (Cao *et al* 2007), etc.

Cobalt hydroxides have been extensively studied over the last decade, owing to their unique physico-chemical properties for electrochemical, magnetic, secondary batteries, and catalytic applications (Kurmoo 1999; Jafarian *et al* 2003; Hou *et al* 2005; Li *et al* 2005). Cobalt hydroxide can be crystallized into a hexagonal layered structure with two polymorphic forms, α - and β -Co(OH)₂ (Ma *et al* 2006). The β -Co(OH)₂ crystal has a brucite-like structure, whereas α -Co(OH)₂ is isostructural with hydrotalcite-like compounds. Generally, this hydrotalcite-like phase is metastable and easily transforms into more stable brucite-like compounds in strongly alkaline media. Accordingly, β -Co(OH)₂ is often selected as additives of alkaline secondary batteries due to its stability and enhanced conductivity when changed to β -CoOOH (Qiao *et al* 2009). In previous work, Li and co-workers synthesized sisal-like, dandelion-like, and rose-like Co(OH)₂ architectures by aggregating of well-arranged nanorods and nanoflakes (Li *et al* 2006). Zeng's group reported the ethylenediamine-mediated synthesis of butterfly-like β -Co(OH)₂ nanocrystals consisting of linear arrays (Sampanthar and Zeng 2002). Zhang *et al* (2005) synthesized needle-like α -Co(OH)₂ and hexagonal β -Co(OH)₂ by changing the reaction environment from nitrogen to oxygen (Zhang *et al* 2000). However, up to now, the preparation of Co(OH)₂ 3D hierarchical structures is still a big challenge. In this study we report our recent efforts on the synthesis of 3D hierarchical β -Co(OH)₂ microspheres through a facile hydrothermal process. The influences of different reaction conditions on the morphology of final products have been discussed in detail.

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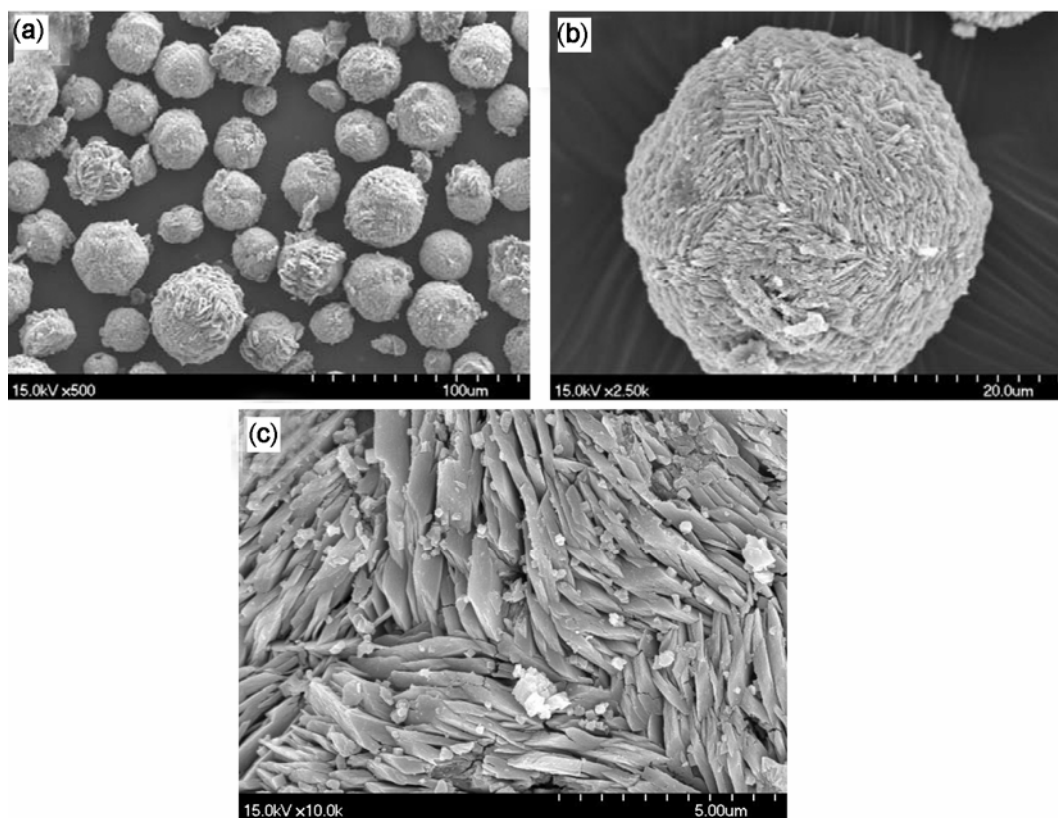


Figure 1. SEM images of $\beta\text{-Co}(\text{OH})_2$ samples. (a) Hierarchical microsphere morphology; (b) individual microsphere; (c) higher magnification SEM image.

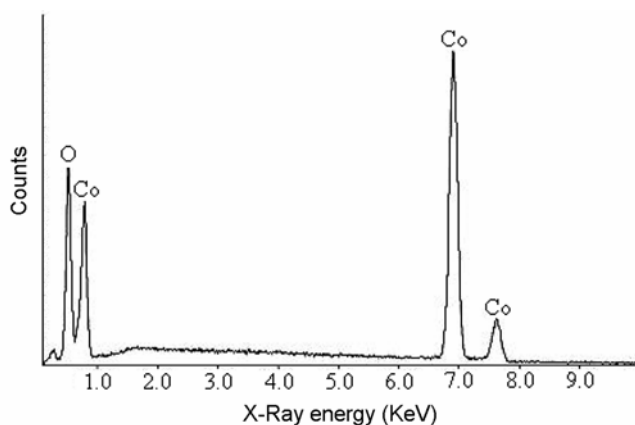


Figure 2. EDS patterns of hierarchical $\beta\text{-Co}(\text{OH})_2$.

2. Experimental

2.1 Sample preparation

Cobalt hydroxide microspheres were prepared by hydrothermal process. In a typical procedure, 4 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 3 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 90 ml of deionized water. When the solution clarified, pH of the solution was main-

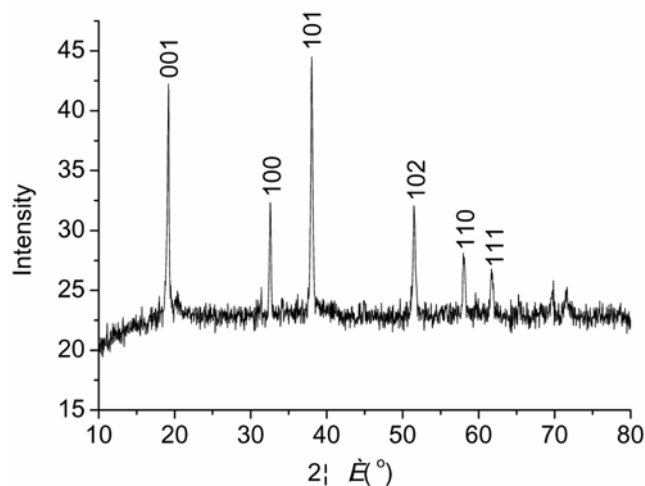


Figure 3. XRD pattern of the as-prepared product. Indexing is based on the structure of $\beta\text{-Co}(\text{OH})_2$.

tained at 9 by adding NaOH. Then the reaction mixture was charged in a 100 ml capacity autoclave with Teflon liner followed by uniform heating at 180°C for 10 h. After the reaction was completed, the autoclave was allowed to cool to room temperature naturally. The solid precipitate was filtered, washed several times with

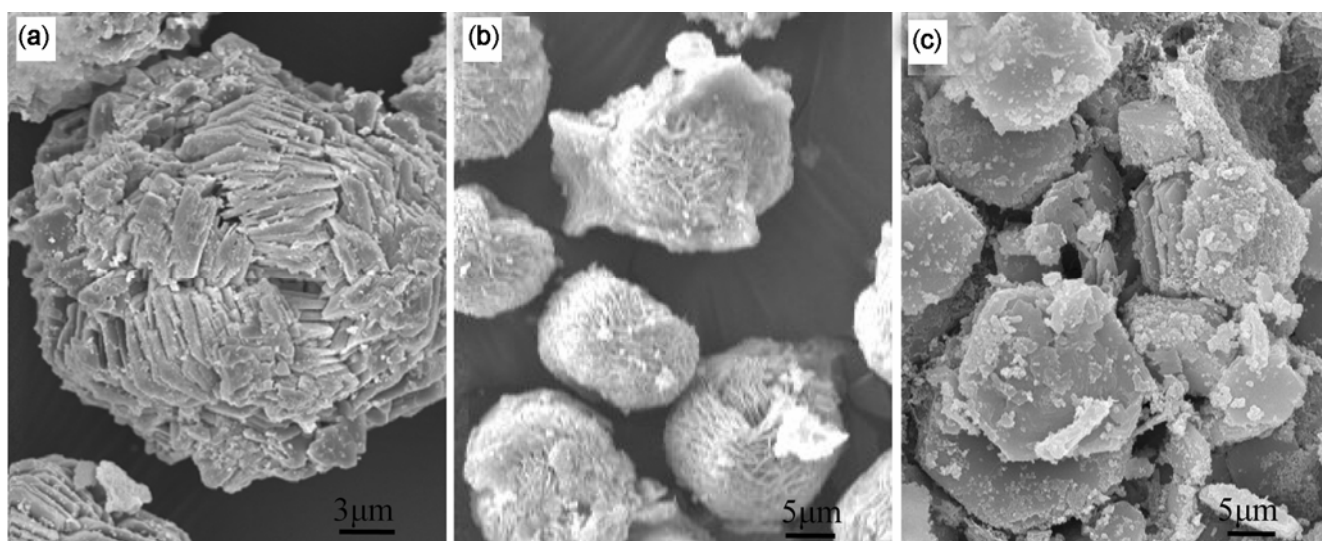


Figure 4. SEM images of as-synthesized sample via pH values: (a) 8, (b) 10 and (c) 11.

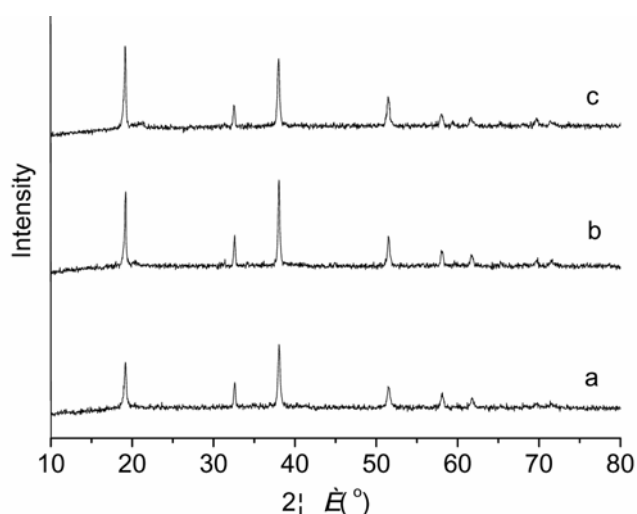


Figure 5. XRD pattern of as-synthesized sample via pH values: (a) 8, (b) 10 and (c) 11.

distilled water and anhydrous ethanol to remove impurities, and then dried at 80°C in air.

2.2 Characterization

The obtained samples were characterized by X-ray powder diffraction (XRD) using a Rigaku D/max- γ B X-ray diffractometer with graphite monochromatized CuK α radiation ($\lambda = 1.54178$ Å) operated at 40 kV and 80 mA. The images of the samples were obtained by scanning electron microscopy (SEM; Hitachi S-4700 15 kV). Energy-dispersive X-ray spectroscopy (EDS) is attached to the Hitachi S-4700.

3. Results and discussion

Figure 1 shows the SEM images of the Co(OH) $_2$ sample which was prepared by CTAB-assisted hydrothermal method. It can be seen that the as-synthesized Co(OH) $_2$ samples exhibit microsphere structure with a diameter range of 20–50 μ m, as shown in figure 1a. Each microsphere is congregated randomly by pieces of nanoplate with both length and width on the order of 2–3 μ m, as shown in the enlarged SEM image (figure 1b). The high magnification SEM image (figure 1c) reveals that the thickness of each plate is in the range of 300–500 nm. The energy dispersive spectrometry (EDS) analysis was employed to determine the composition of hierarchical Co(OH) $_2$. As shown in figure 2, it indicates that the main elements in samples are O and Co. Taking H into consideration, they should, therefore, be attributed to Co(OH) $_2$. The novel hierarchical Co(OH) $_2$ microsphere can be easily obtained by the present facile synthesis route according to the SEM and EDS observation.

The phase and purity of the products were examined by XRD. Figure 3 shows the XRD pattern of as-synthesized Co(OH) $_2$. All the diffraction peaks can be indexed to a pure hexagonal phase of β -Co(OH) $_2$ with lattice parameters of $a = 3.189$ Å and $c = 4.666$ Å, which are in good agreement with the values in the literature (JCPDS card No. 30-0443, $a = 3.191$ Å and $c = 4.664$ Å).

The effect of pH value on the morphology of as-synthesized β -Co(OH) $_2$ sample was further investigated. Figure 4 shows the SEM images of β -Co(OH) $_2$ synthesized by CTAB-assisted but with pH value of 8, 10 and 11, respectively. Figure 4a displays the SEM image of sample made at pH of 8 which shows that the product morphology is hexagonal aggregation. This hexagonal aggregation is a layered assembly of numerous nanoplates.

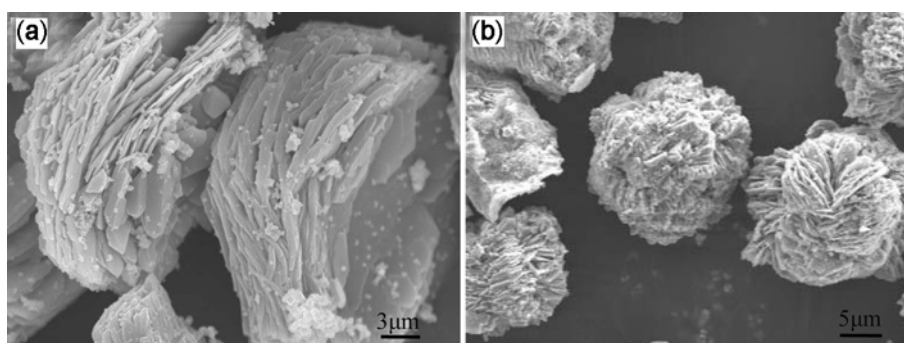


Figure 6. SEM images of samples prepared at different added amounts of CTAB: (a) 0 g and (b) 2 g.

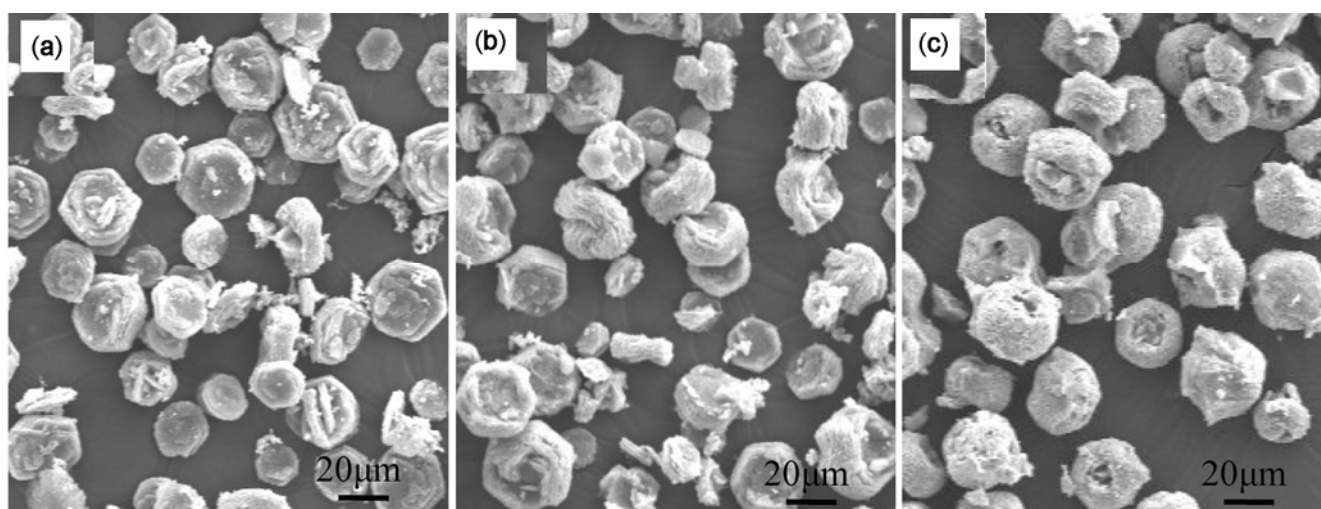


Figure 7. SEM images of as-synthesized β -Co(OH) $_2$ sample obtained via different hydrothermal reaction times at 180°C: (a) 1 h, (b) 4 h and (c) 7 h.

When pH value was increased to 10, as shown in figure 4b, β -Co(OH) $_2$ with imperfect microsphere was obtained. If pH value was increased to 11, only irregular microstructures, not hierarchical β -Co(OH) $_2$ microspheres, were obtained (figure 4c). Figure 3 shows the XRD patterns of samples prepared under different pH values. The β -Co(OH) $_2$ phase can be obtained in the whole pH values range (8–11) under investigation.

In order to understand the function of the CTAB surfactant in the formation of present β -Co(OH) $_2$ microspheres, one control experiment was further performed. In the controlled experiment conducted without using CTAB and keeping the rest of the experimental conditions unchanged, only aggregation of numerous sheets were obtained (figure 6a). When the added amount of CTAB was 2 g, the products were imperfect hierarchical microspheres (figure 6b). When the added amount of CTAB was increased to 3 g, hierarchical β -Co(OH) $_2$ microspheres were the major products (figure 1). Therefore, the use of the appropriate amount of CTAB (3 g) is a cru-

cial prerequisite for the formation of this perfect β -Co(OH) $_2$ microspheres under the selected reaction conditions.

The formation process of hierarchical β -Co(OH) $_2$ microsphere was observed via different hydrothermal reaction times, which was monitored by SEM characteristics. Figure 7 shows the SEM images of the β -Co(OH) $_2$ samples prepared after 1, 4, or 7 h hydrothermal reaction time. For the 1 h sample (figure 7a), β -Co(OH) $_2$ microdisks were formed at the initial stage. Clearly, the β -Co(OH) $_2$ microdisks were assembled from a few layers of sheets. Through 4 h hydrothermal reaction, the β -Co(OH) $_2$ nanoplate further congregated on the microdisks. With the hydrothermal reaction time is increasing, hierarchical β -Co(OH) $_2$ microdisks will be finally formed from assembly of the nanoplates, as shown in figures 7c and 1.

The growth mechanism of crystal is determined by both the internal structure and external conditions such as temperature, pressure, and composition of the solution. It is well known that the shape of the crystals can be con-

trolled by adding chemical capping reagents into the solution (Song *et al* 2006, 2007b). The surfactant might suppress the crystal growth rate in some directions and/or stimulate the growth rate in others. It is believed that pH value has a great influence on the concentration of growth units. In this experiment, pH value of the solution and the cation surfactant CTAB result in the formation of hierarchical β -Co(OH)₂ microsphere structures assembled from nanoplates. The detailed mechanism for the formation of hierarchical β -Co(OH)₂ microspheres is still under investigation.

4. Conclusions

In summary, we reported the fabrication of 3D hierarchical β -Co(OH)₂ microspheres assembled from pieces of nanoplates with the assistance of surfactant CTAB via the facile hydrothermal method. The β -Co(OH)₂ microspheres were composed of nanoplate with both length and width on the order of 2–3 μ m, and thickness in the range of 300–500 nm. Optimum synthetic reaction conditions including amounts of CTAB and pH value have been found for the production of perfect hierarchical β -Co(OH)₂ microsphere. These β -Co(OH)₂ microsphere may find their applications in a variety of areas such as catalysis, electronics, magnetics, secondary batteries, and so on.

References

- Cao M H, He X Y, Chen J and Hu C W 2007 *Cryst. Growth Des.* **7** 170
Chen Z T and Gao L 2008 *Cryst. Growth Des.* **2** 460
Cölfen H and Mann S 2003 *Angew. Chem., Int. Ed.* **42** 2350
Fan S, Li G, Zhang X, Mu H, Zhou B, Gong L, Liang H, Guo I and Guo J 2009 *Cryst. Growth Des.* **9** 95
Hou Y, Kondoh H, Shimojo M, Kogure T and Ohta T 2005 *J. Phys. Chem.* **B109** 19094
Jafarian M, Mahjani M G, Heli H, Gopal F, Khajehsharifi H and Hamed M H 2003 *Electrochim. Acta* **48** 3423
Kanaras A G, Sönnichsen C, Liu H and Alivisatos A P 2005 *NanoLett.* **5** 2164
Kuang D B, Lei B X, Pan Y P, Yu X Y and Su C Y 2009 *J. Phys. Chem.* **C113** 5508
Kurmoo M 1999 *Chem. Mater.* **11** 3370
Lao J Y, Wen J G and Ren Z F 2002 *Nano Lett.* **2** 1287
Li B, Xie Y, Wu C, Li Z and Zhang J 2006 *Mater. Chem. Phys.* **99** 479
Li W, Zhang S and Chen J 2005 *J. Phys. Chem.* **B109** 14025
Li Y, Cao M and Feng Y 2009 *Langmuir* **25** 1705
Ma R, Liu Z, Takada K, Fukuda K, Ebina Y, Bando Y and Sasaki T 2006 *Inorg. Chem.* **45** 3964
Qiao R, Zhang X L, Qiu R, Kim J C and Kang Y S 2009 *Chem. Eur. J.* **15** 1886
Sampanthar J T and Zeng H C 2002 *J. Am. Chem. Soc.* **124** 6668
Shi H, Qi L, Ma J and Cheng H 2003 *J. Am. Chem. Soc.* **125** 3450
Song X C, Zhao Y and Zheng Y F 2006 *Mater. Lett.* **60** 3405
Song X C, Zhao Y and Zheng Y F 2007a *Cryst. Growth Des.* **7** 159
Song X C, Zheng Y F, Yang E and Wang Y 2007b *Mater. Lett.* **61** 3904
Wang D W, Li F, Liu M, Lu G Q and Cheng H M 2008 *Angew. Chem., Int. Ed.* **47** 373
Zhang Z, Sun H, Shao X, Li D, Yu H and Han M 2005 *Adv. Mater.* **17** 42
Zhang L, Dutta A K, Jarero G and Stroeve P 2000 *Langmuir* **16** 7095