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Self-Assembly of ZnO Nanoplatelets into Hierarchical Mesocrystals and Their Photocatalytic Property

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Abstract. In this work, a simple chemical procedure was developed for the preparation of mesocrystals consisting of ZnO nanoplatelets. By simple mixing the aqueous solutions Zn(NO3)2, NaOH and ethanol at certain temperatures, the hierarchical mesocrystals with big at both ends but small in the middle were obtained. After being annealed in air at certain temperatures, the same structured ZnO mesocrystals were generated. The morphology, crystalline structure and chemical composition were characterized using SEM, XRD FT-IR and Raman. The photocatalytic properties of the ZnO mesocrystals were also investigated. It was illustrated that the ZnO mesocrystals show decent photocatalytic performance to the photodegradation of methyl blue.

1. Introduction
Mesocrystals, an ordered superstructure of crystals with mesoscopic size (1-1000 nm), have attracted great attention in the last few years due to their mesoscopic structure offering new opportunities for materials [1]. Within mesocrystals, the interaction between the building blocks, in most cases the small particle, are relatively weaker than the ion by ion or single molecule attachment which exists in conventional single crystals [2, 3]. The mesocrystals show typical hierarchical ordered structural features in which the individual small particles are packed in certain oriented aggregation manner, but preserve their inherent crystalline structure. Thus, the mesocrystals have chemical and physical properties differing from that of the single crystal counterparts. Additionally, owing to their unique size region, the mesocrystals should be easier to process or manipulate than the nanoparticles, which is advantageous for their preparation and application [4, 5].

ZnO, as a smart functional material, is a well-known wide band gap semiconductor. Both the bulk single crystal and nanocrystals have been widely studied and some of them have found practical applications in solar cells, chemical sensors, optoelectronics, and photocatalysis [6-9]. Different mesocrystal structures of ZnO have been synthesized. For instance, Liu et al. obtained uniform-sized, core-shell ZnO mesocrystal microspheres using a facile one-pot hydrothermal method in the presence of water-soluble polymer poly (sodium 4-styrenesulfonate) [10]. Li et al. report on the fabrication of hollow ZnO mesocrystals that form via aggregation of nanometer-sized ZnO particles, and these particles was precipitated from the strongly hydrated tetrabutylammonium hydroxide[11]. Ye et al. prepared hierarchical ZnO mesocrystals from a precursor of synthetic layered basic zinc acetate nanobelts by a facile solution route in the presence of poly (vinyl pyrrolidone) [12]. Nevertheless, the high cost and the relatively complicated procedure of these methods somewhat limit their application
for large scale preparation of ZnO mesocrystals. The properties of ZnO mesocrystals are also worth exploring further.

Herein, we reported a simple, rapid and cost-efficient way to synthesize one hierarchical ZnO precursor mesocrystals with big at both ends but small in the middle by simple mixing the aqueous solutions Zn(NO$_3$)$_2$, NaOH and ethanol at certain temperatures. After being annealed in air at certain temperatures, the same structured ZnO mesocrystals were generated. It was shown that the as-obtained ZnO mesocrystals have excellent photocatalytic activity and anti-optical bleaching properties to photocatalytic degradations of methyl blue.

2. Experimental Section

2.1. Preparation of ZnO mesocrystals

In a typical experiment, 15 ml (0.5 mol/L) Zn(NO$_3$)$_2$ aqueous solution was mixed with 10 ml NaOH (5 mol/L) solution under stirring, after its complete dissolution, the clear precursor solution was obtained. Then, 10 ml ethanol was poured into the clear precursor solution under stirring, and the solution slowly turned milky white. The reaction temperature (10 °C) was adjusted using a cryogenic circulator in the process of reaction. After reaction for 30 min, the solid product was collected by centrifugation, and was washed using deionized water for three times, and then was dried at 80 °C. The as-prepared white solid product was finally annealed at 200 °C in air for 4 h.

2.2. Characterization

The morphologies of as-prepared solid products were characterized using scanning electron microscope (SEM, Verios 460, FEI, America). The crystallinity was evaluated using X-ray powder diffraction (XRD) performed on a D8 Advance diffractometer (Bruker, German). The FTIR spectra were acquired on a Nicolet IS50 FTIR spectrometer (Thermo Fisher, America) with the samples milled in KBr wafer. Raman spectroscopy measurement was examined by laser confocal micro-Raman spectroscopy using LabRam HR Evolution (Horiba Jobin Yvon, Japan) with an excitation laser beam wavelength of 473 nm. The UV-vis absorption was measured using a UV-Vis spectrocope (Shimadzu UV2550, Japan).

2.3. Photocatalytic degradation experimental

The photocatalytic degradations of methyl blue (MB) dye was carried in a photo-reactor equipped (Bilon, Shanghai). The reaction was carried out in quartz tubes under vigorous stirring, which was installed 6 cm away from the irradiation lamp. The lamps were equipped inside a cylindrical Pyrex tube cooled by circulated water. In a typical experiment, ZnO mesocrystals, 50 mg, were dispersed in 100 mL, methyl blue aqueous solution (15 mg/L), and was stirred for 20 min to reach an adsorption–desorption equilibrium of methyl blue onto the ZnO mesocrystals. The reaction was initiated by exposing the quartz tube to a mercury lamp (365 nm, 500 W) at room temperature (20 °C) under the same photoreaction conditions. The reaction process was followed using UV-Vis absorption spectroscopy measurement.

3. Results and discussion

As shown in figure 1a, the solid product of the reaction of Zn(NO$_3$)$_2$ and NaOH in the presence of ethanol at the 10 °C reaction temperature shows a hierarchical morphology with big at both ends but small in the middle. The as-obtained products assume sizes of ~5 μm in length, ~3 μm in big-end thickness and ~1μm in the middle thickness. From the high-magnification image (figure 1b and figure 1c), it can be found that each hierarchical structure is composed of many ordered nanoplatelets and exhibits typical mesocrystal character. The individual nanoplatelets within the mesocrystals assume sizes of ~800 nm in length and ~100 nm in thickness. The nanoplatelets are aggregated together in a side-by-side manner. Obviously, each mesocrystal could exist independently, and no obvious aggregation between the mesocrystals was observed. To elucidate the composition and the crystallinity of the mesocrystals, their XRD patterns were acquired and depicted in figure 1d. The main diffraction peaks of the hierarchical mesocrystals can be indexed to a rhombic phase of Zn(OH)$_2$ (JCPDS card No.
Based on our previous work, a possible formation mechanism for the hierarchical mesocrystals was speculated [9]. Probably, Zn(NO$_3$)$_2$ reacted with NaOH in water at most 10 °C to slowly form first the nanocrystals (clusters) of Zn(OH)$_2$. Meanwhile, ethanol adsorbed onto certain crystalline special faces of the Zn(OH)$_2$ nanocrystals and might further block the growth of the Zn(OH)$_2$ nanocrystals along certain directions leading to the formation of nanoplatelets. On the other hand, the strong interactions between the ethanol molecules on different Zn(OH)$_2$ nanoplatelets drive them to assemble head-by-head and side-by-side way to finally form the hierarchical mesocrystals to reduce the surface energy.

**Figure 1.** (a-b) SEM image of as-obtained hierarchical mesocrystals. (c) XRD patterns of the mesocrystals.

**Figure 2.** (a, b) Low-magnification and (c) high-magnification SEM image of annealed mesocrystals.

It is well known that Zn(OH)$_2$ could be easily decomposed at relatively higher temperature into H$_2$O and ZnO, which may provide more attractive properties than the Zn(OH)$_2$. Thus, the powders of Zn(OH)$_2$ mesocrystals were annealed at 200 °C in air for 4 h. Though the hierarchical morphology with big at both ends but small in the middle and the mesocrystal character of the as-prepared products were both preserved properly after annealed treatment, the surface of the platelets appeared holes which suggested that the as-obtained products have experienced the recrystallization phenomenon (figure 2). The main reason is that the nanoplatelets possess lots of defects due to crystal could not achieve the full growth [13].
The as-obtained mesocrystals are composed of pure ZnO nanoplatelets. This was further confirmed by XRD. As shown in figure 3a, all diffraction peaks can be well indexed to a wurtzite structure (hexagonal) ZnO (JCPDS card No. 36-1451) [9]. The FTIR spectra of as-obtained products showed characteristic bands at 495 cm\(^{-1}\), which is attributed to the absorption of Zn-O bond, also confirm the presence of ZnO [14]. Figure 3c represents the Raman spectrum of the samples at the range of 200 to 800 cm\(^{-1}\) at room temperature, which shows four peaks at 331, 381, 437 and 580 cm\(^{-1}\). The peak at 438 cm\(^{-1}\) corresponds to the optical E\(_{2H}\) high frequency mode, which is the common Raman active peak for wurtzite hexagonal ZnO. These peaks at 331 and 381 cm\(^{-1}\) are assigned to E\(_{2H}\)-E\(_{2L}\) mode and A\(_{1T}\) mode, respectively. The suppressed peak at 581 cm\(^{-1}\) in the spectrum is attributed as E\(_{1T}\) mode caused by impurities and defects. These results further confirm that wurtzite structure ZnO has very good crystal quality [15].

![Figure 3](image1.png)

**Figure 3.** (a) XRD patterns, (b) FT-IR spectra and (c) Raman spectra of annealed mesocrystals.

As a promising photocatalyst, ZnO has been studied for the photodegradation of some organic compounds. The MB, as a common cationic dye in textile industry, is one of the most notorious contaminants in aquatic environments owing to its huge amounts, slow biodegradation, and toxicity. In our study, the photocatalytic activity of the as-obtained ZnO hierarchical mesocrystals samples (50 mg) on the degradation of MB (initial concentration: 15 mg/L, 100 mL) under UV light irradiation was

![Figure 4](image2.png)

**Figure 4.** (a) UV-Vis absorption curves of the concentration of residual MB with different UV light irradiation time. (Inset) the color of the MB solution with different UV light irradiation time. (b) The photocatalytic efficiency curves of three photocatalytic cycles processing.
investigated. The absorption spectrum of MB solution was characterized by its characteristic absorption at 664 nm. Under dark conditions and with diffuse light 20 min, the adsorption–desorption equilibrium of methyl blue onto the ZnO mesocrystals were reach, then the light was turned on. The reaction time was scheduled to be 0, 5, 10, 20, 40 and 60 min, respectively. As shown in figure 4a, the ZnO mesocrystals samples were used for the photodecomposition of MB, and the absorption spectra decrease in intensity rapidly with the extension of exposure time. It revealed that the as-obtained ZnO mesocrystals samples exposure to UV light for 20 min resulted in over 95% degradation of MB, the concentration of MB decreased remarkably. The change in color of the MB solution was also suggested this result in the process of photocatalytic reaction (inset figure 4a). The stability and reusability of ZnO mesocrystals were studied in terms of performing the MB degradation reactions repeatedly three times. The photocatalytic efficiency of ZnO mesocrystals was preserved well (as shown in figure 4b) showing good optical stability. Additionally, the morphology and structure of the mesocrystals were well maintained during the reaction (figure 5).

Experiments also show that ZnO mesocrystals samples can be more readily separated from the slurry system by filtration or decantation after photocatalytic reaction due to their large weight and weak Brownian motion, and the solid catalyst can then be reused. After three repeated cycles of photodegradation of MB with the as-prepared ZnO, the catalyst retains its original photocatalytic activity (figure 4b), confirming ZnO mesocrystals are not photo-corroded or poisoned during the photocatalytic oxidation of the pollutant dye molecules. The most interesting point is that the morphology of the structure remains intact even after the catalysis, as shown in figure 5. The stability of a photocatalyst is important for its practical application. Therefore, the prepared hierarchical ZnO mesocrystals can be regarded as ideal photocatalysts for environmental purification on the industrial scale.

4. Conclusion
The hierarchical ZnO mesocrystals with big at both ends but small in the middle and consisted of nanoplatelets have been prepared successfully, when the aqueous solutions of the Zn(NO$_3$)$_2$ and NaOH were mixed simply in the presence of ethanol at the 10 °C reaction temperature and followed by annealed in air. It was illustrated that the as-obtained ZnO mesocrystals have good stability and
photocatalytic performance in the photodegradation of MB in water. The product exhibited the potential application of photocatalytic ability in pollutant organic compounds treatment. Given the simple and scalable production procedure, and the easy processing, we hope that the as-obtained ZnO mesocrystals may find practical application in photocatalysis and others.

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