NH$_4^+$ directed assembly of zinc oxide micro-tubes from nanoflakes

Weiyi Yang$^1$, Qi Li$^*$, Shian Gao$^1$ and Jian Ku Shang$^{1,2}$

Abstract

A simple precipitation process followed with the heat treatment was developed to synthesize ZnO micro-tubes by self-assembly of nanoflakes composed of nanoparticles. The resulting ZnO micro-tubes demonstrated excellent photocatalytic performance in degrading methylene blue (MB) under UV illumination. It was found that NH$_4^+$ ion played a critical role in directing the assembly of the nanoflakes to form the micro-tube structure. A critical reaction ratio existed at or above which the ZnO micro-tubes could be obtained. For the mixtures of solutions of (NH$_4$)$_2$CO$_3$ and zinc salt, the ratio $(C_{(NH_4)_2CO_3}/C_{Zn^{2+}})$ was 2:1.

Keywords: ZnO micro-tubes, nanoparticles, NH$_4^+$ directed growth, self-assembly

Introduction

The zinc oxide (ZnO) has been widely investigated and utilized in various technical fields, including pigments, rubber additives, gas sensors, varistors, semiconductors, optoelectronic devices, light-emitting diodes, and solar cells, due to its catalytic, electrical, optoelectronic, and photochemical properties [1]. With the development of nanotechnology, nano/micro-sized ZnO had attracted extensive research attentions over the past decade [2-30]. Abundant nanostructure morphologies exist for ZnO, such as flower-like nanostructures [5,26,30], nanorod [3,12-15,21], nanowires [4,18], nanobridges and nanonails [17], tubular microstructural [7], nano/micro-sized particles [9,11,27,28], and micro-tubes [19]. A variety of methods had been developed to synthesize various ZnO nanostructures, including chemical vapor transport and condensation (CVTC) [23], electrodeposition [24], hydrothermal synthesis [25,26], evaporation formation [27], chemical precipitation [28], and aqueous solution deposition [29]. For example, nanohelices, nanosprings, nanorings, and nanobelts had been synthesized by Kong and Wang via a solid-vapor process in 2003, which could have applications as one-dimensional nanoscale sensors, transducers, and resonators [20]. In 2006, Wang and Song synthesized ZnO nanowires array by the vapor-liquid-solid process, which has the potential of converting mechanical, vibrational, and/or hydraulic energy into electricity for powering nanodevices [21].

In this work, a simple precipitation process followed with the heat treatment was developed to synthesize ZnO micro-tube structure by self-assembly of nanoflakes composed of nanoparticles. The formation mechanism of this interesting ZnO morphology was examined by systematically investigating the effects from zinc salt type, precipitation agent concentration, precipitation environment, and precipitation agent type. The study identified a key role played by NH$_4^+$ ion in the directional growth of the micro-tube structure. A critical reactant ratio $(C_{(NH_4)_2CO_3}/C_{Zn^{2+}})$ was found at 2.0:1.0, below which no such micro-tube structure could be obtained. The photocatalytic performance of ZnO micro-tubes was demonstrated by their good photocatalytic degradation effect on MB under UV illumination. With the combination of the special catalytic, electrical, optoelectronic, and photochemical properties of ZnO and this interesting highly porous micro-tube structure, these ZnO micro-tubes may find potential applications in many technical areas.

Experimental section

Materials

Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, >99.0%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, People’s Republic of China) and zinc sulfate heptahydrate

* Correspondence: qili@imr.ac.cn
$^1$Materials Center for Water Purification, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, People’s Republic of China
Full list of author information is available at the end of the article

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(ZnSO₄·7H₂O, ≥99.5%, Kemiou Chemicals Co. Ltd., Shenyang, People’s Republic of China) were used as the zinc source, and ammonium carbonate ((NH₄)₂CO₃, NH₃% ≥40.0%, Sinopharm Chemical Reagent Co., Ltd.) and sodium carbonate (Na₂CO₃, ≥99.5%, Sinopharm Chemical Reagent Co., Ltd.) were used as the precipitation reagents in the synthesis of self-assembled ZnO micro-tubes, respectively. Methylene blue trihydrate (C₁₆H₁₈ClN₃S·3H₂O, Kemiou Chemicals Co. Ltd.) was used as the model organic pollutant for the static photocatalytic degradation experiment with ZnO micro-tubes under UV irradiation. All the reagents were of analytical grade and used as received without further purification.

**Synthesis**

ZnO micro-tubes were synthesized by a simple precipitation method. In a typical synthesis process, a metal alkoxide, Zn(CH₃COO)₂·2H₂O, was dissolved in deionized (DI) water to obtain solution #1 at the concentration of 1 M, and (NH₄)₂CO₃ was dissolved in DI water to obtain solution #2 at the concentration of 1.8 M. While the mixture was stirred vigorously during the precipitation process, 100 mL of solution #1 was dropwise added into 200 mL of solution #2. After the addition of solution #1, the mixture was kept stirring for 30 min, and then the white precipitate was collected by centrifugation, washed with DI water repeatedly until neutral pH, and dried at 60°C to approximately 70°C for a day. The final ZnO product was obtained by calcination of the precipitate at 300°C for 2 h in air. To examine the effect of zinc salt on the morphology of obtained ZnO, an inorganic zinc salt, ZnSO₄·7H₂O, was also used in this synthesis processes with the same experimental setting as Zn(CH₃COO)₂·2H₂O. To examine the precipitation reagent concentration effect on the formation of ZnO micro-tubes, (NH₄)₂CO₃ solutions with different concentrations (from 1.8 to 0.5 M) were prepared and used in the precipitation process to obtain desired C(NH₄)₂CO₃/CZn⁺⁺ ratios. The chemical addition sequence in the precipitation process was examined with both zinc salts at the C(NH₄)₂CO₃/CZn⁺⁺ ratio of 3.2:1.0 to demonstrate the precipitation environment, in which both the addition of the zinc salt concentration into the (NH₄)₂CO₃ solution and the addition of the (NH₄)₂CO₃ solution into the zinc salt solution were adopted. Na₂CO₃ was also used as the precipitation reagent to verify the effect of NH₄⁺ in the formation of ZnO micro-tubes at the C(NH₄)₂CO₃/CZn⁺⁺ ratio of 3.2:1.0 for both zinc salts under the same experimental conditions.

**Characterization**

The crystal structures of the precipitates and ZnO final products were analyzed by the D/MAX-2004 X-ray powder diffractometer (Rigaku Corporation, Tokyo, Japan) with Ni-filtered Cu (0.15418 nm) radiation at 56 kV and 182 mA. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were utilized to study their morphologies. SEM images were obtained with a SUPRA35 Field Emission Scanning Electron Microscope (Carl Zeiss NTS GmbH, Carl-Zeiss-Straße 56, 73447 Oberkochen, Germany). SEM samples were made by dispersing the precipitate or ZnO final product in ethanol, applying drops of the dispersion on a conductive carbon tape, and drying in air for 12 h. Before imaging, the sample was sputtered with gold for 120 s (Emitech K575 Sputter Coater, Emitech Ltd., Ashford Kent, UK). TEM observation was carried out on a JEOL 2010 transmission electron microscope (JEOL Ltd., Tokyo, Japan). TEM observation was carried out on a JEOL 2010 transmission electron microscope (JEOL Ltd., Tokyo, Japan) operated at 200 kV, with point-to-point resolution of 0.28 nm. TEM samples were made by dispersing the precipitate or ZnO final product on a Cu grid. The UV-vis spectrum of ZnO micro-tubes was measured on a UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan).

**Photocatalytic degradation of methylene blue**

The photocatalytic performance of ZnO micro-tubes was examined by their photodegradation of MB under UV irradiation. The initial concentration of MB aqueous solution is 1.46 × 10⁻⁵ mol/L (approximately 4.67 ppm) and a fixed concentration of 1 mg photocatalyst per milliliter. The average intensity of UV (254 nm) irradiance striking the MB solution was ca. 1.52 mW/cm², measured by a Multi-Sense UV-B UV radiometer (Beijing Normal University Photoelectricity Instrumet Plant, Beijing, China). The UV irradiation time varied from 20 to 180 min. At each time interval, ZnO micro-tubes were recovered by centrifugation at 12,600 rpm, and the light absorption of the clear solution was measured by the UV-2550 spectrophotometer. The remaining concentration of MB in the solution could be calculated by the ratio between the light absorptions of photocatalyst-treated and untreated MB solutions. For the comparison purpose, the concentration changes of MB solution were also investigated with the same experimental setup in the absence of ZnO micro-tubes and under UV light illumination, or with the presence of ZnO micro-tubes and no UV illumination.

**Results and discussion**

**ZnO micro-tubes by self-assembled nanoparticles**

Figure 1A shows the X-ray diffraction pattern of the white precipitate after the precipitation reaction between Zn(CH₃COO)₂·2H₂O and (NH₄)₂CO₃ with a molar ratio at 1.0:3.6, which demonstrates that the precipitate obtained by the precipitation reaction is crystallized Zn₄CO₃(OH)₆H₂O. The reaction could be expressed by:
The white Zn₄CO₃(OH)₆·H₂O precipitate demonstrates an interesting tube morphology at micrometer size, which is assembled by nanoflakes composed of nanoparticles (Figure 1B). These micro-tubes have a tripore structure, in which the largest pores are the tubes at micrometer size, the middle ones are the inter-nanoflake pores, and the smallest ones are the pores between nanoparticles in the nanoflakes.

To convert the white Zn₄CO₃(OH)₆·H₂O precipitate to ZnO, a heat treatment was conducted at 300°C for 2 h in air. Figure 1C shows the X-ray diffraction pattern of the white precipitate after the heat treatment, which matches well to the standard diffraction pattern of wurtzite ZnO. The average crystallite size of the hexagonal phase is approximately 13.4 nm, obtained by the

$$4Zn(CH_3COO)_2\cdot2H_2O + 4(NH_4)_2CO_3 = Zn_4CO_3(OH)_6\cdotH_2O \downarrow + 8CH_3COONH_4 + 3CO_2 \uparrow + 4H_2O \quad (1)$$

Figure 1 X-ray diffraction pattern, FESEM, and TEM images. (A) The X-ray diffraction pattern and (B) FESEM image of the white precipitate after the precipitation reaction between Zn(CH₃COO)₂·2H₂O and (NH₄)₂CO₃ with a molar ratio at 1:0.36. (C) The X-ray diffraction pattern, (D) FESEM image, and (E) TEM image of ZnO micro-tubes after the heat treatment of the precipitate in (A).
Scherrer’s formula [31]:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

Interestingly, the white ZnO final product has the similar micro-tube morphology as that of Zn₄CO₃(OH)₆·H₂O. Figure 1D, E shows the FESEM and TEM images of ZnO with different magnifications. From these observations, it is clear that the micro-tube morphology was kept during the heat treatment, while the diameter of these micro-tubes became smaller due to the contraction during the heat treatment. Thus, an interesting micro-tube structure for ZnO could be obtained by a simple precipitation process followed with the heat treatment, which has a highly porous structure and could find potential applications in many technical areas.

Effect of the type of zinc salt on ZnO structure morphology

To investigate the formation mechanism of this interesting micro-tube structure by the assembly of nanoflakes composed of nanoparticles, the zinc salt type effect was first examined. As a metal alkoxide, the acetate ions from Zn(CH₃COO)₂·2H₂O used in the precipitation process may contribute to the formation of this micro-tube structure. To clarify its role in this process, an inorganic zinc salt, ZnSO₄·7H₂O, was chosen to synthesize ZnO under the same experimental conditions. Figure 2A shows the X-ray diffraction pattern of the white precipitate after the precipitation reaction between ZnSO₄·7H₂O and (NH₄)₂CO₃ with a molar ratio at 1.0:3.6, which demonstrates that the precipitate obtained by the precipitation reaction is also crystallized Zn₄CO₃(OH)₆·H₂O. The reaction could be expressed by:

\[ 4\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 4(\text{NH}_4)_2\text{CO}_3 = 4\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O} \downarrow + 4(\text{NH}_4)_2\text{SO}_4 + 3\text{CO}_2 \uparrow + 24\text{H}_2\text{O} \]  

The white Zn₄CO₃(OH)₆·H₂O precipitate obtained from ZnSO₄·7H₂O also demonstrates the similar tube morphology at micrometer size assembled by nanoflakes composed of nanoparticles (Figure 2B). After the heat treatment, similar highly crystallized ZnO micro-tubes were also obtained (Figure 2C, D), although no acetate ions were involved in this synthesis process. No obvious

Figure 2 X-ray diffraction pattern and FESEM images (A) The X-ray diffraction pattern and (B) FESEM image of the white precipitate after the precipitation reaction between ZnSO₄·7H₂O and (NH₄)₂CO₃ with a molar ratio at 1.0:3.6. (C) The X-ray diffraction pattern and (D) FESEM image of ZnO micro-tubes after the heat treatment of the precipitate in (A).
difference was observed on the crystal structure and morphology of the obtained ZnO final product. Thus, the type of zinc salts (organic or inorganic) is not the determining factor on the formation of ZnO micro-tubes.

Precipitation reagent concentration effect on ZnO structure morphology

From the above analysis, the precipitation reagent used in our experiment, (NH₄)₂CO₃, should be the determining factor in the formation of ZnO micro-tubes. To clearly demonstrate its effect, the morphology evolution of ZnO was investigated with the decrease of (NH₄)₂CO₃ to Zn(CH₃COO)₂·2H₂O/ZnSO₄·7H₂O molar ratio in the precipitation reaction, and the results were summarized in Table 1. From Table 1, a critical \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio exists at approximately 2.0:1.0 for the use of either Zn(CH₃COO)₂·2H₂O or ZnSO₄·7H₂O. When the \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio is at or over 2.0:1.0 (up to 3.6:1.0 in current work), ZnO exhibited this interesting micro-tube structure. Below this critical ratio, no micro-tube structure could be obtained. Irregular agglomerated ZnO nanoparticles were obtained when \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) was 1.6:1.0 or 1.2:1.0. When the \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio was 1.0:1.0, ZnO exhibited a sphere-like structure composed of nanoflakes similar to what Wang and Muhammed reported before [26]. Representative FESEM images of these ZnO structures are shown in Figure 3 (with Zn(CH₃COO)₂·2H₂O) and Figure 4 (with ZnSO₄·7H₂O) with the \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio at 2.4:1.0, 2.0:1.0, 1.6:1.0, and 1.0:1.0, respectively, which clearly demonstrated the ZnO structural evolution with the decrease of \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio.

Effect of the precipitation environment on ZnO structure morphology

To further explore the formation mechanism of ZnO micro-tubes, the effect of chemical addition sequence in the precipitation process was examined. Figure 5A shows the FESEM image of ZnO structure obtained at the \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio of 3.2:1.0 when the addition of the Zn(CH₃COO)₂·2H₂O solution into the (NH₄)₂CO₃ solution was adopted in the precipitation process. ZnO micro-tubes self-assembled by ZnO nanoparticles were obtained. However, when the addition of the (NH₄)₂CO₃ solution into the Zn(CH₃COO)₂·2H₂O solution was adopted in the precipitation process, no micro-tube structures were obtained even with the same \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio of 3.2:1.0 (Figure 5B). Similar result was observed with the use of ZnSO₄·7H₂O in this process as demonstrated in Figure 5C, D. Thus, ZnO micro-structure could not be obtained without a (NH₄)₂CO₃-rich environment, no matter which zinc salt was used in the precipitation process.

Effect of the ammonium existence on ZnO structure morphology

Another precipitation agent, Na₂CO₃, was used to further examine the formation mechanism of ZnO micro-tubes in our study. Figure 6A shows the FESEM image of ZnO structure obtained at the \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratio of 3.2:1.0. The addition of the Zn(CH₃COO)₂·2H₂O solution into the Na₂CO₃ solution was adopted in the precipitation process, which provides a Na₂CO₃-rich environment. From Figure 6A, irregular agglomerated ZnO nanoparticles were obtained under such experimental conditions, and no micro-tube structure was obtained. Similar result was observed with the use of ZnSO₄·7H₂O in this process as demonstrated in Figure 6B. Thus, ZnO micro-tubes could be obtained with (NH₄)₂CO₃ as the precipitation reagent with proper \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) ratios, while a similar carbonate precipitation reagent Na₂CO₃ could not produce ZnO micro-tubes.

In the precipitation process, \( \text{CO}_3^{2-} \) ion is one of the key components to produce \( \text{Zn}_4\text{CO}_3(\text{OH})_6\cdot\text{H}_2\text{O} \) precipitate, which could then be converted to ZnO by the heat treatment. To form the micro-tube structure, however, \( \text{CO}_3^{2-} \) ion shows little effect. The experimental result here suggests that \( \text{NH}_4^+ \) ion is the key factor in the formation of this micro-tube structure. Otherwise, the usage of Na₂CO₃ as the precipitation agent

| \( C_{\text{NH}_4\text{CO}_3}/C_{\text{Zn}^{2+}} \) | Zn(CH₃COO)₂·2H₂O | ZnSO₄·7H₂O |
|-----------------|----------------------|----------------------|
| 3.6:1.0         | Micro-tubes          | Micro-tubes          |
| 3.2:1.0         | Micro-tubes          | Micro-tubes          |
| 2.8:1.0         | Micro-tubes          | Micro-tubes          |
| 2.4:1.0         | Micro-tubes          | Micro-tubes          |
| 2.0:1.0         | Micro-tubes          | Micro-tubes          |
| 1.6:1.0         | Irregular agglomerated particles | Irregular agglomerated particles |
| 1.2:1.0         | Irregular agglomerated particles | Irregular agglomerated particles |
| 1.0:1.0         | Sphere-like microstructures consisted of nanoflakes | Sphere-like microstructures consisted of nanoflakes |
should also result in the formation of micro-tube structure as (NH₄)₂CO₃ did. Thus, a possible mechanism could be proposed for the formation of these micro-tubes assembled by nanoflakes composed of nanoparticles based on the above experiment results. In the precipitation process, large amounts of NH₄⁺ ions exist in the reaction mixture, which do not chemically participate in the formation of the Zn₄CO₃(OH)₆·H₂O precipitate. As suggested by Wang and Muhammed [28], NH₄⁺ ions could adsorb onto Zn₄CO₃(OH)₆·H₂O nanoparticles just precipitated from the reaction mixture, form a monolayer on the surface of these nanoparticles, and hold the nanoparticles together by H-bonding. In their work, they observed that rod-shaped particles consisting of several spherical particles aligned in one direction. Here, the interaction between NH₄⁺-coated Zn₄CO₃(OH)₆·H₂O nanoparticles form nanoflakes first, and the interaction between NH₄⁺-coated Zn₄CO₃(OH)₆·H₂O nanoflakes bonds the nanoflakes together in one direction and produce micro-tube structures by self-assembly. This proposed mechanism could explain the huge difference observed on the precipitate morphology by the chemical addition sequence. When the Zn(CH₃COO)₂·2H₂O solution was dropwise added into the (NH₄)₂CO₃ solution, plenteous NH₄⁺ ions existed that could adsorb onto Zn₄CO₃(OH)₆·H₂O precipitate to cover its surface and direct the formation of micro-tube morphology. When the (NH₄)₂CO₃ solution was dropwise added into the Zn(CH₃COO)₂·2H₂O solution, however, not enough NH₄⁺ ions existed that could adsorb onto Zn₄CO₃(OH)₆·H₂O precipitate to cover its surface. Thus, the directional growth of Zn₄CO₃(OH)₆·H₂O was not achievable and no micro-tube structure was obtained.

**Light absorbance property and photocatalytic performance of ZnO micro-tubes**

The optical property of ZnO micro-tubes was investigated by measuring their diffuse reflectance spectra.
From the reflectance data, optical absorbance can be approximated by the Kubelka-Munk function, as given by Equation 4:

\[
F(R) = \frac{(1 - R)^2}{2R}
\]

where \( R \) is the diffuse reflectance [32]. Figure 7A shows the optical absorbance spectrum of ZnO micro-tubes, which demonstrates that these ZnO micro-tubes have a strong absorption when light wavelength is < 400 nm. The insert image in Figure 7A shows the Tauc Plot [32] \( (F(R)h\nu)^n \text{vs} \ h\nu \) constructed from Figure 7A in order to determine the band gap of ZnO micro-tubes. As a direct band gap semiconductor, \( n \) equals 0.5 for ZnO. Extrapolation of this line to the photon energy axis yields the semiconductor band gap of these ZnO micro-tubes at 3.18 eV, which is slightly smaller than the band gap of ZnO powders at 3.37 eV. The red-shift of the light absorption of these ZnO micro-tubes may be attributed to their special micro-tube morphology.

Similar observation had been reported on TiO\(_2\) with a nanotube morphology [33].

The light absorption spectrum suggests that these ZnO micro-tubes may have a good photocatalytic performance under UV irradiation. The photocatalytic activity of these ZnO micro-tubes was investigated by its degradation effect on MB under UV irradiation. Figure 7B summarizes the residue MB concentration as a function of treatment time for three different treatments. When MB solution was under UV illumination without the addition of ZnO micro-tubes, no significant degradation could be observed. With the addition of ZnO micro-tubes, significant degradation still could not be observed when there was no UV illumination. This observation suggests that adsorption of MB will not contribute much to its concentration changes during the photocatalytic degradation treatment. Under UV light illumination, however, photodegradation of MB was clearly observed with the treatment of ZnO micro-tubes. After 3 h of treatment under UV illumination, the color
Figure 5 The FESEM images of ZnO nanostructures obtained at the $\frac{C_{(NH_4)_2CO_3}}{C_{Zn^{2+}}}$ ratio of 3.2:1.0. (A) Zn(CH$_3$COO)$_2$·2H$_2$O solution was added into (NH$_4$)$_2$CO$_3$ solution, and (B) (NH$_4$)$_2$CO$_3$ solution was added into the Zn(CH$_3$COO)$_2$·2H$_2$O solution. (C) ZnSO$_4$·7H$_2$O solution was added into (NH$_4$)$_2$CO$_3$ solution, and (D) (NH$_4$)$_2$CO$_3$ solution was added into ZnSO$_4$·7H$_2$O solution.

Figure 6 FESEM images of ZnO nanostructures obtained with the $\frac{C_{(NH_4)_2CO_3}}{C_{Zn^{2+}}}$ ratio of 3.2:1.0. From the precipitation reaction between (A) Zn(CH$_3$COO)$_2$·2H$_2$O and Na$_2$CO$_3$, and (B) ZnSO$_4$·7H$_2$O and Na$_2$CO$_3$. 

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of the MB solution changed from blue to almost colorless, and the concentration of residue MB was determined to near zero. From the comparison of these three treatments, it is clear that these ZnO micro-tubes have a good photocatalytic activity under UV illumination.

Conclusions
ZnO micro-tube structure was synthesized by a simple precipitation process followed with heat treatment. The micro-tube was formed by self-assembly of nanoflakes of ZnO nanoparticles, creating a highly porous structure. The formation mechanism of ZnO micro-tube structure was investigated, and the key role of NH₄⁺ ion in the directional growth of this micro-tube structure was demonstrated. A critical reactant ratio ($C_{(NH_4)CO_3}/C_{Zn^{2+}}$) was found at 2.0:1.0, below which no such micro-tube structure could be obtained. These ZnO micro-tubes demonstrated a good photocatalytic degradation effect on MB under UV illumination and could find potential applications in many technical areas.

Acknowledgements
This study was supported by the National Basic Research Program of China, Grant No. 2006CB601201, the Knowledge Innovation Program of Chinese Academy of Sciences, Grant No. Y0NS711171, and the Knowledge Innovation Program of Institute of Metal Research, Grant No. Y0NSA111A1.

Author details
1Materials Center for Water Purification, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, People’s Republic of China 2Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

Authors’ contributions
WY carried out the synthesis, characterization, and photodegradation experiments, and participated in the preparation of the manuscript. QL conceived of the study, participated in its design and coordination, and wrote the manuscript. SG participated in the synthesis experiment. JKS participated in the design of the study and the preparation of the manuscript. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

Received: 3 June 2011 Accepted: 11 August 2011
Published: 11 August 2011

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Cite this article as: Yang et al. NH4+ directed assembly of zinc oxide micro-tubes from nanoflakes. Nanoscale Research Letters 2011 6:491.

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