Electronic Supplementary Information for

Facile Synthesis of High Crystalline ZnO Nanorods with Controlled Aspect Ratios and Their Optical Properties

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Materials, Methods, and Characterizations

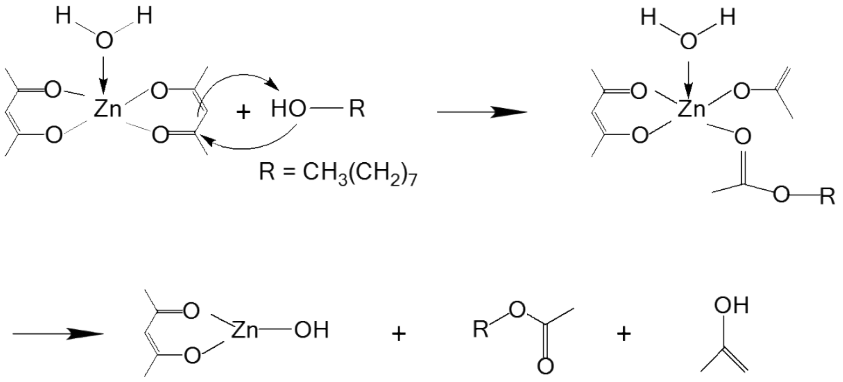
1. Chemicals

Zinc (II) acetylacetonate hydrate ($Zn(acac)_2 \cdot xH_2O$), 1-octyl alcohol (≥99%), octanoic acid (≥99%), and octylamine (99%) were purchased from Sigma-Aldrich. Ethanol (99.5%) and toluene (99.5%) were purchased from Daejung Chemicals. All the chemicals were used as received.

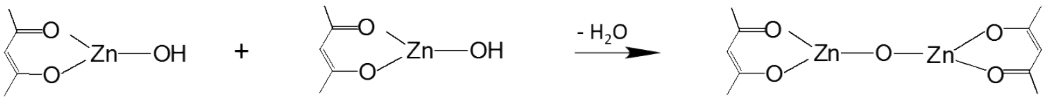
2. Standard protocol for a gram-scale synthesis of ZnO nanorods

A typical synthesis of ZnO nanorods was conducted by heating the mixture of 1 g $Zn(acac)_2 \cdot xH_2O$ and 10 mL 1-octyl alcohol at 150 ^oC for 1 h under vigorous stirring under air atmosphere. The resulting white suspension was cooled to the room temperature, then 10 mL of toluene and 30 mL of ethanol were added to precipitate the product. The ZnO nanorods were collected by centrifugation at 3000 rpm for 10 min and then re-dispersed in toluene for further use. The proposed sequence of reaction steps leading to the formation of ZnO clusters can be shown in Scheme S1.

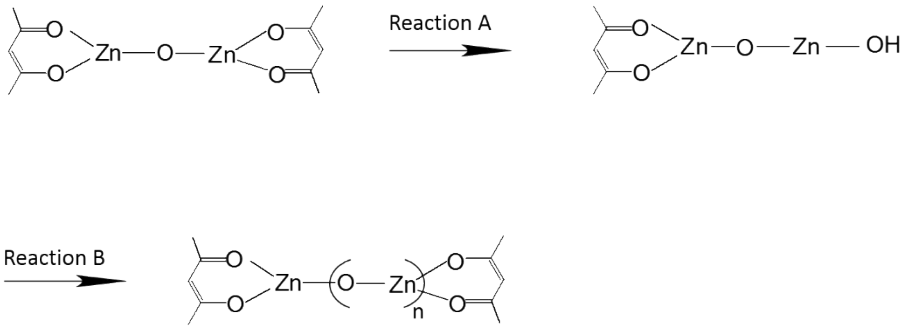
A. Substitution (Hydroxylation)



B. Dehydration-Condensation



C. Cycles of reaction A and B



Scheme S1 Reaction mechanism for the formation of Zn-O cluster: (A) formation of the Zn hydroxyl species and (B) its dehydration, and (C) the formation of the ZnO cluster by a number of cycles of A and B.

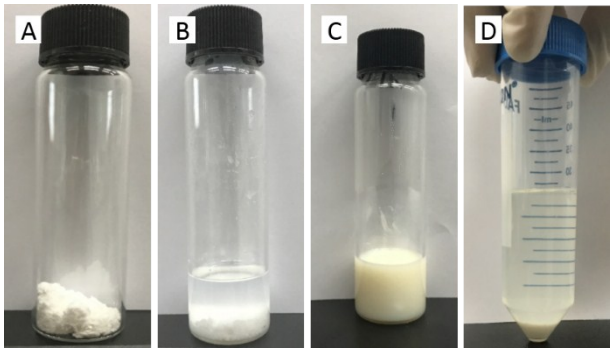


Fig. S1 Photographs of reaction vials containing (A) $Zn(acac)_2 \cdot xH_2O$ powder, (B) a mixture of $Zn(acac)_2 \cdot xH_2O$ in 1-octyl alcohol, and (C) white suspension of ZnO after the reaction, and a conical tube containing (D) ZnO precipitates after the centrifugation.

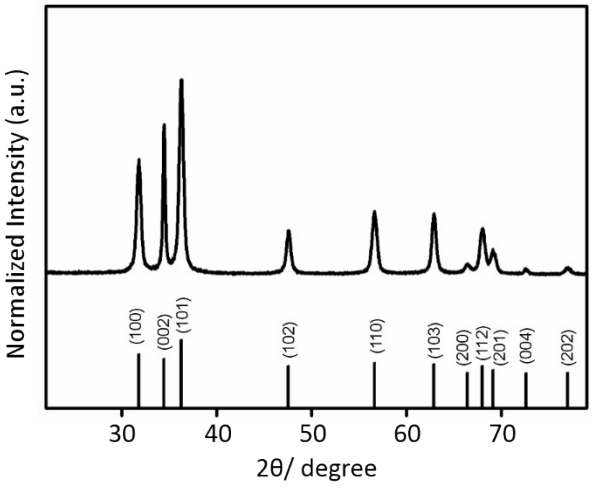


Fig. S2 An XRD pattern of ZnO nanorods synthesized in a standard protocol. The intensity and position for ZnO reference (bottom) were taken from the JCPDS database (JCPDS #36-1451).

2.1 Synthesis of ZnO nanorods using octylamine

ZnO nanorods were synthesized by heating the mixture of 1 g $Zn(acac)_2 \cdot xH_2O$, 1 mL octylamine, and 9 mL 1-octyl alcohol at 150 °C for 1 h under vigorous stirring under air atmosphere. The work-up process is similar to the standard protocol. The proposed chemical reactions leading to the formation of Zn^{2+}-amine complexes in the presence of octylamine (RNH_2, R = C_8H_{17}) are as follows;

$$RNH_2 + H_2O \rightarrow ROH + NH_3 \quad \text{(Eq. S1)}$$

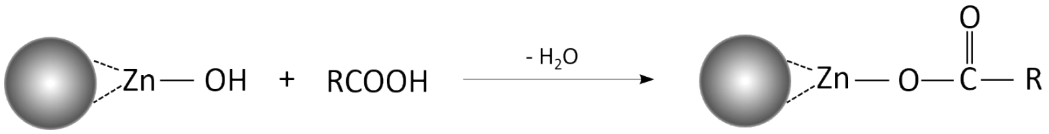
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad \text{(Eq. S2)}$$

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \quad \text{(Eq. S3)}$$

Scheme S2 Proposed surface modification of ZnO with octylamine.

2.2 Synthesis of ZnO nanorods using octanoic acid

ZnO nanorods were synthesized by heating the mixture of 1 g $Zn(acac)_2 \cdot xH_2O$, 1 mL octanoic acid, and 9 mL 1-octyl alcohol at 150 ^oC for 1 h under vigorous stirring under air atmosphere. The work-up process is similar to the standard protocol.



Scheme S3 Proposed surface modification of ZnO with octanoic acid.

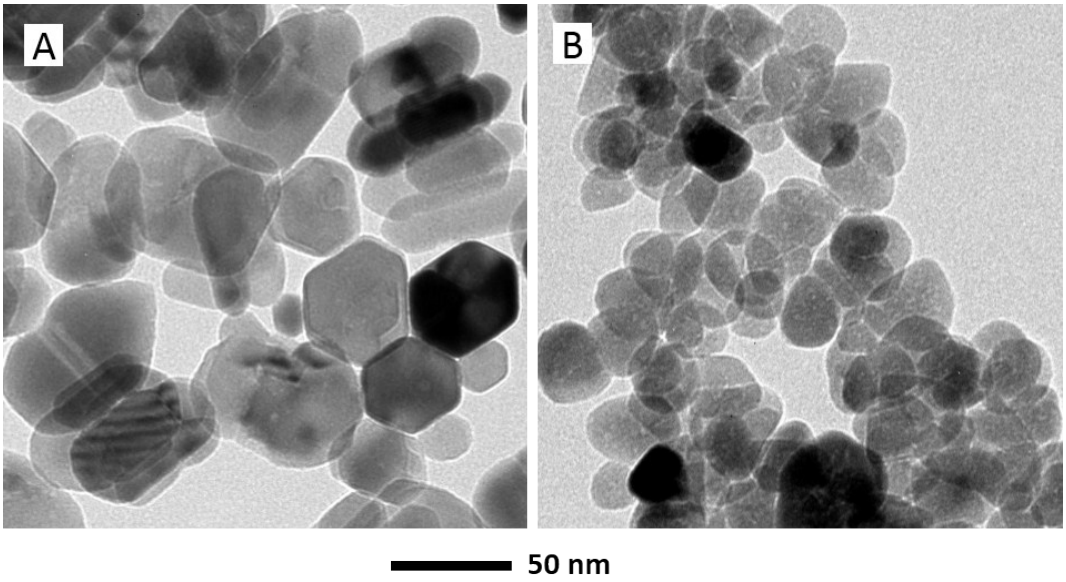


Fig. S3 TEM images of ZnO nanoparticles synthesized by adding (A) 5 mL of octylamine and (B) 1 mL of octanoic acid in the standard protocol.

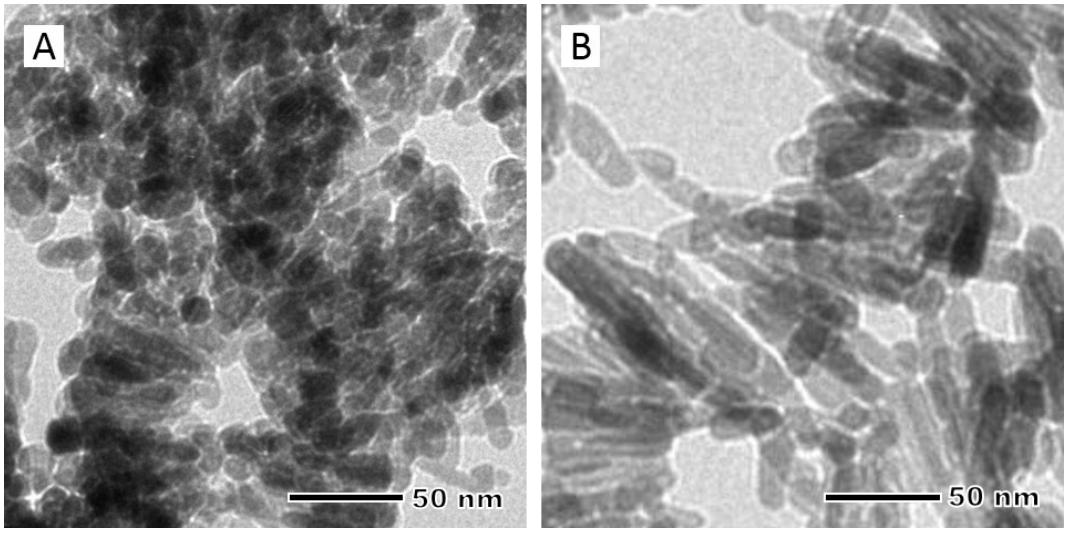


Fig. S4 TEM images of ZnO nanorods obtained at different reaction temperatures of (A) 100 and (B) 130 ^{o}C.

3. Morphological and structural characterizations

TEM images were taken using a JEOL JEM-2100 microscope operated at 200 kV by drop casting the nanoparticle dispersions on carbon–coated copper grids and drying under ambient conditions. The crystal phase of ZnO nanocrystals was characterized by powder XRD using a Bruker AXS D8 ADVANCE diffractometer equipped with a Linxeye 1-D detector (Bruker AXS GmbH). The UV/Vis spectra were measured using a JASCO V-530 UV/Vis spectrophotometer with a scanning wavelength from 250 to 800 nm. The photoluminescence spectra were obtained by exciting the samples with 325 nm photons using a HeCd laser, and the luminescence was detected using a PMT that was attached to a monochromator with a focal length of 500 mm (LabRAM HR-800).

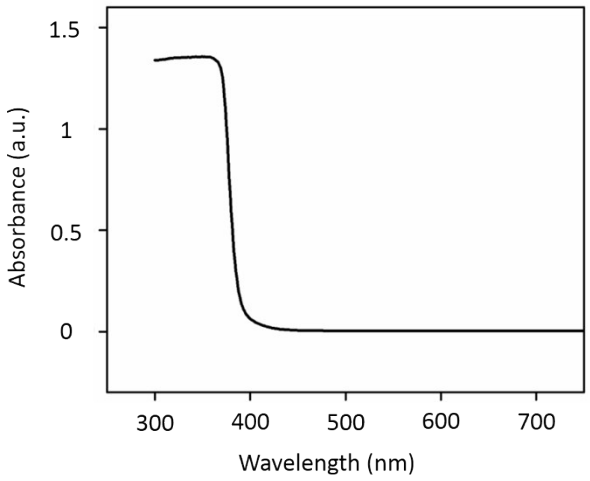


Fig. S5 UV-Vis spectrum for bulk ZnO powder.

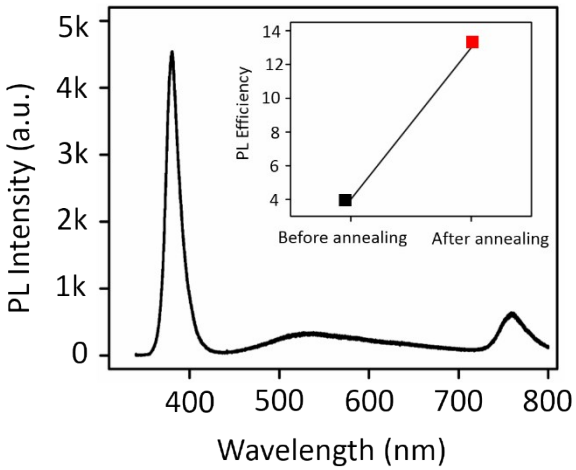


Fig. S6 PL spectrum of ZnO nanorods with aspect ratio of 5.9 after annealing at 300 ^{o}C with the inset showing the PL efficiency.