Electronic Supporting Information for:

**Uniform ZnO Nanorods Derived from the Lithium Ions as Growth Controlling Agent in Non-aqueous Medium**

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**Experimental Section**

**Chemicals:** Oleylamine (OM; >70%, Aldrich), 1-Octadecene (ODE; >95%, Fluka), Zinc acetate dihydrate (Zn(OAc)₂·(H₂O)₂; AR, Sinopharm Chemical Reagent Company), Lithium hydrate (LiOH; AR, Sinopharm Chemical Reagent Company), Lithium acetate (LiOAc; AR, Shanghai Jinghua Bio-tech Co., Ltd.), Lithium carbonate (Li₂CO₃; AR, Sinopharm Chemical Reagent Company), Sodium carbonate (Na₂CO₃; AR, Sinopharm Chemical Reagent Company), Potassium carbonate (K₂CO₃; AR, Sinopharm Chemical Reagent Company), ethanol (AR), cyclohexane (AR). All chemicals were used as received without further purification. All the nanocrystals were synthesized by using standard air-free procedures.

**Synthesis of uniform ZnO nanorods:** A typical procedure is described as follows: a given amount of Zn(OAc)₂·(H₂O) (1 mmol) was added into 10 mmol of OM and 20 mmol of ODE as solvent, in a three-necked flask (100 mL) at room temperature. Then, the slurry was heated to 100 °C to remove water and oxygen with vigorous magnetic stirring under vacuum for several minutes in a temperature-controlled electromantle, and thus form an optically transparent solution. The resulting mixture was heated to 160 °C under argon protection, then, a suitable amount of alkali metal salts (one of LiOAc, LiOH, Li₂CO₃, Na₂CO₃, K₂CO₃) dispersed in 10 mmol of OM was injected into the solution. After that, the solution was heated to a temperature to 310 °C at a heating rate of 15 °C/min and kept for 60 min under argon atmosphere. After cooling to room temperature, the nanocrystals were precipitated by adding an excess amount of the absolute ethanol into the reacted solution, followed by washing with ethanol and cyclohexane, drying in air at 60 °C. The as-formed nanocrystals were easily redispersed in various apolar organic solvents (e.g. cyclohexane). The yields of all the obtained nanocrystals were about 65–75%.

**Instrumentation.** The X-ray diffraction (XRD) patterns were recorded on a D/MAX-3 (Japan) diffractometer with a slit of 1/2° at a scanning rate of 4° min⁻¹, using Cu Kα radiation (λ= 1.5406 Å) in the range of 20–80°. Samples for transmission electron microscopy (TEM) and scanning electron microscopy (SEM, Hitachi S-570, Japan) analysis were prepared by drying a drop of nanocrystal dispersion in cyclohexane on amorphous carbon-coated copper grids. Particle sizes, shapes, and high-resolution TEM (HRTEM) characterization was performed with a Philips Tecnai F20 (FEG-TEM, USA) operated at 200 kV. The Uv-Vis absorption spectra of the nanocrystals were obtained on a Perkin Elmer/Lambda 40 Uv-Vis spectrometer (USA) (the nanocrystals dispersions were filled into a quartz cell (1 cm path length), and pure cyclohexane...
The metal contents in the nanocrystals were determined by a Leeman Labs Profile spec (USA) inductively coupled plasma atomic emission spectrometer (ICP-AES). Room-temperature Raman spectra of the samples were collected on a Jobin Yvon Raman Lab RAM HR800 spectrometer (France) excited with Ar⁺ 488 nm and He-Cd 325 nm laser beams equipped with a grating of 2400 grooves/mm, an Olympus BX41 microscope (50 objective lens) and a charge-coupled device detector. FTIR spectra of the samples (prepared by directly depositing some of the product solutions in cyclohexane onto a KBr wafer) were obtained with a EQUINOX-55 spectrophotometer (Germany). Room-temperature photoluminescence fluorescence spectra of the nanocrystals were recorded on a Jobin Yvon Raman Lab RAM HR800 spectrometer excited with the He-Cd 325 nm laser beams.

**Fig. S1** XRD patterns of pure ZnO nanoparticles and ZnO nanorods with different amount of LiOAc as growth agent in the reaction medium.
Fig. S2 Raman spectra of the as-obtained ZnO nanorods excited with (a) Ar⁺ 488 nm and (b) He-Cd 325 nm lasers. In Figure S2(a), the Raman peak at 433 cm⁻¹ is attributed to the ZnO nonpolar optical phonons of high-E₂ mode, which is one of the typical peaks of wurtzite ZnO.¹ The band at 327 cm⁻¹ is assigned to the overtone of A₁, the bands at 584 cm⁻¹ corresponds to E₁ symmetry with LO modes. When excited with He-Cd 325 nm laser beam, the Raman spectrum consists of four bands with frequency shifts at multiples of the 1LO zone-center with frequency of 580 cm⁻¹ (Figure 2(b)). The other three resonance bands are observed at 1140, 1710, and 2296 cm⁻¹ in turn, which are attributed to typical multiphonon processes.² It should be pointed out that there is no detectable signal corresponding to any other lithium species in the Raman spectra, the nanocrystals keep the same structure as the ZnO.³

Table 1 ICP (Inductively Coupled Plasma Atomic Emission Spectrometry) data of as-obtained ZnO nanorods with different amount injections of LiOAc precursor, indicating the absence of the lithium ions in the material after its washing using deionized water.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Li/Zn (molar ratio)</th>
<th>ICP results</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn (µg/ml)</td>
</tr>
<tr>
<td>ZnO: 5%mol Li</td>
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<td>176</td>
</tr>
<tr>
<td>ZnO: 10%mol Li</td>
<td>10%</td>
<td>216</td>
</tr>
<tr>
<td>ZnO: 15%mol Li</td>
<td>15%</td>
<td>112</td>
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**Fig. S3** TEM images of ZnO nanorods obtained from the injection different amount of LiOAc (a) 0.05 and (b) 0.10 mmol LiOAc into 1 mmol Zn(OAc)$_2$·(H$_2$O)$_2$ and OM/ODE solvents for reaction 1 h at 310 °C, the as-obtained ZnO nanorods have the sizes of (106.2±17.3) nm × (39.7±3.6) nm for 0.05 mmol LiOAc and (102.4±21.3) nm × (30.7±3.0) nm for 0.10 mmol LiOAc, respectively.

**Fig. S4** FTIR spectra (EQUINOX-55) of Zn(OAc)$_2$·(H$_2$O)$_2$, OM/ODE solvents, and as-prepared ZnO (15%LiOAc) nanorods dispersed in cyclohexane. The presence of strong acyclic C-H stretching at 2930 cm$^{-1}$ and 2860 cm$^{-1}$ in ZnO (15%LiOAc) nanorods indicated the existence of OM. The C=O asymmetric stretching mode in Zn(OAc)$_2$ at 1447 cm$^{-1}$ shifted slightly to 1457 cm$^{-1}$ by ~10 cm$^{-1}$ when OM was added to from ZnO (15%LiOAc) nanorods. We believed this was an indication of the formation of an intermediate Zn(OAc)$_2$–OM complex. Additionally, the two peaks at 1378 and 1635 cm$^{-1}$ in the IR spectrum of ZnO (15%LiOAc) nanorods were attributable to C-N stretch of OM, respectively. Based on the IR analysis of ZnO (15%LiOAc) nanorods, it was confirmed that these ZnO (15%LiOAc) nanorods were possibly coated by OM organic molecule.$^4$
Fig. S5 TEM images of ZnO nanoparticles when using (a) Na$_2$CO$_3$ and (b) K$_2$CO$_3$ as growing agents in OM/ODE solvents.

Fig. S6 Structural model of ZnO polar structure (red: Zn, gray blue: O).
Fig. S7 Plot of the electrical resistance as a function of temperature, as obtained during heating to given temperatures at a slow heating rate. Herein, we used a multimeter to probe the electrical conductance of the reaction solution, and then, to monitor the dissolving process of lithium precursors (here: LiOAc) in OM solvent, with two Pt electrodes directly immersed in the solution. The solutions were classified as follows: highly conductive for resistance $R<15$ MW, and nonconductive for $R>200$ MW. Figure S7 shows that the resistance of the solution decreased gradually with increasing temperature, meaning that Li$^+$ ions were released in the OM solvent at elevated temperatures.

References:


