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## Zinc Oxide Nanostructures Derived from a Simple Solution Method for Solar Cells and LEDs

Periyayya Uthirakumar\* and Chang-Hee Hong

*School of Semiconductor Science and Chemical Technology, Semiconductor Physics Research Center, Chonbuk National University, Chonju 561-756, South Korea.*

\* Corresponding author: Tel: +82-63-270-3928; Fax: +82-63-270-3585.

E-mail: [uthirakumar@gmail.com](mailto:uthirakumar@gmail.com).

**Abstract :** A simple solution method has been proposed in which the specific impacts of solvent characteristics on the growth of zinc oxide (ZnO) nanoparticles were revealed. The particles aggregation is a major drawback in hydrothermal method that was greatly suppressed in relatively less polar reaction solvents. As for as application is concern, highly dispersible ZnO nanomaterials was subjected to be used as an active material for dye sensitized solar cell (DSSC), due to their higher internal surface area. Also, the deposition of ZnO nanomaterials layers on the commercially available blue/green light emitting diodes (LEDs) were fabricated to improve the light extraction efficiency, without disturbing the basic structure of LED.

### 1. Introduction :

Nanomaterials have attracted a great deal of attention due to the unique physical properties, owing to their size effect, and their promising application in nanoscaled devices. Due to its large bandgap, ZnO is an excellent semiconductor material for applications considered for other wide bandgap materials such as GaN and SiC. In addition to this, due to the extreme large exciton binding energy, the exciton in ZnO is thermally stable at room temperature than other semiconductor materials like GaN (25 meV) and ZnSe (22 meV), and thus ZnO (about 60 meV) has significant advantages in optoelectronic applications such as for ultraviolet (UV) lasing, UV photonic devices, sensors and piezoelectric devices etc [1-3]. In order to compete with conventional solid state processes, much attention has to be given to prepare micron to nano-scaled ZnO particles in various synthetic routes, such as hydrothermal methods [4,5] and solution method [6-9]. Such routes are attractive because of their mild synthetic conditions, low cost, and ease of mass production. Among them, a simple and effective method to obtain very fine nanomaterials could be the better alternative for the future applications. In advance, selecting a cheap precursor with relatively a low operating temperature may

further tune to simplify the nanomaterial synthesis. Hence, we are intentionally working in this field to optimize a simple and effective technique to synthesize very fine and individual ZnO nanoparticles.

## 2. Experimental :

In the typical procedure, 50 mg of zinc acetate dihydrate was dissolved completely in 25 ml of methanol, using ultra-sonication at room temperature. The clear transparent solution was diluted with equal volume of (25 ml) of *p*-Xylene and heated to 60 °C. The reaction was continued for about 10 hrs, white ZnO particles were slowly crystallized, filtered and washed with excess methanol for at least three times to remove the starting materials or impurities, if any, and dried at 120°C. Similarly, the other non-polar hydrocarbon solvents such as *n*-Hexane, Ether were used in place of *p*-Xylene to investigate the specific impacts of solvent characteristics on the growth of ZnO nanostructures. The details about solvent characteristics were summarized in Table 1.

Table 1. Summarized reaction recipes and their morphologies of isolated ZnO particles.

Sample code	ZnHe	ZnXy	ZnEt
Primary solvent	Methanol	Methanol	Methanol
Co-solvent	<i>n</i> -Hexane	<i>p</i> -Xylene	Diethyl ether
Total volume (ml)	25 + 25	25 + 25	25 + 25
Polarity index of solvents	5.1 + 0	5.1 + 2.5	5.1 + 2.8
Average polarity index	2.6	3.8	4.0
Water miscibility (%)	0.001	0.02	6.9
Extent of aggregation	No	No	No
Morphology	Snowflake-like	Sphere-like	Cage-like

## 3. Results and discussion :

Water immiscible non-polar hydrocarbon solvents such as *n*-Hexane, *p*-Xylene and Ether, was diluted with a polar solvent (methanol), to reduce the average polarity of the medium to 2.6, 3.8 and 4.0 in ZnHe, ZnXy, ZnEt, respectively. Fig. 1 shows the high magnified FESEM and TEM images of ZnO nanoparticles of ZnXy. The FESEM pictures clearly show the uniform size distribution of ZnO nanoparticles. Most of the crystals are found to be individual particles rather than agglomerated particles in Fig. 1(a). The average particle size is approximately measured to be around 15 nm. This was further confirmed by the TEM images, as shown in Fig. 1(b-c). The lattice resolved HRTEM image explores that there is no crystalline defects such as dislocations and stacking faults were present in the ZnO nanoparticles, as shown in Fig. 1(c). The spacing between the adjacent lattice planes is 0.26 nm, corresponding to the distance between two (0 0 0 2) crystals planes [10].

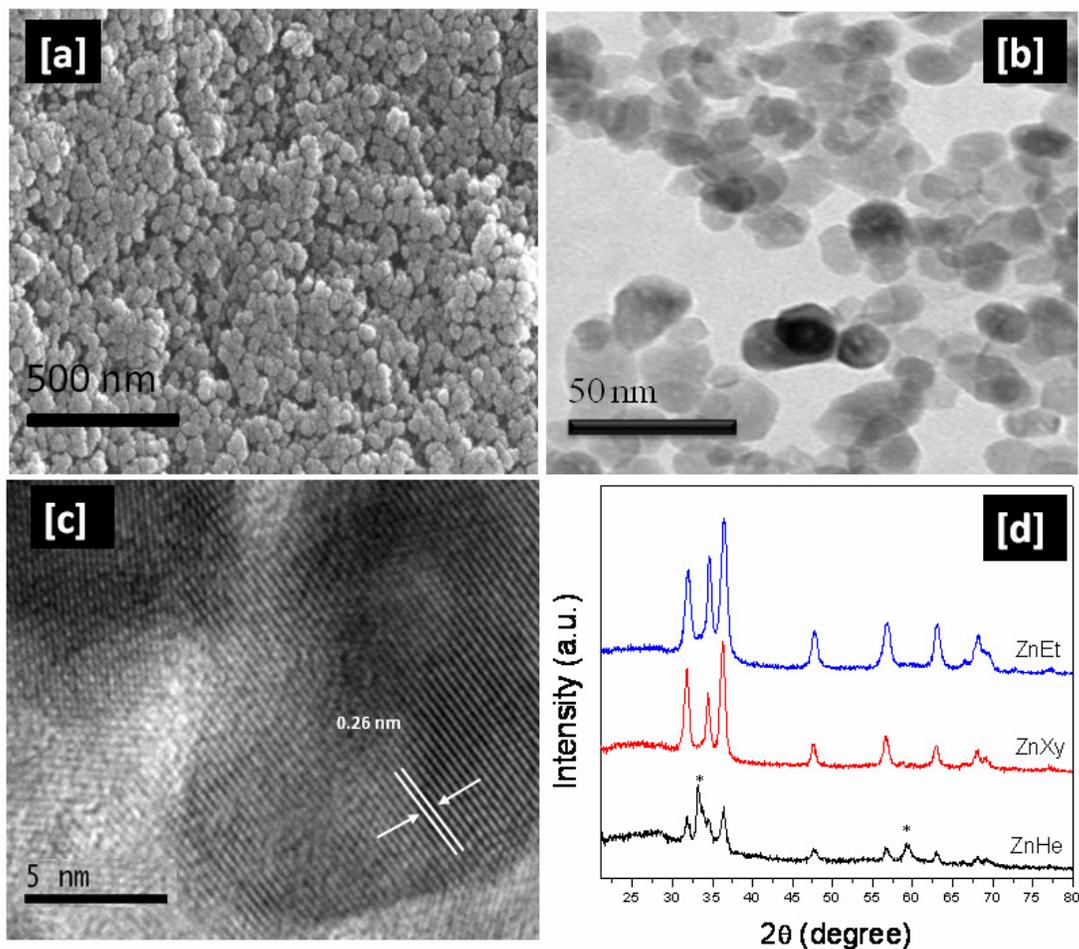


Figure 1. (a) FESEM, (b) TEM and (c) HRTEM images of ZnO nanoparticles isolated from ZnXy. XRD spectra of ZnO particles isolated from ZnHe, ZnXy and ZnEt (d).

Fig. 1(d) depicts the X-ray diffraction spectra of the ZnO particles crystallized with respect to different non-polar hydrocarbon solvent mixture. No typical diffraction peaks corresponding to other impurities have been found in ZnXy and ZnEt samples. However, a couple of new peaks were appeared in ZnHe, which corresponds to ZnO intermediates  $[Zn_5(OH)_8(CH_3COO)_2]$ , as indicated by a star mark in Fig. 1(d) [7]. The appearance of ZnO intermediate peaks is probably resulted from an incomplete decomposition of zinc acetate precursor, due to the combined effect of lesser polarity index of the reaction medium and immiscibility between the reaction solvents (methanol and n-hexane).

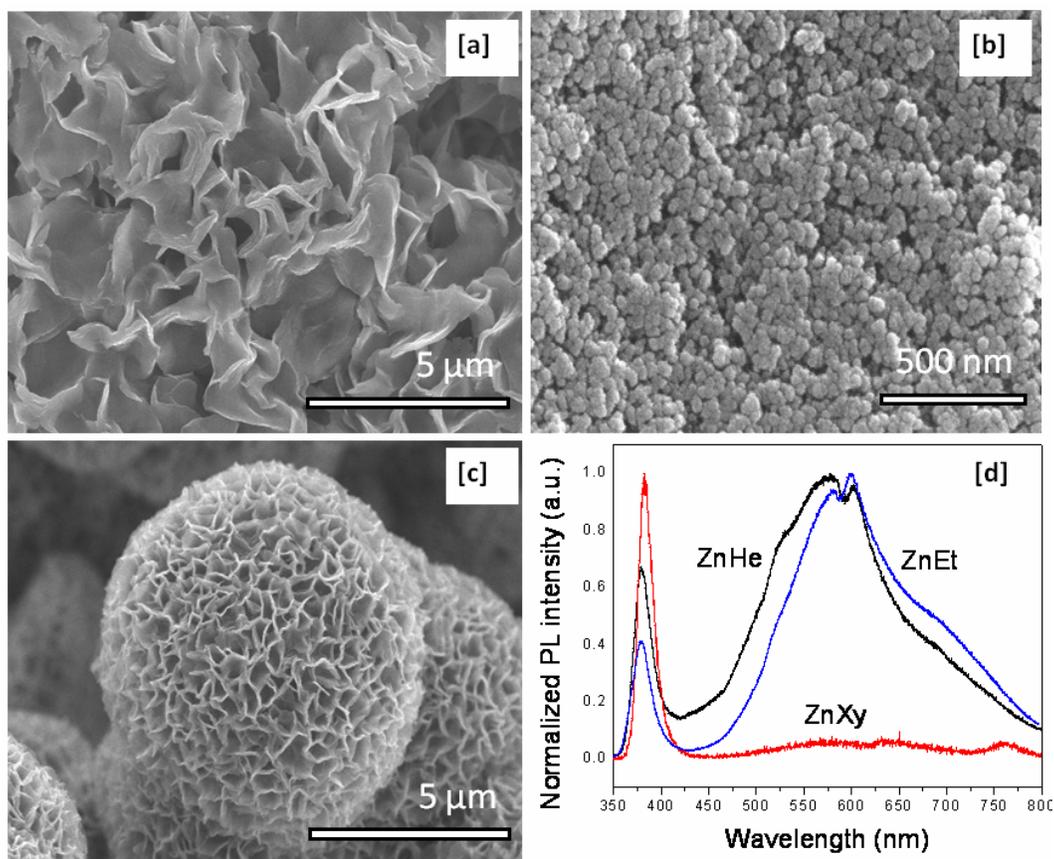


Figure (2) : FESEM images and room temperature PL spectra of ZnO particles isolated from (a) ZnHe, (b) ZnXy and (c) ZnEt.

The FESEM micrographs clearly show remarkably different morphologies of ZnO materials prepared from different non-polar hydrocarbon solvents, as shown in Fig. 2. The shape of the ZnO particles obtained from ZnHe looks snowflake-like structure. A special type of porous ZnO materials (Cage-like) morphology was observed from ZnEt. Very stable and aggregation free ZnO nanoparticles were crystallized from ZnXy. In contrary, full of agglomerated ZnO nanoparticles was resulted from only in methanol, which composed of very fine ZnO nanoparticles [9]. Fig. 3(d) depicts the room temperature photoluminescence (PL) spectra of ZnO particles prepared from different solvents. ZnXy showed a very strong UV band-edge emission with almost no defect emission that indicates high purity ZnO nanoparticle formations. But, there is a broad and wide PL signal observed in the range covered from 500 to 700 nm, along with a UV band-band edge emission in both ZnHe and ZnEt.

### 3.1. Dye sensitized solar cells :

DSSC device was fabricated using ZnO nanoparticles obtained from ZnXy materials as an active layer. The current-voltage (I-V) behavior was measured while the cells were irradiated by AM 1.5 simulated sunlight with a power density of  $100 \text{ mW/cm}^2$ , to

investigate the performances of the DSSC device. Fig. 5(a) shows the photocurrent density vs voltage curves. The power conversion efficiency (PCE) was calculated from the equation,  $PCE (\eta) = J_m V_m / P_{inc}$ , where  $J_m$  is the maximum current,  $V_m$  is the maximum voltage, and  $P_{inc}$  is the incident light power. PCE value from the DSSC fabricated with  $ZnXy$  nanoparticles showed 1.166 %. The higher PCE probably attributed to the higher surface area of the nanoparticles, which ultimately resulted in increasing adsorption of dye molecules and light harvesting [11].

### 3.2. Light emitting diodes :

For LED application, the light extraction efficiency of the device was improved by deposition of ZnO nanoparticles ( $ZnXy$ ) layer on the commercially available blue LED. Well-known blue light emitting InGaN-GaN epitaxial layers, mesa-structure LEDs with the area of  $350 \times 350 \mu m^2$  have been fabricated and a simple spin coater was used to deposit the ZnO nanoparticle layers. To improve the light extraction efficiency (LEE) of the device, a single, two and three layers were coated on blue LED. The light output power of LEDs before and after ZnO layers was measured by a high-speed LED tester and measurement system. Fig. 5(b) represents the improvement of radiometric power (RP) and total luminous flux (TLF) of the device with respect to number of ZnO layers. Interestingly, the RP and TLF were observed to be maximum improvement of 3.8 and 3.4 %, respectively, from the double ZnO layer sample, when compare to bare blue LED chip. Higher LEE from the ZnO nanoparticles was attributed due to increased surface roughness that causes angular randomization of the photons, leads the probability of photons escaping from the LED is increased and thus an increased integrated intensity.

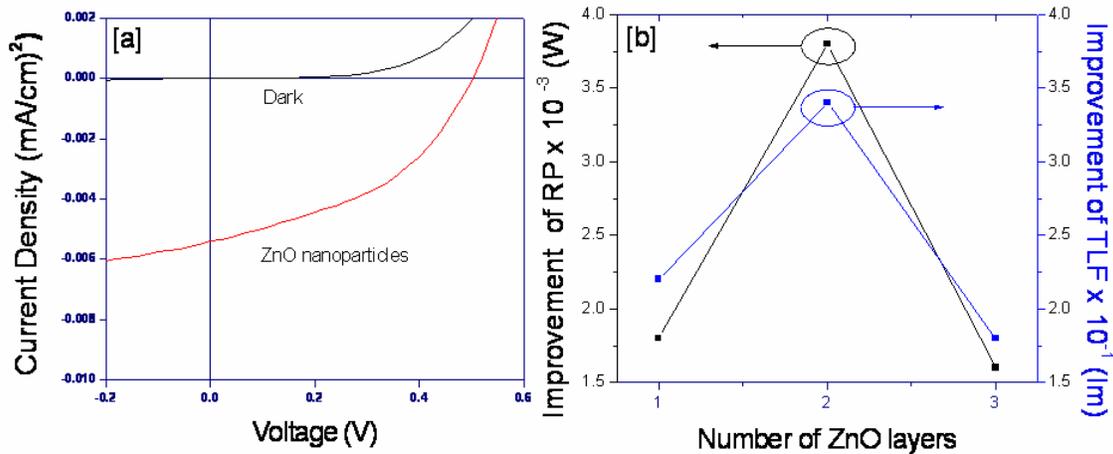


Figure (3) : (a) Photovoltaic behavior of active ZnO nanoparticles and (b) Improved output power with respect to number of ZnO layers.

### 4. Conclusions :

Highly dispersible ZnO nanoparticles have been successfully synthesized by controlling the reaction solvent characteristics, at relatively very low temperature in a simple solution

method. The average polarity index of the reaction medium was controlling the decomposition of zinc acetate precursors to generate a pure ZnO particle. Very slow crystallization of ZnO particles in the non-polar hydrocarbon solvents is responsible for the UV band edge emission. A stable dispersion of ZnO nanoparticles was used as an active component in DSSC and effective scattering layer in LED to improve the light extraction efficiency.

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