

# Synthesis of ZnO Nanorods Arrays on ITO and Their Photoelectrochemical Performance

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Tapered ZnO nanorod arrays are synthesized on indium-tin oxide (ITO) using a two-step hydrothermal method. The influence of the growth temperature on the structure, morphology and photoelectrochemical (PEC) performance is investigated. The synthesized nanorods having an average diameter of about 100 nm are found to be nearly perpendicular to the substrate and exhibit good PEC properties. Our results suggest that the growth temperature is a crucial parameter to determine the physical and chemical properties of the nanorod arrays.

**Keywords:** ZnO, Nanorod, Photoelectrochemical, Optical Properties.

## 1. INTRODUCTION

One-dimensional (1-D) ZnO nanomaterials such as nanorods (NRs), nanowires (NWs) and nanotubes (NTs) have received considerable attention due to the wide and direct bandgap (3.37 eV) and large exciton binding energy (60 meV).<sup>1–4</sup> Owing to the higher surface-to-volume ratio and carrier mobility than the bulk or film counterparts, ZnO NR/NW arrays have huge potential in applications such as dye sensitive solar cells (DSSC), nanogenerators, light emitting devices (LED), and so on.<sup>5–8</sup> ZnO NR arrays have been synthesized by many methods such as chemical vapor deposition (CVD), metalorganic vapor phase epitaxy (MOVPE), electrochemical deposition, hydrothermal methods, aqueous solution methods, and so on.<sup>2,5,6,9–11</sup> Among these methods, hydrothermal or aqueous methods are advantageous for the synthesis of ZnO NW or NR arrays due to the low growth temperature (lower than 100 °C).<sup>12,13</sup> There have been many reports on the synthesis, optical, and structural characterization of ZnO NR arrays but there have been few investigations on the PEC properties so far to the best of our knowledge. In this study, we report the hydrothermal synthesis of ZnO NR arrays with a diameter of ~100 nm on an indium tin oxide (ITO) substrate on which a thin ZnO seed layer has been deposited electrochemically. The effects of the growth temperature on the morphology, structural, and optical properties are investigated. It is found that the ZnO

NR arrays exhibit good PEC performance indicative of good potential in DSSC applications.

## 2. EXPERIMENTAL DETAILS

A 20–30 nm thick ZnO seed layer was prepared on the ITO substrates at room temperature (RT) by electrochemical deposition for 1 min. The electrolyte consisted of a mixture of a 20 mM zinc nitrate aqueous solution and 7.5 mM hexamethylenetetramine (HMT). Afterwards, the coated substrates were placed downward in kettles filled with 40 ml of a 25 mM aqueous solution of zinc nitrate and HMT. The hydrothermal reactions took place in the high-pressure kettles at temperature of 50, 70, 90, and 120 °C for 20 h without stirring. The crystal structure and morphology of the NR arrays were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM, FEI Sirion 200 FEG). Room temperature photoluminescence (PL) measurements were performed using a Xe lamp (300 nm) as the excitation source. The optical absorption measurements were performed using a UV-near-IR grating spectrometer (UV 4100).

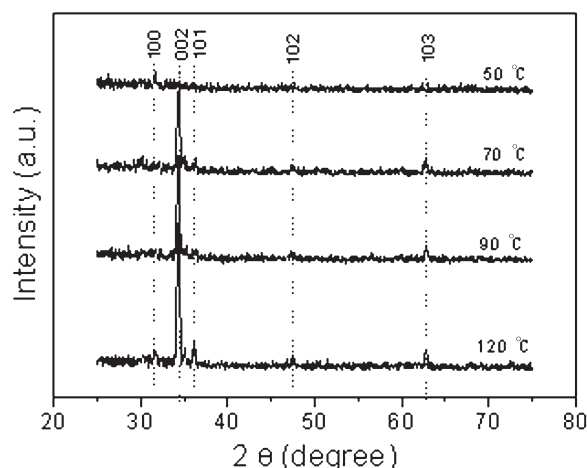
Prior to the PEC measurements, a conductive silver epoxy was employed to provide good electrical contact to the copper wire. Another nonconductive epoxy was applied to the edge of the samples. The PEC study was performed in a standard three-electrode configuration with a platinum plate as the counter electrode and Hg-Hg<sub>2</sub>Cl<sub>2</sub> (SCE) as the reference electrode. A 0.5 M aqueous Na<sub>2</sub>SO<sub>4</sub> solution served as the electrolyte. The PEC characteristics were measured with white light emitted from

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a 500 W Xe lamp. The measured light irradiance was 100 mW/cm<sup>2</sup>.

### 3. RESULTS AND DISCUSSION

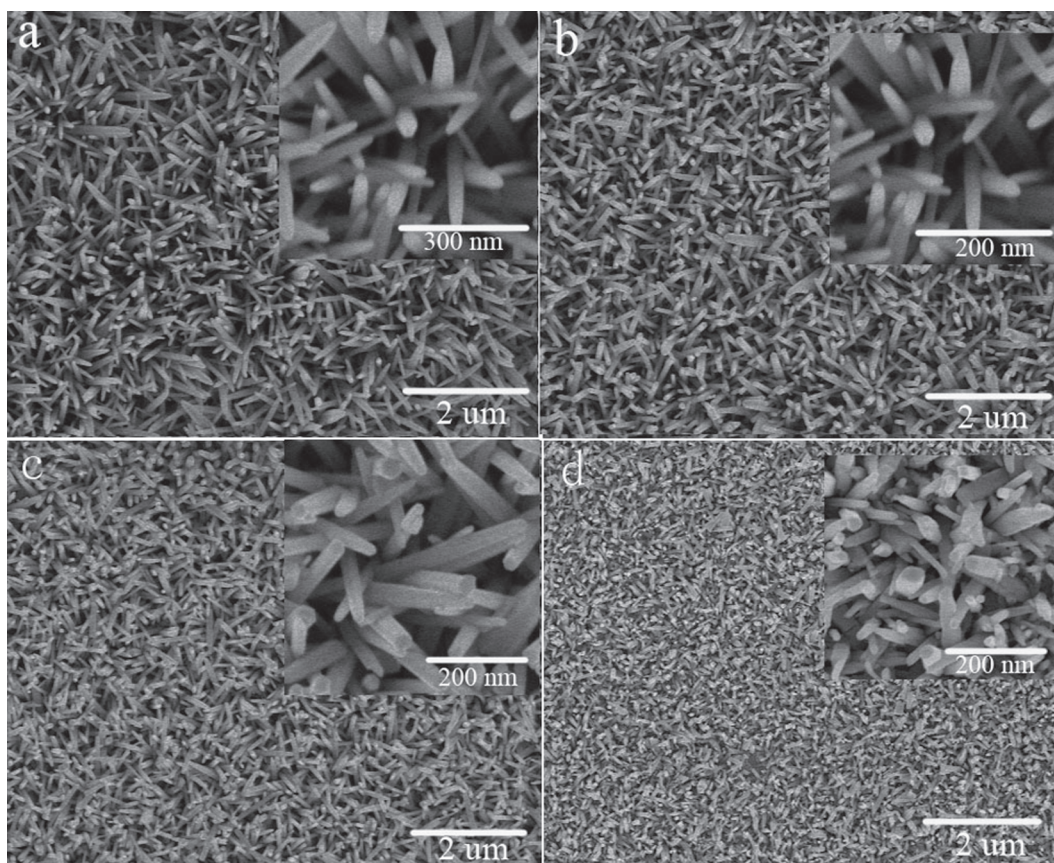
Figure 1 shows the planar-view SEM images of the ZnO NR arrays fabricated on the ITO at different reaction temperatures. The hexagonal morphology can be observed clearly from the top view SEM images. The NR arrays have uniform size (diameters of about 100 nm) and shape and cover a rather large area. As the temperature increases, the density and length of the NR arrays increase correspondingly, resulting in larger surface-to-aspect ratios. The behavior can be attributed to an increase in the growth rate at an elevated temperature. It is also found that all the nanorods exhibit a tapered structure. The higher the growth temperature, the larger is the diameter ratio of the stem to tip. As a result, the sample prepared at 120 °C exhibits the sharpest contrast between the tip and stem, that is, a needle-like structure. The nanorods fabricated at 50 °C are short, randomly orientated, and distributed sparsely. In a typical hydrothermal reaction, the precursors are depleted gradually with time and a higher reaction temperature leads to a faster depletion rate of the reactants. As the solvent concentration decreases, the growth rate of the



**Fig. 2.** XRD patterns of the ZnO NRs arrays grown on ITO substrates at 50–120 °C.

nanorods' sidewall diminishes significantly resulting in a thinner tip and eventually a tapered structure.

Figure 2 depicts the XRD patterns of the ZnO NR arrays produced at various temperatures. All the diffraction peaks can be indexed to the (100), (002), (101), (102) and (103) crystalline orientations of the hexagonal phase. This is due to the ensemble of rods since no crystallized characteristics

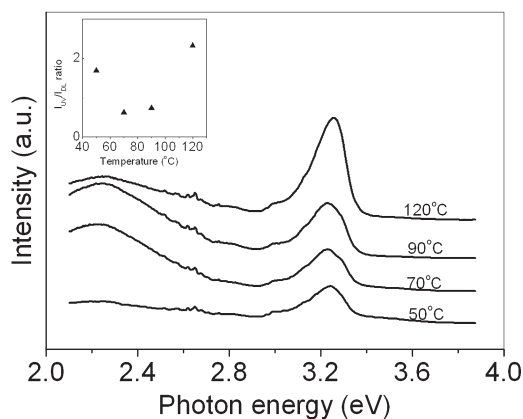


**Fig. 1.** FESEM images of the ZnO NRs arrays grown on ITO substrates at (a) 120 °C, (b) 90 °C, (c) 70 °C, and (d) 50 °C.

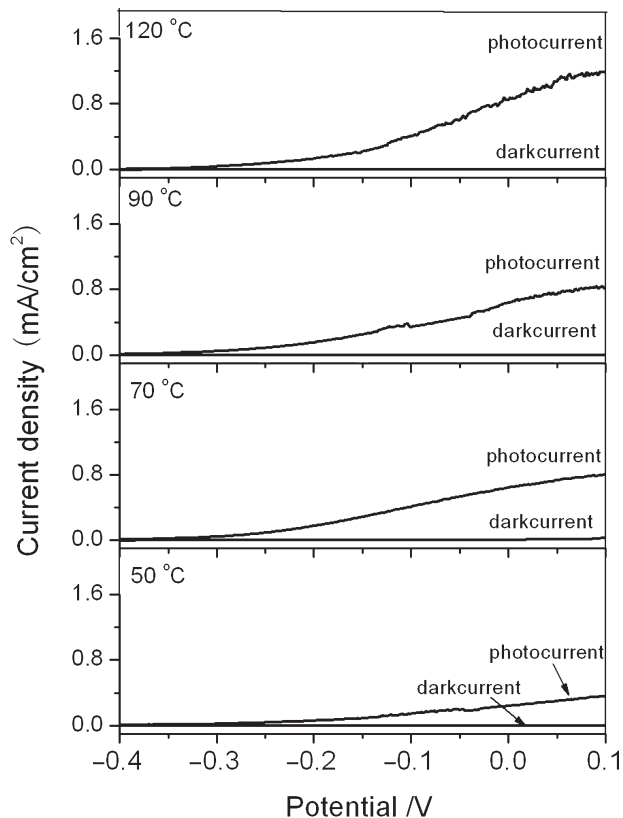
are observed from the seed layer. The sample synthesized at 50 °C show many weak diffraction peaks indicative of a disordered nanorod array. However, the XRD patterns acquired from the samples produced at higher temperature are dominated by the (002) peak, indicating a vertical ZnO nanorod array along the *c*-axis. It can be shown by our other studies that vertical ZnO NR arrays can also be synthesized on other substrates such as copper, brass, PET, and silicon by the same method.

Figure 3 shows room-temperature PL spectra of the ZnO NRs arrays. All the spectra are dominated by strong ultraviolet (UV) luminescence located at 3.2–3.3 eV as well as broad visible emission at about 2.5 eV related to deep-level defects. It should be noted that the increase in the temperature from 70 to 120 °C leads to a blue shift in the UV peaks and an increase in the ratio ( $I_{\text{NBE}}/I_{\text{DL}}$ ) of the NBE to DL emission. The sample prepared at 120 °C exhibits the highest energy of UV luminescence  $\sim 3.26$  eV and the largest UV-to-visible ratio  $\sim 2.3$ , indicative of the best crystalline quality. In comparison, the UV peak of the sample synthesized at 50 °C is located at  $\sim 3.245$  eV and the ratio  $I_{\text{NBE}}/I_{\text{DL}}$  is  $\sim 1.7$ . Both values are a little higher than those of the one synthesized at 70 °C. The anomalous behavior results from the effect of the ITO substrate due to rather weak PL density of the nanorods. Since ITO has a wider band gap ( $\sim 3.6$  eV) than ZnO, peak broadening and blue-shifting of the UV peak are unavoidable. As a result, the UV peak of the sample synthesized at 50 °C is found to blue-shift and increase compared to the one prepared at 70 °C.

Figure 4 shows the typical photocurrent versus potential results for the ZnO NR electrode in the dark and under white light illumination in the 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte. Note that the dark current of the samples is rather low (on the order of  $10^{-4}$  mA/cm<sup>2</sup>) whereas clear enhancement in the current density is observed under illumination. ZnO which is a typical *n*-type semiconductor shows the characteristics of an increase of the anodic photocurrent with increased applied potential as illustrated by the curves. The current is rather low in the absence



**Fig. 3.** RT PL spectra of the ZnO NRs arrays grown on ITO substrates at 50–120 °C.



**Fig. 4.** Typical photocurrent versus measured potential for ZnO NR arrays electrode in dark and under white light illumination in 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte. The scanning rate is 1 mV/s. The working electrode is the ZnO NR arrays.

of illumination but increases largely under illumination. The low dark current, regardless of the applied potential, is attributed to the relatively low carrier density in the as-grown NRs. UV illumination gives rise to a large number of extrinsic carriers giving rise to a longer lifetime of the carrier recombination. Furthermore, the polarity in the surface layer results in separation of the electron–hole pairs, and the excess electrons above the conduction band maximum (CBM) move into the circuit under external potential producing a photocurrent. The left holes are transferred to  $\text{OH}^-$  producing  $\text{O}_2$ . The increase in the lifetime enables more excess electrons to take part in the process, leading to a notable increase in the current compared to the dark current. A large photocurrent to dark current ratio denotes high photoelectron activity or efficiency in the photoelectron conversion in the ZnO NRs. It should also be noted that the samples prepared at higher temperature produce a larger photocurrent which can be attributed to the larger surface-to-aspect ratio.

In summary, ZnO NRs arrays have been synthesized on ITO substrates using a simple hydrothermal method. The growth temperature plays a significant role in the morphology, crystallization, optical, and PEC properties. The sample prepared at 120 °C exhibits the best PEC properties and largest photocurrent to dark current ratio.

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