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# Solution processed ZnO rectangular prism as an effective photoanode material for dye sensitized solar cells

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ABSTRACT

Well crystalline ZnO rectangular prism (ZnO-RP) nanomaterials were synthesized by a low temperature solution process and employed as photoanode materials for the dye sensitized solar cells (DSSCs). Synthesized nanomaterials featured the define rectangular prism morphology with the average thickness of ~100 nm and possessed typical hexagonal wurtzite structure. ZnO-RP photoanode presented a reasonable conversion efficiency ($\eta$) of ~3.3% along with high short circuit current ($J_{SC}$) of ~8.91 mA/cm$^2$, open circuit voltage ($V_{OC}$) of ~0.725 V and fill factor ($FF$) of ~0.51 in DSSC. The rectangular shape of ZnO could provide high surface to volume ratio for dye absorption and light harvesting efficiency, which significantly resulted in high $J_{SC}$ and conversion efficiency of DSSC.



## 1. Introduction

A dye sensitized metal oxides semiconductor assembled photo-electrochemical device, called dye-sensitized solar cell (DSSC) is elicited as a new generation photovoltaic technology owing its high solar to electricity conversion efficiency with ease of fabrication and low production cost [1–3]. In DSSC, metal oxide semiconducting based photoanode is one of most important component for enhancing sunlight absorption, electron excitation and light harvesting efficiency [4]. The interfacial, dynamic and structural properties of photoanode present the significant impact on the charge transport and photovoltaic properties of DSSC [5]. Several reports already investigated on the mechanisms of DSSCs in terms of morphology, structure and optical properties of $TiO_2$ and other metal oxide semiconducting materials [6–8]. So far, various metal oxides semiconducting nanomaterials such as $SnO_2$, ZnO, $Nb_2O_5$, etc. employed as photoanode materials for improving the charge collection and injection of charges in DSSC [9–11]. Apart from the other metal oxides, ZnO nanomaterials are highly impressive alternative photoanode materials to $TiO_2$ nanomaterials because of their environmentally friendly nature and easily manufacture at high purity with high crystallinity at low temperature condition.

ZnO semiconductor is receiving tremendous attentions owing to its high versatility and multi-functionality along with a wide band gap ($E_g$) and a large exciton binding energy [12]. ZnO nanomaterials display a diverse range of technological and practical applications in electrical, light-emitting diodes, solar cells, gas sensors, chemical sensor, and so on [13–16]. The excellent properties such as optoelectronics, peizoelectronic, and bio-compatible of ZnO nanomaterials are tending them to use in various electrochemical and photoelectrochemical applications [5]. Due to their excellent dielectric, ferroelectric, piezoelectric, pyroelectric properties, the ZnO-based nanograined materials find numerous applications, particularly, in photocatalysis, chemical sensors, memory resistors and photovoltaics [17]. In particular, the morphologies of ZnO nanomaterials are easily tailored in the form of nanorods, nanoflowers, nanosheets, nanobelts etc. by changing the synthetic and parametric tools [18–22]. Moreover, ZnO nanomaterials is often believed to be a compatible photoanode material to $TiO_2$ for DSSCs. ZnO nanoparticle thin films based photoanode demonstrated a low conversion efficiency of 0.4% due to the slow the absorption mechanism especially at longer wavelength [22]. 2D ZnO nanostructures, such as nanobelts and nanosheets, are expected to be alternative materials because they have shown enhanced optical, structural, and morphological which believe that these morphologies might show significant impact on the improvement in conversion efficiency of DSSCs [23]. In the present paper, we report on the synthesis of well-crystalline ZnO-RP nanomaterials by a low temperature solution process and utilizes as photoanode materials for the fabrication of DSSCs. The synthesized

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crystalline ZnO-RP nanomaterials has been extensively characterized in terms of morphology, structure, optical, dye loading and photovoltaic properties.

## 2. Experimental

In a typical procedure, 0.5 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was dissolved in deionized (DI) water and then slowly added 0.3 M diethylamine ($((C_2H_5)_2NH)$) solution under continuous stirring. The pH of whole reaction mixture was adjusted to 10 by the dilute NaOH solution. Afterward, the whole reaction mixture was transferred into Scott Duran bottle and closed tightly. The packed bottle placed into laboratory oven and maintained the temperature at 80 °C for 8 h. At the end of heating, white precipitates were obtained, which was washed with methanol several times and dried at 60 °C for 24 h to form ZnO powder products. The ZnO-RP nanomaterials were applied as photoanode materials for DSSC. For DSSC fabrication, the ZnO-RP nanomaterials based thin film was prepared as described in elsewhere [5]. In brief, the prepared ZnO-thin film on fluorine doped tin oxide (FTO) glass was dipped into the ethanolic dye solution (0.3 mM, bis (2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium, N719 dye) for dye sensitization to achieve ZnO photoanode. The counter electrode (CE) was manufactured by depositing Pt thin layer on FTO glass using ion sputtering. Then the Pt CE was placed over ZnO photoanode which were sealed using 60 μm thick surlyn film by pressing over the hot plate at 80 °C. Finally, a specific composition of redox electrolyte (0.5 M LiI, 0.05 M $I_2$, and 2 M tert Butyl pyridine in acetonitrile) was injected into the cell by syringe through the holes of CE. The performance of fabricated DSSC was analyzed by measuring the current density ($J$)–voltage ($V$) characteristics under 100 mW/cm$^2$ (1.5AM), as described elsewhere [5].

## 3. Results and discussions

The synthesized ZnO nanomaterials have been morphologically examined by field emission scanning electron microscopy (FESEM, Hitachi S-4700) and transmission electron microscopy (TEM, JEM-2010-JEOL, Japan). Fig. 1(a) depicts the low magnification FESEM image of synthesized ZnO nanomaterials, which reveals well defined and uniform rectangular prisms like morphology. Recently, it has reported that the physical properties of pure and doped nanograined ZnO are strongly counted on the existence of defects like interphase boundaries and grain boundaries [17,24]. It can be seen in Fig. 1(a), the synthesized ZnO-RP nanomaterials are indeed nanograined which contain very developed grain boundaries and free surfaces. At high magnification (Fig. 1(b)), each rectangular prism possesses the average size of ~200–300 nm with average thickness of ~100 nm. Similar morphology is seen in the low resolution TEM image (Fig. 2(c)), confirming the formation of rectangular prism like morphology. The high resolution (HR)–TEM (Fig. 1(d)) of ZnO-RP shows well defined lattice structures with the average two adjacent fringes of ~0.26 nm, which corresponds to (1 0 0) plane of the wurtzite ZnO structure. This observation further confirms in the selected area electron diffraction (SAED) patterns of ZnO-RP.

Crystalline nature of synthesized ZnO-RP was determined by X-ray diffraction pattern (XRD, Rigaku, Cu $K\alpha$, $\lambda = 1.54178$ Å) with range of 20–70°. Fig. 2(a) shows the XRD of ZnO-RP, showing visible diffraction peaks at 31.9, 34.7, 36.4, 47.7, 56.7, 62.9, 66.5, 68.1, and 69.2°, which are absolutely matched to the typical ZnO wurtzite crystal structure (JCPDS no.: 36-1451) [25]. However, no other diffraction peaks are detected in XRD pattern of ZnO-RP, indicating no impurities in synthesized ZnO-RP. Additionally, Moreover, the grain boundaries in synthesized ZnO-RP nanograins might originate from the existence of amorphous surficial, interfacial and inter-granular layers in ZnO-RP,

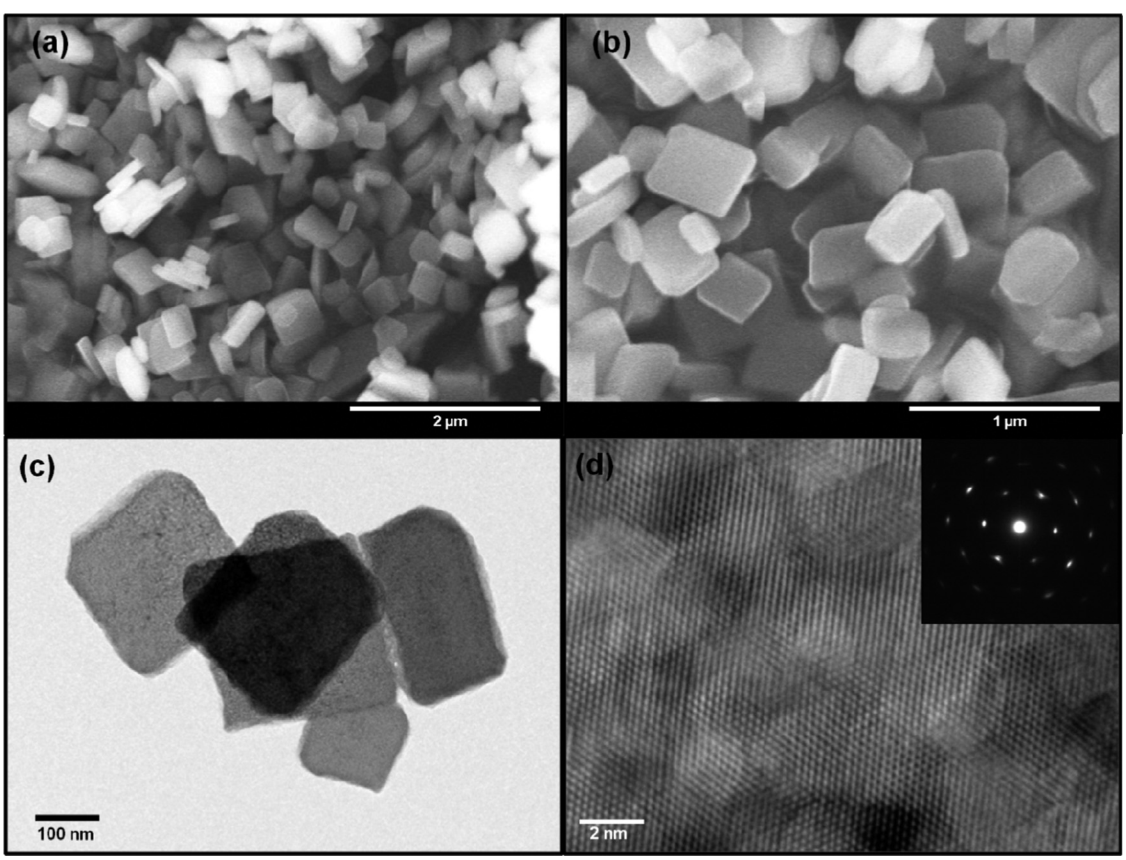


**Fig. 1.** FESEM images at low (a) and high (b) magnification mode, and TEM (c) and HRTEM (d) images of synthesized ZnO-RP nanomaterials.