

# Defects free growth of zinc oxide nanowires on indium doped tin oxide (ITO) substrate for hydrogen production through electrochemical water splitting

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We report the rational synthesis design and characterization of defect free growth of zinc oxide (ZnO) nanowire arrays on ITO substrate for hydrogen generation through photoelectrochemical water splitting. In comparison to ZnO nanowires synthesized by using conventional hydrothermal method, the ZnO nanowires synthesized by special design in which substrate is suspended upside down in the Teflon autoclave show significantly improved photocurrent in the entire potential window. Moreover, ZnO nanowires synthesized by special design have low photocurrent saturation potentials as compared to ZnO nanowires synthesized by using conventional hydrothermal method indicating very efficient charge separation and transportation. These results suggest ample potential of defect free ZnO nanowire arrays in PEC water splitting applications.

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*Keywords:* ZnO nanowire, ITO substrate, PEC water splitting applications

## 1. Introduction

During the last few decades, hydrogen energy as renewable and clean energy have become one of the utmost important and popular subjects of research at a global level due to its environmentally friendly nature and high gravimetric energy. Among various techniques, hydrogen production through photoelectrochemical water splitting by using semiconductor metal oxides based photoelectrodes is one of the most promising method due to its eco-friendly nature and relatively low operating temperature [1-6]. As an electrode material for photoelectrochemical water splitting, zinc oxide (ZnO) based nanostructured materials have been received considerable attention due its outstanding performance [1, 7-12]. The environment friendly nature, low cost and non-toxicity makes ZnO as a superior candidate among commonly existing semiconductors. Moreover, ZnO possess extremely rich morphologies and 10-100 times higher carrier mobility as compared to titanium oxide (TiO<sub>2</sub>) which facilitates the electron transfer and reduces electrical resistance [13, 14]. ZnO nanostructures for the electrode material for photoelectrochemical water splitting has been synthesized by using various method such as chemical vapor deposition, hydrothermal etc. The techniques based on hydrothermal method does not requires any sophisticated equipment's or special experimental conditions and become one of the more commonly used method for the synthesis of ZnO nanostructures[15-17]. However, it is very hard to minimize the native defects in ZnO nanostructures which are typically arises by hydrothermal technique, the existence of the inherent defects in ZnO such as oxygen vacancy and zinc interstitial limits optoelectronic and

photonic applications. Hence, it is essential to enhance the quality of the one dimensional ZnO nanostructures grown by hydrothermal technique comparable to that of other commonly existing sophisticated vapor phase techniques and should be applicable for all the substrates. In order to solve the aforementioned problem, we modified the hydrothermal method in which the substrate containing ZnO seed layer is suspended upside down in the Teflon autoclave using a specially designed support. The synthesized ZnO nanowires shows much higher performance as compared to ZnO nanowires grown by using conventional hydrothermal process, in which the ZnO seed layer coated substrate was placed upside down in the Teflon autoclave.

## 2. Experimental methods

All chemicals, methanol, Zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), Zinc acetate dihydrate (Zn(OOCCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O), Potassium hydroxide (KOH), Hexamethylenetetramine (HTMA) and Polyethylenimine (PEI) are purchased from Sigma Aldrich and used as received. The seed layer solution of ZnO was prepared by mixing 0.001M methanolic solution of Zn(OOCCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O with 0.005M solution of KOH [18]. The seed solution was then spin coated on ITO substrate with a spinning rate of 4000 rpm for 20 seconds. This process was carried out for three times to achieve the desire thickness of the seed layer on ITO substrate. After each coating the ITO substrate was dried at 140 °C on hotplate. For the synthesis of ZnO nanowires, 0.001 M of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.005 M of HMTA and 70 mg of PEI were mixed and stirred magnetically for 4 hours. For the

synthesis of defect free growth of ZnO nanowires, the seed layer coated ITO substrate was suspended upside down in the Teflon autoclave using a specially designed support designed for this experiment and the hydrothermal reaction was performed at 95 °C for 4 hours. For comparison we also synthesized ZnO nanowires on ITO substrate by using conventional method in which substrate is suspended upside down in the Teflon autoclave at the bottom of a Teflon autoclave. After the reaction, ITO substrate containing ZnO nanowires was washed with deionized water and dried on hotplate at 80 °C.

### 3. Results and discussion

The morphology of ZnO nanowires grown on ITO substrates by hanging them above from the bottom of the Teflon vessel was observed at different magnifications by using FE-SEM and the results are presented in Fig. 1. It can be seen from Fig. 1 that ZnO nanowire on ITO coated glass substrate have average diameter and length of 100 nm and 2.5 $\mu$ m respectively. Fig. 2 shows the FE-SEM images of ZnO nanowires grown directly by positioning the ITO coated glass substrate upside down. The typical diameter and length of the substrate grown inside the autoclave was found to be 50-70 nm and 0.5-0.7 $\mu$ m. The X-ray diffraction pattern for the as grown ZnO nanowire arrays on ITO coated glass substrate are shown in Fig. 3. All the peaks were indexed to the hexagonal wurtzite ZnO crystalline phase [space group: P63 mc] and the lattice parameter values estimated to be  $a = 3.249\text{\AA}$  and  $c = 3.60\text{\AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  which are in well agreement with the literature (JCPDS No. 86-0120). The appearance of sharp peaks indicates that ZnO nanowires are highly crystalline in nature. The optical properties of the as grown ZnO nanowires on ITO coated glass substrate were determined using room temperature PL spectroscopy on different substrates grown under similar experimental condition are shown in the Fig. 4. It is well known from many reports typically there are two bands have appeared in the PL spectra of ZnO. The first one belongs to near band edge emission in the ultra violet region which originates from the recombination of free excitons through exciton-exciton collision process and the second is deep level emission in the visible region arised from impurities and structural defects in the crystal due to oxygen vacancy (Od) and zinc interstitial (Zni). Regarding the blue-green emission of ZnO nanostructure, it has already been demonstrated that radial recombination of photogenerated holes with singly ionized oxygen vacancies in the surface lattice of ZnO. This explanation well agreed with the theoretical calculation using first principles method and proposed that oxygen vacancies have comparatively low formation enthalpy, hence, the electron-hole radioactive recombination occurring easily at the vacancies [20, 21]. The crystalline quality of the ZnO nanostructure is usually related with the PL spectrum. From our experiment it is very clear that nanowire arrays grown by hanging both ITO coated glass substrates contain very low deep level emission (DLE) as shown in Fig. 4. The most plausible

reason for the low DLE is effective control of surface recombination of photogenerated carriers by avoiding the interfacial strain between substrate containing seed layer and Teflon wall. However, as grown ZnO nanowire by directly placing the substrate upside down into the autoclave shows very broad near band edge emission with more deep level emission (Fig. 4). The water splitting properties of as grown ZnO nanowires on ITO substrate is studies under UV light illumination as shown in the Fig. 5. The dark scans for ZnO nanowires synthesized by special design in which substrate is suspended upside down shows a rather small background current density in entire voltage range from -0.8 to 1 V. However, under illumination the photocurrent density of ZnO nanowires synthesized by special design in which substrate is suspended upside down increases significantly in entire voltage range from -0.8 to 1 V which is much large than that of ZnO nanowires grown by conventional hydrothermal method (1.94 mA/cm<sup>2</sup>). The results suggest by controlling the defects in ZnO nanowires during the synthesis, we can significantly enhances the activity of ZnO nanowires. The photocurrent responses toward light ON-OFF cycling of ZnO nanowires synthesized by special design in which substrate is suspended upside down is shown in Fig. 5(b). It can be seen from Fig. 5(b) that ZnO nanowires shows a steady and prompt photocurrent generation during ON and OFF cycles of illumination. This result demonstrates that by controlling the defect in ZnO nanowires during the synthesis can effectively enhance the photocatalytic activity of ZnO nanowires along with outstanding chemical stability.

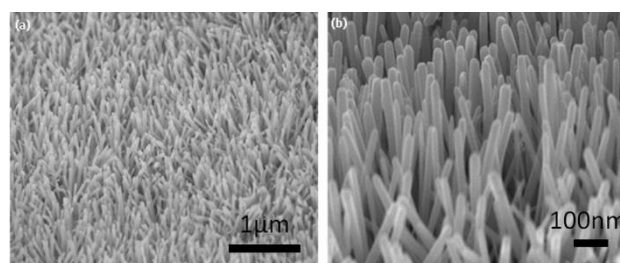


Fig. 1. FE-SEM images of the zinc oxide (ZnO) nanowires on ITO coated glass substrate by hanging inside the autoclave synthesized at 95 °C for 4 hours.

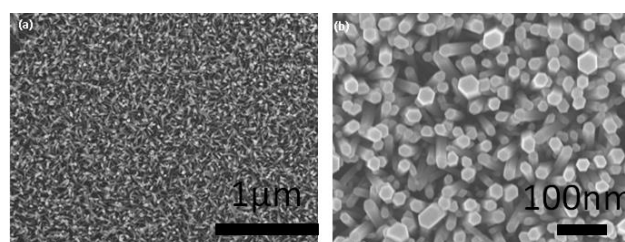


Fig. 2. FE-SEM images of the zinc oxide (ZnO) nanowires on ITO coated glass substrate directly by placing upside down inside the autoclave synthesized at 95 °C for 4 hours.

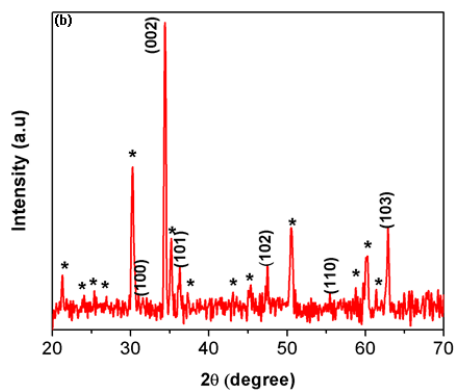


Fig. 3. X-Ray diffraction analysis of as grown zinc oxide (ZnO) nanowires on ITO coated glass substrate.

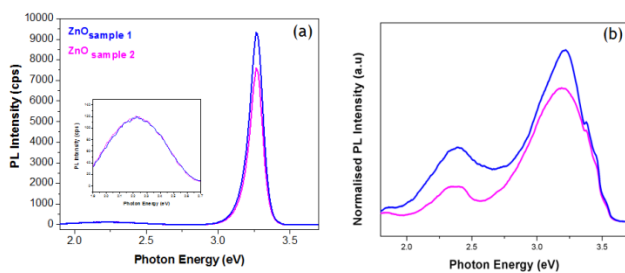


Fig. 4. Room Temperature photoluminescence studies of the as grown zinc oxide (ZnO) nanowires on ITO coated glass substrate (a) by hanging inside the autoclave (b) by placing the substrate directly upside down.

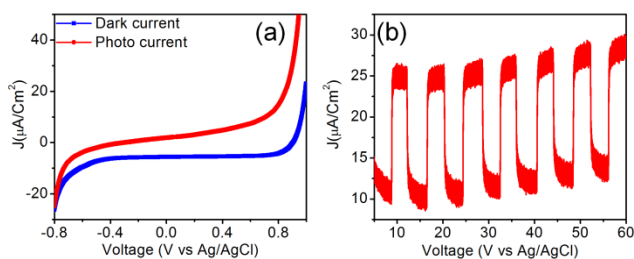


Fig. 5. Current versus voltage characteristics of zinc oxide (ZnO) nanowires grown on ITO coated glass substrate (a) Photo current transient responses of ZnO nanowires grown on ITO coated glass substrate.

#### 4. Conclusion

Green and efficient conversion and storage of earth abundant natural resources into usable energy is the greatest challenge for materials scientist. Currently we are at a stage where the existing materials already reached the inherent limits and it is a high time to think about new material architectures by controlling size, shape and geometry as well as composition for sustainable energy in future. In the current project we synthesized defects free architectures of most comely used ZnO material while establishing a balance between different material properties to achieve optimum results for the realization of

the practical applications of ZnO photocatalyst for photocatalytic hydrogen evolution from water splitting.

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