

Appendix A

Miscellaneous work

In this chapter, the work on ZnO nanorods based electrodes has been discussed for hydrogen evolution and storage. These studies suggest the possibility of ZnO nanorods as hydrogen storage media in alkaline conditions.

A.1 ZnO NANOROD ELECTRODES FOR HYDROGEN EVOLUTION AND STORAGE

The molecular hydrogen (H_2) has been investigated intensively as an alternative to the fossil fuels because of its high specific heat of combustion. The hydrogen fuel cells may offer particular advantages for transportation because of its reduced weight, superior energy conversion efficiency and ecological friendliness [Veziroglu and Barbir, 1995]. Energy-efficient hydrogen production and safe storage remains the key technological obstacle for H_2 based economy. The steam reforming of hydrocarbons is used for large scale H_2 production. However, this process is not economical and also the produced hydrogen is not pure enough to use directly for an application. In contrast, electrolysis of water has been used to produce relatively pure and economical hydrogen which can be used directly in fuel cells. Also, this hydrogen is free from carbon monoxide, usually present in steam reforming process and is detrimental to the proton exchange membrane of fuel cells [Rossmesl *et al.*, 2007]. In the hydrogen evolution reaction (HER) [Roberge, 2008], Iron (Fe) and Ni (nickel) electrodes are used because of their relatively high H_2 evolution overpotentials (380 and 480 mV, respectively). In spite of high overpotentials, the process is energy intensive and consumes huge electricity [Shan *et al.*, 2008; De Giz *et al.*, 1995; Wang *et al.*, 2005; Arul, 2000; Qing *et al.*, 2003, 2004; de Souza Roberto *et al.*, 2007; Joanna and Antoni, 2007]. In recent years, numerous studies have focused, on the quest for new electrode materials presenting higher electrocatalytic efficiency for HER [Rosalbino *et al.*, 2005; Metikos-Hukovic *et al.*, 2006; Hu, 2000]. Many semiconductor oxides, such as TiO_2 , WO_3 , ZnO, $SrTiO_3$, Fe_2O_3 , Cu_2O , SiO_2 , etc., have been tested (in both bulk and nano form), for such applications [Satsangia Vibha *et al.*, 2008; Bjorksten *et al.*, 1994; Zaban *et al.*, 2000; Aroutiounian *et al.*, 2005; Rau Greg, 2004; El-Meligi and Ismail 2009]. There are few studies on the oxidation activities on ZnO as well as the ability of ZnO nanorods (NRs) to store the hydrogen [Cox *et al.*, 2001; Cox *et al.*, 2001; Hofmann *et al.*, 2002; Ip *et al.*, 2003; Kiliç and Zunger, 2002; Lee *et al.*, 2006; Van de Walle, 2002; Van De Walle, 2001; Van De Walle CG, 2000]. ZnO has also been investigated for photocatalytic anodes in solar-powered photo-electro-chemical (PEC) electrolysis, where H_2 is generated directly by using a metal cathode and a semiconducting anode for water splitting [Yan *et al.*, 2007; Wolcott *et al.*, 2009]. In this section, we will discuss the HER electrocatalytic efficiency and the hydrogen storage capability of high quality PLD-grown ZnO NRs on Si (100) substrates (ZnO NR /Si (100)) in both acid and alkaline electrolytes.

A.1.1 Experimental Details

Vertical arrays of self-forming, catalyst-free, ZnO NRs were grown on Si (100) substrates using Pulsed Laser Deposition (PLD), by Rogers et al and reported in details elsewhere [Rogers *et al.*, 2011]. The crystalline quality of ZnO nanostructures was investigated using X-Ray Diffraction (XRD) measurements, performed in a Panalytical MRD Pro system using a Cu K_α source, a four-bounce Ge monochromator in the incident beam path and a “triple-axis” monochromator in the diffracted beam path. Sample morphology was studied using a Hitachi

S4800 Field Emission-Scanning Electron Microscope (FE-SEM). The room temperature Photo Luminescence (PL) measurement was carried out using 325 nm HeCd laser emission line. Electrochemical studies were made using ZnO (NR)/Si (100) as the cathode (working electrode), a platinum wire as the anode and Ag/AgCl as a reference electrode. Electrical connections were made to the ZnO NR/Si (100) by soldering a copper wire to the Si. The fabricated electrochemical cells were tested using both 1M H₂SO₄ acidic and 8.5M KOH alkaline electrolytes. All cyclic voltammetry measurements are conducted using an Iviumstat spectro-electro-chemical workstation in the three electrode assembly (details are discussed in section 3.3.10.1).

A.1.2 Results and Discussion

The X-ray diffraction measurements were collected in $2\theta/\Omega$ and Ω scans and results are shown in Figure A.1. The broadened multi-peak diffraction at $2\theta \sim 34.47^\circ$ suggests that the lattice parameter 'c' has increased from $\sim 5.192 \text{ \AA}$ to $\sim 5.200 \text{ \AA}$. There is also some higher-angle broadening at the base of the peak, as shown in Figure A.1a, suggesting the contribution from smaller c lattice parameters as well. The disorders in these nanostructures, especially for the less dense a-b plane at the base of the NRs (and thus a larger lattice parameter 'a') may be the main reason for the observed large variation in the lattice parameters [Sandana *et al.*, 2011]. The Ω scan measurement is also shown in Figure A.1b which is symmetrical with a Full-Width Half Maximum (FWHM) of 0.47° . These measurements explain that NRs are highly c-axis oriented.

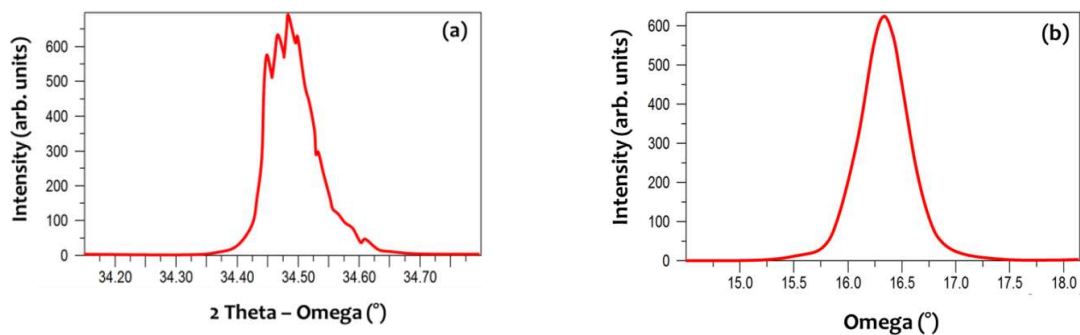


Figure A.1 : XRD (a) $2\theta/\Omega$ and (b) Ω scans for the (0002) peak of the ZnO NRs grown on Si (100).

Figure A.2(a) shows an FE-SEM image of the top surface of ZnO NRs on Si substrate. These rods are vertically aligned with diameters ranging from 100 nm to 300 nm, and a pitch of about 400 nm. The rods lengths were varied in between $\sim 1 \mu\text{m}$ to $\sim 2 \mu\text{m}$ by controlling the growth parameters. The room temperature photoluminescence spectrum for the ZnO NRs on Si (100) substrate is shown in Figure A.2(b). Strong main emission peaked at 3.176 eV, corresponds to the wurtzite ZnO near band edge emission (NBE), with FWHM about 110 meV. The additional peak at 3.3eV, has been observed, as shoulder peak and may correspond to the oxygen defects, especially oxygen vacancies consistent with the reported literature [Tam *et al.*, 2006; Wu and Liu, 2002].

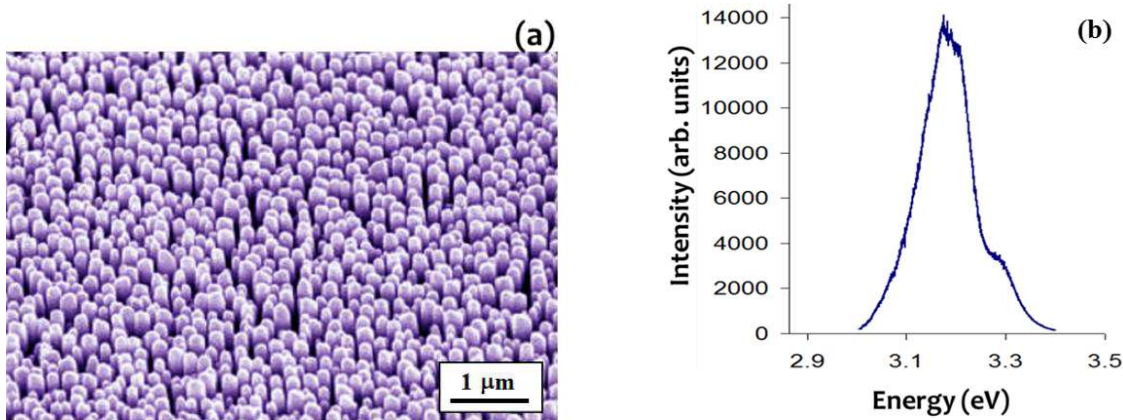


Figure A.2 : (a) FE-SEM image of vertical ZnO nanorod array grown by PLD on a Si (100) substrate. (b) Room temperature photoluminescence spectrum for the ZnO NR grown on Si (100).

The cyclic voltammetry plots for ZnO NRs/Si (100) in 1M H₂SO₄ and 8.5 M KOH are shown in Figures A.3 (a & b). These observations suggest that H₂ evolution is irreversible in acidic, whereas reversible in basic conditions.

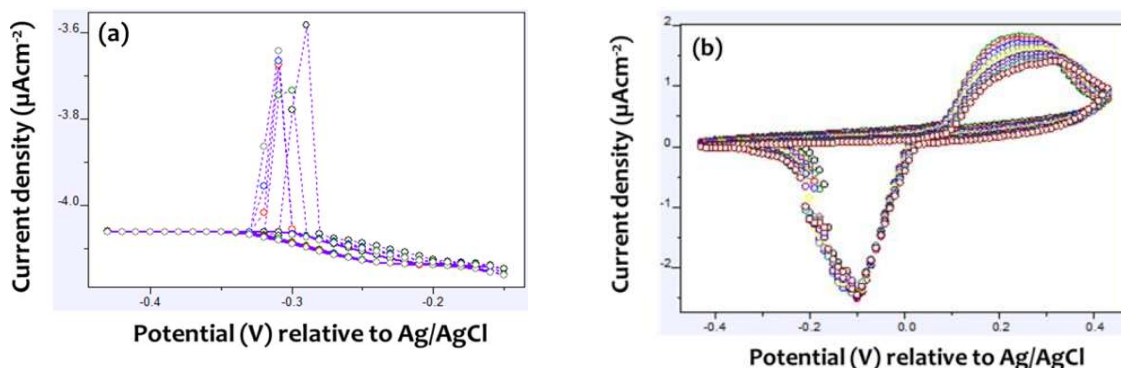


Figure A.3 : (a) Cyclic Voltammetry plots for a ZnO NR/Si (100) working electrode in 1M H₂SO₄ at a 10mV/s scan rate for five cycles. (b) Cyclic voltammetry plots for a ZnO NR / Si (100) working electrode in 8.5M KOH at 10mV/s scan rate for five cycles.

Figure A.3 (a) show the irreversible nature of the voltammogram. To understand the hydrogen evolution reaction (HER) in an acidic electrolyte, three reactions mechanism are considered such as Volmer (electrosorption), Heyrovsky (electrodesorption) and Tafel (recombination) mechanisms [Harrington and Conway, 1987]. The electron transfer process for each mechanism is summarized in Table A.1 for acidic medium. Considering the similar possibility at the surface of ZnO NRs (Table A.1), hydrogen may form and escape through the solution, and that's why there is no reversible process in these voltammogram. It could also be possible that the generated H₂ may get trapped in the ZnO NRs due to Van der Waal's forces. The slight agitation would then be likely to release this physisorbed H₂.

Table A.1 : Mechanism of H₂ evolution in acidic medium

Mechanism	Metal Surface	ZnO Surface
Volmer	$H_3O^+ + e^- + M \rightarrow MH + H_2O$	$H_3O^+ + e^- \rightarrow ZnO...H + H_2O$
Heyrovsky	$H_3O^+ + e^- + MH \rightarrow M + H_2$	$H_3O^+ + e^- + ZnO...H \rightarrow ZnO + H_2O$
Tafel	$2MH \rightarrow 2M + H_2$	$2ZnO...H \rightarrow 2ZnO + H_2$

Hydrogen evolution mechanism in the alkaline medium on both metal surface and ZnO surface are given in Table A.2 for the three possible mechanisms. The hydrogen evolution reaction is reversible and reproducible under alkaline conditions. The measured reversible cyclic voltammograms are shown Figure A.3b.

Table A.2 : Mechanism of H₂ evolution in basic medium

Mechanism	Metal Surface	ZnO Surface
Volmer	$H_3O^+ + e^- + M \rightarrow MH_{ads} + OH^-$	$H_2O + e^- + ZnO \rightarrow ZnO...H + OH^-$
Heyrovsky	$MH_{ads} + e^- + H_2O \rightarrow M + OH^- + H_2 \uparrow$	$ZnO...H + e^- + H_2O \rightarrow H_2 \uparrow + ZnO + OH^-$
Tafel	$MH_{ads} \rightarrow 2H + H_2 \uparrow$	$2ZnO...H \rightarrow 2ZnO + H_2 \uparrow$

If out of these three steps, Heyrovsky electrochemical desorption step becomes the rate-determining step (RDS) (i.e. evolution of H₂ from ZnO surface is the RDS), the resident time that an H atom is hydrogen-bonded to the O of ZnO will increase and hence the cathodic peak will be smaller and broader. During the anodic cycle the peak current increases and a shift in peak potential between cathodic and anodic peaks is observed, $\Delta E_{shift} = 0.15$ V. This shift can be attributed to the existence of ZnO-H species after a cathodic sweep and evolution of H₂ is occurring in anodic sweep via recombination of ZnO-H rather than electrochemical desorption. This hypothesis is consistent with the high electronegativity of O, which would assist to hold the H atom strongly in ZnO lattice via hydrogen bonding. When an anodic potential is applied afterwards, the bonded H would start recombining with neighboring H species, bound to ZnO and thus promote the evolution of H₂.

A phenomenological thermodynamic analysis can be carried out for the above HER mechanisms of ZnO NRs surfaces in (i) an acidic and (ii) an alkaline medium to obtain the energy required for the reaction to proceed (the activation energy, ΔG_{eq}), as well as to investigate the energies of each process occurring during the reaction.

Case (i) Acidic medium

The standard exchange current density for HER on s, p and d metal surfaces ($i_{0(HER)}$) can be written as [Harinipriya and Sangaranarayanan, 2002]

$$i_{0(HER)} = \left(\frac{FC_{H^+} + k_b T}{Ah} \right) \exp \left\{ -\frac{\Delta G_{H^+-s}}{2SN_{H^+}RT} - \frac{F\chi_e^s}{2RT} + \frac{F\xi\Phi_M}{RT} \right\}, \quad (A.1)$$

where F is faraday constant in C/mol, C_{H^+} represent the concentration of H⁺ ions in mol/liter, k_b denote Boltzmann constant in J/K, T is the ambient temperature in K, A indicates the area of the electrode in cm², h is the Planck's constant in Js, ΔG_{H^+-s} is the hydration energy of H⁺ ions in J/mol, SN_{H^+} is the hydration number of H⁺ ions, R is the Gas constant in J/K/mol, χ_e^s being the surface potential of electrons (excess energy required for the electrons to cross solution/electrode interface and vice versa) in eV, ξ is a dimensionless constant and Φ_M is the workfunction of the electrode (in eV) under consideration. The free energy of activation ($\Delta G_{eq}(HER)$ (eV)) and heterogeneous rate constant are explained elsewhere [Harinipriya and Sangaranarayanan, 2002]. $\xi = 0.17$, irrespective of the cathode material. The free energy of the solution for protons (protonium ion, ΔG_{H^+-s} (eV)) and the electron surface potential in solution (χ_e^s (eV)), are reported as 9.357 eV and 0.4 eV, respectively [Trasatti, 1976, 1972a; Marcus, 1991]. The hydration number (SN_{H^+}) is given as 5 and from Figure A.3a, peak current density for the HER on the ZnO NRs in 1M H₂SO₄ is -3.7 μAcm^{-2}

(ii) Alkaline medium

The free energy of activation and heterogeneous rate constant are represented in details of published work [Harinipriya *et al.*, 2012]. The exchange current density can be given as,

$$i_0 = \frac{nFC_{OH^-} - k_b T}{Ah} \exp \left\{ -\frac{(1+\beta)E^0}{RT} + \frac{\Delta G_{mH}^{form}}{RT} - \frac{\Delta G_{H-H}^{form}}{RT} + \frac{pH\beta nF}{RT} \right\}, \quad (A.2)$$

where $\beta = 0.5$ is the symmetry factor of the reaction, E^0 is the standard reduction potential

of H⁺ to H₂. From the above expression for $i_{0(HER)}$, the actual free energy change involved in the storage of H atoms in ZnO NRs can be evaluated from electrochemical data. From Figure A.3b, if the anodic peak current is considered to be responsible for the recombination of ZnO...H species leading to hydrogen evolution, then $i_{0(HER)}$ is taken to be 2.5 μAcm^{-2} . Upon substituting C_{OH^-} as 8.5, pH as 15, ΔG_{H-H}^{form} and E^0 are reported as 4.518 eV and 0.245 V [Lide, 1987] with

respect to the Ag/AgCl electrode. The free energy change involved in the bonding of hydrogen to ZnO as ZnO...H (ΔG_{mH}^{form}) is calculated using equation (A.2) and is ~192.086kJ/mol (this value is approximately three times higher than the O-H...O type hydrogen bonding in water) [Vinogradov and Linnel, 1971].

A.2 CONCLUDING REMARKS

Vertically arrays of nanorods with preferential c-axis orientation of ZnO were grown on the native oxide on the surface of Si (100) substrates with strong NBE emission peaked at 3.176 eV. Cyclic voltammetry analysis indicated that H can be stored in ZnO NRs via formation of ZnO-H bonding in a strongly alkaline medium.

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