ZnO Nanorod Electrodes for Hydrogen Evolution & Storage

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ABSTRACT

Due to the attractive combination of a relatively high specific heat of combustion with a large specific energy capacity, molecular hydrogen (H_2) is being investigated for use as an alternative to fossil fuels. Energy-efficient H_2 production and safe storage remain key technical obstacles to implementation of an H_2 based economy, however.

ZnO has been investigated for use as an alternative photocatalytic electrode to TiO_2 for solar-powered photo-electro-chemical (PEC) electrolysis, in which H_2 is generated by direct water splitting in a cell with a metal cathode and a semiconducting anode.

In this investigation, ZnO NR grown on Si (100) substrates by pulsed laser deposition were investigated for use as electrodes in the Hydrogen Evolution Reaction (HER). The electrochemical potential and Fermi energy of the ZnO NR were estimated from the electrochemical current density in acid and alkaline solutions via phenomenological thermodynamic analysis. As well as acting as an effective electrocalytic cathode, the ZnO NR appear to operate as a hydrogen reservoir. These results indicate that the ZnO NR have excellent potential for the storage of evolved H_2.

Keywords: ZnO, Nanowires, Hydrogen Evolution Reaction, Pulsed Laser Deposition, Cyclic Voltammetry

1. INTRODUCTION

Due to the attractive combination of a relatively high specific heat of combustion with a large specific energy capacity, molecular hydrogen (H_2) is being investigated for use as an alternative to fossil fuels [1]. Energy-efficient H_2 production and safe storage remain key technical obstacles, however, to implementation of an H_2 based economy.

Although industrial H_2 production is dominated by steam reforming of hydrocarbons, the energy costs of this process are relatively high and the purity is insufficient for fuel cell applications. H_2 produced by electrolysis is better adapted for fuel cell use because it is free of carbon monoxide contamination, which acts as a poison in proton exchange membrane fuel cells [6]. ZnO has been investigated for use as an alternative photocatalytic electrode to TiO_2 for solar-powered photo-electro-chemical (PEC) electrolysis, in which H_2 is generated by direct water splitting [2, 3].

In this investigation, the electrocatalytic hydrogen generation efficiency and the hydrogen storage capability of ZnO NR grown on Si (100) substrates by Pulsed Laser Deposition (PLD) [4, 5] were investigated.

2. EXPERIMENT

Vertical arrays of self-forming, catalyst-free, ZnO NRs were grown on Si (100) substrates using PLD, which is known for the synthesis of oxide materials with excellent crystal quality [4]. The growth conditions were as described elsewhere [5].

Sample morphology was studied using a Hitachi S4800 Field Emission-Scanning Electron Microscope (FE-SEM). The crystal quality of the nanostructures was investigated using X-Ray Diffraction (XRD) performed in a Panalytical MRD Pro system using a Cu Kα source, a four-bounce Ge (220) monochromator in the incident beam path and a three bounce Ge (220) monochromator in the diffracted beam path. Optical properties were studied via Room Temperature (RT) PhotoLuminescence (PL) with the 325 nm emission line of a HeCd laser.

Electrochemical studies were made using the ZnO NR / Si (100) as the cathode (working electrode), 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 cells were tested using both acidic and alkaline electrolytes: (1) 1M H_2SO_4 and (2) 8.5 M KOH, respectively. Deionised water, obtained using a Millipore purification system, was used for the dilution.

Cyclic voltammetry was conducted using a Iviumstat spectro-electro-chemical workstation with a three electrode assembly.

3. RESULTS & DISCUSSION

Figure 1 shows an SEM image of a typical region of the ZnO NRs.
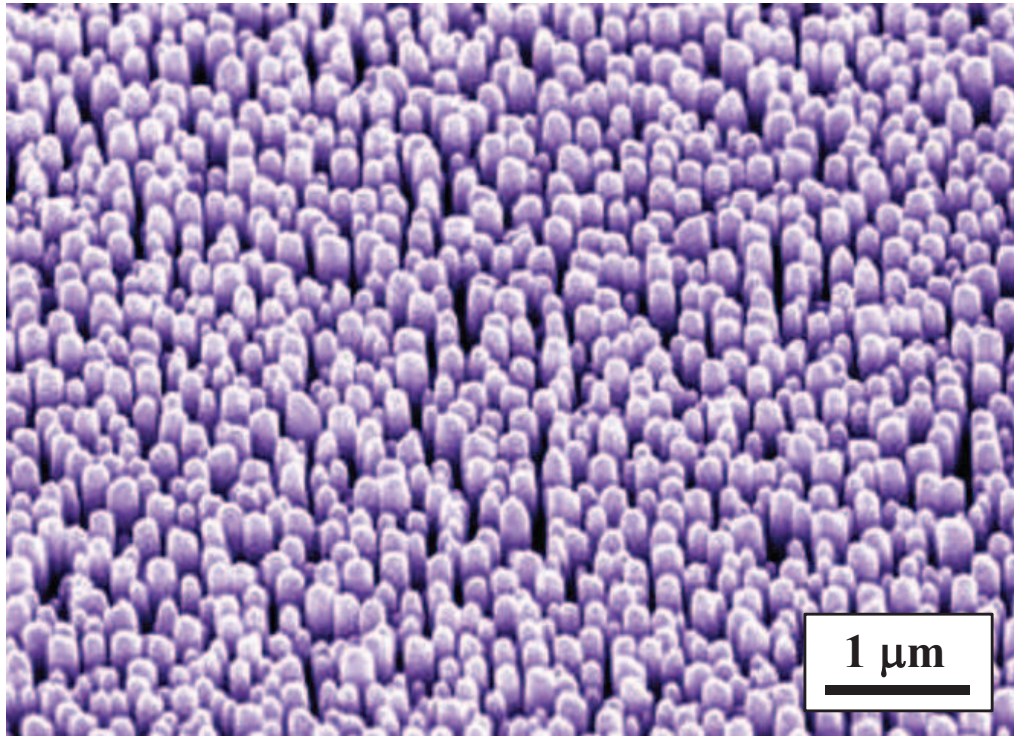
Figure 1 SEM image of vertical ZnO NR array grown by PLD on a Si (100) substrate.

The rods are vertically aligned, are between about 1 μm and 2 μm in length, have a diameter of between about 100 and 300 nm and a pitch of about 400 nm. Figure 2 shows XRD 2 θ/Ω & Ω scans for the (0002) peak of the ZnO NR grown on Si (100).
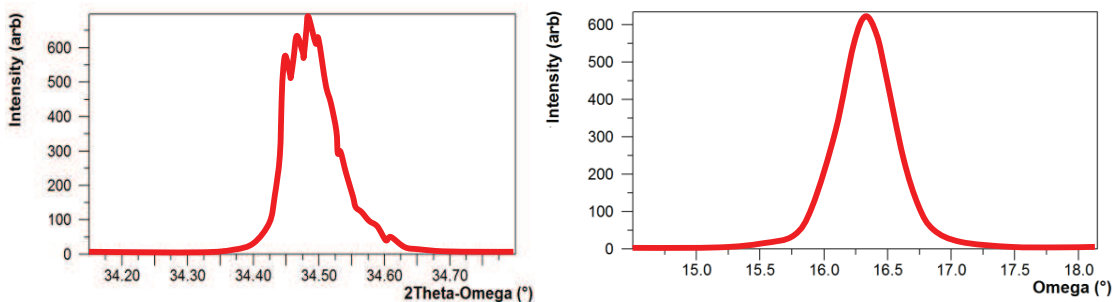
Figure 2: XRD 2 θ/Ω & Ω scans for the (0002) peak of the ZnO NR grown on Si (100).

The 2θ/Ω peak has a broadened multi-peak form, which is indicative of a variation in the c lattice parameter for the different NRs (between ~5.192 and ~5.200 Å: which is slightly lower than might be expected for relaxed wurtzite ZnO) [7]. There is also some higher-angle broadening at the base of the peak, which is indicative of a contribution from regions with a smaller c lattice parameter. This could be due to disorder at the start of nanostructure growth creating a less dense a-b plane at the base of the NRs (and thus a larger a lattice parameter) [8]. The Ω scan shows a much more

symmetrical peak, with a Full Width Half Maximum (FWHM) of 0.47°. This suggests that the NRs were significantly more c-axis oriented than the author's previously reported ZnO grown on Si (111) substrates (thin films [9] and NR arrays [10]). It should be noted that there was no attempt to remove the native amorphous SiO_2 oxide layer present on the Si (100) substrate surface.

The RT PL spectrum for the ZnO NR / Si (100) is shown in Figure 3.
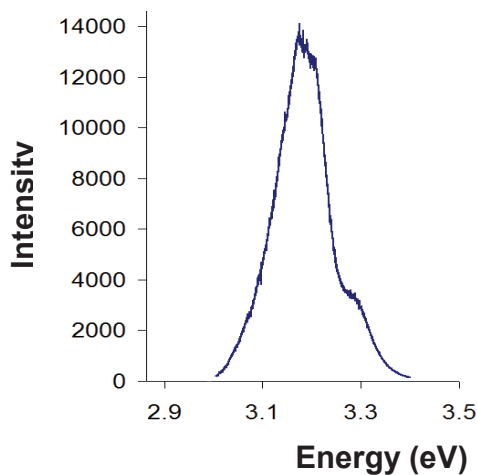
Figure 3 RT PL spectrum for the ZnO NR grown on Si (100).

The spectrum shows a strong main emission peaked at a wavelength (λ_{MAX}) of about 3.176 eV, which is consistent with near band edge emission (NBE) from wurtzite ZnO. The FWHM is about 110 meV.

The cyclic voltammetry plots for ZnO NRs / Si (100) in 1M H_2SO_4 and 8.5 M KOH are shown in Figures 4 and 5, respectively.

a) Potential (V) relative to Ag/AgCl   b) Potential (V) relative to Ag/AgCl
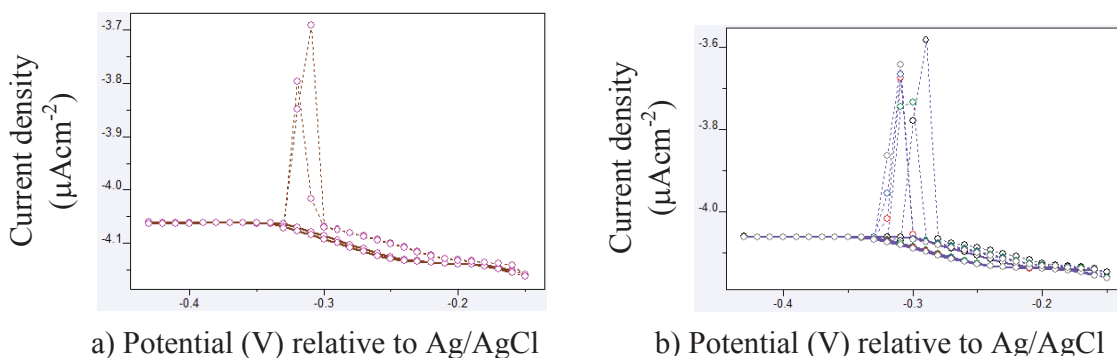
Figure 4: Cyclic Voltammetry plots for a ZnO NR / Si (100) working electrode in 1M H_2SO_4 at a 10mV/s scan rate. The plots for (a) two and (b) five cycles illustrate the poor reproducibility of the results. The reference electrode was Ag/AgCl and the counter electrode was a Pt wire.
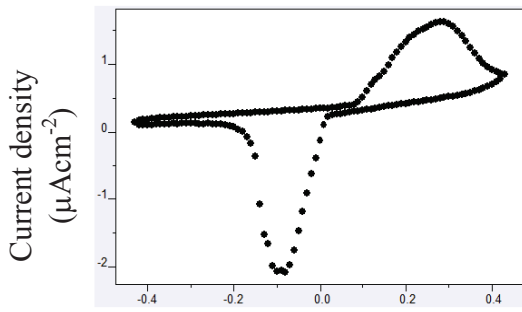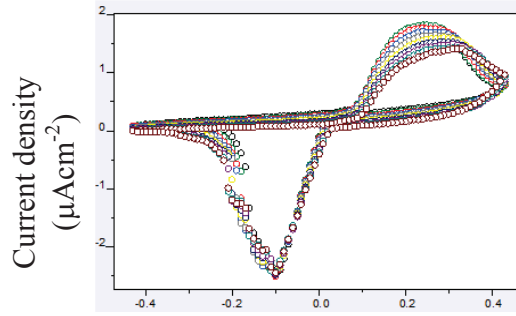
a) Potential (V) relative to Ag/AgCl   b) Potential (V) relative to Ag/AgCl

Figure 5: Cyclic voltammetry plots for a ZnO NR / Si (100) working electrode in 8.5M KOH at 10mV/s scan rate. The plots for (a) one and (b) ten cycles illustrate the reproducibility of the results. The reference electrode was Ag/AgCl and the counter electrode was Pt wire.

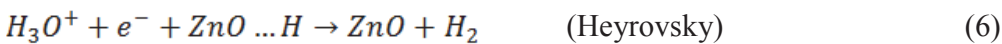The cyclic voltammetric studies revealed, highly irreversible evolution of H_2 in the acidic electrolyte while reversibility was maintained in the basic electrolyte. Figures 5 a and b show the variable/irreversible nature of the voltammogram. In general, HER in an acidic electrolyte involves three reaction steps: Volmer (electrosorption), Heyrovsky (electrodesorption) and Tafel (recombination) [11].

$$H_3O^+ + e^- + M \rightarrow MH + H_2O \qquad \text{(Volmer)} \qquad (1)$$

$$H_3O^+ + e^- + MH \rightarrow M + H_2 \qquad \text{(Heyrovsky)} \qquad (2)$$

$$2MH \rightarrow 2M + H_2 \qquad \text{(Tafel)} \qquad (3)$$

If the same mechanisms are assumed to occur at the surface of ZnO NRs, H_2 gas is formed and escapes through the solution and does not get reduced in the cathodic cycle of the voltammogram. It is also possible, however, that the H_2 may be trapped by the ZnO NRs due to Van der Waal's forces. Slight agitation would then be likely to release the physisorbed H_2.

$$H_3O^+ + e^- \rightarrow ZnO \ldots H + H_2O \qquad \text{(Volmer)} \qquad (4)$$

$$2ZnO \ldots H \rightarrow 2ZnO + H_2 \qquad \text{(Tafel)} \qquad (5)$$

$$H_3O^+ + e^- + ZnO \ldots H \rightarrow ZnO + H_2 \qquad \text{(Heyrovsky)} \qquad (6)$$

The mechanism of H_2 evolution in the alkaline medium, is different. From Figures 6 a and b, it is clear that the HER is reversible in nature and is reproducible. The mechanism of HER in an alkaline medium is as follows:

$$H_3O^+ + e^- + M \rightarrow MH_{ads} + OH^- \qquad \text{(Volmer electrochemical discharge)} \qquad (7)$$

$$MH_{ads} + e^- + H_2O \rightarrow M + OH^- + H_2 \uparrow \qquad \text{(Heyrovsky electrochemical desorption)} \qquad (8)$$

$$2MH_{ads} \rightarrow 2M + H_2 \uparrow \qquad \text{(Tafel catalytic recombination)} \qquad (9)$$

Assuming the same HER mechanism as for metal surfaces (above), the reaction for a ZnO surface can be expressed as follows:

$$H_2O + e^- + ZnO \rightarrow ZnO \ldots H + OH^- \text{(Volmer electrochemical discharge)} \qquad (10)$$

$$ZnO \ldots H + e^- + H_2O \rightarrow H_2 \uparrow + ZnO + OH^- \quad \text{(Heyrovsky electrochemical desorption)} \quad (11)$$

$$2ZnO \ldots H \rightarrow 2ZnO + H_2 \uparrow \qquad \text{(Tafel catalytic recombination step)} \qquad (12)$$
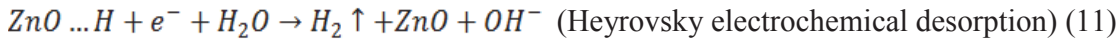
If out of the three steps, the Heyrovsky electrochemical desorption step becomes the rate-determining step (rds) (i.e. evolution of H_2 from ZnO surface is the rds), the resident time that an H atom is hydrogen-bonded to the O of ZnO will increase and hence the cathodic peak will be smaller and broader. 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 H_2 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 act to hold the H atom strongly in ZnO lattice via hydrogen bonding. When an anodic potential is then applied, the H would start recombining with neighbouring H species bound to ZnO and thus promote the evolution of H_2.

A phenomenological thermodynamic analysis can be done for the above HER mechanisms of ZnO NR surfaces in (i) an acidic and (ii) an alkaline medium in order to obtain the energy required for the reaction to proceed (the activation energy, $\Delta G^{\neq}_{eq}$), as well as to investigate the energetics of each process occurring during the reaction.

3.1 Acidic medium

It is well established in the literature that the standard exchange current density for HER on sp and d metal surfaces ($i_{0(HER)}$) can be written as [12]

$$i_{0(HER)} = \left(\frac{FC_{H^+}k_bT}{Ah}\right) exp\left\{-\frac{\Delta G_{H^+-s}}{2SN_{H^+}RT} - \frac{F\chi_e^S}{2RT} + \frac{F\xi\Phi_M}{RT}\right\} \qquad (13)$$

where F is the Faraday constant in C/mol, C_{H^+} represents the concentration of H^+ ions in mol/liter, k_b denotes the Boltzmann constant in J/K, T is the ambient temperature in K, A indicates the area of the electrode in cm^{-2}, h is 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 is 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 ($\Delta G^{\neq}_{eq(HER)}$ (eV)) is given by :

$$\Delta G^{\neq}_{eq(HER)} = \frac{\Delta G_{H^+-s}}{2SN_{H^+}} + \frac{F\chi_s^e}{2} - F\xi\Phi_M \qquad (14)$$

and the heterogeneous rate constant is given by

$$k_{et} = \frac{k_b T}{h} exp \left\{ -\frac{\Delta G^{\neq}_{eq(HER)}}{RT} \right\}$$ (15)

where $\Delta G^{\neq}_{eq(HER)}$ is the equilibrium free energy of activation for HER in J/mol and k_{et} is the heterogeneous rate constant in s⁻¹. The value of the constant ξ is 0.17 irrespective of the cathode material. The free energy of 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 [13-15]. The solvation number for protons in water (i.e. the hydration number (SN_{H^+})) is given as 5. From figures 5 (a) and (b), the peak current density for the HER on the ZnO NRs in 1M H_2SO_4 is -3.7 μAcm^{-2} and by roughly approximating it for i_0 in equation (13), the Φ for the ZnO NRs can be estimated. By employing the value for Φ_M obtained in equation (14), the $\Delta G^{\neq}_{eq(HER)}$ of the ZnO NRs can be estimated. Upon substitution of the above given values of ΔG_{H^+-s}, χ^e_s, SN_{H^+} in equation (13), the value of Φ for the NR is calculated to be 3.113 eV. From equation (14), the $\Delta G^{\neq}_{eq(HER)}$ for the ZnO NRs is estimated to be 0.60649 eV. This value suggests that there may be scope for improved performance by engineering of the ZnO NR bandgap to a lower value.

3.2 Alkaline medium
If the following steps are considered to occur in the HER for the ZnO NRs in the alkaline medium:
(a) reduction of H^+ to atomic H
(b) formation of ZnO…..H
(c) recombination of ZnO…..H to form ZnO and H_2

then the free energy of activation can be written as

$$\Delta G^{\neq} = \Delta G^0_{red,\frac{H^+}{H_2}} + \Delta G^{form}_{O…H} + 2\Delta G^{break}_{O…H} + \Delta G^{form}_{H-H}$$ (16)

where $\Delta G^0_{red,\frac{H^+}{H_2}}$ denotes the standard free energy change for the reduction of H^+ to H_2 in kJ/mol, $\Delta G^{form}_{O…H}$ represents the free energy change involved in the formation of ZnO…H bond in kJ/mol, $\Delta G^{break}_{O…H}$ indicates the free energy change during the breaking of ZnO…H bond in kJ/mol and ΔG^{form}_{H-H} is the free energy change for the formation of H – H bond in kJ/mol.

Therefore,

$$\Delta G^{\neq} = \Delta G^0_{red,\frac{H^+}{H_2}} + \Delta G^{form}_{O…H} - 2\Delta G^{form}_{O…H} + \Delta G^{form}_{H-H}$$ (17)

Thus,

$$\Delta G^{\neq} = \Delta G^0_{red,\frac{H^+}{H_2}} - \Delta G^{form}_{O…H} + \Delta G^{form}_{H-H}$$ (18)

Since, the heterogeneous rate constant in $\sec^{-1}$ can be written as:

$$k_{et} = \frac{k_b T}{h} exp\left\{-\frac{\Delta G^0_{red,\frac{H^+}{H_2}}}{RT} - \frac{\Delta G^{form}_{O...H}}{RT} + \frac{\Delta G^{form}_{H-H}}{RT}\right\} \quad (19)$$

and $i_{0(HER)}$ can be given as:

$$i_0 = \frac{nFC_{OH^-}k_b T}{Ah} exp\left\{-\frac{\Delta G^0_{red,\frac{H^+}{H_2}}}{RT} + \frac{\Delta G^{form}_{O...H}}{RT} - \frac{\Delta G^{form}_{H-H}}{RT} + \frac{\beta nFE_e}{RT}\right\} \quad (20)$$

where C_{OH^-} is the concentration of OH⁻ ions in mol/lit.
Upon rewriting, this becomes,

$$i_0 = \frac{nFC_{OH^-}k_b T}{Ah} exp\left\{-\frac{(1+\beta)E^0_{red,\frac{H^+}{H_2}}}{RT} + \frac{\Delta G^{form}_{O...H}}{RT} - \frac{\Delta G^{form}_{H-H}}{RT} + \frac{pH\beta nF}{RT}\right\} \quad (21)$$

where β is the symmetry factor of the reaction and always taken as 0.5, $E^0_{red,\frac{H^+}{H_2}}$ is the standard reduction potential of H⁺ to H_2.

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 and hence k_{et} and the $\Delta G^{\neq}$ for H storage in the ZnO NRs can also be estimated.

From Figure 6b, 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 $2.5 \mu A cm^{-2}$. Upon substituting C_{OH^-} as 8.5, pH as 15 (this is possible in the case of high concentration alkaline solution where pOH is negative and pH = 14 − pOH, thus pH>14, this could be attributed to the ion pair formation at high concentrations), ΔG^{form}_{H-H} is reported as 435.99kJ/mol (4.518 eV) [16], $E^0_{red,\frac{H^+}{H_2}}$ as 0.245 V [16] with respect to the Ag/AgCl electrode, in equation (21), the free energy change involved in the bonding of hydrogen to ZnO as ZnO...H ($\Delta G^{form}_{O...H}$) is calculated as 192.086kJ/mol (this value is approximately three times higher than the O-H...O type hydrogen bonding in water) [17].

4. CONCLUSION

SEM, XRD and PL study of ZnO grown on the native oxide at the surface of Si (100) substrates revealed self-forming, catalyst-free, vertical arrays of NR with a marked preferential c-axis orientation (Ω scan FWHM of 0.47°) and strong NBE emission, peaked at 3.176 eV. Cyclic voltammetry studies made using the ZnO NR / Si (100) as the cathode and Pt as the counter electrode, Ag/AgCl as reference revealed that the NR act as effective electrocatalytic cathodes for the HER. Phenomenological thermodynamic analysis indicated that H can also be stored in ZnO NRs via formation of ZnO-H bonding. A bond energy of 192.086 kJ/mol was estimated.

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