

### Supporting informations

#### EXPERIMENTAL DETAILS FOR ZnO NANONAILS

ZnO nanonails have been synthesized by a simple thermal evaporation method using metallic zinc powder as a source of zinc in the presence of oxygen without the use of any metal catalyst or additives.<sup>[22, 23]</sup> The source material loaded into a reactor was rapidly heated up to the temperature ranges of 580-700 °C under a flow of high-purity nitrogen gas at the rate of 200 sccm (standard cubic centimeter per minute). When the furnace temperature reached to a desired growth temperature, the oxygen gas was introduced into the reactor at a flow rate of 10 sccm during the whole growth period. The typical growth time for the synthesis of these ZnO nanonails was 60 min. After the growth process, the white colored products were collected for structural and optical characterization and fabrication of hydrazine sensor. The structural properties of as-grown nanonails were examined using scanning electron microscope (SEM), X-ray diffraction (XRD) patterns, and high-resolution transmission electron microscopy (HRTEM) equipped with the selected area electron diffraction (SAED) patterns. Room-temperature Raman-scattering and photoluminescence studies, respectively measured with the Ar<sup>+</sup> (513.4 nm) and He-Cd (325nm) laser lines as the exciton sources have been performed to examine the optical properties of as-grown ZnO nanonails.

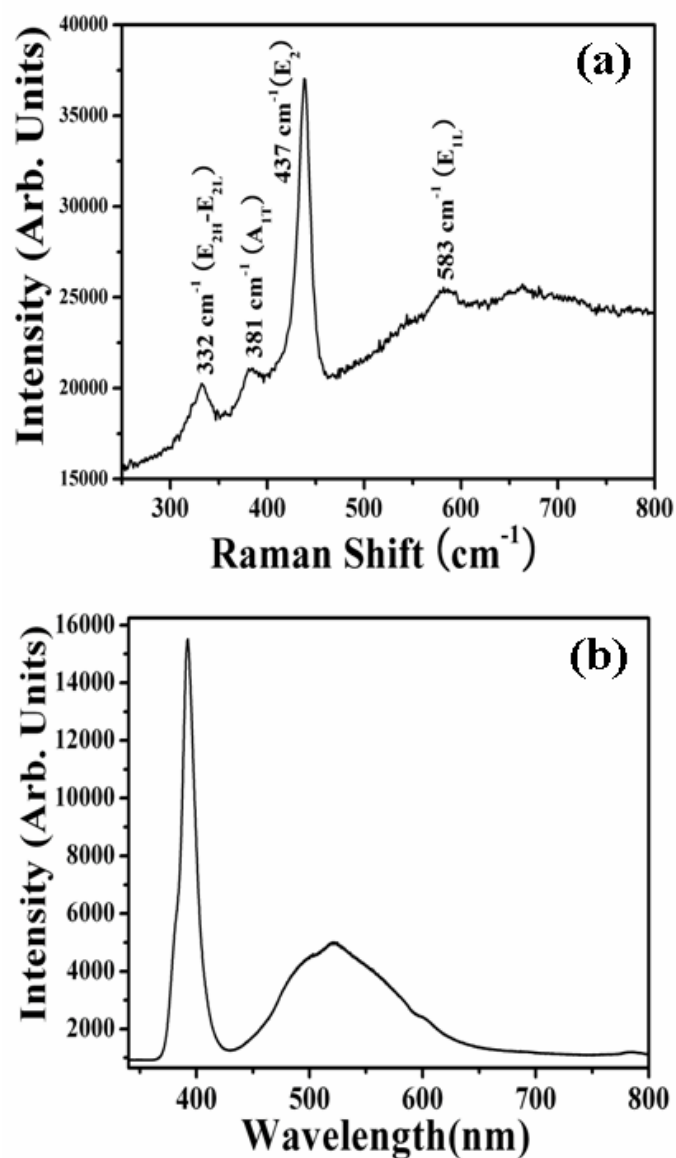
To fabricate the hydrazine sensor, the as-grown ZnO nanonails were coated onto the surface of a gold (Au) electrode with the area of 2.0 mm<sup>2</sup>. The prepared ZnO nanonails/Au electrode was wetted by phosphate buffer solution (0.1 M PBS) with pH=7.4 and dried gently by the high purity nitrogen gas. After drying the modified

ZnO/Au electrode, a 5  $\mu\text{l}$  (5 weight %) Nafion solution was dropped onto the electrode and dried for 24 h at 4  $^{\circ}\text{C}$  to form a film on the modified electrode like net-coating. For the amperometric experiments, aliquots of hydrazine (from 0.2 - 3  $\mu\text{M}$ ) were injected into the stirred electrolyte solution and each addition of hydrazine resulted in a rapid increase in the current. When not in use, the ZnO-modified gold electrodes (i.e., Nafion/ ZnO/Au electrodes) were stored in PBS (pH=7.4) at 4  $^{\circ}\text{C}$ . The electrochemical experiments were carried out at room- temperature using an electrochemical analyzer (SHIn 2000, EQCM, Korea) with a conventional three-electrode configuration: a working electrode (ZnO-modified gold electrode with the area of 2  $\text{mm}^2$ ), a Pt wire as a counter electrode and Ag/AgCl (saturated KCl) as a reference electrode. Prior to the experiments, the working electrode was polished with the 0.05  $\mu\text{m}$  alumina slurry and then sonicated in de-ionized water.

### **Raman-scattering and room-temperature photoluminescence spectrum for the as-grown ZnO nanonails**

Figs. (a) and (b) show the Raman-scattering and room-temperature photoluminescence (PL) spectra of as-synthesized ZnO nanonails measured with measured with the  $\text{Ar}^+$  and He-Cd laser lines at exciton wavelengths of 513.4 nm and 325 nm, respectively. A strong and dominant peak at 437  $\text{cm}^{-1}$  attributed to be as the Raman active optical-phonon  $E_2$  mode of ZnO crystal, and a very suppressed and small peak at 583  $\text{cm}^{-1}$ , assigned as  $E_{1L}$  mode appeared due to the formation of defects such as zinc interstitials and oxygen vacancies, etc, have been observed. Furthermore, in the room-temperature PL spectrum, a strong and high intensity peak of UV emission at 381 nm and a suppressed and broad green emission at 521 nm attributed to oxygen vacancy was

observed. Therefore, the observed Raman-scattering and PL results confirm that the synthesized ZnO nanonails have good crystal quality, with a wurtzite hexagonal phase and exhibit a good optical properties with very less structural defects.



(a) Typical Raman-scattering and (b) room-temperature photoluminescence spectra from the as-grown ZnO nanonails

### **Detection of hydrazine using the hexagonal-shaped ZnO nanorods modified gold electrodes**

The hexagonal-shaped ZnO nanorods were grown onto the Au-coated silicon substrate as reported earlier [1]. To fabricate the hydrazine chemical sensors, the as prepared ZnO nanorods were firstly transferred from the silicon substrate to the standard gold electrode commonly used in electrochemistry. The modification of the Au electrodes, for the detection of the hydrazine was same as employed in the case of ZnO nanonails.

Figure 1 shows a typical amperometric response of the hexagonal-shaped ZnO nanorods-modified gold electrode (Nafion/ZnO nanorods/Au electrode) on successive addition of hydrazine (from 0.2 – 2.4  $\mu\text{M}$ ) to a continuously stirred 0.01 M PBS solution (pH 7.4) at an applied potential in the range of -0.5 to 0.4 V. A rapid and sensitive response by changing the hydrazine concentration and an obvious increase in the oxidation current upon successive addition of hydrazine was observed from the fabricated ZnO nanorods based amperometric sensors. The modified electrode achieved 95% steady state currents with in 10 s.



Figure 1. Amperometric response of the Nafion/hexagonal-shaped ZnO nanorods/Au electrode with successive addition of hydrazine into 0.01 M PBS buffer solution (pH = 7.4). The applied potential was in the range of -0.5 to +0.4 V vs. Ag/AgCl (sat'd KCl) reference.

Figure 2 shows the calibration curve of the fabricated hexagonal-shaped ZnO nanorods based amperometric hydrazine sensor. The response current increases as the concentration of hydrazine increases, and saturated at a high hydrazine concentration value of  $\sim 1.65 \mu\text{M}$ .

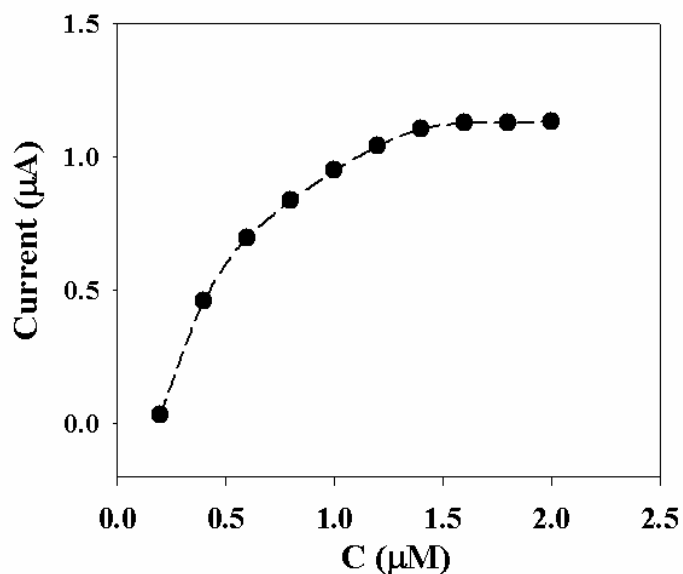


Figure 2. Typical calibration curve of the fabricated hexagonal-shaped ZnO nanorods based amperometric hydrazine sensor. The plot of Current vs Concentration (C) exhibits that the current saturated at a high concentration value of hydrazine ( $\sim 1.65 \mu\text{M}$ ).

Figure 3 exhibits the typical plot of  $1/\text{Current}$  ( $1/I$ ) versus  $1/\text{Concentration}$  ( $1/C$ ) which exhibits a linear relationship with the steady state current and hydrazine concentration. Moreover, under the optimized condition, the steady state current showed a linear relationship with the hydrazine concentration in the range of 0.2 to 2.0  $\mu\text{M}$ . The correlation coefficient ( $R$ ) was estimated to be 0.9914. The sensitivity of the hexagonal-shaped ZnO nanorods modified amperometric hydrazine sensor, from the slope of calibration curve, was found to be  $4.76 \mu\text{A}/\text{cm}^2 \mu\text{M}^{-1}$  and the detection limit was estimated, based on signal to noise ratio, 2.2  $\mu\text{M}$ .

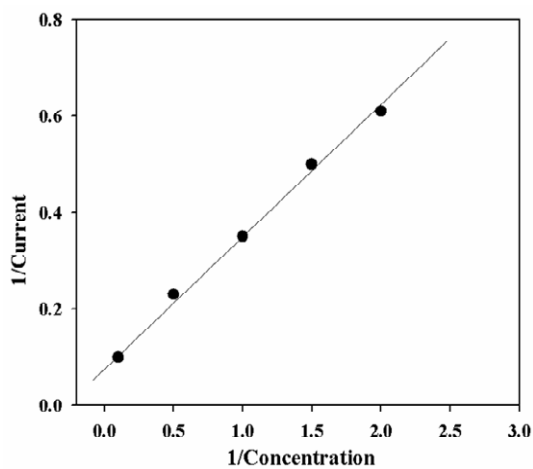


Figure 3. The plot of  $1/\text{Current}$  ( $1/I$ ) versus  $1/\text{Concentration}$  ( $1/C$ ) exhibiting a linear relationship with the steady state current and hydrazine concentration

## References

- [1] A. Umar, S. H. Kim, J. H. Kim and Y. B. Hahn, *J. Nanosci. Nanotech.* 2007, **7**, (In press)