Detection of Zn^{2+} ion with UV light activated ZnO nanorods

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Abstract: ***Monitoring of Zn^{2+} ion in water is very important as it is a vital cation in the human body excess of which can be fatal. ZnO nanorods grown over interdigitated Cu electrodes can be used as an efficient Zn^{2+} ion detector in presence of UV light. This paper reports the response of the ZnO nanorods based sensor to water samples containing different concentration of Zn^{2+} ions.***

Keywords: *Sensor, ZnO nanorods, Zn^{2+} ions, interdigitated electrodes*

1. Introduction

Zinc ion is a vital cation present in the human body for the regulation of biological processes and other bodily functions [1]. The human body contains about 2-3 g on average of zinc. However, an excess of zinc above the normal level is dangerous to one's health which can even cause death [2]. Therefore, monitoring of zinc ions in water is very important for our health.

Recently, nanostructures based sensors have attracted the attention of researchers because of high sensitivity. One-dimensional (1D) nanostructures such as nanowires, nanorods (short nanowires), nanofibres, nanobelts, and nanotubes have been of intense interest in research because of their higher surface area to volume ratios [3].

In this paper, ZnO nanorods are used for detection of zinc ions in water as it is a semiconductor material with direct wide band gap energy (3.37 eV) and a large exciton binding energy (60 meV) at room temperature [4]. ZnO is also biocompatible, biodegradable, and biosafe for medical and environmental applications [5]. ZnO nanorods act as an efficient sensing material under UV illumination as it is a good UV absorber [6].

2. Experimental

2.1 Fabrication of the Zn ion sensor

The Zn ion sensor was fabricated by growing ZnO nanorods on Cu electrodes as shown in Fig. 1. These interdigitated electrodes were made on a printed circuit board by a normal PCB design method. The UV sensitive ZnO nanorods were grown on the electrodes following a chemical synthesis route starting from ZnO nanoparticles as explained below. When the device was illuminated with UV light, photo generated carriers in ZnO nanorods drifted to the finger electrodes under biased condition.

2.2 Synthesis of ZnO nanoparticles

For the nanoparticles dispersion, at first 20ml of 4mM zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$, Merck, 99% purity] was prepared using ethanol [C_2H_5OH, Merck, 99% purity] as the solvent. This solution was then heated under

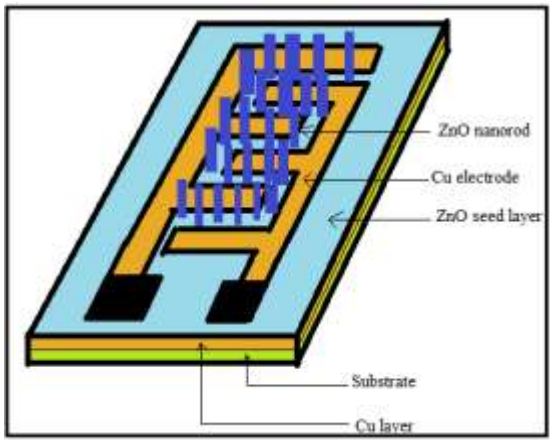


Fig. 1 ZnO nanorods on interdigitated electrode

rigorous stirring at 50°C for an hour. Another 20mL of fresh ethanol is then added to the solution to dilute it. At room temperature, 20mL of 2mM sodium hydroxide with ethanol as solvent was added to the diluted solution under mild stirring for half an hour.

This mixture was then placed in a water bath at 50-60^{o}C for an hour. The mixture was then cooled to room temperature [7].

2.3 Seeding of ZnO nanoparticles

Before the seeding of the nanoparticles the substrate was preheated at 120^{o}C for 1-5 hours. The substrate which is the interdigitated electrode was then dipped in a concentrated colloidal dispersion of ZnO nanoparticle for 15 minutes. Three such dippings were required and after each dipping, the substrate was then washed with deionized water to remove the loosely bound particles and was then heated at 120^{o}C for 15 minutes [8].

2.4 Growth of ZnO nanorods on the seeded substrate

For the growth of the nanorods, the seeded substrate was placed inverted in a petri dish

containing equimolar solution of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$, Merck, 99% purity] and hexamine [$C_6H_{12}N_4$, Merck, 99% purity]. This was kept in a hot air oven at 90^{o}C keeping the active layer down for 5 hours. This solution was to be changed after every 5 hours and the growth was continued upto 15 hours. After the completion of the growth, the substrate was washed thoroughly with deionized water and post annealing was done at 120^{o}C for an hour [9,10].

2.5 Preparation of Zinc ions solution

Zinc acetate dihydrate $Zn(CH_3COO)_2.2H_2O$, Merck, 99% purity] was used in the preparation of Zn^{2+} solution. Different concentrations (1000 ppm, 500 ppm, 250 ppm and 125 ppm specifically) of zinc ions were prepared by mixing appropriate amounts of zinc acetate dehydrate in deionized water.

2.6 Characterization

Transmission electron microscopy (TEM) was carried out to determine the size of ZnO nanoparticles using a TECNAI G2 20 S-TWIN TEM operated at 200 KV. Size of the ZnO nanorods was obtained from the SEM image using JEOL JSM 6390LV SEM.

2.7 Sensor set-up

The set-up for zinc ion detection using ZnO nanorods is shown as a schematic in Fig. 2. In this technique, in presence of UV light, a few drops of test water sample are dropped onto the sensor containing the thin film of ZnO nanorods. The change in voltage across the sensor depending on the concentration of zinc ions present in the solution is then obtained, which is then further amplified.

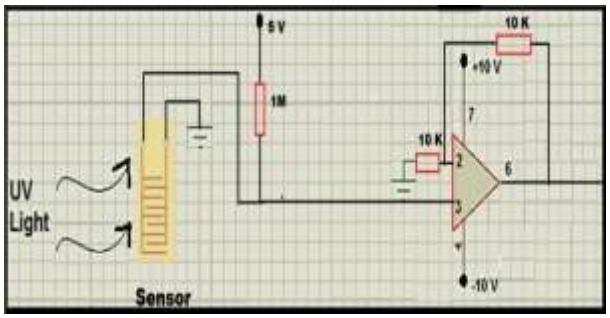


Fig. 2 Sensor set-up

3. Results and Discussion

Fig. 3 (a) shows the TEM image of the as-synthesized nanoparticles and fig.3(b) shows SEM image of the ZnO nanorods grown on the Cu interdigitated electrodes.

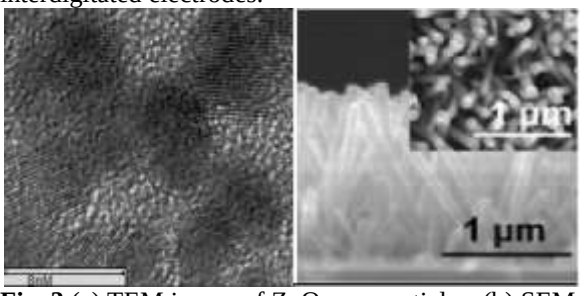


Fig. 3 (a) TEM image of ZnO nanoparticles, (b) SEM image of ZnO nanorod

The UV response of ZnO nanorods is influenced by the adsorption and desorption of oxygen on its surface during UV illumination. O_2 molecules from the ambient are adsorbed onto the nanorods surface by capturing free electrons from ZnO. When the UV light is incident on the surface of the nanostructure, electron-hole pairs are photogenerated. Nanorods due to its large surface area facilitate a fast surface reaction process as the photogenerated hole reacts with negatively charged adsorbed oxygen. As a result, the electron of the pair is left in the conduction band, which increases the conductivity of the nanostructures. When the UV illumination is turned off, the oxygen molecule recombines with the electron, leading to a decrease in film conductivity.

The reactions involved in the process are shown below:-

$$O_2 + e^- \rightarrow O_2^- \quad \text{.....(1)}$$

where O_2 is an oxygen molecule, e^- is a free electron and O_2^- is an adsorbed oxygen on the surface of nanorods.

$$h\upsilon \rightarrow h^+ + e^- \quad \text{.....(2)}$$

where hU is the photon energy of UV light, h^+ is a photogenerated hole in the valence band and e^- is a photogenerated electron in the conduction band.

$$O_2^- + h^+ \rightarrow O_2 \quad \text{.....(3)}$$

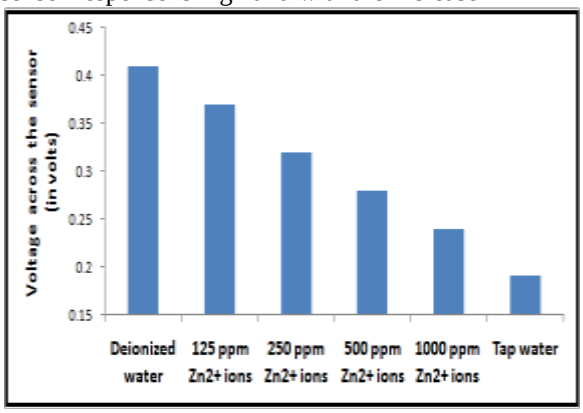
Where photogenerated hole reacts with negatively charged adsorbed oxygen.

The sensor was tested for deionized water and tap water along with the water samples prepared with zinc ions. The results obtained from the sensor system which is made up of these UV sensitive nanorods are shown in table I.

Table I: Response of the sensor

Type of solution		Voltage across sensor (in volt)	Op-amp o/p (in volt)
No water		0.84	3.10
Deionized water		0.41	0.75
Zn^{2+}	125 ppm	0.37	0.65
	250 ppm	0.32	0.53
	500 ppm	0.28	0.44
	1000 ppm	0.24	0.37
Tap water		0.19	0.28

The values from table I are plotted on a graph shown in fig.4. It is found that in presence of deionized water which is devoid of any ions, the sensor response is high and with the increase in



concentration of Zn^{2+} ions, the voltage drop across the sensor decreases. This happens due to the decrease in resistance across the sensor with the increase in concentration of metal ions. Further, unpurified tap water, which contains lots of metal ions, voltage drop across the sensor decreases even more.

4. Conclusion

ZnO nanorods grown over interdigitated electrode array have been successfully applied for detecting Zn^{2+} ions in presence of UV light. The change in voltage across the sensor can be used as parameter for determination of concentration of Zn^{2+} ions present in water sample.

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