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DNA quartz crystal microbalance biosensor based on ZnO nanostructure

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Nanostructured ZnO was synthesized using sol-gel method. The structural properties of the synthesized ZnO were studied using X-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD patterns of the synthesized powder confirm the Wurtzite-structure of ZnO without any impurity phase. The crystallite size of the powder was estimated using Scherrer formula and observed to be 31 nm. The various concentrations of DNA were immobilized over ZnO using physical interactions. The quartz crystal microbalance (QCM) study reveals that the frequency shift depends on the concentration of immobilized DNA molecules. This suggests that synthesized nanostructured ZnO could be used as DNA sensing application.

Keywords: *ZnO, DNA, Biosensor, Quartz crystal microbalance, nanostructure*

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1. Introduction

In recent years, there is growing interest to fabricate biosensors based on inorganic materials [1]. Among them, ZnO based sensors gave attracted considerable attention because of their unique electrical, optical and biocompatibility properties [2,3]. ZnO is n-type semiconductor with optical band gap of ~3.4 eV which makes it also suitable for photoconductivity and photocatalytic activity [4]. Recently, much attention has been paid for the fabrication of nanostructured materials because of their improved sensitivity due to high surface to volume ratio compared to bulk counterpart [1].

Wang et al [5] have used ZnO nanowires for ammonia sensing application. It was observed that ZnO nanowires have high sensitivity to ammonia in the range of 40–1000 ppm. An electrochemical DNA biosensor based on zinc oxide (ZnO) nanoparticles and multi-walled carbon nanotubes (MWNTs) were fabricated [6]. An electrochemical biosensor based on nanostructured ZnO for the quantitative detection of an extremely small amount of glucose was developed [7]. The immobilization of negatively charged glucose oxidase was realized over nanostructured ZnO through electrostatic interaction. Umar et al [8] have fabricated cholesterol biosensor using flower shaped ZnO structure. Erol et al [9] have synthesized nanostructured ZnO using sol-gel technique for humidity sensing application. The relative sensitivity of the ZnO nanoparticles-based humidity sensor was determined by electrical resistance measurements.

In this paper, we report the DNA sensing characteristics of nanostructured ZnO using quartz crystal microbalance (QCM) technique. QCM is very sensitive mass device which is very promising because of its low cost and compact design. The electrostatic interaction between nanostructured ZnO and DNA were used to immobilize DNA over ZnO.

2. Experimental

2.1. Preparation of nanostructued zinc oxide

Nanostructured zinc oxide was synthesized using sol-gel method. In typical synthesis, zinc acetate dihydrate was dissolved in 2-methoxyethanol (0.5 M) under constant magnetic stirring for 10 minutes and then, monoethanolamine (0.5 M) was added as a stabilizer during the stirring. The above solution was stirred constantly for two hours. The obtained gels were calcinated in a tube furnace for 5 h at 400 ºC.

2.2 Fabrication of quartz crystal microbalance biosensor

The quartz crystal microbalance biosensor was prepared as follows, the quartz crystal was ultrasonically cleaned by acetone, ethanol and deionize water baths. After cleaning process, it was dried with N_2 gas. The ZnO nanopowders were stirred in ethanol solution and then, ultrasonically dispersed. The nanopowders were coated on the surface of quartz crystal by drop casting method.

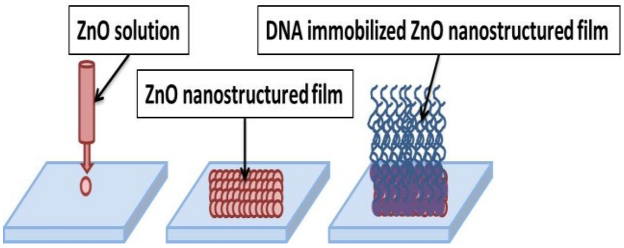

Fig.1. Schematics of DNA immobilization on ZnO

The DNA nonactivated DNA oligonucleotid was immobilized onto the ZnO by physical adsorption technique and this process was repeated for various microliter volumes of DNA solution (Fig.1). The modified electrode was kept overnight for DNA immobilization and subsequently washed with buffer solution, and dried in nitrogen environment. The structural properties of the ZnO and DNA deposited on gold coated onto quartz crystal investigated by Park System XE-100E atomic force microscopy (AFM). Fig.2 show the surface morphology of DNA on ZnO nanoparticles. The sensor measurements were done using a QCM200 Quartz Crystal Microbalance.

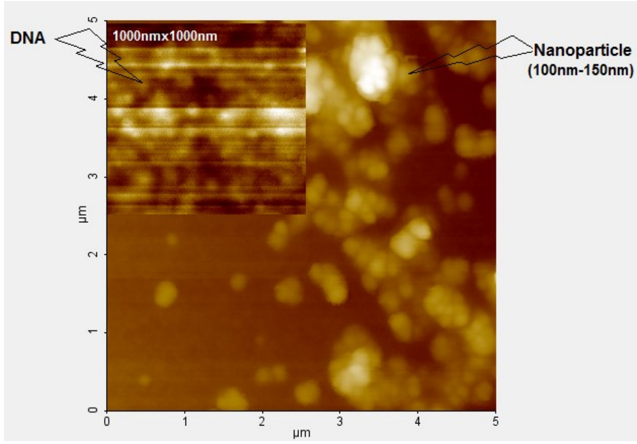

Fig.2. AFM image of DNA immobilized onto the ZnO particles

3. Results and Discussion

The XRD diffraction patterns of the synthesized ZnO powder is shown in Fig.3. The observed diffraction peaks of the synthesized powder can be indexed within experimental error as hexagonal ZnO phase (Wurtzite-structure) with lattice constants of a = 3.2510 Å and c = 5.2065 Å. The observed peak positions and lattice constants are in good agreement with the JCPDS file of ZnO (JCPDS cards No.36-1451). The sharp intense peaks of ZnO also confirm the good crystalline nature of the powder. No other impurity phase was observed in the XRD patterns of the powder. The average particle size (D) of the powder was calculated using the Scherrer equation [9],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the x-ray wavelength, β is the full width at half maximum, and θ is the diffraction angle of the XRD spectra The average particle size was estimated to be 31 nm. This suggests that the ZnO film is a nanomaterial.
Fig.4 shows the frequency shift (Δf) curves with time for control, ZnO, and ZnO with various concentrations of DNA. As seen in the Fig.4, the frequency shift of DNA immobilized onto ZnO is increased with increase in the DNA concentration. The results confirm that ZnO based QCM sensors are very sensitive to the amount of DNA immobilized over ZnO film. The shift in the frequency is related to the mass loading on the QCM sensor and can be expressed by the following equation [10]

$$\Delta f = -2.26 \times 10^{-6} \left(\frac{f^2 \Delta m}{A} \right) \tag{2}$$

where f (MHz) is the fundamental frequency of the unloaded crystal, Δm (g) is the mass loading, and A (cm^2) is the surface area of the electrode. Fig.5 shows the variation of mass loading (Δm) as a function of time for various concentrations of DNA. As seen in the Fig.5, mass loading is dependent on the concentration of DNA. Fig.6 shows the frequency shift dependence of DNA concentration. The DNA sensor indicates a linear behavior until to 15 µl. After 15 µl, a rapid increase in frequency shift. The obtained results suggest that synthesized nanostructured ZnO could be used as DNA sensing applications.

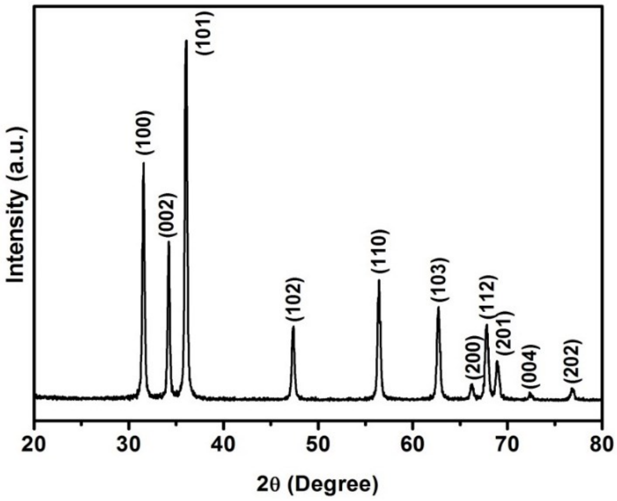

Fig.3 XRD patterns of ZnO nanoparticles

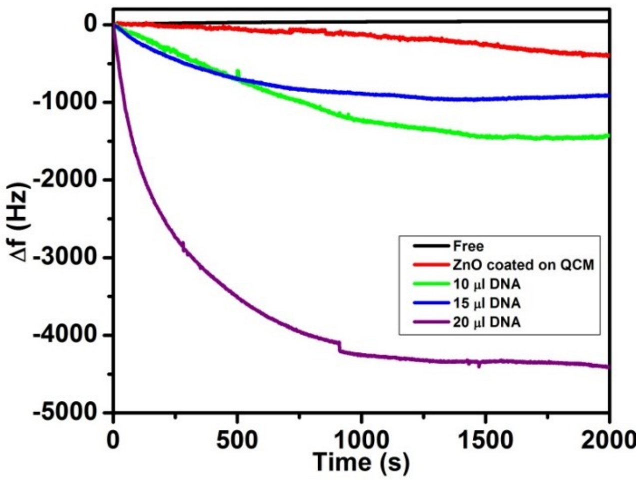

Fig. 4 Time dependence frequency shift for various films

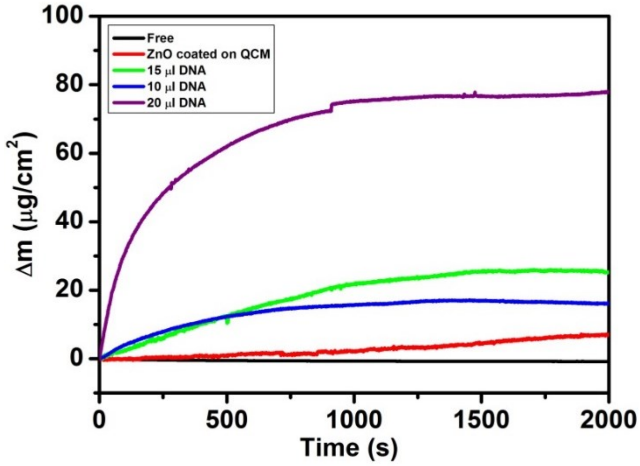

Fig. 5. Time dependence mass loading of various films

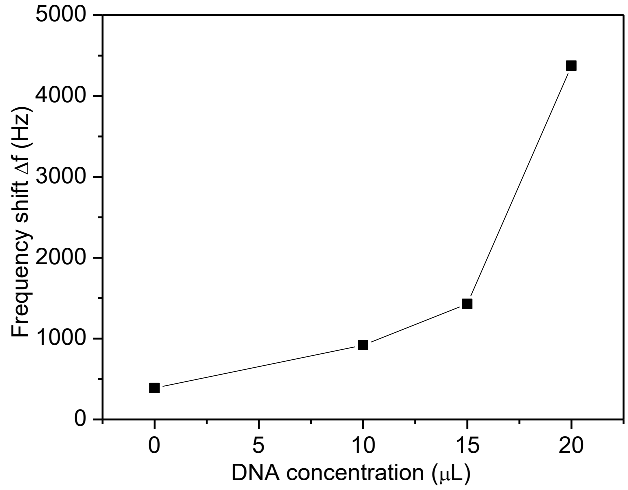

Fig.6. Frequency shift dependence of DNA concentration

4. Conclusion

Nanostructured ZnO was used for the fabrication of DNA sensor. The particle size of the synthesized ZnO was estimated using XRD patterns and observed to be 31 nm. Different concentrations of DNA were immobilized over ZnO. The frequency shift and mass loading study with time show that the response of the senor is dependent on the concentration of DNA molecules. The present study reveals that the synthesized ZnO could be used as DNA sensor

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