Electrochemical and Solid-State Letters, **10** (1) J1-J3 (2007)
1099-0062/2006/10(1)/J1/3/$20.00 © The Electrochemical Society

ZnO-Based Cyclodextrin Sensor Using Immobilized Polydiacetylene Vesicles

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We report that polydiacetylenes (PDAs) vesicles were successfully immobilized and chemisorbed on single crystal ZnO surfaces. Immobilized PDAs on ZnO were found to be sensitive to temperature and selectively sensitive to α- and γ-cyclodextrins. This approach is attractive for the on-chip integration of various types of sensors, ultraviolet light emitting diodes, and transparent electronics with PDAs.

Manuscript submitted June 2, 2006; revised manuscript received June 30, 2006. Available electronically November 1, 2006.

Recently there has been intense interest in the development of ZnO for applications in ultraviolet (UV) light emitters, transparent high power electronics, transparent electrodes in displays, and in photovoltaic devices, piezoelectric transducers, and chemical and gas sensing.[1-5] In addition, ZnO is lattice matched to InGaN at an In composition of 22%, allowing for integration of the two materials to provide enhanced functionality.[1] An example would be combining visible or UV light-emitting diodes with fluorescent chemical or biological detectors and off-chip wireless communications circuitry. ZnO of reasonable quality can also be deposited at lower growth temperatures than GaN, leading to the possibility of transparent junctions on cheap substrates, such as glass. This may lead to low-cost UV lasers with important applications in high-density data storage systems, solid-state lighting where white light is obtained from phosphors excited by blue or UV light-emitting diodes, secure communications, and biodetection. ZnO is attractive for sensing applications because of its wide bandgap (3.2 eV), the availability of heterostructures, the ease of synthesizing nanostructures and the biosafe characteristics of this material. Recently, the first applications in pH sensor and gas sensor using ZnO were published.[4,5] ZnO is a transparent substrate, which makes it easier to monitor the chemistry occurring on the surface from backside using the optical spectroscopy, compared with opaque GaAs and Si substrates. For these reasons, there is significant interest in ZnO-based chemical and biological sensors.

After the first report of polydiacetylene (PDA) supramolecules as an influenza virus sensor, the applications of PDAs as chemosensors and biosensors have been a subject of much recent research.[6-8] Polydiacetylene has been known for its unique property that "blue-phase" polydiacetylene does not fluoresce but its counterpart "red-phase" is fluorescent. The phase transition from blue-phase to red-phase happens in response to many stimuli from environments such as temperature,[7] pH,[8] and ligand-receptor interactions.[9] We recently reported the unique effects of cyclodextrins on the formation and colormetric transition of polydiacetylene vesicles as well as the new approach for the immobilization of PDA on glass.[10-12] Furthermore, the functionalized PDAs can be used as chemosensors to monitor ion, glucose, protein and *E. Coli.*[13] Because the immobilized PDA supramolecule showed better sensitivity against smaller amount of target analytes than PDA solution, it would be advantageous to integrate immobilized PDA in micrometer-size regions with ZnO-based devices.

Experimental

The bulk ZnO hexagonal-phase single crystals from Cermet, Inc. were 1 cm^2 in dimension and were nominally undoped with 300 K electron concentration of $9 \times 10^{16}\ cm^{-3}$ and mobility of 200 $cm^2/V\ s$. To immobilize PDA on the ZnO surface, the ZnO was first cleaned with acetone and ethanol. Then, the Zn-face surface of ZnO was treated using an ozone plasma for 30 min to remove surface hydrocarbons. After ozone treatment, ZnO was dipped in an amine solution (3-aminopropyltriethoxysilane:ethanol = 1:10 in volume ratio) for 4 h. When the contact angle was measured against pure water (pH 5.5, room temperature) after this process, it was 65.5° (Fig. 1). Then, it was dipped in a solution containing 1 mg *N*-hydroxysuccinimidobiotin dissolved in 1 mL dimethysulfoxide and 3 mL phosphate buffered saline (PBS; pH 7.2). for 2 h and avidin for another 2 h. At this point, the surface of ZnO was ready for the immobilization of supramolecules (here, vesicles) after the treatments of biotin and avidin (Fig. 2a). To make self-assembled surface patterns of the vesicles, PCDA-ABA (10,12-pentacosadiynoic acid-aminobutyric acid):PCDA-biotin(10, 12-pentacosadiynoic acid-2,2′-(ethylenedioxy)-bis-(ethylamide)-biotin)) =9:1 was used to fabricate vesicles through a standard sonication method.[14] The size distribution of the vesicles was measured by light scattering to be mono-modal and the average size was ~169 nm. A microarrayer (Nano-plotter from Gesim) was employed for patterning to immobilize vesicle on the ZnO surface. After the supramolecule (self-assembled PCDA-ABA:PCDA-Biotin) was deposited on the ZnO surface, the supramolecule/ZnO hybrid structure was exposed to UV light of 254 nm for polymerization at the intensity of 1 mW/cm^2 for 5 min. Finally, the formed PDA supramolecular surface pattern arrays were immobilized and chemisorbed on ZnO surface (Fig. 2b). To confirm the immobiliza-

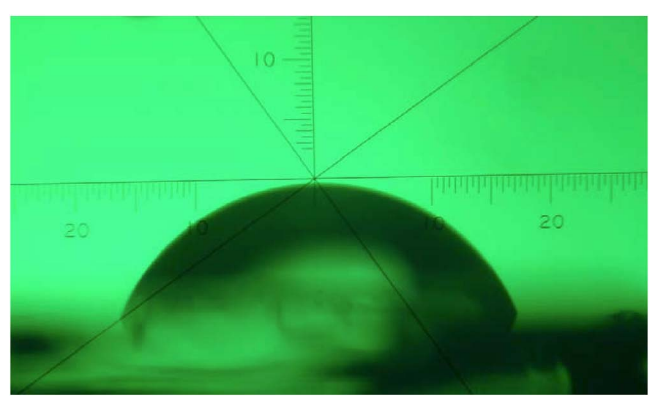

Figure 1. (Color online) Contact angle measurement against pure water (pH 5.5, room temperature) after dipping in amine solution for 4 h.

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