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A new nano-worm structure from gold-nanoparticle mediated random curving of zinc oxide nanorods

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ABSTRACT

Creating novel nanostructures is a primary step for high-performance analytical sensing. Herein, a new worm like nanostructure with Zinc Oxide-gold (ZnO/Au) hybrid was fabricated through an aqueous hydrothermal method, by doping Au-nanoparticle (AuNP) on the growing ZnO lattice. During ZnO growth, fine tuning the solution temperature expedites random curving of ZnO nanorods and forms nano-worms. The nano-worms which were evidenced by morphological, physical and structural analyses, revealed elongated structures protruding from the surface (length: 1 μm; diameter: ~100 nm). The appropriate peaks for the face centred cubic gold were (111) and (200), as seen from X-ray diffractogram. The strong interrelation between Au and ZnO was manifested by X-ray photoelectron spectroscopy. The combined surface area increment from the nanoparticle radii and ZnO nanorod random curving gives raise an enhancement in detection sensitivity by increasing bio-loading. 'Au-decorated hybrid nano-worm' was immobilized with a probe DNA from Vibrio Cholera and duplexed with a target which was revealed by Fourier Transform Infrared Spectroscopy. Our novel Au-decorated hybrid nano-worm is suitable for high-performance bio-sensing, as evidenced by impedance spectroscopy, having higher-specificity and attained femtomolar (10 fM) sensitivity. Further, higher stability, reproducibility and re-generation on this sensing surface were demonstrated.

1. Introduction

Success in nanotechnology has been driven in most cases by bottom-up and top-down approaches with inter- and multi-disciplinary strategies (Gopinath et al., 2009; Fujimaki et al., 2010; Nomura et al., 2013; Simpson et al., 2011). These two approaches are highly involved in the creation of nanostructures, evidenced by a complete platform for research and development, forms roads from laboratory to Industry and bridging the gaps in all disciplines (Balakrishnan et al., 2015; Dong et al., 2010; Gopinath et al., 2008a; 2008b; Lakshmipriya et al., 2013). In laboratory conditions, bottom-up or self-assembly approaches, involving nanofabrication by chemical or physical forces operating at the nanoscale level to assemble basic units into complete structures, met great success (Li et al., 2011; McAlpine et al., 2007). In the recent years, with these approaches, nanostructured metal oxides have been the focus for biosensor development (Köck et al., 2014; Perumal and Hashim, 2013; Solanki et al., 2011). Among various types of nanostructured metal/semiconductor hybrids that have been developed, nanostructured Zinc oxide (ZnO) has been intensively studied because of its unique nano-morphology, functional biocompatibility, chemical stability, sensitivity, non-toxicity, and high catalytic properties (Foo et al., 2013; Jiang et al., 2014). Furthermore, ZnO nanostructures possess excellent electrical properties, which are suitable for fast and accurate sensing applications (Ali et al., 2012; Tak et al., 2014). The biocompatibility characteristics exhibited by ZnO is highly desired for surface functionalization and interfacing with chemical and biological compounds at pH extremes (Haarindraprasad et al., 2015; Liu et al., 2008; L. Wang et al., 2010a). Recently, optical, electrical and magnetic properties of ZnO nanostructure have been reported to be enhanced through the incorporation of novel metal nanoparticles, with advantages for improvements in biosensing characteristics owing to their potential for enhanced catalytic activity, surface to volume ratio and multiple functionality (Khoa et al., 2015; Kumar et al., 2015). It is expected that the judicious application of nanoscale structures via these combinations with novel metals, will yield new

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strategies and avenues for diagnosis and therapeutics (Geng et al., 2012; Lee et al., 2011). ZnO nanostructures prepared by bottom-up approach are catalytically synthesized by chemical and physical vapour depositions and vapour liquid solid method, where structures are assembled from basic units into larger structures (Suh et al., 2010; Wang et al., 2005). Unfortunately, bottom up approach through this method is not promising due to several limitations, such as low yield assembly, catalyst dependence, high cost and limited lab-settings, which require knowledge of complicated technologies (Bai et al., 2013; Kashif et al., 2013). Looking at ease of fabrication, sol–gel spin coating combined with an aqueous hydrothermal technique is an easy and convenient method for the synthesis of various ZnO nanostructures through the bottom-up approach. This technique has promising advantages, such as capability for production upscaling at low temperatures and production of epitaxial, anisotropic nanostructures (Polsongkram et al., 2008; Zhang and Que, 2010). Using this method and varying the growth parameters, such as reaction temperature, solution molarity, and pH, various ZnO nanostructure can be formed (Foo et al., 2014; Kashif et al., 2012; Perumal et al., 2015; Tak et al., 2014). However, there has not been much focus on the ZnO/Au hybrids to create novel nanostructures through the hydrothermal growth method. Herein, we report a new structure formation through AuNP mediated random curving of ZnO nanorod. In this study, we took the advantage of ZnO/Au properties and generated a new hybridized nanostructure possessing worm-like morphology on a silicon substrate. We demonstrated a simple, low-cost hydrothermal growth method to synthesize ZnO/Au hybrid worm, generated by doping Au on the ZnO nanorods. Further, the effects of AuNP on the surface topology, structural and optical characteristics of ZnO/Au hybrid nano-worm has been investigated. This study involves the process to obtain nano-worm like structure, the way developed remarkably creates an avenue for other new nanostructure creations.

2. Methods

2.1. Fabrication of Interdigitated Electrodes (IDEs)

A p-type silicon wafer was cleaned using RCA1, RCA2 and BOE to remove organic and inorganic contaminations and native oxide layer on the wafer surface (Adam and Hashim, 2014; Balakrishnan et al., 2014). Next, the silicon wafer was rinsed and cleaned with deionized water. 200 nm thick SiO_2 layer was produced on the cleaned wafer surface using a wet oxidation furnace. Using a conventional lithography process, an IDE device of 7 mm × 5 mm in size was patterned using negative resists (NR7-6000PY) on the SiO_2/Si substrate. A thermal evaporator (Auto 306 thermal evaporator; Edwards High Vacuum International, Wilmington, MA, USA) was used to deposit a Titanium/Au (500/3000Å) layer on the SiO_2/Si substrate and were patterned through lift-off process. Eventually, the negative photoresist sacrificial layer which formed was removed using acetone. In this work, an IDE with 16 fingers was fabricated where the width and length of each finger was 0.1 and 3.9 mm, respectively, and the spacing between the two adjacent fingers was 0.1 mm.

2.2. Preparation of ZnO thin films (ZnO-TFs)

ZnO-TFs were prepared using spin coating technique as follows; 8.78 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 200 ml of ethanol solvent (ZnO seed solution sol–gel). The concentration of ZnO was kept constant as 0.2 M. The mixed solution was then vigorously stirred with a magnetic stirrer at 60 °C for 30 min. The stabilizer, MEA was added drop by drop to the ZnO solution with constant stirring for 2 h. Finally, the transparent and homogenous solution were stored for aging at room temperature. The aged ZnO sol gel was deposited onto the IDE device by using a spin coating technique at a speed of 3000 rpm for 20 s. The deposition process of seed layer was repeated for 3 times to get a thicker ZnO thin film. For each deposition process, the coated ZnO thin films were dried at 150 °C for 20 min to remove the organic residuals that might exist on the ZnO thin films. The coated ZnO thin films were then annealed in a furnace under ambient air at 300 °C for 2 h to get highly crystallized ZnO.

2.3. Preparation of ZnO-TF–Au Nanohybrids

ZnO-TF–Au nanohybrids were prepared by a sputtering method. To form ZnO-TF–Au nanohybrids, Au wetting layer were physically deposited by a Sputter coater (EMS550X) with Au target and rotating stage. The detailed experimental condition is: electric current is kept at 25 mA, for 2–8 min and the Argon process vacuum level was kept at 10^{-2} mbar. Hence, we obtained Au- decorated ZnO TFs forming ZnO-TF–Au nano-hybrids.

2.4. Preparation of ZnO/Au hybrid nano-worm by hydrothermal method

ZnO Nano-worm like structure was formed using hydrothermal growth methods. For hydrothermal growth of ZnO/Au hybrid nano-worm, the prepared substrate with seed layer coated (ZnO-TF–Au nanohybrids) was submerged backward inside growth solution using Teflon sample holder. 25 mM of growth solution were prepared by mixing zinc nitrate hexahydrate and hexamethyltetramine in de-ionized water. The growth process was done inside a vacuum oven at 97 °C for 3 h. The prepared hydrothermal growth ZnO/Au hybrid nano-worm were cleaned with Isopropanol and de-ionized water to remove residual salt prior to annealing in furnace under ambient air at 300 °C for 2 h.

2.5. DNA immobilization and hybridization

The ZnO/Au hybrid nano-worm electrodes were cleaned and dried under nitrogen gas and used to fabricate DNA biosensor to detect *Vibrio cholera*. The direct immobilization of probe DNA on the electrode surface was achieved by dispensing 10 μL of 1 μM probe DNA solution in Tris- EDTA buffer for 3 h followed by washing the electrode and then rinsing with sterile double distilled water. The DNA hybridization was accomplished by dispensing the probe modified electrodes into different concentrations of test DNAs (complementary, non-complementary and mis-matches). The electrodes were washed upon hybridization process to remove any unbound target before measurements were taken. The complete immobilization process of thiolated probe DNA and hybridization with target is schematically illustrated in Fig. 2. The electrodes hybridized DNA was regenerated by rinsing the surfaces with hot (95 °C) deionized water for 2 min, followed by rapid cooling in ice bath. The surface was repetitively hybridized and regenerated with target for reusability test. The stability of probe DNA electrodes was studied for 4 weeks by performing the assay on a daily basis. Electrodes were stored in 4 °C when not in use.

3. Results and discussion

Utilizing a self-assembly bottom-up approach and nanoscale fabrication a new ZnO nanostructure possessing worm-like morphology was synthesized on silicon substrate. The doping of ZnO-TF with AuNPs (before the hydrothermal growth), created a new surface topography with the nano-worm structure. The heating