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Gold nanoparticle immobilization on ZnO nanorods via bi-functional monolayers: A facile method to tune interface properties

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ABSTRACT

We demonstrated the functionalization of one dimensional (1-D) zinc oxide nanorods (ZnO NRs) using bi-functional organic molecules to create hybrid structures with surface functionalities and tuneable organic/inorganic interface. Bi-functional molecules with carboxylic acid, thiol and silane end groups and amine termination had been employed to functionalize the NRs by forming carboxylate, thiolate and hydroxylation bonds, respectively, with ZnO. The surface textures of NRs were preserved even after functionalization. The functionalized NRs were decorated with gold nanoparticles (AuNPs) and the hybrid structures exhibited a quenched blue shift ultraviolet emission which depended on the distance between the ZnO surface and the AuNPs. The NR functionalization with bi-functional molecules and decoration of NPs, and surface morphologies were analyzed using x-ray photoelectron spectroscopy, field emission scanning electron microscopy and transmission electron spectroscopy. These hybrid structures can play a vital role in tuning the interface properties and have potential applications in future photovoltaics, chemical sensors, biomarkers, and wavelength based biosensors.

1. Introduction

One-dimensional (1D) semiconducting metal oxide nanostructures have attracted attention because of their unique electrical, optical, and magnetic properties that are different from those of the respective bulk counterparts, as well as their potential applications in mesoscopic research and nanodevices [1–3]. Among many inorganic semiconductor 1D nanomaterials, zinc oxide (ZnO), a II–VI semiconductor with a wide band gap of about 3.37 eV (at 300 K) and a large free exciton binding energy of 60 meV, is an excellent electronic and photonic material with promising applications such as in dye-sensitized solar cells, field emission devices, sensors, catalysis and light-emitting diodes [4]. In recent years, the organic functionalization of ZnO NRs is of great interest to form organic/inorganic hybrid structures in order to modify the surface properties and to tune the interface for efficient intra-molecular energy and electron transfer between organic and inorganic molecules [5–7].

Many approaches such as chemical vapor deposition, spin coating and dip coating have been employed to modify and functionalize the ZnO surface. Owing to the fact that metal oxides exhibit variable surface energies, wetting of the ZnO surface by organic molecules has to be carefully considered in order to ensure that interpenetration and uniform anchoring will occur. One of the possible strategies involves covalent bonding of the organic molecules using different surface chemistries in order to ensure that the ZnO organic interface is conducive to promote charge transfer [8,9]. Such hybrid systems exhibit many characteristic properties which can be used in applications such as biological sensors, light-emitting diodes, and solar cell devices [10,11].

Organic monomers with single and bi-functional groups have been widely used for surface modifications to tune and enhance electronic/optical properties, improve surface wettability, create dielectric layers and polar groups at the metal–oxide interfaces and in hybrid structures [12–14]. More particularly, bi-functional organic molecules possess the advantage of creating linkages for further molecular attachments, anchoring of nanoparticles and bio-molecules [15,16]. Ruankham et al. demonstrated that the ZnO NR surface grafted with a small organic molecule (indolin D205 dye) created dipole moments directed away from the ZnO surface in hybrid ZnO/poly(3-hexylthiophene) (P3HT) solar cells, thereby suppressing the reverse saturation dark current density and charge recombination which significantly improved the power conversion efficiency [17]. Taratula et al. functionalized the surface of ZnO nanotips covalently by bi-functional

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C16 carboxylic acids with alkyl chain of thiol and imide group exposed outwards which later acted as linkers to covalently bind DNA molecules for deployment as biosensors [18]. In this work, we have provided different pathways for surface functionalization of ZnO NRs using bi-functional molecules and allowing them for further decoration.

Hybrid nanostructures containing both AuNPs and ZnO are very attractive due to their novel and enhanced properties in applications such as photocatalysis, sensors, photovoltaics and surface plasmonic resonance [19–22]. Bora et al. fabricated dye-sensitized solar cells of ZnO NRs decorated with in-situ citrate-reduced AuNPs forming a Schottky barrier at the ZnO/Au interface, inducing higher optical absorptions due to the surface plasmon absorption of AuNPs, and thereby enhancing the power-conversion efficiency [23]. Udawatte et al. prepared well-defined Au/ZnO NP composites by modifying ZnO with preformed AuNPs protected with bi-functional glutathione ligand which significantly enhanced the charge separation by extracting electrons from the photoexcited ZnO and consequently improved the photocatalytic activity of the composites [24].

Though the hybrid structures possess enhanced electronic and optical properties, the main challenge is to synthesize these structures on substrates with control over the dimensions and functionalities while maintaining the morphology, so that the physical and chemical properties of the material can be tailored to deliver predictable and controllable performance [25,26]. In this work, we have adopted a simple two-solution approach—successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) to synthesize vertical ZnO NRs [27]. Subsequently, the NRs were grafted with various organic molecules possessing bi-functional end groups and the terminal amine end group allowed the decoration of AuNPs. These hybrid structures grafted with molecular thin films and anchored AuNPs create defined interfaces with enhanced electronic/optical properties.

2. Experimental details

2.1. Self-assembled monolayer (SAM) formation and decoration of AuNPs

The ZnO seed layer and NRs were prepared as reported in our earlier works (See supplementary information) [27]. The synthesized NRs were then chemically grafted with bi-functional molecules and decorated with AuNPs by two sequential steps (Scheme 1). Firstly, bi-functional molecules were grafted on ZnO NRs by immersing silicon wafers containing the ZnO NRs in a 3 mM p-aminophenyltrimethoxysilane (APhS) solution of toluene for 6 h/5 mM 6-aminocaproic acid (ACP) solution of methanol for 12 h/5 mM 4-aminothiophenol (ATP) solution of dichloromethane for 12 h, respectively (See supplementary information, Fig. S1 for the detailed schematic of chemical binding of SAMs on ZnO NR). All the reactions were carried out at room temperature. After immersion, the substrates were then rinsed copiously with the respective solvents and sonicated in the solvent for 2 min to remove loosely bound molecules. The substrates were then dried in a nitrogen stream and stored. Trimethoxysilane terminated APhS formed SAMs on ZnO surface by hydroxylation with surface hydroxyl groups [10].

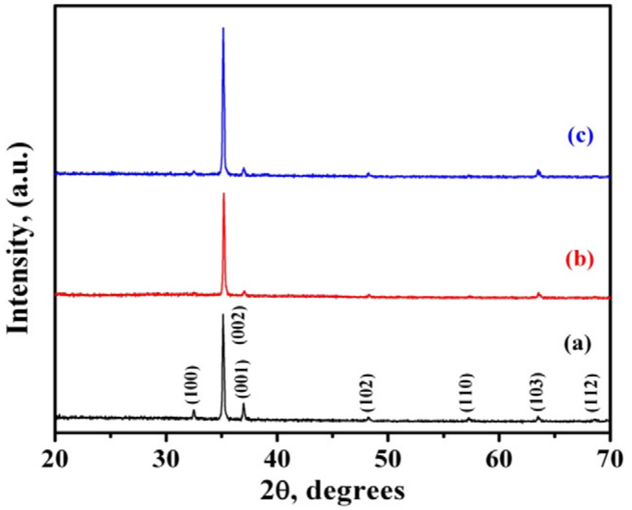


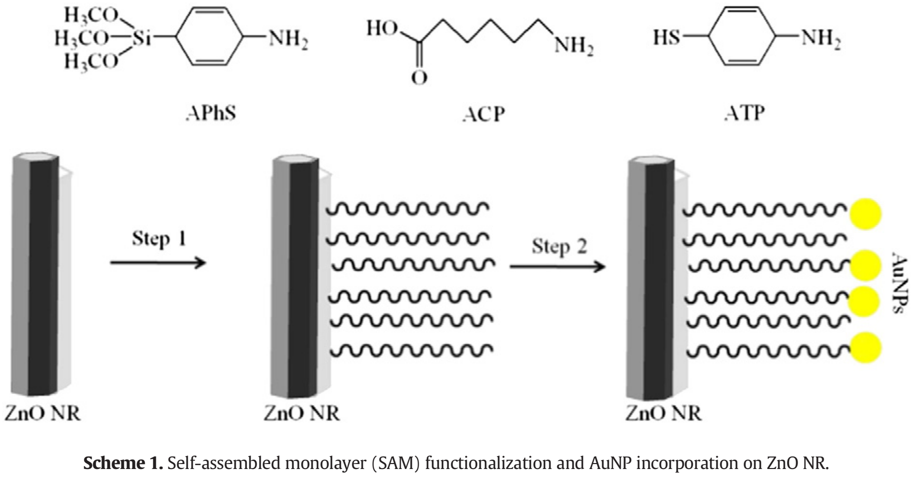
Fig. 1. XRD patterns of functionalized ZnO NRs with AuNP incorporated (a) APhS, (b) ACP and (c) ATP.

The acid terminated ACP assembled through the carboxylate mono/bi-dentate coordination bonds with Zn atoms [13,18], whereas thiolate (Zn—S) bond formation occurred in ATP immobilization [12,28]. Amine terminated SAMs were formed on the NRs as a result of these reactions. The AuNPs were prepared by the citrate reduction approach and the particle size was 14.5 ± 4 nm (see supplementary information, Fig. S3) [29]. The functionalized ZnO NRs were immersed in the AuNP solution for the following durations: 6 h for APhS modified NR, 12 h for ACP- and ATP-modified NRs. Finally, the substrates were rinsed in copious amount of water and dried in nitrogen. The citrate reduced AuNPs have the tendency to attach to amine terminated SAMs [30].

3. Result and discussion

3.1. Structural and morphological analysis of SAM coated ZnO NRs

The X-ray diffraction (XRD) pattern of ZnO seed layer and NRs grown on silicon wafers showed the preferential growth of nanostructures along the [002] orientation at 34.64° along the direction of c-axis (see supplementary information, Fig. S2). The ZnO nanostructures possessed wurtzite structure. The field emission scanning electron



Scheme 1. Self-assembled monolayer (SAM) functionalization and AuNP incorporation on ZnO NR.