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Synthesis and surface modification of hybrid multiblock gold–nickel–polypyrrole nanorods by poly(fluorene) and their optical properties

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ABSTRACT

We have demonstrated that hybrid multiblock nanorods (MBNs) consisting of gold, nickel, and polypyrrole were prepared by electrochemical deposition method using anodized aluminum oxide as a template. Thiol substituted poly(fluorene) was synthesized through Ni(0)-mediated polymerization. Thiol substituted poly(fluorene) was used for the surface modification of MBNs. The as-synthesized thiol substituted poly(fluorene) and surface modified MBNs were characterized by NMR, SEM, AFM, TEM, TGA, XRD, GPC and XPS. Optical properties of the prepared materials were investigated via UV–vis Spectroscopy and photoluminescence spectroscopy. The poly(fluorene) and surface modified MBNs were showing fluorescence decay life time of 3.47 and 2.77 ns, respectively.

Introduction

Nanometer-scale, one-dimensional (1D) structures have generated a great deal of interest as potential building blocks for nanostructured materials, composites, nanoscale electronic devices, ultrahigh-density magnetic recording systems and optical devices. One-component systems are now quite common. There are many experimental approaches to fabricate nanorods such as seed-mediated growth method, lithographic, vapor phase synthesis, photoreduction and electrochemical deposition. Gold nanoparticles are of particular interest, as they are one of the most stable metal nanoparticles and possess fascinating properties, including their ability to assemble in multiple shapes, and size related electronic and magnetic properties, leading to a wide range of applications, including catalysis and biology. The optical properties of gold nanoparticles are tunable throughout the visible and near-infrared region of the spectrum as a function of nanoparticle size, shape, aggregation state and local environment.π-Conjugated materials with electronically rigid backbones have attracted considerable interest in both academic research and industrial applications due to increasing potential as active components for a wide range of electronic and optoelectronic devices. In the past decade, fluorene-based oligomers and polymers have found a rich variety of applications in the field of optoelectronics, such as organic light-emitting diodes, organic field effect transistors and organic solar cells, etc. Fluorene based material possess high thermal stability, good solubility, high hole mobility and facile functionalization at the C-9 position of fluorene [1–3].

Modification of the surface of gold nanorods with fluorophores results in strong surface enhanced Raman scattering and is important for designing biological sensors [4] and optoelectronic devices [5]. The binding of chromophores on the metal surface results in the quenching of the excited state. Energy transfer and electron transfer are the main deactivation channels for the excited molecules on the metal surfaces. The potential usefulness of surface modified gold nanorods in these fields, as well as the bottom-up approach of nano science and technology, is a considered key in the preparation of novel building blocks and materials for the 21st century [6–9].

Electrochemical deposition offers marked advantages over other methods for synthesis of one dimensional nano structures, as this method have a high growth rate. But there are relatively few examples of methods for synthesizing multicomponent 1D materials made from both inorganic and organic materials. In this work hybrid multiblock nanorods (MBNs: gold (Au)–nickel (Ni)–polypyrrole (PPy)) were fabricated by electrochemical deposition of Au, Ni and PPy into the channels of AAO template.

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The block length of the gold, nickel and polypyrrole structures was controlled by controlling the number of coulombs that are passed in the experiment. Here in, we present the synthesis of thiol pendant monomer (fluorene: TF) and thiol pendant conjugated polymer (poly(fluorene): PTF) were prepared. The resulting thiol functional group of the monomer and conjugated polymers are able to self-assemble onto MBNs. The surface modified MBNs were analyzed by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), X-ray Photoelectron Spectroscopy (XPS), UV–vis Spectroscopy and Photoluminescence Spectroscopy (PL). The results indicate that the MBNs based on organic–inorganic hybrid junctions possess very interesting morphological and optical properties, thus they are more suitable and promising for the fabrication of high performance optoelectronic devices.

Experimental

Materials

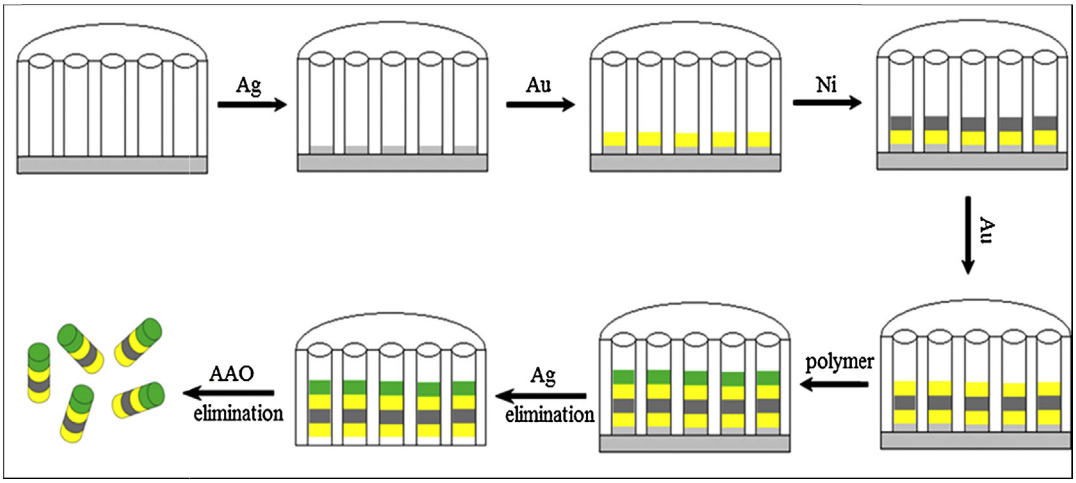
Au and Ag plating solutions (pure gold sg-10, high speed silver) (Transgene). Ni plating solution (matt plating solutions) (Hantechpmc). Fluorene, ferric chloride, bromine, potassium hydroxide, 1,6-dibromohexane, tetrabutylammonium bromide, potassium thioacetate, bis(1,5-cyclooctadiene) nickel(0), 2,2′-bipyridyl, 1,5-cyclooctadiene, pyrrole and lithium perchlorate (Sigma-Aldrich), nitric acid (Daejung Chemicals & Metals), sodium hydroxide (Samchun Pure Chemicals) and solvents were used as received. Anodized aluminum oxide (AAO, d = 25 mm, pore size = 0.2 μm) template (Whatman International Ltd).

Measurements and characterization

All electrochemical depositions were performed on an Autolab (PGSTAT128N, USA) equipped with a three-electrode system (counter electrode: Pt wire, reference electrode: Ag/AgCl (3 M KCl)). TGA was performed on SCINCO (TGA 1000) series thermal analyzer system at a heating rate of 10 °C/min from ambient to 700 °C under nitrogen atmosphere. The particle morphology and structural properties of the prepared samples were further elucidated by SEM (Horiba, EX-250), the prepared sample was sputtered on a carbon disc with the help of double-sided adhesive tape and sputter-coated with a thin layer of Au to prevent sample from charging problems. Absorption spectra was obtained using a single-beam UV–vis Spectroscopy (Hewlett Packard 8453, USA). The Nuclear Magnetic Resonance (NMR) spectra for the products were recorded using Varian 300 MHz-NMR (USA) with $CDCl_3$/DMSO as solvent and TMS as a internal reference. The molecular weight of the prepared PTF was determined by means of Gel Permeation Chromatography (GPC) in an Agilent GPC–SEC Analysis System, Agilent Technologies, (Santa Clara, USA) fitted with MIXED-A Columns (Agilent Technologies) using polystyrene standards for the calibration and tetrahydrofuran (THF) as the solvent at room temperature with a flow rate of 1.0 mL/min. The phase purity of synthesized materials was studied using X-ray diffraction (XRD). XRD profiles of the MBNs were obtained on X-ray diffractometer (Rigaku, SmartLab, Japan). The surface characterization of MBNs and PTF–MBNs were carried out at room temperature using a non-monochromatized Al-$K\alpha$ X-ray source by Thermo VG Scientific, K-alpha XPS instrument (USA). TEM measurement was performed by casting sample dispersion on carbon coated copper grids and allowing it to dry at room temperature. TEM measurement measurements were done on FE-TEM, JEM-2100F (HR) (JEOL LTD, Japan). Three-dimensional structures of the PTF–MBNs surfaces were observed with SPM-9700 scanning probe microscope (Shimadzu, Kyoto, Japan). PL spectra were obtained on a LabRAM HR UV–vis-NIR (Japan) photoluminescence microscope. Time-resolved PL spectra was utilized to measure lifetime using FLS920 fluorescence spectrometer (Edinburgh Instruments).

Electrodeposition of hybrid multi-block nanorods (MBNs)

Prior to AAO template, 400 nm thick Ag was thermally evaporated on one side as a conducting layer as shown in Scheme 1, AAO template was sandwiched between a piece of alumina foil and an insulating O-ring (d = 1 mm) was assembled in a PTEE cell as working electrode, Ag/AgCl electrode as reference electrode and Pt wire as counter electrode to establish three electrode configuration. Au and Ni deposition was carried out at "−0.95 V" (vs Ag/AgCl) applied potential. PPy deposition was carried out at (0.2 M pyrrole, 0.3 M lithium perchlorate), +0.75 V (vs Ag/AgCl) applied potential. The length of the Au, Ni and PPy nanorods were controlled by monitoring the charge passing through the cell. The Ag component was selectively etched with concentrated nitric acid and the template was subsequently immersed in a 3 M sodium hydroxide solution to dissolve the AAO template and release the synthesized MBNs. Released MBNs underwent a repeated several-step rinse process, which includes solvent renewal and ultrasonic dispersing. A schematic representation of the fabrication of MBNs process was illustrated in Scheme 1.



Scheme 1. Synthesis of the hybrid MBNs.