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Full Length Article

Effect of ZnO core electrodeposition conditions on electrochemical and photocatalytic properties of polypyrrole-graphene oxide shelled nanoarrays

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ABSTRACT

Novel hybrid core-shell nanoarchitectures were fabricated by a simple two-step electrochemical approach: first ZnO nanorod core was electrodeposited from $Zn(NO_3)_2$ solution; further, the core nanoarray was coated with a shell based on polypyrrole hybridized with graphene oxide by electropolymerization. The properties of the core/shell nanoarchitectures were studied as a function of the core properties induced by electrodeposition parameters. The ZnO nanostructures showed improved crystallinity and c-axis preferred orientation with increasing cathodic deposition potential while the increased deposition duration resulted in a morphology transition from nanorod to pyramidal shape. The electrochemical activity of the core/shell arrays was found to increase with the deposition potential of ZnO core but decreased when morphology changed from nanorod to pyramid shape. The photocatalytic results showed improved activity for the core/hybrid shell nanoarrays with respect to ZnO and ZnO/PPy ones. The degradation rate for methylene blue decreased with prolonged deposition duration of the core. The obtained results highlight the importance of electrochemical tuning of ZnO-based core/shell nanoarrays for improved performance in electrochemical and photocatalytic applications.

1. Introduction

Amongst the inorganic semiconductors, zinc oxide (ZnO) has been widely studied for potential application in functional devices thanks to the wide band gap, large exciton binding energy and transparency [1,2]. Thanks to its unique structural anisotropy, various oriented nanostructures, including nanowires, nanorods, nanoplates, nanosheets, etc. can be fabricated and incorporated into devices [3–5]. The morphology-dependent properties of ZnO nanomaterials favorable in various applications such as electrochromics, sensing devices, or solar cells triggered the focus onto ZnO nanoarrays (NAs) with one-dimensional morphology because the efficiency of some applications is directly related to the surface area and orientation of the ZnO, e.g., improved electrolyte diffusion was reported for energy storage, fast response for electrochromic applications, improved sensing property due to increased surface area or enhanced performance of solar cells devices especially due to providing direct conduction pathway for electron transport [6]. The interest in fabrication of new ZnO nanostructures has been growing due to new applications relying on size and shape. Lately, pyramidal shape ZnO re-attracted interest in the solar cell community because of increased light scattering and simplicity of wet-chemistry approaches for which the key strategy is the tailoring the surface chemistry of the semipolar side facets during crystal growth.

On the other hand, surface engineering attracted much interest for boosting performance of ordered ZnO nanostructures, as it is commonly related to the presence of surface defects. Hybridization of ZnO with graphene may provide an ideal photocatalytic

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system to accelerate the charge transfer from photocatalyst to the liquid–solid interface by taking advantage of graphene's unique electron transport property, superior chemical stability, high specific surface area and high transparency [7–9]. Many studies also reported enhanced interfacial charge transfer, minimized contact recombination, and improved collection capabilities in solar cells by modification of ZnO NAs with shells made of inorganic semiconductors [10], and various organic materials [11,12]. The nanoarchitectures based on ZnO core and conducting polymer (CP) shells represent one of the most promising materials from both fundamental and technological view points as they exhibit attractive properties that favor their application in various fields such as energy storage, electronics, optics or catalysis [13–17]. One the main disadvantages of ZnO – the instability under illumination – can also be addressed by enveloping in CP shell [18]. The confinement in CPs or carbon shells was also indicated to boost the capacitance of metal oxides [19].

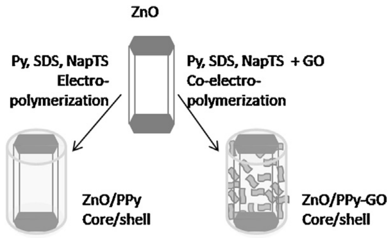
From the wealth of synthetic approaches including wet chemistry, magnetron sputtering, pulsed laser deposition, chemical vapor deposition, etc., the electrochemical deposition techniques have often been preferred for growing one-dimensional NAs of both ZnO and conducting polymers due to their low cost, mild conditions and accurate process control [20,21]. Although synthesis of ZnO nanostructures has been widely explored, it is necessary to study the relationship between electrodeposition conditions and the growth of ZnO with well-controlled crystalline morphology for exploring a high effective and simple route to prepare novel nanostructures for practical applications. Moreover, in regards to ZnO/CP core/shell NAs, the studies till present involved ZnO NAs only as templates for the fabrication of oriented CP nanostructures [16,17,22,23]. Thus, the research on ZnO/CP-rGO NAs lacks important understanding of the influence of hybrid interface on the capabilities and limitations of such NAs. On the other hand, graphene oxide (GO) could serve as a suitable filler for CP coatings thanks to its hydrophilicity and improved conductivity due to oxygen containing functional groups and further improve architecture performance [24].

Therefore, in this paper we report about the optimization of the properties of hybrid CP-GO coated ZnO NAs in relation to ZnO core morphology. Polypyrrole (PPy) was selected due to its many desirable features including low-cost, environmental stability and large scale processability [25]. The morphology of ZnO was tailored by electrodeposition from $Zn(NO_3)_2$ precursor in absence of a seed layer. As the ratio between the OH^- generation rate and Zn^{2+} diffusion is the main parameter controlling the growth mechanism of ZnO from nitrate-based solutions, here the addition of $NaNO_3$ and modulation of deposition potential and charge were carried on in order to induce varying morphologies. To the best of our knowledge, this is the first kind of report as an attempt to highlight the importance of adjusting the parameters of electrochemical procedures towards the tailoring of key properties of ZnO for enhancing properties of ZnO core/PPy-GO hybrid shell arrays.

2. Experimental

2.1. Materials

The chemicals were purchased from Aldrich, Merck or Alfa Aesar and used as such. All solutions were prepared with double-distilled water. Indium-doped tin oxide (ITO) coated conducting glass slides (~10 Ω/sq, Solar Energy Technology Co, Ltd, Wuhan Jinge, China) were degreased with detergent and consecutively cleansed in distilled water, acetone, and isopropanol before use by means of ultrasonic treatment.



Scheme 1. A schematic illustration of the fabrication of the ZnO/PPy-GO nanorod core/hybrid shell NAs.

2.2. Synthesis of GO

Graphite oxide was prepared by modified Hummers method as presented in our previous works [26]. Before use, graphene oxide dispersion ($0.1\ mg\ mL^{-1}$) was obtained by ultrasonic treatment of graphite oxide in a surfactant solution (sodium dodecyl sulfate (SDS), 20 mM) for 30 min.

2.3. Synthesis of ZnO NAs

All the electrochemical procedures were performed using a potentiostat (Versastat 3, Princeton Applied Research) in a classical three-electrode configuration, using the ITO slides, a Pt plate and a saturated Ag/AgCl electrode as the working electrode, the counter electrode, and the reference electrode, respectively. The ZnO NAs were synthesized on ITO substrate from 0.1 M $NaNO_3$ containing 10 mM $Zn(NO_3)_2$ at 75 °C by using the constant potential deposition mode. The deposition potential and duration were varied from −0.95 V to −1.05 V and 10 min to 40 min, respectively.

2.4. Fabrication of ZnO/PPy-rGO core/shell nanoarchitectures

Herein, the sequential electrodeposition approach depicted in Scheme 1 for the electrochemical coating of the ZnO NAs in a hybrid PPy-rGO shell was preferred as it has the advantage of tailoring the inorganic/organic interface during the formation of the nanoarchitecture and the random dispersion of the semiconducting nanoparticles in the polymeric shell is avoided by the formation of highly oriented ZnO array at the surface of the substrate first [27]. The ZnO NA was coated with a PPy-rGO sheat by in-situ co-electrochemical polymerization method and for comparison purpose, the polymeric shell was also deposited in absence of GO. Briefly, the electrolyte used for electropolymerization was obtained by mixing a solution of sodium *p*-toluenesulfonate (NapTS, 0.05 M) of pyrrole (Py, 0.1 M) containing SDS surfactant (20 mM) and the GO dispersion under ultrasonic treatment. Prior to each deposition, the ZnO NAs were wetted for 10 min in the electropolymerization electrolyte by means of ultrasounds. The nanohybrid polymeric coating was deposited at constant applied current density of $0.5\ mA\ cm^{-2}$ at room temperature for 100 s. After electro-coating, the hybrid nanoarchitectures were thoroughly rinsed with high pure deionized water five times to remove any impurities.

2.5. Characterization

The structural characterization of the nanoarchitectures was performed by X-Ray diffraction (XRD) spectra (D2 Phaser, Bruker) with the Cu Kα line of 1.54 Å. The distributions of the composites were characterized by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Spectrum 100, Perkin Elmer). Raman spectra were recorded using a microscope with a 514-nm laser (inVia, Renishaw). X-ray photoelectron spectroscopy (XPS) measurement was performed using a VG ESCA-LAB 220i-