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Short communication

Sonochemical assisted synthesis of RGO/ZnO nanowire arrays for photoelectrochemical water splitting

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ABSTRACT

This article presented the synthesis of a hybrid nanoarchitecture material composed of reduced graphene oxide (RGO) multiple sheets and ZnO nanowire arrays (NWAs) formed on an arbitrary ZnO coated fluorine doped tin oxide (FTO) substrates via pulse sonication and hydrothermal approach. The NWAs have high aspect-ratio, high density, apt positioning and well-ordered formation. FESEM images demonstrated that RGO layers have been effectively intercalated between and on the accessible surfaces of the ZnO NWAs. The diameter of ZnO nanowires is 80–150 nm and length about 1–2 μm. Raman spectrum of hybrid material exhibited characteristic D and suppressed G peaks for graphene and E_2 mode at 437 cm^{-1} for ZnO NWAs. UV–visible spectrum indicated slight red shift towards visible range after formation of RGO/ZnO NWAs heterostructure. The Photoelectrochemical results indicated higher current densities for RGO/ZnO NWAs heterostructure due to water oxidation reaction at the working electrode compared to pristine ZnO NWAs.

1. Introduction

Atomic layers of RGO has been the attracted incredible interest due to their fascinating properties in many industrial and commercial electronic devices, chemical sensors, optical devices, energy storage, and composite materials [1–6]. On the other hand, one-dimensional (1D) metal oxide nanostructures, such as nanobelts, nanowires, nanorods, and nanoneedles represents significant type of tiniest dimension nanomaterials for smooth transport of electron and excitons and expected as building blocks for advanced functional nanoelectronics and nanosystems [7–10]. Among various metal oxide semiconductors, Zinc oxide (ZnO) is extensively investigated due to its fascinating electronic, optical, catalytic, photoelectrochemical, sensing and photovoltaic properties [5,11–13].

However recently more attention has been devoted to the formation of hybrid nanostructured nanomaterials, composed of interactively both inorganic and organic components, with multiple functionalities and enhanced catalytic properties compared to single component materials [11,14–16]. This inimitable class of hybrid nanostructured materials can not only maintain significant features of both components but also offers the potential to engineer the significant properties of the hybrid materials by the combining their functional components. The distinguished properties of ZnO utilized in hybrid materials to get better outcomes. Among hybrid materials, semiconductor RGO/ZnO nanostructures emerging as distinctive class of materials, where RGO enhanced bulk properties of pristine ZnO and provides supportive electrical, optical and catalytic properties [5]. Recently various groups have successfully engineered RGO/ZnO hybrid materials for different applications [17–23]. The physiochemical properties of hybrid materials greatly influenced the synthetic approach. Therefore, adopting suitable synthetic technique can be helpful to achieve desired architecture with enhanced characteristics semiconducting and optical properties. Among the various synthetic techniques, sonochemical assisted method has emerged as an intriguing method to fabricate different semiconductor materials with unique morphologies [24]. The eminent acoustic cavitation phenomenon arose from ultrasonic waves, in which energy is transferred to the solution, responsible for the formation of miniscule bubbles. Later, these bubbles collapse and harvest temporary micro-level hot spots. This phenomenon is highly exothermic and elevates the solution temperature and pressure as much as ~5000 K and ~1800 atm with cooling rate of 109 K/s respectively [25–27]. This high temperature and pressure accelerate the physical melding of the hybrid materials.

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In this work, we have efficiently synthesized hybrid RGO/ZnO NWAs nanoarchitectures on FTO substrate by low temperature hydrothermal and pulse sonication deposition technique. Detailed structural characterization of ZnO and RGO/ZnO NWAs investigated by FESEM, EDX, XRD and Raman techniques. The optical properties studied by UV–Vis spectroscopy and photoresponse measurement of pristine and hybrid ZnO NWAs carried out by photoelectrochemical (PEC) techniques.

2. Experimental section

2.1. Synthesis of ZnO NWAs

ZnO NWAs were prepared on FTO (fluorinated tin oxide), substrate by aqueous solution. For the synthesis of ZnO NWAs, analytical grade zinc nitrate hexahydrate [Zn $(NO_3)_2{\cdot}6H_2O$] (Sigma Aldrich) and hexamethylenetetramine [HMTA; $C_6H_{12}N_4$] (Sigma Aldrich) were used as reagents without further purification. In a typical reaction, the mixture of 0.1 M aqueous solution of Zn $(NO_3)_2{\cdot}6H_2O$ and HMTA were mixed and transferred into hydrothermal vessel and kept in laboratory oven at 85 °C for 4 h. The ZnO/FTO glass substrate immersed upside down in the hydrothermal vessel. The pH of the solution is maintained at 6. After the successful growth of ZnO NWAs on FTO substrate, the system was cooled to the room temperature slowly and the ZnO deposited substrate is rinsed with DI water and then dried at room temperature for 2 h. To achieve high crystalline product the ZnO deposited FTO substrate calcined at 400 °C for optimum time.

2.2. Ultrasonic intercalation of RGO in ZnO NWAs

In order to design RGO/ZnO NWAs nanohybrid architecture, initially the RGO prepared by modified hummer method, well dispersed in ethanol (2 wt%) to make a suspension [28]. The suspension sonicated until obtained well-dispersed RGO solution. The as prepared ZnO NWAs on FTO substrate introduced to the homogenous RGO dispersed suspension and pulse sonication technique employed for appropriate interaction of RGO in the nanogaps of ZnO NWAs. The sequence of pulse kept at 15 s ON and 15 s OFF. This sequence followed for 10 complete ON/OFF pulse cycles. Due to this vigorous vibrational energy treatment through sonication, it was assumed that the RGO well intercalated in ZnO NWAs, which later confirmed by their physicochemical characterizations. This intercalation of the RGO into the ZnO NWAs framework remains strongly dependent on the time and amplitude of ultrasonic treatment.

2.3. Material characterization

The surface morphology of the heterostructure examined by field emission scanning electron microscope (FESEM). Chemical composition investigated by the energy dispersion spectroscopy (EDX). The crystalline phase of RGO/ZnO NWAs were explored by X-ray powder diffraction (XRD) with Cu Kα X ray radiation (λ = 0.15406 nm). Raman spectra of heterostructure were recorded with a LabRAM HR high-resolution Raman spectrometer (Horiba–Jobin Yvon) using a He–Ne laser (λ = 632.8 nm) with D1 filter to reveal their structural properties. The optical properties measured with UV/Vis spectrophotometer at room temperature within the wavelength range 300–800 nm.

2.4. Photoelectrochemical characterization

The PEC water splitting experiments were carried out in 0.5 M sodium sulfate (Na_2SO_4) (Sigma Aldrich) electrolyte in DI water. Photocurrent was measured in a standard three electrode configuration cell, where RGO/ZnO NWAs was used as working electrode, platinum foil as counter electrode and Ag/AgCl as reference electrode respectively. The potential and current of the photoelectrode controlled by a potentiostat (Autolab). The samples were illuminated by an artificial sunlight simulator (Oriel Newport) equipped with xenon lamp to simulate AM 1.5 illumination (100 mW/cm^2). However, only the visible portion of light spectrum used by filtering the UV portion by help of UV Cut-off filter i.e. the visible portion of solar light glittered on the working electrode.

3. Results and discussions

3.1. Growth of RGO/ZnO heterostructure NWAs

Fig. 1(a–d) provided schematic diagram for the formation of RGO/ZnO heterostructure NWAs. In the initial step, reaction between ZnO precursor and HMTA leads to uniform distribution of ZnO seeds on the FTO conducting surface. These seeds served as nucleating sites for ZnO NWAs growth in specific directions. HMTA plays pivotal roles in this reaction. First, it provides OH^- ions to achieve the precipitation reaction by help of thermal degradation [29]. Secondly, HMTA also acts as a pH buffer and provides basic environment by releasing OH^- ions through decomposition in hydrothermal reaction, the rate of which is inversely proportion to the pH of the solution [30]. Thirdly, HMTA direct only (001) epitaxial growth, by attacking on the nonpolar facets of the ZnO NWs and averts excess Zn^{2+} ions to these sites [32]. Thus, HMTA organize the seed distribution and redirect the ZnO NWAs growth in specific dimension in the following steps. Fig. 1d, shows the schematic of intercalated RGO in ZnO NWAs gaps after pulse sonication treatment of 10 cycles.

Fig. 2 shows XRD pattern of ZnO NWAs grown on FTO substrate. All the peaks (100), (002), (101), (102) and (110) of XRD spectrum revealed purely wurtzite hexagonal phase of ZnO. Moreover, XRD peaks designated by star were referred to FTO substrate. The FTO substrate almost covered by ZnO thick film, thus their characteristic peaks are mostly disappeared or faded. Fig. 3(a) and (b) shows low and high magnification micrographs of ZnO NWAs grown on the FTO substrate after initial hydrothermal treatment. The diameter of each nanowire is about 60–80 nm and their length up to 1.5 μm respectively. ZnO NWAs are uniform in their size, well ordered and partially oriented on the substrate. High-magnification image showed NWAs are not densely packed but have smaller nanogaps between them, which can be important for incorporation or intercalation of RGO monodispersed layers. Fig. 3(c) and (d) show top view FESEM micrographs of RGO/ZnO NWAs heterostructure. These micrographs reveal effective intercalation or stacking of RGO on the surface of ZnO NWAs. High magnified micrographs (Fig. 3(d)) revealed that the ZnO NWAs embedded within RGO monolayers and their tips can be seen within those layers upon keen observation, suggesting their successful intercalation. ZnO exhibited tapering features and their diameter and length is about 80–150 nm and 1–2 μm respectively. It is important to note that ZnO arrays have large aspect-ratio due to dense ZnO thin film (seed layer). ZnO NAs with smaller dimensions does not stand pulse sonication and detaches from the substrate eventually. The EDX spectrum in Fig. 4 showed peaks for Zn, O, C, Si, Sn and In elements. Presence of Zn, C and O with elemental ratios >20% (% EDX is provided in supplementary materials) confirms the formation of RGO/ZnO NWAs heterostructures, while the rest elemental peaks are appeared due to the constituents of FTO coated glass.

Raman spectrum provided in Fig. 5 to understand RGO/ZnO NWAs heterostructure formation. Fig. 5(a) shows the Raman spec-