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Electrochemical synthesis of core-shell ZnO/CdS nanostructure for photocatalytic water splitting application

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Abstract

We have successfully synthesized ZnO NRs and ZnO/CdS core-shell structures by a facile two step chemical routes viz. electrodeposition and chemical bath deposition. Plane ZnO nanorods films were deposited by using three electrode electrodeposition on FTO glass substrates. The ZnO/CdS core-shell structures were deposited by immersing plane ZnO nanorod films into a bath containing precursor solution of CdS in chemical bath deposition. Formation of ZnO NRs and ZnO/CdS core-shell structures has been confirmed by UV-Visible absorption, Raman spectroscopy and scanning electron microscopy. The synthesized ZnO NRs and ZnO/CdS core-shell structures has been also characterized for photoelectrochemical (PEC) properties, Mott-Schottky analysis, electrochemical impedance spectroscopy (EIS) and efficiency measurements of PEC system. It has been found that the photocurrent conversion efficiency in water splitting is higher for ZnO/CdS core-shell photoanode than ZnO NRs photoanode. These results suggest that addition of CdS with ZnO NRs is beneficial in increasing the visible light absorption and to enhance the photocurrent conversion efficiency in water splitting. Thus, ZnO/CdS core-shell configuration can be a prospective candidate for efficient PEC splitting of water.

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1. Introduction

Zinc oxide (ZnO) is a group II-VI compound semiconductor material with a direct wide band gap of ~ 3.37 eV and a large exciton binding energy of ~ 60 meV at room temperature [1]. It is a promising material with broad applications in optoelectronics, transistors, UV sensors, biosensors, gas sensors, photo-catalyst etc. due to its excellent opto-electronic properties. One-dimensional (1D) nanostructures of ZnO such as nanoparticles [2, 3], nanotubes [4], nanoflowers [5], nanowires [6], tetrapods [7], nanorods [8], doughnuts [9], nanodisks, nanoplates, nanospheres and hemispheres [10-15] nanosheets [16], etc. are ideal photo-catalysts because of their large surface-to-volume ratio. To sensitize ZnO, cadmium sulphide (CdS) is an excellent material due to its advantages for visible light harvesting, high abundance and low-cost production. Especially it has an appropriate band alignment with ZnO [17, 18]. The band alignment of ZnO with CdS results highly efficient separation of photo-generated charge carriers. However, ZnO/CdS have rarely been explored for the visible-light driven applications.[19,20] The core shell nano-composites have a lot of advantages over planar thin films semiconductor junction such as large surface area for photons to interact with material and to reduce electron hole recombination losses.

The ZnO has higher carrier mobility and hence addition of CdS layer with ZnO as a visible active layer enhances the light absorption process. The synthesized hierarchical morphologies ZnO/CdS core-shell structure shows a prominent visible-light-driven performance under the light irradiation. The ability to form 1D nanostructures of ZnO with uniform CdS shell layers is a key step toward the realization of high-efficiency photoelectrochemical (PEC) cells.[20,21] Here, we report synthesis of ZnO nanorods (ZnO NRs) and ZnO/CdS core-shell by a facile two step chemical routes. The morphology, optical properties, and PEC performance of ZnO NRs and ZnO/CdS core-shell have been investigated in view of their use in water slitting.

2. Experimental

2.1. Synthesis of ZnO NRs and ZnO/CdS core-shell

ZnO nanorods were synthesized on FTO glass substrate by simple, cost effective and environment friendly electrodeposition method. The FTO substrate, Pt foil and SCE were used as working, counter and reference electrodes respectively. The required electrodeposition parameters are such as deposition potential, time, temperature and molarities were optimized for well aligned, dense and uniform growth of ZnO nanorods. The aqueous solution of equimolar zinc nitrate [$Zn(NO_3)_2.6H_2O$] and hexamethylenetetramine (HMT) (both AR grade, 99.99% pure) precursors were kept at temperature ~ 80 ^{0}C throughout experiment. A constant potential ~ - 0.75 V was applied for 4 hours to grow sufficiently high dense nanorods on the substrate surface.

The CdS thin films were deposited independently on FTO glass substrate by using CBD method. For synthesis of CdS films specific molarities of cadmium sulphate ($CdSO_4$), thiourea and ammonium hydroxide were kept constant to maintain pH of solution at 11. Then ZnO NRs films were dipped inside a solution at temperature 70 ^{0}C and finally CdS shell layer was grown with optimum thickness on ZnO nanorod films. The synthesized films were removed and dried under air flux.

2.2. Characterization of ZnO NRs and ZnO/CdS core-shell

The surface morphology of the films was investigated using a JEOL JSM-6360A scanning electron microscope (SEM) with operating voltage 20 kV. The optical band gap of the films was deduced from absorption and was measured using a JASCO, V-670 UV-Visible spectrophotometer in the range of 200-800 nm. Raman spectra were recorded with Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range 150-900 cm^{-1}. The excitation source was 632.8 nm line of He-Ne laser. The power of the Raman laser was kept less than 5 mW to avoid laser induced crystallization on the films.