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Synergetic impact of surface plasmon hot electron and CuS nanolayer of CuS/Au/ZnO core-shell nanorods for the degradation of toxic pollutant

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ABSTRACT

CuS/Au/ZnO core-sell nanorods (NRs) have been synthesized by a novel and facile chemical method in an aqueous medium. The CuS/Au/ZnO NRs showed higher catalytic activity as compared to the ZnO NRs, Au/ZnO NRs, and CuS/ZnO NRs. The wavelength-dependent photocatalytic activity of the CuS/Au/ZnO NRs confirmed that the Au NPs act as the surface plasmon generated photocatalytic activity boosters and that CuS performs as a co-catalyst. The photocurrent generation and photo-electrochemical study further exhibited higher photocurrent generation and reduction of charge transfer resistance due to the synergistic impact of the Au NPs and CuS coating on the ZnO NRs.

Introduction

Environmental purification by effective utilization of solar energy through semiconductor photocatalytic nanomaterials to degrade toxic organic pollutants could facilitate global sustainability. Under ultraviolet (UV) irradiation, among the different efficient photocatalyst nanomaterials, zinc oxide (ZnO) is most commonly used for air and water purification, as it has many advantages including availability, lack of toxicity, great efficiency, photochemical stability, and robustness [1–5]. However, its visible blindness and high level of electron-hole pair recombination limit its usefulness as an efficient photocatalyst under solar light irradiation [6]. Therefore, improving the poor ability of ZnO to absorb visible light and to separate excitons is essential for ZnO to be a powerful photocatalyst.

Recently, to improve the visible photocatalytic activity of ZnO, the incorporation of metal nanoparticles (NPs), such as gold (Au) or silver (Ag), onto the ZnO surface has been reported. Hot electrons are generated by localized surface plasmon resonance (SPR) and transferred to the conduction band (CB) of ZnO over the Schottky barrier with the metal NPs [7–11]. This energy barrier can considerably suppress the charge recombination between the electrons present in ZnO and the holes in metal NPs, and can increase the probability for successive chemical reactions and thereby affect the performance of the photocatalyst [12,13]. Additionally, to further enhance photocatalytic efficiency, ZnO one-dimensional nanostructures such as nanorods, nanotubes, nanobelts, and nanowires have shown some inherent advantages, such as a fast collection of photogenerated charge carriers [14,15]. ZnO NRs is a wide band gap semiconductor material with unique optical, electronic, chemical, and physical properties. The one-dimensional (1D) structure of these materials confers some advantages, such as large aspect ratio, unidirectional electron mobility, and lower charge recombination rates.

Ultimately, to use all of the solar energy incident on the earth, ZnO can be incorporated with a visible light-active semiconductor material with a narrow band gap to absorb visible light and produce electron-hole pairs; the junction between ZnO and the semiconductor can efficiently separate the electron-hole pair for use in the catalytic chemical reaction [16–18]. There have been many reports about visible light-active photocatalysts, such as Cu_2O, CuS, PbS, CdS, CdTe, and CdSe, which can act as sensitizers with high absorption coefficients, broad absorption ranges, and different morphologies to modify the band gaps of the materials [19–25]. Sensitizers using elements like cadmium and lead are not suitable for practical application because of their toxicity. Thus, it is desirable to use a sensitizer that consists of nontoxic elements. Specifically, copper sulfide (CuS), which is a p-type semiconductor material with a narrow band gap of 2.2 eV and wide visible light absorption, has been noticed because of its chemical stability and excellent photocatalytic performance [26–28]. The most important feature of an incorporated visible light-absorbing nanomaterial is a core-shell shape that can assist the motion of the electrons or holes from the core to the shell, or vice versa, thereby leading to

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restricted charge recombination and enhanced charge separation by inducing energy band bending under the built-in electric field at the interface [29,30]. However, the optical thickness of the nanoscale sensitizer is too thin to abundantly absorb incident visible light, so a proper optical design is required to elongate the light path and produce a highly efficient photocatalyst.

Herein, we introduce a new strategy to combine the SPR effect and a visible light-absorbing material to maximize the catalytic performance of ZnO. In this combination, there are three key advantages: hot electron generation with a metal Schottky junction in the SPR effect, visible light absorbance with a p-n junction potential in a visible sensitizer, and a light scattering effect by SPR resulting in an increased light path in the sensitizer. To demonstrate the synergistic effect of the Au NPs and CuS shell on the catalytic activity of CuS/Au/ZnO NRs we synthesized a novel and facile method to synthesized CuS/Au/ZnO NRs core-shell nanostructure. The Au NPs was used for the SPR effect and a thin CuS shell as a visible light-absorbing nanomaterial. Further, we proposed a growth mechanism of CuS/Au/ZnO NRs. The time-dependent catalytic activity of Au/ZnO NRs, CuS/ZnO NRs, and CuS/Au/ZnO NRs were evaluated by the degradation of toxic organic pollutant. The absorption, photoluminescence, electrical conductivity, and electrochemical impedance of all the nanomaterial have been investigated systematically. Further, the effect of excitation wavelength on catalytic activity of Au/CuS/ZnO NRs has been explored, as well as its photo stability and recyclability has been studied systematically.

Experimental section

Reagents

Chloroauric acid ($HAuCl_4$, 99.99%, Sigma Aldrich), sodium borohydride ($NaBH_4$, ≥98%, Sigma Aldrich), sodium citrate dehydrates (99%, Sigma Aldrich), MO (99.8%, Sigma Aldrich), methanol (98%, Merck), copper(II) nitrate hydrate (99.999%, Sigma Aldrich), sodium sulfide (98%, Sigma Aldrich), TiO_2 powder (Degussa, P-25), 3-mercaptopropionic acid (MPA, >99%, Sigma Aldrich) and DI water (HPLC grade, Merck) were used as received without any further purification.

Characterization

Photoluminescence (PL) measurements were performed using a fluorescence spectrophotometer (Cary Eclipse). UV–vis absorption spectra were recorded using a UV–vis spectrophotometer (Hitachi U-3900 H). The surface morphologies of the nanomaterials were studied using transmission electron microscopy (TEM, JEM-200 CX). The crystal structures of the nanomaterials were analyzed by X-ray diffraction (XRD, Philip-X'Pert X-ray diffractometer) using Cu Kα as the X-ray source (λ = 1.5406 Å). The chemical compositions of nanomaterials were analyzed by XPS (K-alpha, Thermo U.K.) using Al Kα radiation (1486.6 eV) and a carbon 1s peak at 284.8 eV was consider as a reference. The amperometric studies were carried out with a CHI 680 electrochemical workstations (CH Instruments Co., USA). The impedance studies were carried out in the frequency range between 0.01 Hz and 100 kHz with an AC signal of 10 mV amplitude under simulated solar light source. Pt wire was used as a counter electrode, saturated Ag/AgCl as a reference electrode, and ZnO NRs, Au/ZnO NRs, CuS/ZnO NRs, and CuS/Au/ZnO NRs were individually employed as working electrodes. A 0.1 M Na_2SO_4 solution was used as the electrolyte.

Photocatalytic and photoconductive activity

The photocatalytic activities of pure ZnO NRs, CuS/ZnO NRs, CuS/Au/ZnO NRs and P25 (TiO_2) spin coated ITO, were evaluated by

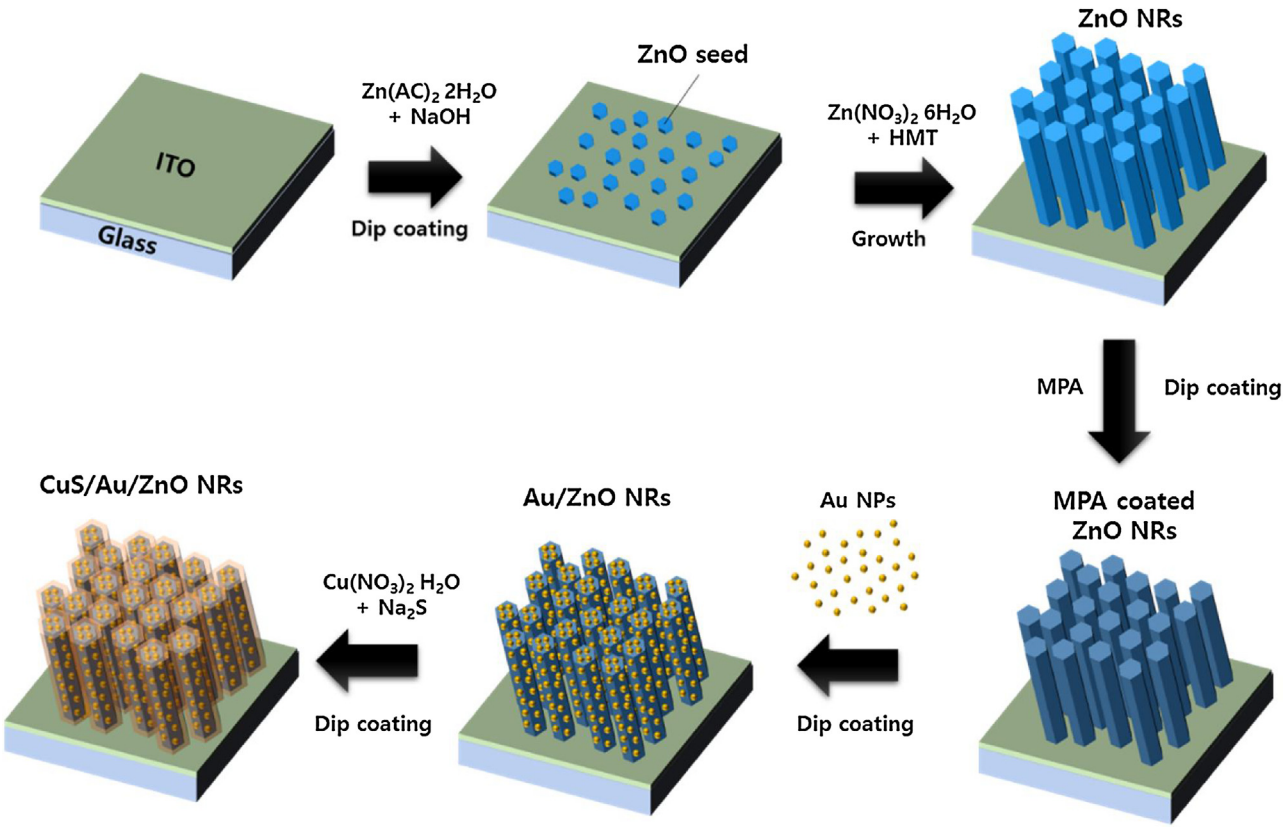

Fig. 1. Schematic diagram for the synthesis of CuS/Au/ZnO NRs.

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