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Facile synthesis of a novel full-spectrum-responsive $Co_{2.67}S_4$ nanoparticles for UV-, vis- and NIR-driven photocatalysis

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ABSTRACT

Sparked by growing pollution issues, research aiming at a better harvesting of solar energy in photocatalysts for environmental remediation has been thriving. In this study, a novel mixed valence state of $Co_{2.67}S_4$ nanoparticles with full-spectrum-responsive photocatalytic activity had been fabricated via a facile solvothermal route. The as-synthesized samples were systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV–vis-NIR diffuse reflection spectroscopy (UV–vis-NIR DRS). The photocatalytic performance of as-obtained samples had been investigated by the degradation of methylene blue (MB) in aqueous solution. The $Co_{2.67}S_4$ nanoparticles with the particle size of 5–20 nm could degrade MB with the efficiency of 64%, 84% and 68% under the UV light, visible light and near-infrared light exposure, respectively. Furthermore, a possible photocatalytic mechanism toward the near-infrared region had been proposed to be that the Co^{2+}/Co^{3+} redox couple played vital parts in the photocatalytic activity of $Co_{2.67}S_4$. This study provides a novel full solar spectrum-responsive photocatalyst for solar-light utility and environmental remediation.

1. Introduction

As a free, abundant and non-polluting resource, solar energy has been deemed as one of the most promising renewable energy sources all over the world [1–4]. For the better use of solar energy, numerous investigations of photocatalysts have been implemented [5–7]. However, it is still a challenging task to exploit a photocatalytic materials with efficient broad spectrum harvesting and conversion for solar light, especially the near-infrared (NIR) wavelength [8–10]. So far, the response of photocatalysts have been mostly confined in the spectrum from UV to visible wavelength, whereas the near-infrared light which reaches nearly 44% in the solar spectrum has been rarely harvest [11–15].

The pioneering investigations of such near-infrared light photocatalysts have been basically focused on the up-conversion luminescence of rare earth materials for the past 30 years. Upon the near-infrared excitation at 980 nm, the rare earth materials could generate upconverted emission peaks changing from near-infrared to UV or visible region of the spectrum [16–21]. Served as an intermedium, the up-conversion materials can convert NIR excitation light into visible or UV emission light to excite corresponding photocatalysts. After that, the forceful oxidative holes and reductive electrons could be generated for the photocatalytic reaction [12,16]. Nevertheless, the quantum efficiency of up-conversion photocatalyst was limited, owing to its extremely narrow absorption band of light at 980 nm [22,23]. Therefore, many other photocatalysts which possessed Vis-NIR or NIR photocatalytic activity come into being, such as WS_2, Bi_2WO_6 and $Cu_2(OH)PO_4$ [24,25]. However, to date, $Co_{2.67}S_4$ photocatalyst, a kind of transition-metal sulfides with full-spectrum-responsive photocatalytic activity, has not been investigated.

Recently, the transition-metal sulfides were regarded as a type of promising candidates, owing to the distinctive and irreplaceable cracking electronic, magnetic, and photovoltaic properties in energy, catalysis, and electricity [26–29]. Cobalt sulfides (Co_mS_n), a significant kind of complicated transition-metal sulfides, possess

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diverse chemical formulas and various crystalline phases, such as CoS_2, CoS, Co_9S_8, Co_3S_4, Co_3S_2, and $Co_{1-x}S$ [27,30–32]. Moreover, Co_mS_n have exhibited excellent potentiality in energy storage and conversion devices, such as electrochemical capacitors, catalysts for fuel cells, dye-sensitized solar cells and cathode materials for lithium-rechargeable batteries [33–35]. Furthermore, the quantum chemical calculations revealed that the surface structure of Co_mS_n (e.g., CoS) could create electron transfer pathways for oxygen reduction kinetics, which facilitated for the improvement of catalytic activity [36]. Up to now, most investigations of Co_mS_n have been focused on the electrochemistry, and rarely utilized in photocatalysis and waste-water treatment.

Recently, our group had reported the facile synthesis of Sb_2S_3/ultrathin g-C_3N_4 sheets heterostructures embedded with g-C_3N_4 quantum dots with enhanced NIR-light photocatalytic performance [37]. Besides, metal sulfides-based composites including $Sb_2S_3/Sb_4O_5Cl_2$, In_2S_3@MIL-125(Ti), SnS_2-$MgFe_2O_4$/rGO and metal sulfides quantum dots on MIL-125(Ti) had been synthesized by hydrothermal method, solvothermal method and photodeposition strategy, respectively. These photocatalysts had shown excellent visible light photocatalytic activity [38–42]. In this study, a novel full-spectrum-response photocatalyst $Co_{2.67}S_4$ was fabricated by a facile solvothermal method, which exhibited great optical absorption in a broad range of 240–2200 nm, covering the wave band of UV, visible and NIR region. The obtained photocatalysts were characterized by SEM, TEM, XRD, XPS and UV–vis-NIR DRS [43]. The $Co_{2.67}S_4$ nanoparticles with mixed valence had realized great photocatalytic property for methylene blue (MB) degradation under UV, visible and NIR irradiation. The degraded MB wastewater samples were characterized by three dimensional fluorescence excitation-emission matrix (3D EEM) and gas chromatography-mass spectrometry (GC–MS). Moreover, a possible mechanism toward the near-infrared light has been proposed.

2. Experimental section

2.1. Materials

Cobalt chloride ($CoCl_2{\cdot}6H_2O$), Sodium sulfide ($Na_2S{\cdot}9H_2O$), Ethylene glycol ($C_2H_6O_2$) and Methylene blue (MB, $C_{16}H_{18}N_3SCl$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were of analytical grade and used as received without any further purification.

2.2. Synthesis of $Co_{2.67}S_4$ nanoparticles

$Co_{2.67}S_4$ nanoparticles were synthesized by means of a facile solvothermal procedure. In general, 1 mmol of $CoCl_2{\cdot}6H_2O$ and 2.2 mmol of $Na_2S{\cdot}9H_2O$ were dissolved in 40 mL ethylene glycol at room temperature. Then, the mixtures were stirred for 30 min to form a homogeneous solution. Afterwards, all of the mixtures were transferred into a 50 mL Teflon-lined autoclave for 24 h at 150 °C, 180 °C and 200 °C. When the autoclave cool to room temperature, the as-synthesized black products were collected by centrifugation, washed with distilled water and absolute ethanol, subsequently, to remove any ionic residual. Finally, the products were dried under vacuum at 60 °C overnight.

2.3. Characterization

The powder X-ray diffraction (XRD) patterns of $Co_{2.67}S_4$ nanoparticles were carried out with Bruker AXS D8 advance diffractometer operating with Cu-Ka radiation (λ = 1.5406 Å) to investigate the crystal structure of the samples under 40 kV, 250 mA. The surface elemental composition and valence state of the sample was implemented by X-ray photoelectron spectroscopy (XPS), which were recorded on a Thermo ESCALAB 250Xi instrument, and the binding energies of adventitious carbon (284.8 eV) were applied for charge correction. Transmission electron microscopy (TEM, JEOL JEM-1230) and scanning electron microscope (SEM, JEOL JSM-6700) images were applied to investigate the morphology and structure of the obtained samples. The materials was uniformly dispersed into absolute ethanol by ultrasound method, and the solution was evenly dropped on the copper grids. After drying, the copper grids was observed by Transmission electron microscopy (TEM), the chemical composition was examined via energy-dispersive X-ray spectroscopy (EDS) attached to the TEM. UV–vis-NIR diffuse reflectance spectra (UV–vis-NIR DRS) of the samples were recorded on a UV–vis-NIR spectrophotometer (U4100, Hitachi) with an integrating sphere attachment within the range of 240–2200 nm and $BaSO_4$ was used as the reflectance standard.

2.4. Photocatalytic activity test

The photocatalytic activities of the $Co_{2.67}S_4$ nanoparticles were estimated by the photodegradation of MB under UV, visible and near-infrared light irradiations supplied by a 300 W Xenon lamp (Beijing China Education Au-light, Co., Ltd.). The light source (14 V, 16 A, 15 cm) far away from the photocatalytic reator. Typically, the photocatalytic degradation was actualized in a 250 mL beaker, containing 100 mL MB solution (10 mg L^{-1}) and 50 mg photocatalyst. To dispel the effect of adsorption on the experimental results, the solutions were magnetically stirred for one hour in a dark condition to achieve the adsorption-desorption equilibrium under room air conditions. Moreover, a 300 W Xenon lamp was applied as the UV light, visible light and near-infrared light source, under assistance of filters to ensure the light < 400 nm as UV source, light of 400–760 nm as visible source as well as the light < 760 nm were cut off by filter as near infrared source. Every periodic interval of 20 min, 4 mL aliquots were drawn out and centrifuged to remove the particles. The residual MB concentrations were detected at 664 nm by a UV–vis spectrophotometer (UV-2250, SHIMADZU Corporation, Japan). In the experiment of oxidative species detection, the holes, $^{\bullet}OH$ and $^{\bullet}O_2^-$ generated during the photocatalytic process were resolved by sodium oxalate, isopropanol and N_2-saturated condition respectively. The degraded MB wastewater samples were characterized by EEM spectroscopy (F-4600, Hitachi). Scanning emission spectra was acquired from 200 to 800 nm by varying the excitation wavelength from 200 to 800 nm at 10 nm increments. The chemical constituents of the dichloromethane extract of degraded MB wastewater samples were determined by GC–MS analysis. GC–MS was run on a GCMS-QP2010 Plus spectrometer (30 m × 0.25 mm × 0.25 μm; SHIMADZU, Japan) with helium (2.0 mL/min) as carrier gas.

3. Results and discussions

3.1. Characterizations on $Co_{2.67}S_4$ nanoparticles

Firstly, the crystal phase compositions and purity of as-obtained samples were characterized by X-ray diffraction (XRD), as shown in Fig. 1. It can be clearly seen that all of the diffraction peaks could be well corresponded with the cubic phase of $Co_{2.67}S_4$, which matched well with the standard XRD patterns (PDF#97-010-9368), and no impurity peaks were identified. Moreover, the lattice parameters could be calculated to be a = 9.44 Å, and the XRD spectrum also showed four peaks located at 2θ = 31.4°, 38.1°, 50.2° and 55.0°, corresponding to the (311), (400), (511) and (440) planes of $Co_{2.67}S_4$. After photodegradation, no obvious changes of the XRD patterns