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Photoelectrocatalytic reduction of nitrobenzene on Bi-doped $CuGaS_2$ films

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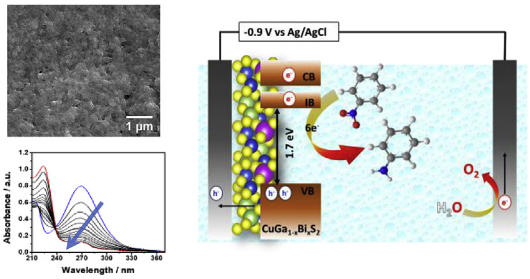
HIGHLIGHTS

- Facile and fast approach to prepare Bismuth-doped $CuGaS_2$ nanocrystals.
- Bismuth-doping enhanced optical properties of the chalcogenide semiconductor.
- Photoelectrocatalytic reduction of nitrobenzene under visible light irradiation.
- High conversion and high selectivity to aniline using Bi-doped $CuGaS_2$.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrobenzene, a toxic nitroaromatic, a feedstock compound to the production of many commercially relevant chemicals were photoelectrocatalytically reduced into aniline on a photoelectrode comprised by a bismuth-doped $CuGaS_2$ nanocrystallyne thin films on molybdenum. The activity of the photoelectrodes were compared to the reaction performed on undoped-$CuGaS_2$ films, and they were carried out under illumination with an applied bias potential at 0.9 V. Aniline was highly selectively obtained with 83% of conversion for reaction times of 100 min when using Bi-doped $CuGaS_2$, representing higher conversion of nitrobenzene and yield to aniline than the undoped photoelectrode. The catalytic performance of the doped films remained stable for a set of 5 consecutive experiments. These results indicate Bi-doped $CuGaS_2$ as a promising material to be applied in the photoelectrocatalytic reduction of nitrobenzene into aniline through the direct pathway mechanism, using solar light illumination.

1. Introduction

Nitrobenzene (NB) derivatives are a class of compounds that find high applicability in the production of many commercially relevant chemicals, such as dyes (Rao et al., 2003), explosives (Tan et al., 2017), pesticides (Keum and Li, 2004) and perfumes (Ma et al., 2017), to name a few. In the pharmaceutical industry, NB derivatives can be used as precursors in different synthesis routes (Roberts et al., 2017) such as in the paracetamol synthesis (Khan et al., 2017; Marsac et al., 2017) for instance. A major cause of concern due to the large use of nitroaromatics by the industry is the persistent presence of such pollutants in wastewater effluents and the toxicological implications to the human health (Zhu et al., 2007). NB have already been linked to anemia, skin irritation and presumably have carcinogenic nature (Kovacic and Somanathan, 2014; Li et al., 2017a). According to United States Environment Protection Agency (USEPA), its maximum allowed concentration in wastewater must not exceed 20 ppb (Lowenbach et al., 1979; Liu et al., 2017a; b). Over the past decades, many research groups

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have reported different strategies to manage nitroaromatics in aqueous effluents, such as physical (Wu et al., 2017), biological (Li et al., 2017b; Yuan et al., 2017), and chemical degradation techniques (Bai et al., 2017; Yang et al., 2018). It is commonly pointed as an effective and environmentally friendly strategy to convert the toxic nitrobenzene into a low toxic and easy to mineralize aminoaromatic derivative (Liu et al., 2017a; b). In this sense, several investigations have reported the usage of noble metals (Au, Pt) and transition metals (Ru, Cu, Ni) in the production of aniline and intermediates (nitrosobenzene, phenylhydroxylamine, azobenzene) from the heterogeneous catalytic hydrogenation of nitrobenzene (Sheng et al., 2016). However, some of these methods require the employment of elevated temperatures and H_2 pressure conditions in order to obtain satisfactory yields of aniline (Qusti et al., 2014). As an alternative, electrochemical reduction of nitrobenzene to aniline over noble metal electrodes (Pt, Au) has also been reported. The main drawback of the electrocatalytic approach is the low current efficiencies obtained since nitrobenzene reduction takes place at considerably highly negative values of overpotential, in such a way that the undesired hydrogen reduction reaction also occurs concomitantly (Marken et al., 1996; Seshadri and Kelber, 1999). To overcome this issue, many studies have focused in the development of cathodic materials able to promote the nitrobenzene reduction at lower overpotentials (Song et al., 2007).

On the other hand, photocatalysis has attracted much attention since TiO_2 electrodes began to be employed in the light-assisted decomposition of water into hydrogen and oxygen (Fujishima and Honda, 1972). It expanded the investigations on using photochemical catalysis, not only for water splitting (Kanakaraju et al., 2015; Gao et al., 2017a; b; Gromboni et al., 2017), but also for organic pollutants degradation (Alves et al., 2018), carbon dioxide reduction to fuels (Gao et al., 2017a; b), among other organic reactions (Wang et al., 2017). This technique provides prominent advantages including non-toxicity, low cost, no secondary pollution and thorough mineralization. In addition, photocatalysis can be performed under solar illumination as a renewable and alternative energy resource.

The photoelectrocatalysis combines electrocatalysis and photocatalysis, where a system containing a photoelectrode is activated by light illumination with an application of a constant bias potential. In this system, the photocatalyst can be easily recovered and recycled for consecutives treatments after use (Xie et al., 2016; Garcia-Segura and Brillas, 2017).

The photoelectrocatalytic efficiency on organic pollutant remediation is directly related to the semiconductor selected as photoelectrodes. In this work, a thin filme of $CuGaS_2$ on molybdenum is used as photoelectrode. $CuGaS_2$ is a chalcogenide (Cu-III-S_2 family) (Tablero and Marron, 2010) with a 2.4 eV band gap (E_g) (M. Han et al., 2016a, b) of chalcopyrite-like structure (Song et al., 2015; Guo et al., 2016). Its optical absorption can be enhanced to produce photocatalysts that are active in the visible light range when doped with transition metals (Ti (Hashemi et al., 2014; Jing et al., 2016; Lv et al., 2014), Cr (Chen et al., 2013), Ce (Xiao et al., 2015) and Fe (Koskelo et al., 2016)), post-transition (Sn (Song et al., 2015; Han et al., 2016a; b)), and 15 group elements (N, P, As, Sb) (Han et al., 2016a; b). Han et al. (Han et al., 2016a; b). Inspired by the aforementioned strategy herein we present the development of a Bi-doped $CuGaS_2$ nanocrystals and its catalytic performance evaluation towards the selective reduction of nitrobenzene into aniline, using a photoelectrocatalytic approach.

2. Experimental

2.1. Chemicals

In this work the following chemicals were used: copper (I) chloride (CuCl, 97%, Sigma Aldrich), gallium sulfate ($Ga_2(SO_4)_3 \cdot 18H_2O$, 99.99%, Aldrich), sulfur powder (S, 99.5%, Acros), bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$, 98%, Sigma Aldrich), oleylamine (OLA) (70%, Sigma Aldrich), molybdenum foil (Mo 0.1 mm, Sigma Aldrich), nitrobenzene (NB) (99.98%, Vetec Quimica Fina).

2.2. Synthesis of Bi-doped $CuGaS_2$ chalcopyrite nanocrystals

Bi-doped $CuGaS_2$ nanocrystals were prepared according to the procedure reported in our previous work (Andrade and Mascaro, 2018). In the procedure, 0.5 mmol of CuCl, 0.24 mmol of $Ga_2(SO_4)_3 \cdot 18H_2O$, and 0.01 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ were added to 8 mL of OLA into a three-neck flask. In a separate flask, 1 mmol of sulfur powder was dissolved in OLA (2 mL). Both flasks were attached to a Schlenk line, previously purged of oxygen and water by pulling vacuum at room temperature for 10 min. The flasks were heated to 240 °C using a sand bath, and then, the reaction was initiated by the rapid transfer of the sulfur precursor into the metals solution. The reaction mixture was refluxed for 1 h and allowed to cool to room temperature. The nanocrystals were separated by precipitation, adding excess ethanol followed by centrifugation at 8000 rpm for 10 min. Thereafter, the nanocrystals were redispersed in chloroform and centrifuged at 7000 rpm for 5 min. To remove excess OLA, the product was again precipitated with ethanol, centrifuged and finally, stored in hexane.

2.3. Spray-deposition of nanocrystals on Mo substrates

For depositing Bi-doped $CuGaS_2$ films on a Mo foil, a spray system was assembled using an airbrush tool attached to a compressed air line (10 mL min^{-1}), used as solution carrier (Fig. SM-1). The nanocrystals hexane solutions (0.012 mg mL^{-1}) were sprayed for 2 s (spray flow = 33 μL s^{-1}) on preheated Mo substrates (5 mm × 10 mm) on a hotplate at 80 °C. This process was then repeated 20 times, with 1 min intervals between the deposition sessions for evaporation of the remaining solvent.

2.4. Bi-doped $CuGaS_2$ nanocrystals and nanocrystalline films characterization

The organization at long-distance and structure of the chalcogenides were determined by X-ray powder diffraction (XRD) analysis, performed with Cu Kα radiation (40 kV, 30 mA) using a Shimadzu model XRD 6000 diffractometer with 0.5°, 0.5°, 0.3 mm slits for entrance, scattering and exit, respectively, at room temperature. The UV–Vis spectra of the nanocrystals solutions were measured between 300 and 2000 nm in a quartz cell with a 1 cm path length, using a Cary 5G Varian UV–Vis–NIR spectrophotometer. Transmition electron microscopy (TEM) and high-resolution (HRTEM) images were obtained using a Tecnai G2 F20 X-Twin 200 kV FEI. Films thicknesses and semiquantitative elemental analysis were estimated by scanning electron microscopy (SEM, Inspect F50 model, FEI) coupled with energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha spectrometer using monochromatic Al Kα (1486.6 eV) radiation.

2.5. Photoelectrocatalytic reduction of nitrobenzene on $CuGa_{1-x}Bi_xS_2$ films

Photoelectrocatalytic experiments were carried out in a quartz cell equipped with an Ag/AgCl reference electrode, a Pt counter electrode, and $CuGa_{1-x}Bi_xS_2$ films supported on Mo with a 0.25 cm^2 average active area, as working electrode. The electrodes were immersed in 3.5 mL electrolyte solution, containing 80 μM