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Mechanochemistry of copper sulfides: Characterization, surface oxidation and photocatalytic activity

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Abstract

In the present study, the mechanochemically prepared covellite, CuS and chalcocite, Cu_2S nanocrystals are compared in detail. Concretely, the SEM, EDS, N_2 adsorption, UV-Vis, PL, FTIR, ZP measurements, PCCS, XPS and DTA/TG were used. SEM, EDS and elemental mapping has shown that the agglomerates containing nanoparticles of the corresponding phases were formed as a result of milling. The nitrogen adsorption method has documented richer surface properties in the case of CuS sample. The specific surface area values were 2.7 $m^2.g^{-1}$ and 1.4 $m^2.g^{-1}$ for CuS and Cu_2S, respectively. UV-Vis and PL measurements have shown that these materials might be suitable for optoelectronic applications, as the optical bandgaps were 1.92 eV and 3 eV for CuS and Cu_2S, respectively. FTIR spectrum of CuS exhibited the peak at 621 cm^{-1}, which is characteristic for this material. ZP values were more negative in the case of CuS and PCCS has confirmed the finer character of this sample (x_{50} values were 680 nm and 617 nm for Cu_2S and CuS, respectively). XPS method documented the surface oxidation of the prepared Cu_2S. The thermal stability measurement up to 550 °C has shown that Cu_2S does not undergo significant changes (only 1.4% weight loss was observed), whereas CuS is losing sulfur and is transformed into digenite and chalcocite (14.3% weight loss was observed). The mechanochemically synthesized copper sulfides show high activities in photodecolorization of Methyl Orange dye under visible light irradiation, as Cu_2S was able to completely decompose the dye in 150 min and CuS caused 80% decomposition after the same time of treatment.

Keywords: copper sulfide; covellite; chalcocite; mechanochemistry; characterization; photocatalytic activity

1. Introduction

Among copper sulfides, covellite, CuS and chalcocite, Cu_2S are the most common. These compounds in the form of nanoparticles are extensively studied today, because of their possible utilization in various applications, including biomedical ones [1]. As an example, their application in photothermal ablation can be mentioned [2]. Further applications are as photocatalysts [3, 4], hydrogen gas sensors [5], absorbers for solar cells [6, 7], energy storage devices [8] or thermoelectric materials [9, 10].

There are many synthetic pathways to copper sulfide nanocrystals, like hot injection method [11], hydrothermal [12] and solvothermal synthesis [13],