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Short communication

Electronic and photoluminescent properties of Mn-doped Cu_2S nanostructures for possible photocatalytic applications

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ABSTRACT

Hexagonal nanostructures of crystalline Cu_2S and Mn-doped Cu_2S synthesized hydrothermally in this report are examined. SEM micrographs display an anisotropic nature in pristine and Mn-Cu_2S nanostructures. Pristine Cu_2S material displays the emission at 497 nm while as the Mn-incorporation leads to a stokes shift of ~ 15 nm. The broad peak with high intensity at 511 nm in the PL is ascribed to the incorporation of 10 %-Mn into Cu_2S nanostructures. Energy gap decrease in 10 %-Mn-Cu_2S was observed from the optical absorption and the electronic structure simulations, simultaneously. Where a strong spin polarization with indirect transitions is observed within the range of visible light spectrum due to spin crossover of partial Mn-d states from spin up to spin down channels. Mn induced spin interactions shift the Fermi level (EF) towards the conduction band with a gap of 1.53 eV in high spin state and 0.31 eV in low spin state. Pristine copper sulphide nanostructures and the optimal doped sample's ability to dynamically regulate their fluorescence and hole doping density could potentially result in their successful integration into optical switches and solar systems.

1. Introduction

The controlled nanoscale engineering of bulk semiconductors with precise size, structure, and compositional uniformity has been intensively pursued for diverse applications spanning micro-nanoelectronics, photocatalysis, photovoltaics, and biomedicine. Despite significant advances, achieving such precision remains a formidable challenge in materials science, particularly for implementation in functional devices [1–3]. The characteristics of nanostructures significantly depends up on their morphological features and sizes, as their physical and chemical properties in bulk are quite different [4,5]. 2D-heterostructures or monolayer designing and construction has attracted much interest in the fundamental as well as applied research. Among several metal chalcogenide nanostructures, the copper (I) sulfide (Cu_2S) is regarded as a prospective material for future applications in optoelectronic devices [3,6–8]. Copper sulfide (Cu_2S) is a p-type binary chalcogenide semiconducting material with five stable phases at ambient temperature, Such as; anilite ($Cu_{1.75}S$), chalcocite (Cu_2S), digenite ($Cu_{1.8}S$) djurleite ($Cu_{1.96}S$) and covellite (CuS) [9]. Cu_xS (1:2) was reported to have an energy band gap that ranged from 1.2 to 2.5 eV [10]. Copper sulfide has been widely used in various applications due to its superior properties, including thin-film photovoltaics, gas sensors, photodetectors, ion batteries, superconductors, etc. [2,3,6,7]. Different methods were used to synthesized Cu_2S which include spray pyrolysis, electrochemical deposition, atomic layer deposition [11], consecutive ionic stratum adsorption and reaction [12], microwave assisted chemical bath precipitation [13], thermal steaming and chemical vapor deposition [14], etc.

The electronic structure engineering of chalcocite (Cu_2S) nanostructures through transition-metal doping offers a powerful approach to tailor their electronic and optical properties for advanced applications. In this study, we demonstrate the synthesis of highly uniform Cu_2S and Mn-doped Cu_2S heterostructures with controlled dimensions using a low-cost, environmentally benign hydrothermal method. To the best of our knowledge, this work presents the first systematic investigation of how Mn incorporation governs the electronic structure and photoluminescent behavior of Cu_2S-based materials. Furthermore, employing

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