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Electronic structure, photocatalytic and electrochemical performance of chalcogenide quantum dots loaded on reduced graphene oxide: (Cu_2MnSnS_4/rGO)

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ABSTRACT

In the present article, facile and novel synthesis of Cu_2MnSnS_4/reduced-graphene (CMTS/rGO) nanocomposites is achieved. X-ray diffraction (XRD), Raman analysis, X-ray photoelectron spectroscopy (XPS) were explored to test the supposed formation. CMTS semiconductors grow within a tetragonal symmetry and rGO crystallize into hexagonal phase. CMTS particle size is very small having dimensions around 10–12 nm and corroborates with the average particle size calculated from the SEM. The TEM micrograph of rGO consists ~10 nm thick nanosheets. The composite materials exhibit 2D morphology with 17 nm thick rGO nanosheets holding CMTS quantum dots (9 nm). Electronic structure modulations with rGO specify the replication of energy band gaps with experimental agreements. Photocatalytic activity against malachite green (MG) enhances from 74 % (CMTS) to 95 % (CMTS/rGO). In addition, the electrochemical measurements demonstrate the specific capacitance for 10 % CMTS/rGO (870 F/g) is about four times larger than that of pure CMTS (268 F/g). Our results prompt the evidence of possible applications and further research in photocatalysis via graphene reduction.

1. Introduction

Several attractive traits, such as the presence of earth abundant and non-toxic metals and appropriate absorption characteristics for absorber materials, are shared by Cu_2MnSnS_4 and the extensively studied Cu_2ZnSnS_4 for photovoltaic applications [1]. Recently, Cu_2ZnSnS_4 has gained interest as a potential absorber material. Nevertheless, band gap fluctuations are brought on by cation disorder in Cu_2ZnSnS_4, which may restrict the current efficiency levels of Cu_2ZnSnS_4-based solar cells [2,3]. The presence of multiple secondary phases in reactive co-sputtered thin-film Cu_2MnSnS_4 samples with varying cation concentrations and high temperature annealing is confirmed through previous XRD and Raman measurements. Earlier crystal structure calculations validate the preference for stannite crystal structure over kesterite; nevertheless, more validation taking cation disorder into account is required [4,5]. Since, low-dimensional materials outperform their bulk equivalents in terms of electronic properties, solar cell and energy storage efficiency [6,7]. Their performance can be effectively improved via nano-engineered quantum dot formations, which allows modulation of crystal structure as well as electronic energy levels of a material. For stannite (kesterite), the direct band gap of Cu_2MnSnS_4 is calculated to be 1.52 eV (1.62 eV), which is in line with the range of the band gaps that may be detected using spectrophotometry, which is 1.42–1.59 eV. Composition or cation substitution can affect the kinetic parameters (the cation exchange energy and the activation energy for the cation exchange), which can help to lessen cation disorder [2,3].

A diverse range of chalcogenide materials, CZTS (Cu_2ZnSnS_4) and CMTS (Cu_2MnSnS_4) nanomaterials were explored for charge storage as well as photocatalytic applications include metal oxides, sulphides, hydroxides, nitrides, etc. [8–13]. However, the heterostructuring of reduced graphene (rGO) with Mn replacement in CMTS not only optimizes their electronic structure but improves the optical and photocatalytic properties as well. The idea that the cation disorder among the Cu and Mn cations should be reduced compared to antisites involving Cu and Zn cations in Cu_2ZnSnS_4 is part of the interest in Cu_2MnSnS_4 as a potential absorber in solar cells [2]. This is because the cation radii of Cu and Mn are not as similar as the cation radii of Cu and Zn in the irrespective configuration. This ought to lessen the severity of the problem

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