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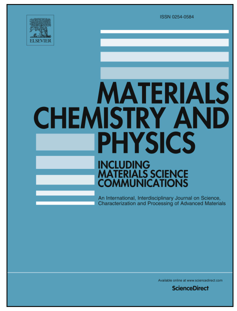

Nitrogen-doped ZnS nanoparticles: Soft-chemical synthesis, EPR statement and quantum-chemical characterization

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ABSTRACT

Nanocrystalline ZnS is a well-recognized semiconducting material for photocatalysis, current photogeneration, white luminophors and efficient fluorescence sensorics. Chemical bath deposition from aqueous solutions is an affordable method for fabrication of ZnS nanostructures and composite materials thereof. Here, the one-step route is proposed for deposition of nitrogen-doped ZnS nanoparticles, prepared formerly only via high-temperature ZnS nitridation. The nanoparticles are characterized by XRD, EPR and UV/Vis spectroscopic methods. The origin, chemical state and localization of nitrogen impurity within the ZnS lattice are elucidated using quantum-chemical calculations. The emergence of nitrogen in ZnS lattice is related to NH_4^+ ions grabbed to the Zn sublattice from parent aqueous solution.

Keywords: ZnS nitridation; chemical bath deposition; EPR spectroscopy; quantum-chemical calculations

1. INTRODUCTION

Nanocrystalline ZnS is an attractive semiconductor nano-photocatalyst for advanced treatment of wastewater contaminated with hazardous organic pollutants under ultraviolet (UV)-light irradiation [1,2], eco-friendly component of buffer thin films in Cu_2ZnSnS_4/$Cu_2ZnSnSe_4$ solar cells [3], material for white-light-emitting phosphors with high quantum efficiency [4] and a highly efficient fluorescent sensors for detecting glyproteins present in the complex biological or biomedical samples [5]. However ZnS exhibits optical activities only under near UV light irradiation, since it is a wide band gap semiconductor (E_g~3.60-3.80eV). Furthermore, as an important part of II-VI semiconductor photocatalysts, ZnS suffers from a problem of stability during the photocatalytic processes [6, 7]. The photocorrosion of ZnS is initiated due to the positively-charged holes h^+ which tend to oxidize S^{2-} in ZnS lattice [7]. The reducing of oxidative capability of h^+ is the key to prevent ZnS from photocorrosion. Thus the low sunlight utilization degree and the poor stability during photocatalytic process limit the wider application of ZnS as photoactive material.

Doping - the intentional introduction of impurities into a material - is fundamental to controlling the properties of semiconductors [8]. Element-doping has become a well-known route to form localized energy levels in the band-gap E_g, tuning E_g and improving the visible light absorption by semiconductor [9]. Numerous research groups are now successfully attempting to incorporate metal and non-metal heteroelements (Mo [9], Ni [10], Sn [11], Cu [12, 13], Mn [12], N, C [14], etc) into ZnS nanocrystals. Both metal and non-metal doping has been