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Brief Note

Solution prepared O-doped ZnS nanocrystals: Structure characterization, energy level engineering and interfacial application in polymer solar cells

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ABSTRACT

Doping impure atoms into host semiconductor nanocrystals is used to tune the properties and functions of semiconductor nanocrystals (NCs). Here, we demonstrate a solution method for preparing O doped ZnS (ZnS(O)) colloidal NCs. The as-prepared NCs have been proved to be consistent with the crystal structure of ZnS and Zn 3d-O 2p hydrization existed in the as-prepared NCs as certified by O k-edge X-ray absorption spectra (XAS). The average size was measured to be about 8.5 nm by Transmission Electron Microscope (TEM). The role of pyridines was to control the size and tune the surface property. By doping oxygen into ZnS lattice, the energy levels of as-prepared NCs were moved down, giving a better band alignment for photovoltaic application. When it was applied to modify ZnO interlayer and form ZnO/ZnS(O) bilayer in the polymer solar cells (PSCs), the optimal power conversion efficiency (PCE) of the device based on ZnO/ZnS(O) reached 8.85% (8.59 ± 0.49%), which increased by 10% compared to ZnO-only control device with the optimal PCE of 8.00% (7.46 ± 0.54%). The novel approach has been proved to be facile and scalable, paving the way for synthetizing O doped semiconductor nanocrystal.

1. Introduction

Nanoscale semiconductors have attracted much attention over the past decades due to their size- and shape-dependent properties compared with their bulk counterparts (Mane and Lokhande, 2010). As the size decreases, the energy band gap (E_g) increases accordingly, resulting in a blue shift of the absorption wavelength. This is known as quantum size effect. Zinc sulfide (ZnS), an important wide band gap (3.6 eV) semiconductor, has been extensively investigated (Chai et al., 2007; Monroy et al., 2003; Quan et al., 2007) and widely used in many fields such as cathode ray tube (CRT) (Ozawa et al., 2005), field emission display phosphors (Fang et al., 2007; Villalobos et al., 2002), electroluminescent devices (Shen and Wang, 2012) and infrared (IR) windows. However, the improper energy levels restrict the application of ZnS NCs in the photovoltaic field. The lowest unoccupied molecular orbital (LUMO) level of ZnS NCs is 3.1 eV higher than that of ZnO NCs, which inhibits electron transfer from electron donor to ZnS in polymer solar cells (PSCs).

Doping is a widely used technological process in material science. It involves incorporating dopants into the host lattice to yield materials with desirable properties and functions. In recent years, doping impure atoms into host semiconductor NCs provides a controlled way to tune the optical, luminescent, electronic, magnetic, and other properties (Goudarzi et al., 2009; Cao, 2011; Mocatta et al., 2011; Norris et al., 2008). For instance, Ni^{2+} doped CdS NCs improved their photocatalytic activity and durability compared with original undoped ones (Luo et al., 2012). And the electrical conductivity of Cu_2ZnSnS_4 NCs can be enhanced through extra Cu^{2+} doping (Yang et al., 2012). Additionally, there have been three different main opinions regarding modification mechanism of metal oxides doped with nonmetals: (1) Band gap narrowing; (2) Impurity energy levels; and (3) Oxygen vacancies. The absorption of semiconductor NCs can be changed by nonmetal doping. Chen et al. reported that H doped TiO_2 NCs increased the absorption region of solar illuminance by hydrogenation of a disordered layer on the nanocrystal surface (Chen et al., 2011).

Due to the large E_g and the excellent transmission property in the visible region, ZnS is probably the most important host matrix for varieties of dopants. So far, numerous literatures have been reported on the synthesis of metal doped ZnS NCs (Mn-doped, Co-doped, Cu-doped, Cd-doped etc.) (Jayanthi et al., 2007; Kudo and Sekizawa, 2000; Zhang

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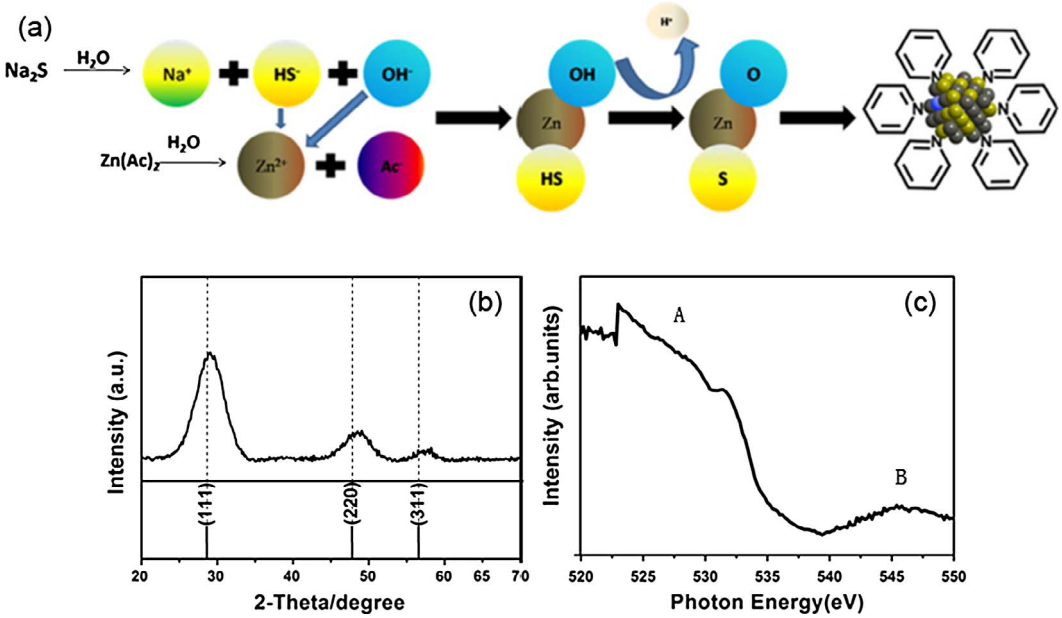

Fig. 1. (a) The synthesis route of the O doped ZnS NCs. (b) XRD pattern of the O doped ZnS NCs. The vertical tick indicates the positions of the reflexes from the cubic phase of ZnS (JCPDS No. 05-0566). (c) O k-edge X-ray absorption spectra of the O doped ZnS NCs. A is the pre-edge of the O K-edge spectrum and B is the featured peak at 546 eV.

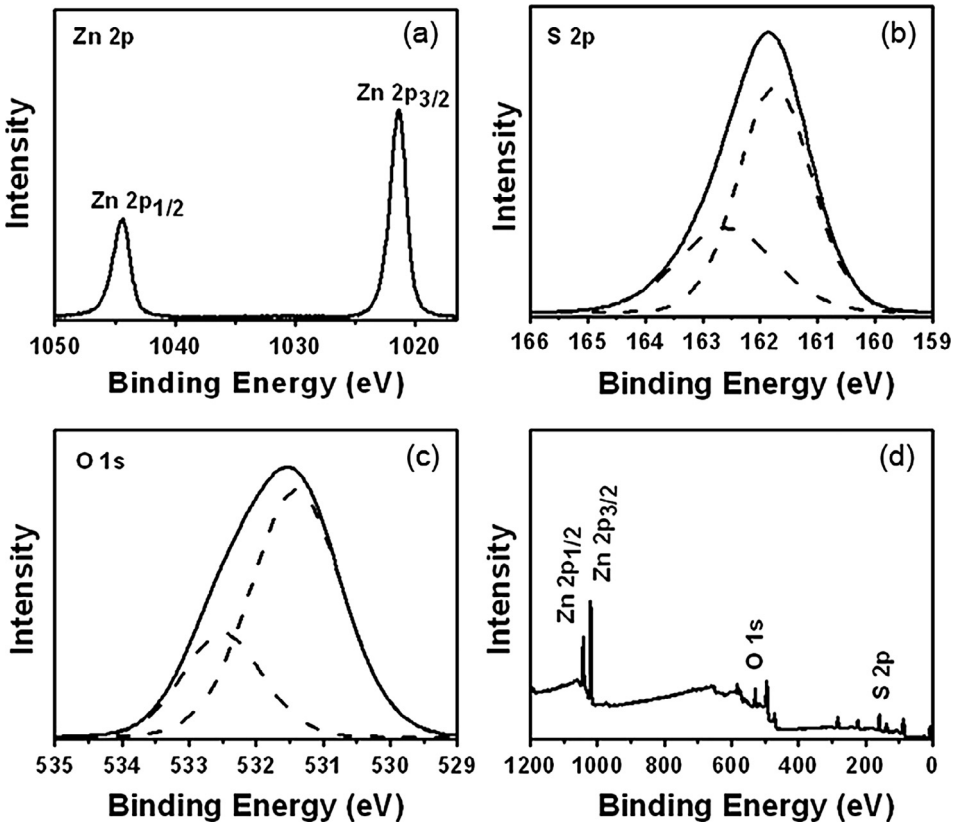

Fig. 2. XPS spectra of the O doped ZnS NCs. (a) Zn 2p XPS acquisition, (b) S 2p XPS acquisition and (c) O 1s XPS acquisition. (d) Full spectra of the O doped ZnS NCs.

et al., 2011; Duan et al., 2018). After doping with different metal elements, varieties of luminescent properties of ZnS NCs have been observed when the NCs were excited by UV, X-rays, and electro-luminescence (Zhao et al., 2004). In addition, some of the doped ZnS NCs are promising candidates as bio-nanocomposites (Makhal et al., 2012; Wu et al., 2010) and diluted magnetic semiconductors (Jadraque et al., 2013; Sapra et al., 2005). According to the density functional theory, ZnS NCs were calculated to exhibit good photocatalytic activity or magnetic behavior by doping nonmetal such as C or N, etc. (Jang et al., 2009; Muruganandham and Kusumoto, 2009; Chen, 2011; Fan et al., 2009). Compared to metal doped ZnS NCs, there has been less attention on the nonmetal doped ZnS NCs, because it is difficult to be achieved in the synthesis process by using conventional chemical methods. Usually, it is accomplished by relatively complicated procedures or harsh conditions (Yu et al., 2011; Grün et al., 1999; Cho et al., 2010; Chen and Burda, 2008). Moreover, doping oxygen into ZnS NCs may be an effective means to improve electron transfer from electron donor to ZnS in ploymer solar cells. But, the methods of doping oxygen into ZnS NCs