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Synthesis and properties of colloidal Cu_2CdSnS_4 nanocrystals

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Abstract: Colloidal Cu_2CdSnS_4 nanocrystals were synthesized by a facile solution chemistry method. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-vis-NIR absorbance spectroscopy measurements indicated that the Cu_2CdSnS_4 colloidal nanocrystals have uniform size-distribution and good crystalline quality with a tetrahedral coordinated structure. The stoichiometric ratio Cu/Cd/Sn/S is about 2.07:0.75:1.26:3.92 in Cu_2CdSnS_4 nanocrystals, and the chemical states of Cu, Cd, Sn and S elements are of +1, +2, +4 and −2, which correspond with the states in the molecular formula of Cu_2CdSnS_4. The band gap of Cu_2CdSnS_4 nanocrystals is estimated to be ~1.3 eV by extrapolating method.
Key words: colloidal nanocrystal; Cu_2CdSnS_4; photovoltaic materials; solar cell
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胶体 Cu_2CdSnS_4 纳米晶的合成与其性质研究

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摘要:用简易的溶液化学方法合成了胶体 Cu_2CdSnS_4 纳米晶.透射电子显微镜(TEM),扫描电子显微镜(SEM),能谱(EDS),X射线衍射(XRD),X射线光电子谱(XPS)和UV-vis-NIR吸收光谱测试表明 Cu_2CdSnS_4 胶体纳米晶具有均一的尺寸分布和良好的结晶性,并具有四面体结构.纳米晶中Cu/Cd/Sn/S的化学计量比约为2.07:0.75:1.26:3.92,Cu、Cd、Sn和S四种元素的化学态分别为+1、+2、+4和−2价,与 Cu_2CdSnS_4 分子式中的化学态一致.通过外推法估算 Cu_2CdSnS_4 纳米晶的禁带宽度为~1.3 eV.
关　键　词:胶体纳米晶;Cu_2CdSnS_4;光伏材料;太阳能电池
中图分类号:TN304+.2　　**文献标识码**:A

Introduction

In the past decades, colloidal nanocrystals have been applied in nanocrystal-based lasers[1], LEDs[2] and photodetectors[3]. Comparing with the traditional thin-films by using electro-deposition, co-sputtering, or co-evaporation[4-5], colloidal nanocrystals-based thin films are flexible by means of dip coating or drop casting on the desired substrate[6-8]. In addition, the roll-to-roll processing based on colloidal nanocrystals is an important method for cost-effective and flexible solar cells. Therefore, the colloidal nanocrystal inks, including $CuInSe_2$, $Cu(In,Ga)Se_2$, $CuInS_2$, and Cu_2ZnSnS_4[6-8] are the most potential photovoltaic materials in the roll-to-roll processing for the cost-effective solar cells.

Cu_2CdSnS_4 has a tetrahedral coordinated structure and a large absorption coefficient over 10^4 cm^{-1}[9].

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The band gap of Cu_2CdSnS_4 is ~1.37 eV, near the optimum direct band gap of 1.5 eV for efficient light absorption[10]. This makes Cu_2CdSnS_4 one of the most promising materials for photoelectric application. Moreover, thermoelectric properties of Cu_2CdSnS_4 and $Cu_2CdSnSe_4$ have been explored and exploited[11]. Due to their supply-abundant elements and excellent photoelectric properties, Cu_2ZnSnS_4 and Cu (In, Ga) (Se, $S)_2$ (CIGS) nanocrystals have been widely prepared as alternative photovoltaic materials[6-8]. However, Cu_2CdSnS_4 nanocrystals and even thin-films are, to our knowledge, rarely reported[9-10] though they are expected to be potential for the advanced photovoltaic and thermoelectric applications[9-11]. Herein, we describe the preparation of colloidal Cu_2CdSnS_4 nanocrystals by using a facile solution chemistry method. All measurements including TEM, SEM, EDS, XRD, XPS and UV-vis-NIR indicated that the Cu_2CdSnS_4 nanocrystals are good crystalline with a band gap of ~1.3 eV.

1 Experiment

All chemicals were used as received without any further purification. The reactions were performed under argon. In a typical synthesis of Cu_2CdSnS_4 nanocrystals, 0.5 mmol (0.0495 g) of copper (I) chloride (CuCl, ACROS, 99% extra pure purified), 0.25 mmol (0.065 g) of cadmium acetate hydrate ($(CH_3CO_2)_2Cd \cdot xH_2O$, Aldrich, ≥99.99%), 0.25 mmol (30 μl) of tin (IV) chloride ($SnCl_4$, ACROS, 99%), 1 mmol (0.032 g) sulfur (S, ACROS, 99.999%) and 12 ml of oleylamine ($C_{18}H_{37}N$, ACROS, 80~90%) were added into a three neck flask connected to a Schlenk line. This precursor mixture was heated to 130℃ and degassed under argon flow for 30 minutes, and formed a dark-blue solution. Then, the reaction solution turned into black when heated and annealed at 300℃ for 5 minutes. Finally, the production was taken out and injected into 40 ml of ethanol, and centrifuged at 8000 rmp/min for 5 minutes. The precipitates were collected and re-dispersed in chloroform, then 20 ml of acetone was added into the solution. The precipitates were re-collected and then re-dispersed in chloroform to form a stable solution after centrifuged at 12000 rmp/min for 3 minutes.

TEM images were taken on JEM-2100F equipped with Gatan 832 CCD at an accelerating voltage of 200 kV. TEM specimens were prepared by dropping Cu_2CdSnS_4 nanocrystals dispersed in chloroform onto carbon-coated copper TEM grids. SEM image was acquired using FEI Sirion 200 with an energy dispersive X-ray analysis. XRD pattern was performed on Bruker D8 Discover X-ray diffractometer. XPS data were obtained using PHI 5000 VersaProbe X-ray photoelectron spectrometer for surface analysis. UV-vis-NIR absorbance spectrum was collected on a Lambda 900 (PerkinElmer) with a scanning velocity of 240 nm/min.

2 Results and discussion

Figure 1(a) and Figure 1(b) are TEM images and size distribution of typical Cu_2CdSnS_4 nanocrystals with an average size of 19.8 nm and a standard deviation of 1.8 nm. It is shown that the nanocrystals have uniform size distribution and slightly irregular shape. High resolution TEM (HRTEM, Figure 1 (c)) shows clear crystalline planes of a single Cu_2CdSnS_4 nanocrystal. A polycrystalline-circle that results from the diffraction of different crystalline planes is shown in selected-area electron diffraction (Figure 1(d)). The average diameter of Cu_2CdSnS_4 nanocrystals is ~20 nm as shown in SEM image (Figure 2(a)), that is consistent with the result of TEM. EDS implies the stoichiometric ratio of Cu/Cd/Sn/S in nanocrystals is 2.07:0.75:1.26:3.92, which approaches 2:1:1:4 in Cu_2CdSnS_4 chemical formulation as depicted in Figure 2(b). The peak of silicon comes from the substrate.

The structure and chemical states of Cu_2CdSnS_4 nanocrystals are investigated by XRD and XPS. XRD pattern (Figure 3) indicates that the nanocrystals have a tetrahedral diffraction pattern (JCPDS 29-0506). In Cu_2CdSnS_4 each cation bonds to four sulfur anions, and each sulfur anion bonds to four cations to form a tetrahedral structure[11]. There are nine diffraction peaks in XRD pattern corresponding to (110), (112), (200), (202), (114), (204), (312), (224) and (316) planes at 2θ = 22.73°, 28.00°, 32.25°, 36.22°, 40.61°, 46.76°, 54.84°, 57.91° and 75.22°, respectively, in Figure 3. Meanwhile, the size of nanocrystals calculated from the full width at

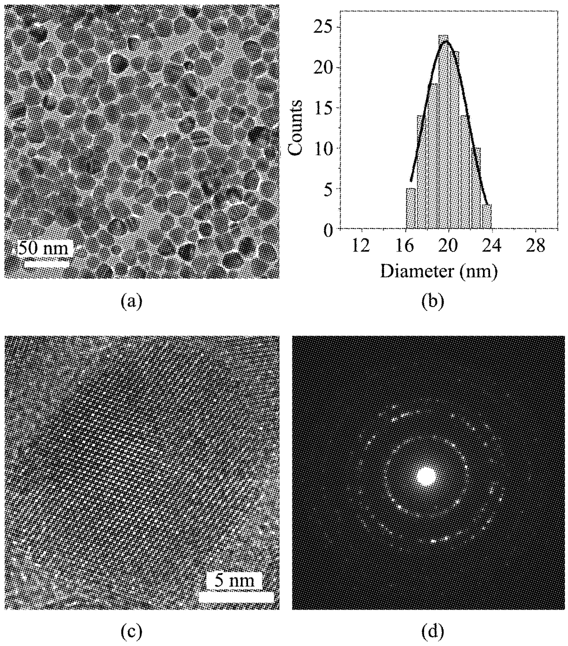

Fig. 1 (a) Overview TEM image (b) the diameter distribution of nanocrystals derived from TEM image (c) HRTEM image of one Cu_2CdSnS_4 nanocrystal (d) selected-area electron diffraction (SAED) pattern

图 1 (a)总体 TEM 图 (b)根据 TEM 图得到的纳米晶粒径分布图 (c)一个 Cu_2CdSnS_4 纳米晶的 HRTEM 图 (d)选区电子衍射(SAED)图

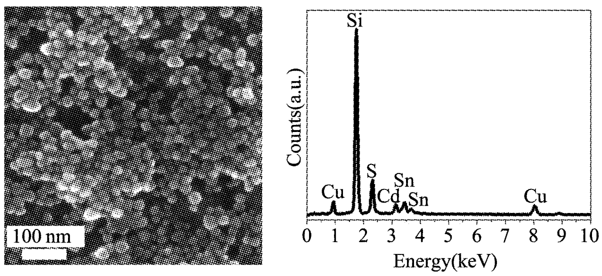

Fig. 2 SEM (a) and EDS (b) of Cu_2CdSnS_4 nanocrystals. All samples were nanocrystal films and prepared on silicon substrates. The peak around 1.8eV in Fig. 2(b) is from silicon substrate

图 2 Cu_2CdSnS_4 纳米晶的 SEM(a)和 EDS(b)图. 所有的薄膜样品为纳米晶沉积在硅片衬底上形成的. 图 2(b)中硅峰来自衬底

half maximum (FWHM) of the (112) plane according to Scherrer formulation is 19.3 nm, consisting with the statistic result from TEM images.

Figure 4 presents the XPS results of four elements. The sulfur 2p3/2 and 2p1/2 peaks in the spectrum are located at 161.5 eV and 162.7 eV (Figure 4 (a)), which are consistent with the 160 ~ 164 eV range for S in sulfides. The copper(I) XPS spectrum

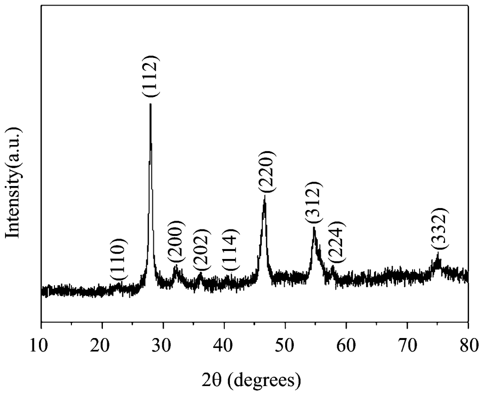

Fig. 3 XRD pattern; XRD samples were nanocrystal films and prepared on monocrystalline silicon substrates

图 3 X 射线衍射谱;XRD 薄膜样品利用纳米晶在单晶硅衬底沉积上制备而成

(Figure 4(b)) shows two narrow and symmetric peaks at 932.1 eV and 952.0 eV, indicative of Cu(I) with a peak splitting of 19.9 eV in agreement with the standard splitting of 19.8 eV. The cadmium 2p peaks located at 404.9 eV and 411.7 eV show a peak separation of 6.8 eV, in agreement with the standard splitting of 6.76 eV, suggesting Cd(II) (Figure 4(c)). The tin 3d5/2 and 3d3/2 peaks located at 486.2 eV and 494.6 eV, with a splitting of 8.4 eV indicates Sn(IV) (Figure 4(d). The XPS of cadmium and tin with asymmetric peaks are resulted from the cadmium-deficient and tin-rich in composition. EDS implies the stoichiometric ratio of Cu/Cd/Sn/S in nanocrystals is about 2.07:0.75:1.26:3.92, which approaches 2:1:1:4 in Cu_2CdSnS_4 chemical formulation. Therefore, the main chemical states of four elements are +1, +2, +4 and −2, that correspond with the states in Cu_2CdSnS_4 chemical formulation (Figure 4).

The optical properties of Cu_2CdSnS_4 nanocrystals are characterized by UV-vis-NIR absorbance spectroscopy shown in Figure 5. It is estimated that the band gap of Cu_2CdSnS_4 nanocrystals is ~1.3 eV by plotting the square of the absorption coefficient α multiplied by the photon energy $h\nu$, versus $h\nu$ in the inset. The band gap of ~1.3 eV nearly corresponds with the value reported in the literature (1.37 eV)[10]. It is shown that the nanocrystals are composed of pure Cu_2CdSnS_4 phase according to absorbance spectroscopy because the band gaps of CdS and Cu_2SnS_3 are 2.5 and 0.93 eV, respectively[12].

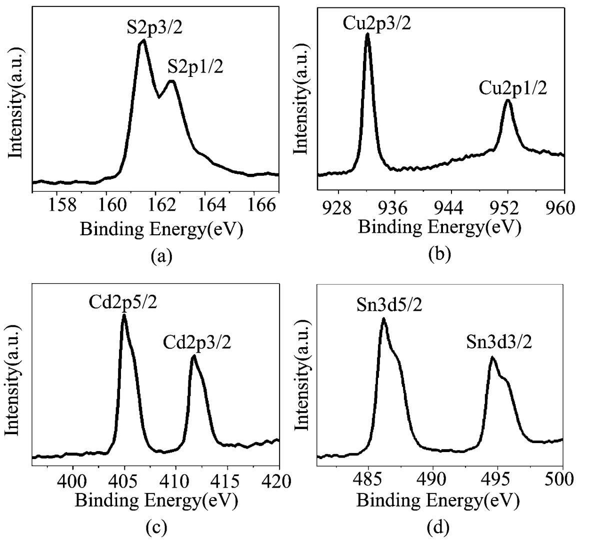

Fig. 4 XPS of Cu_2CdSnS_4 nanocrystals (a) S 2p3/2 and 2p1/2 peaks (b) Cu(I) 2p3/2 and 2p1/2 peaks (c) Cd 2p5/2 and 2p3/2 peaks (d) Sn 3d5/2 and 3d3/2 peaks
图4 Cu_2CdSnS_4纳米晶的 XPS 图 (a)所有元素的 XPS 谱 (a)硫的2p3/2 和 2p1/2 峰 (b)铜(I)的2p3/2 和 2p1/2 峰 (c)镉的2p5/2 和 2p3/2 (d)锡的3d5/2 和 3d3/2 峰

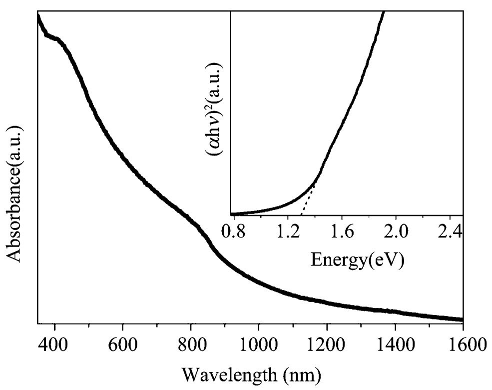

Fig. 5 UV-vis-NIR absorbance spectroscopy of Cu_2CdSnS_4 nanocrystals. The inset is plotted by $(\alpha h\nu)^2$ (the square of the absorption coefficient α multiplied by the photon energy hν) versus hν
图5 Cu_2CdSnS_4纳米晶的 UV-vis-NIR 吸收光谱. 插图以 $(\alpha h\nu)^2$(吸收系数 α 和光子能量 hν 乘积的平方)和光子能量 hν 为坐标作出

3 Conclusions

We have demonstrated the preparation of colloidal Cu_2CdSnS_4 nanocrystals by use of several ordinary precursors. TEM, SEM, EDS, XRD, XPS and UV-vis-NIR measurements indicate that the Cu_2CdSnS_4 nanocrystals have been successfully synthesized with uniform size-distribution, good crystalline quality and tetrahedral coordinated structure. The stoichiometric ratio in nanocrystals of Cu/Cd/Sn/S is about 2.07:0.75:1.26:3.92, and the chemical states of four elements Cu, Cd, Sn and S are of +1, +2, +4 and −2, which correspond with the chemical states of four elements in Cu_2CdSnS_4 molecular formula. It is estimated that the band gap of Cu_2CdSnS_4 nanocrystals is ~1.3 eV according to UV-vis-NIR absorbance spectra.

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