

## Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals for Use in Low-Cost Photovoltaics

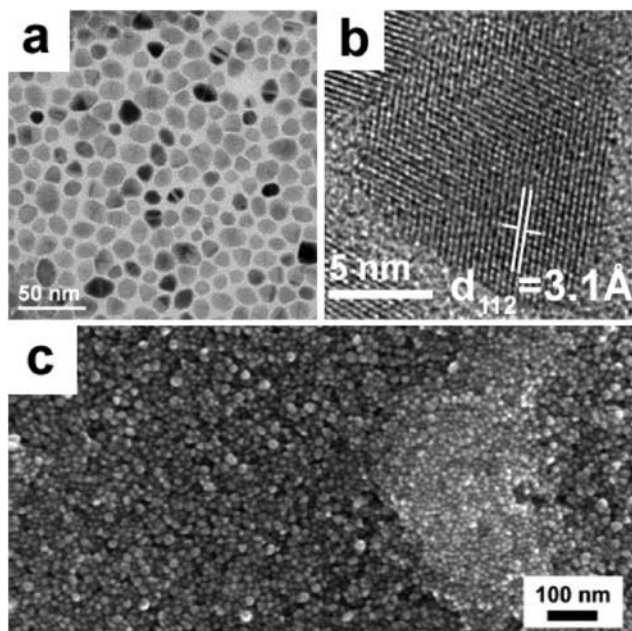
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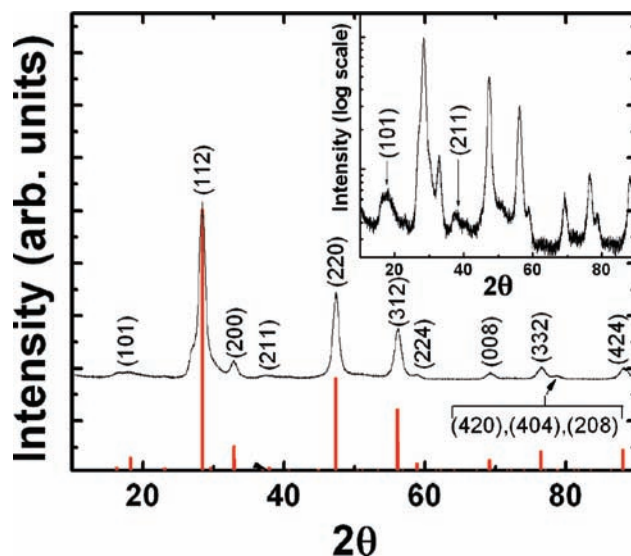
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New photovoltaic (PV) materials and manufacturing approaches are needed for meeting the demand for lower-cost solar cells.<sup>1,2</sup>  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) is one promising new material.<sup>2,3</sup> Its crystal structure and optical properties (band-gap energy of  $\sim 1.5$  eV; absorption coefficient of  $\sim 10^4$   $\text{cm}^{-1}$ ) are similar to those of  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS), one of the most successful thin-film PV materials with demonstrated power conversion efficiencies (PCEs) of nearly 20% and commercial use.<sup>3,4</sup> However, unlike CIGS, which requires relatively rare In and Ga, CZTS is composed of abundant elements.<sup>2,3</sup> CZTS PV devices have been made with PCEs of up to 6.7%.<sup>3</sup>

The highest-efficiency PV devices of CIGS and CZTS are obtained by vapor deposition, which imposes a substantial cost on the technology.<sup>1</sup> Alternative processing strategies with reasonable success have included electrochemical and chemical-solution deposition.<sup>5–7</sup> These techniques, however, still require relatively demanding processing conditions (e.g., high-temperature reactive sintering or the use of harsh chemicals such as hydrazine) to reach reasonable efficiencies.<sup>5–7</sup> A different approach is to prefabricate the PV material as a nanocrystal dispersion—a solar paint—that can be printed, sprayed, or dip-coated, ideally without the need for



**Figure 1.** (a, b) TEM and (c) SEM images of CZTS nanocrystals. In (b), the nanocrystal is imaged down the  $[\bar{1}10]$  crystallographic zone axis. TEM images and EDS data were obtained on carbon-coated Ni grids (200 mesh, Electron Microscopy Sciences) using a JEOL 2010F transmission electron microscope equipped with an Oxford INCA EDS detector. SEM images were obtained using gold-coated soda lime glass substrates with a Zeiss Supra 40 VP scanning electron microscope operated at 1–10 keV.



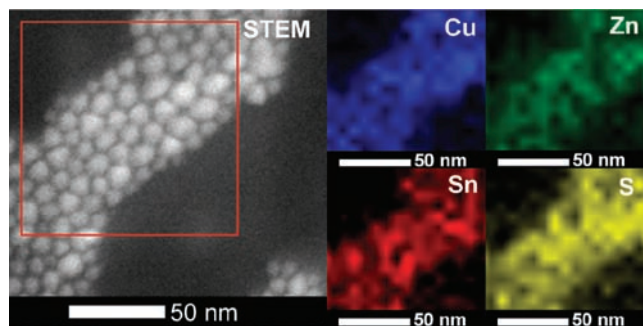
**Figure 2.** XRD pattern of CZTS nanocrystals [Cu  $K\alpha$  radiation ( $\lambda = 1.54$  Å)]. The red reference pattern was simulated with CaRIne Crystallography 3.1 software using space group *I4* and lattice parameters  $a = b = 5.427$  Å and  $c = 10.848$  Å for kesterite CZTS (JCPDS no. 26-0575). XRD data were acquired on a Bruker-Nonius D8 Advance powder diffractometer with samples on quartz substrates, scanning at 6 deg/min in 0.02° increments for  $\sim 12$  h.

intensive postdeposition processing.<sup>8–17</sup> Solar paints could enable continuous roll-to-roll processing under mild conditions on nearly any type of surface.

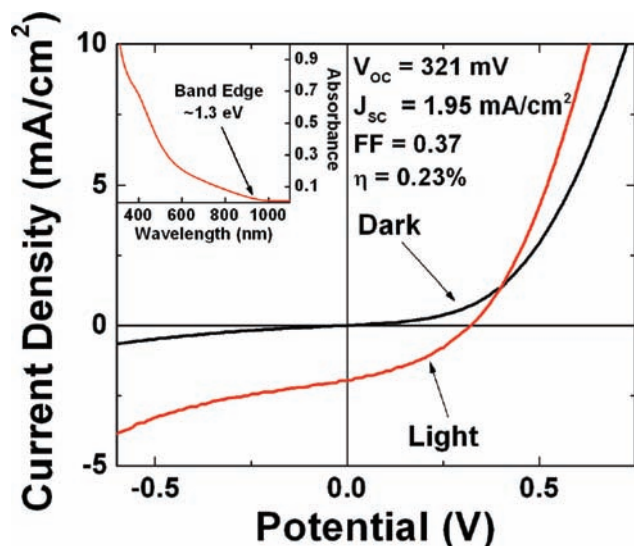
Recently, CIGS nanocrystals have been synthesized with controlled stoichiometry and used in the fabrication of PV devices with reasonable efficiencies.<sup>10,11,14</sup> Here we demonstrate the synthesis of CZTS nanocrystals and their implementation in functioning PV devices.

The CZTS nanocrystals were made by high-temperature arrested precipitation in the coordinating solvent, oleylamine (OLA). Copper(II) acetylacetonate [ $\text{Cu}(\text{acac})_2$ ], zinc acetate [ $\text{Zn}(\text{O}_2\text{CCH}_3)_2$ ], tin(II) chloride dihydrate [ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ], and elemental sulfur (S) were combined in OLA and heated to 280 °C for 1 h under an inert atmosphere.<sup>18</sup> Figure 1 shows transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of a typical CZTS nanocrystal sample. The particles are crystalline and have an average diameter of  $10.6 \pm 2.9$  nm and a slightly irregular, faceted shape.

The average composition of the nanocrystals determined by energy-dispersive X-ray spectroscopy (EDS) analysis of 25 nanocrystals was  $\text{Cu}_{2.08}\text{Zn}_{1.01}\text{Sn}_{1.20}\text{S}_{3.70}$ . The nanocrystals are slightly tin-rich and sulfur-deficient. Scanning transmission electron microscopy (STEM)–EDS elemental mapping of a field of nanocrystals (Figure 3) confirmed that Cu, Zn, Sn, and S are evenly distributed among



**Figure 3.** STEM–EDS elemental map of CZTS nanocrystals. The images were obtained on a Tecnai G2 F20 X-Twin microscope at an accelerating voltage of 200 kV.



**Figure 4.** Current–voltage characteristics of a CZTS nanocrystal PV device. Inset: room-temperature UV–vis–NIR absorbance spectrum of CZTS nanocrystals dispersed in toluene. PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer.  $I$ – $V$  data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

the nanocrystals and that there is no noticeable compositional distribution among the nanocrystals. The band-gap energy determined from the absorbance spectrum of a nanocrystal dispersion (Figure 4, inset) is 1.3 eV, which is close to the bulk literature value of  $\sim 1.5$  eV for CZTS.<sup>19</sup>

X-ray diffraction (XRD) (Figure 2) showed that the nanocrystals are composed of CZTS with the kesterite structure.<sup>20,21</sup> Kesterite has a tetragonal unit cell, with sulfur atoms located in a face-centered-cubic sublattice. The Cu, Zn, and Sn atoms occupy half the tetrahedral interstitial sites within the S sublattice, with compositional order.<sup>20</sup> Similar to chalcopyrite CIGS, kesterite CZTS exhibits diffraction peaks in addition to those observed from the compositionally disordered sphalerite compound, such as the (101) and (211) peaks.<sup>20,22</sup>

PV devices were fabricated with the CZTS nanocrystals. Like CIGS, CZTS films are typically p-type,<sup>3</sup> and test devices were fabricated with a layered structure composed of Au/CZTS/CdS/ZnO/indium tin oxide (ITO).<sup>23</sup> The CZTS layer was deposited by spray coating of a toluene dispersion. The nanocrystal layer was not annealed. Figure 4 shows the PV response of a typical device

having an open-circuit voltage ( $V_{oc}$ ) of 321 mV, a short-circuit current density ( $J_{sc}$ ) of 1.95 mA/cm<sup>2</sup>, a fill factor (FF) of 0.37, and a PCE ( $\eta$ ) of 0.23% under AM 1.5 conditions.

In summary, a synthetic method for producing CZTS nanocrystals has been developed. PV devices fabricated with these CZTS nanocrystals exhibited PCEs of up to 0.23%. While the efficiency of these devices is low, the absorber layers were not processed after deposition with any high-temperature or chemical means. Further optimization of the synthesis and device fabrication should lead to increased PV efficiency.

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