Solar Energy Materials and Solar Cells xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Dual use of Cu_2ZnSnS_4 in solar cells and energy storage devices

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ARTICLE INFO

Keywords:
CZTS
Solar cells
Energy storage
Dual use

ABSTRACT

Both energy harvesting and storage are similarly constrained by materials availability and economics. Herein, we explore the dual use of earth-abundant and low cost Cu_2ZnSnS_4 (CZTS) inks not only for solar cells but also energy storage devices. In this report, we only focus on less addressed but important novel issues. One is the effect of CZTS layer thickness on solar cell performance. The other is the properties of CZTS as a supercapacitor electrode. For solar cells, a study of the effect of CZTS thickness on device performance of 55 solar cells revealed that the highest efficiencies are achieved at a CZTS thickness of approximately 0.37 μm. For energy storage, we achieved a highest reported areal (and specific) capacitance of 2.67 F/cm^2 (1709 F/g) for CZTS. The dual use of CZTS for both energy harvesting and storage opens opportunities such as cheaper devices arising from economics of scale accompanying increased CZTS inks production.

1. Introduction

Energy harvesting and energy storage are the foundations for the application of renewable energies. Cu_2ZnSnS_4 (CZTS) is a well known promising solar cell material that has attracted great attention in recent years. However, the energy storage ability of this material is seldom reported. In this paper, we will report the dual use of this material for solar cells (energy harvesting) and supercapacitors (energy storage).

One reason why solar cells have attracted much interest as an alternative energy source to fossil fuels is because of its potential to become a significant contributor to global energy supply [1]. By covering 0.16% of the Earth's land surface with 10% efficient solar cells, sufficient energy can be harvested to meet the world's energy needs [2]. However, terawatt-scale deployment of solar cells is constrained by materials availability and economics [3]. To this end, solution-processed solar cell materials including CZTS, offering the advantages of earth-abundant composition and low cost, are positioned. Numerous approaches have been attempted to fabricate solution-processed CZTS solar cells [4–11].

Recently, we proposed and succeeded in the synthesis of CZTS nanocrystal (NC) inks in using formamide and the fabrication of CZTS thin films from these inks [12,13]. This approach offers the advantages of increased safety (compared to hydrazine) and lower carbon content in the CZTS NCs (since surfactants with long hydrocarbon chains are avoided). However, the conditions necessary to prepare CZTS solar cells from these inks are not clear and these will be investigated and reported herein.

In addition to energy harvesting, energy storage is necessary in the application of renewable energies. For example, solar is an intermittent energy source and it supplies energy only during the day and the energy supplied varies with changes in weather conditions (e.g. cloud cover). As such, without energy storage, conventional baseload power plants (such as those that utilize fossil fuels) must be kept operating to maintain grid stability [14]. This limits the extent to which solar energy contributes to our energy supply unless grid-scale energy storage is developed. At such large-scales however, materials availability and economics become important considerations. Since both energy harvesting and storage are faced with similar constrains, it is of interest to investigate the dual use of earth-abundant and low cost CZTS NC inks in energy harvesting and storage. Such dual applications of CZTS will be exciting because it opens opportunities such as cheaper devices arising from economics of scale accompanying increased CZTS inks production.

In this work, the dual application of CZTS NC inks in energy harvesting and storage (solar cells and energy storage devices respectively) is explored. The CZTS NC inks are discovered to be suitable for both. For solar cells, we found that the highest efficiencies are achieved at an intermediate thickness of approximately 0.37 μm. For energy storage supercapacitors, we first demonstrate here that CZTS can have a high areal (and specific) capacitance of 2.67 F/cm^2 (1709 F/g).

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http://dx.doi.org/10.1016/j.solmat.2017.07.003
Received 14 February 2017; Received in revised form 29 June 2017; Accepted 9 July 2017

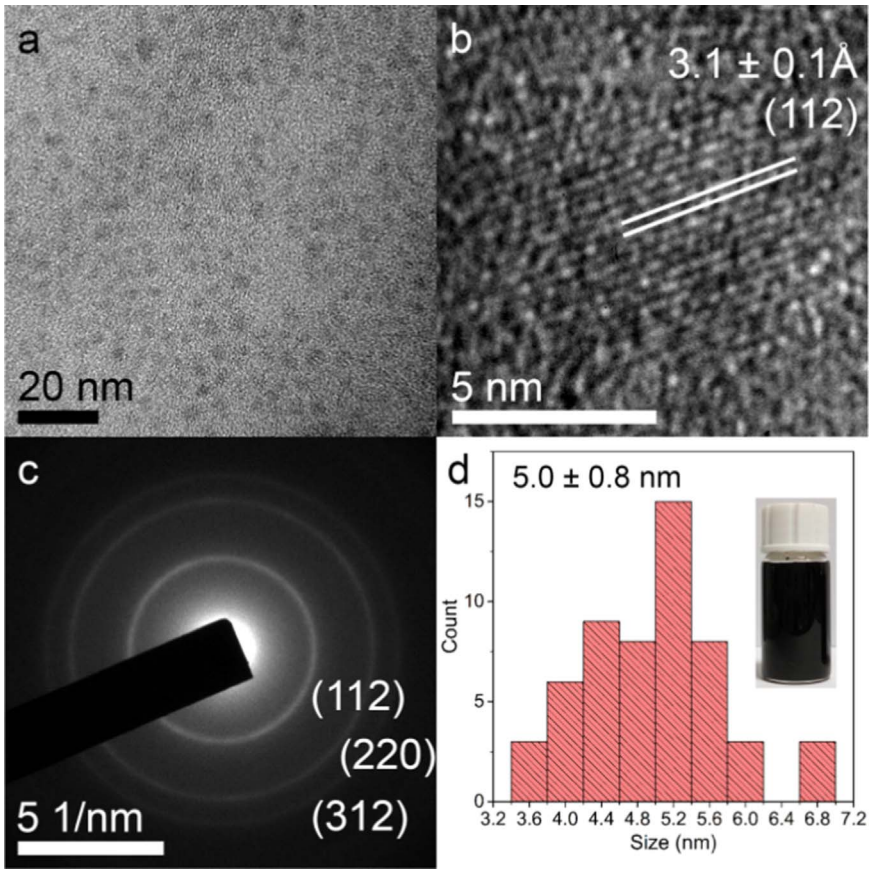

Fig. 1. (a) TEM, (b) HRTEM, (c) SAED, and (d) size histogram of CZTS NCs. Number of NCs measured for (d): 55.

2. Experimental

2.1. Synthesis of NC inks

CZTS NC inks were prepared by dissolving thioacetamide (13.2 mmol, 98%, Sigma-Aldrich) in formamide (10 mL, 99.0 + %, Sigma-Aldrich) in a three-necked flask. After degassing, the solution was heated to 170 °C, following which $Cu(Ac)_2{\cdot}H_2O$ (0.6 mmol, 99.0%, Fluka), $ZnCl_2$ (0.39 mmol, 98 + %, Sigma-Aldrich), and $SnCl_2$ (0.4125 mmol, 98%, Sigma-Aldrich) dissolved in formamide (2.5 mL) were injected and reacted for 2 min. As-synthesized CZTS NCs were washed twice by repeated precipitation, centrifugation and redispersion. Details can be found in our previous report [12].

2.2. Solar cell fabrication

To fabricate CZTS solar cells, CZTS NCs were suspended in ethanol using an ultrasonic bath, spin-coated onto cleaned Mo foils (0.025 mm thick, 99.95%, Alfa Aesar), compacted under a pressure of around 60 MPa, and sulfurized at 600 °C for 30 min. Details can be found in our previous reports [12,13]. Next, 50–70 nm of CdS was grown on the sulfurized CZTS thin-films via chemical bath deposition·H_2O (121.69 mL), $CdCl_2$ (2.23 mL, 0.1 M, 99 + %, Fluka), and NH_4OH (18.62 mL, 28%, Alfa Aesar) were added to a jacketed beaker maintained at 65 °C and kept under magnetic stirring. The samples were then immersed before adding thiourea (7.47 mL, 1.5 M, 99 + %, Sigma-Aldrich). After 17 min, the samples were rinsed using deionised water and dried using N_2 gas. Next, 100 nm of intrinsic ZnO followed by 200 nm of ITO was deposited via RF magnetron sputtering at a sputtering power of 50 W and pressure of 3.6 mTorr. The sheet resistance of ITO is approximately 30 Ω/sq. Finally, the front contact was prepared by dabbing silver paint on the ITO layer.

2.3. Supercapacitor fabrication

The working electrode was prepared by dispersing 65 wt% of CZTS NCs, 25 wt% of carbon black (Graphene Supermarket), and 10 wt% of polyvinylidene difluoride (PVDF) in dimethylformamide (DMF) under magnetic stirring followed by ultrasonication. Ni foam was then immersed in the slurry and mixed under magnetic stirring. After 15 min, the Ni foam was taken out, dapped to remove excess slurry, and dried in air at 50 °C for 12 h.

2.4. Characterization

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) were performed by using a JEOL JEM-2010F TEM at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed by using a Zeiss Supra™ 40 FESEM equipped with an In-lens SE detector and an Oxford X-Max Silicon Drift Detector (50 mm^2). SEM and EDX measurements were performed at an accelerating voltage of 5 and 15 kV respectively. Current density-voltage (J-V) measurements were performed at AM1.5 by using a Newport Oriel Class A Solar Simulator, calibrated using a standard Si reference cell. Electrochemical measurements were performed by using a PARSTAT MC Multi-Channel Electrochemical workstation. The prepared electrode was used as the working electrode, a platinum plate was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode. 1 M KOH was used as the electrolyte.

3. Results and discussion

CZTS ink has been obtained following the process described in Section 2.1, and the electron microscopy and diffraction