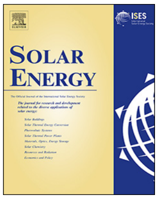
Solar Energy 169 (2018) 505–511

Contents lists available at ScienceDirect

Solar Energy

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



N-doped carbon@Cu nanocomposites as counter electrode catalysts in quantum dot-sensitized solar cells

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ARTICLE INFO

Keywords:
Quantum dot solar cells
MOF-derived carbons
N-C@Cu composites

ABSTRACT

To improve the catalytic activity of carbons in counter electrodes (CEs), Cu nanoparticles (NPs) were introduced into mesoporous N-doped carbons (N-C) derived from metal-organic frameworks (MOFs) to prepare the composites of N-C and Cu NPs (N-C@Cu) *via* impregnation and subsequent reduction method in this work. The obtained N-C@Cu composites with 2–4 nm Cu NPs uniformly distributing in N-C were deposited onto fluorine doped tin oxide (FTO) substrates by screen-printing to fabricate CEs in quantum dot solar cells (QDSCs). The N-C@Cu CEs exhibit higher electrocatalytic activity than both pristine N-C/FTO and commonly used Cu_2S/FTO CEs, which could be ascribed to the synergistic effect between Cu_xS NPs with the excellent electrocatalytic ability and MOF derived N-C with high graphitization, large hydrophilic surface as well as the abundant dopant active sites on the reduction of polysulfide. The superior performance of N-C@Cu composites results in an improved fill factor and a high short circuit current density. Based on optimized N-C@Cu CEs and Zn-Cu-In-Se quantum dot sensitizers, the QDSCs obtained present a promising power conversion efficiency of 9.23%, significantly superior to those of pristine N-C/FTO (7.20%) and Cu_2S/FTO (8.89%) CEs based QDSCs.

1. Introduction

With the increasing demand of renewable energy sources, converting solar energy to electricity by virtue of photovoltaic technology is one of the effective strategies to relieve energy crisis and environmental pollution (Graetzel et al., 2012; Wu et al., 2015a). Quantum dot solar cells (QDSCs), being regarded as one of the most promising third generation solar cells, exhibit outstanding properties, such as tunable band gap of quantum dot (QD) materials, solution processability, low-cost facile fabrication and multiple exciton generation possibility (Nozik et al., 2010; Kamat, 2013; Jiang et al., 2014; Carey et al., 2015; Blas-Ferrando et al., 2015; Du et al., 2016a; Yang et al., 2016). Typically, liquid-junction QDSCs consist of QD sensitized photoanode (Santra and Kamat, 2013; Xin et al., 2015; Wang et al., 2018), polysulfide electrolyte (Chakrapani et al., 2011; Feng et al., 2016) and counter electrode (CE) (An et al., 2017; Wu et al., 2015b; Li et al., 2014a; Kumar et al., 2016). Among them, a CE serves as a pivotal part to complete electrical circuit by collecting photoinduced electrons from external circuit and catalyzing the reduction of polysulfide (S_n^{2-}) to sulfide (S^{2-}) at the interface between CEs and electrolyte (Xin et al., 2011; Meng et al., 2015a; Peng et al., 2015; Xia et al., 2017). With the initiative to improve the power conversion efficiency (PCE) of QDSCs, it is an urgent task to optimize the CE catalyst materials (Wang and Tian, 2016; Hwang and Yong, 2015).

Carbonaceous materials would be the promising candidates for the fabrication of CEs on account of the competitive prices, good conductivity and corrosion inertness for the reduction of polysulfide electrolyte (Ye et al., 2015; Wu et al., 2015b; Chen and Shao, 2016; Meng et al., 2017). Pure carbon materials, such as hollow core/mesoporous shell carbon, mesocellular carbon foam, carbon nanofiber, graphene and active carbon, have been applied as electrocatalysts in QDSCs (Fan et al., 2010; Seol et al., 2011; Sudhagar et al., 2011; Fang et al., 2011; Zhang et al., 2010). Unfortunately, limited by the inherent features of relatively low specific surface area and/or insufficient active sites, pure carbon based CEs usually show inferior electrocatalytic activity (Duan et al., 2015). By view of the synergistic effects of different catalyst components, the development of carbon composite catalysts has been proven to be an efficient approach to improve the catalytic ability of CEs (Li et al., 2014a,b; Radich et al., 2011; Guo et al., 2016; Liu et al., 2017). For example, electrospun carbon nanofiber heteroarchitectures/CuS (EC/CuS) composite was successfully prepared by Li et al. and utilized as CE catalysts, producing an efficiency of 3.86% for QDSCs (Li et al., 2014b). Kamat et al. employed reduced graphene oxide (RGO)/Cu_2S composites to fabricate CEs, producing an unsurpassed PCE of

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https://doi.org/10.1016/j.solener.2018.04.048
Received 6 March 2018; Received in revised form 10 April 2018; Accepted 23 April 2018

4.4% at that time with CdSe QDs as sensitizers (Radich et al., 2011). Also, the composites of carbons and copper sulfide prepared through solid grinding method were attempted to be used as CEs. With CdSeTe QDs as sensitizers, the QDSCs achieved PCE up to 8.40%, higher than that of pure carbon based devices and comparable to that of the commonly used Cu_xS/brass CEs (Guo et al., 2016). Alternatively, the heteroatom doping has been proven to be another efficient way to improve the catalytic activity of carbons (Dong et al., 2012; Meng et al., 2015b; Jiao et al., 2017; Meng et al., 2018; Li et al., 2018). Recently, mesoporous N-doped and Co, N-bidoped carbon materials were employed as CE catalysts by our group (Jiao et al., 2017; Li et al., 2018). Due to their homogeneously dispersed active dopants, good conductivity as well as large hydrophilic surface area, the heteroatom doped carbons exhibit greatly enhanced catalytic activity for polysulfide reduction compared to pure mesoporous carbons (Dong et al., 2012; Jiao et al., 2017; Li et al., 2018). In light of the inherent characteristics of heteroatom doped carbons and the benign catalytic performance of Cu_xS, the introduction of Cu_xS nanoparticles into heteroatom doped carbons might be conducive to the further enhancement of photovoltaic performance of QDSCs.

In this regard, the composites of N-doped carbons (N-C) and Cu nanoparticles (NPs), N-C@Cu, were prepared by impregnation and subsequent reduction method and attempted to fabricate CEs in QDSCs in this work. Metal-organic frameworks (MOFs), especially N-rich zeolitic imidazolate frameworks (ZIFs), recently have been considered to be versatile precursors/sacrificial templates for the preparation of various homogeneous hetero-doping carbons with predetermined functionalities (Zhou et al., 2015; Jiang et al., 2011; Chaikittisilp et al., 2013; Chen et al., 2015; Salunkhe et al., 2016; Gu et al., 2017). Considering that the heteroatom doped carbons derived from ZIFs possess desirable characters for the catalysts in QDSCs such as high hydrophilic surface area and uniform distributed catalytic active sites, ZIF-8 was utilized, herein, as precursors to prepare mesoporous N-C *via* carbonation method (Scheme 1) (Salunkhe et al., 2016; Chen et al., 2016). The N-C obtained were used as supports for the immobilization of Cu NPs to synthesize N-C@Cu composites that were then screen printed onto fluorine doped tin oxide (FTO) substrates to fabricate CEs. Benefiting from the synergetic effects between N-C and Cu_xS NPs on the polysulfide reduction, N-C@Cu composite materials present more excellent catalytic activity for the reduction of polysulfide species in electrolyte compared with N-C derived from ZIF-8. With N-C@Cu/FTO CEs associating with Zn-Cu-In-Se (ZCISe) QDs as sensitizers, a desirable average PCE of 9.07% (open-circuit voltage V_{oc} = 0.628 V, short-circuit current density J_{sc} = 26.48 mA·cm^{-2} and fill factor FF = 0.545) has been observed on the cells constructed, which is superior to those of the commonly used Cu_2S/FTO (8.88%) and pristine N-C/FTO (7.11%) based devices.

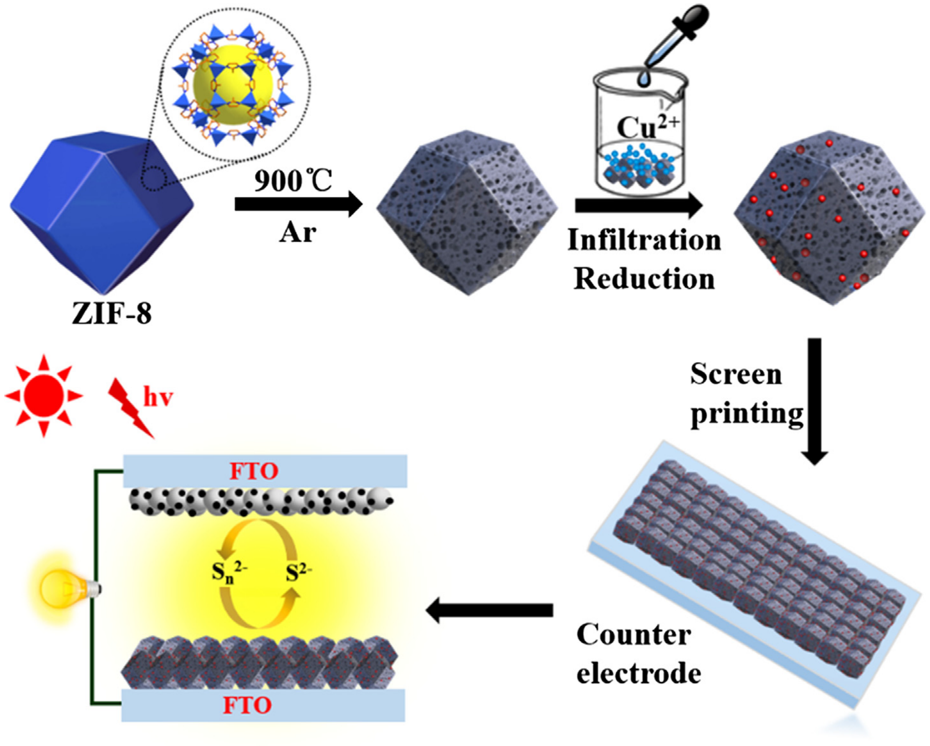
2. Experimental section

2.1. Materials

Zinc acetate ($Zn(OAc)_2·2H_2O$, 99.99%), copper nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, 99%) and diphenylphosphine (DPP, 98%) were obtained from J&K. Selenium powder (200 mesh, 99.99%), oleylamine (OAm, 80–90%), 1-octadecene (ODE, 90%) and poly(vinylpyrrolidone) (PVP, M_w = 8000) were purchased from Aldrich. Copper iodide (CuI, 99.998%), indium acetate ($In(OAc)_3$, 99.99%) and 3-mercaptopropionic acid (MPA, 97%) were received from Alfa Aesar. 2-methylimidazole (99%) and hydrazinium hydrate (80%) were bought from ACROS Organics and Aladdin, respectively. Zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$, 99%), methanol (99.5%) and sulfuric acid (H_2SO_4, 98%) were obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd. Copper sulfate anhydrate ($CuSO_4$, 98.5%) was purchased from Shanghai Titan Scientific Co., Ltd.

2.2. Synthesis of ZCISe QDs

Oil-soluble ZCISe QDs were synthesized by hot-injection method following the procedures reported (Du et al., 2016a; Zhang et al., 2017). First, Zn precursor solution was prepared by mixing Zn $(OAc)_2·2H_2O$ (110 mg, 0.5 mM), OAm (0.5 mL) and ODE (4.5 mL) at



Scheme 1. Scheme illustration of the synthesis of N-C@Cu nanocomposites for electrode catalyst in QDSCs.