Materials Letters 166 (2016) 251–254

Contents lists available at ScienceDirect

Materials Letters

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

Excellent photoelectric properties and charge dynamics of two types of bulk heterojunction solar cells

S. Wang, X.Y. Liu*, Y.Z. Gu*

Institute of Microsystem, School of Physics and Electronics, Kaifeng 475004, China

A R T I C L E I N F O

Article history:
Received 23 October 2015
Received in revised form
16 December 2015
Accepted 21 December 2015
Available online 22 December 2015

Keywords:
Solar energy materials
Surface photovoltage
Photoelectric property
Energy storage and conversion

A B S T R A C T

Photochemical charges generation, separation, and transport at nanocrystal interfaces are central to energy conversion for solar cells. Here, α-Fe_2O_3/$Cu_4Bi_4S_9$ (α-Fe_2O_3/CBS), α-Fe_2O_3/$Cu_4Bi_4S_9$-reduced graphene oxide (α-Fe_2O_3/CBS–RGO), and bulk heterojunction (BHJ) solar cells were fabricated. The signals of steady state and electric field-induced surface photovoltage spectroscopy indicate that α-Fe_2O_3/CBS–RGO exhibits the higher photovoltaic response than α-Fe_2O_3/CBS. Besides, the highest efficiencies of α-Fe_2O_3/CBS–RGO and α-Fe_2O_3/CBS cells are 6.8% and 3.1%, respectively. The internal relations of photoelectric properties to some factors, such as film thickness, RGO conductive network, energy level matching, etc., were discussed in detail. Qualitative and quantitative analyses further verified the comprehensive effect of RGO and other factors. The exploration to understand the transport mechanism of photogenerated charges will promote the RGO application in BHJ solar cells and photovoltaic community.

1. Introduction

$Cu_4Bi_4S_9$ (CBS) exhibits excellent optical stability, broad optical absorption, and superior photoelectric properties. Recently, the photovoltaic response of single crystal CBS nanoribbons with one-dimensional (1D) nanostructure has been reported [1,2]. However, pure CBS suffers from short hole-diffusion length and high electron–hole recombination rate, inhibiting its promising applications as electron donor. Reduced graphene oxide (RGO) or graphene is a crystalline allotrope of carbon with a two-dimensional (2D) structure, in which carbon atoms are packed densely in a regular sp^2-bonded atomic-scale hexagonal pattern [3,4]. Due to its unique structure (atomic thick carbon layer) and properties, such as remarkably high electron mobility at room temperature, high specific surface area, high thermal conductivity, etc. [5], we attempt to improve the separation of photogenerated charges in CBS with incorporation of RGO. α-Fe_2O_3 is especially attractive as electron acceptor due to its stability, abundance, cost effectiveness, as well as suitable band gap and valence band edge position [6,7]. In our work, α-Fe_2O_3/CBS and α-Fe_2O_3/CBS–RGO, as well as bulk heterojunction (BHJ) solar cells were fabricated to further explore the charge dynamics and the actual transfer process [8–12].

2. Experimental

The fabrication of CBS nanoribbons has been reported in our work [2]. Different CBS–RGO were prepared by incorporating RGO into CBS colloid with various RGO (0.4, 0.8, 1.2, 1.6, 2.0 and 2.4 wt%). For the synthesis of heterojunction, α-Fe_2O_3 sol was deposited onto ITO by a spin-coating method [2,13]. Same process was repeated five times and α-Fe_2O_3 was annealed at 500 °C for 1 h to obtain the high crystallinity film. Then CBS and CBS–RGO were spin-coated onto α-Fe_2O_3 to fabricate α-Fe_2O_3/CBS and α-Fe_2O_3/CBS–RGO. These heterojunctions were maintained in an autoclave at 180 °C for 30 h.

The morphology and microstructure were observed by scanning electron microscopy (SEM, JSM-5600LV) and high resolution transmission electron microscopy (HRTEM, JEM-2010), respectively. Steady state surface photovoltage spectroscopy (SPS) is a home-built apparatus to measure the photovoltaic response. Electric field induced surface photovoltage spectroscopy (EFISPS) is a technique that combines the electric field effect with the SPS method. The *I–V* characteristics of cells were measured under illumination with a sun simulator at AM 1.5.

3. Results and discussion

The surface morphology of CBS–RGO is shown in Fig. 1(a). As seen, RGO with 1.6 wt% can fully incorporate with CBS and a dense contact between two components has formed. It is also suggested that CBS nanoribbons are very clear with lengths up to several

* Corresponding authors.
E-mail addresses: lxy081276@126.com (X.Y. Liu), yzgu@henu.edu.cn (Y.Z. Gu).

http://dx.doi.org/10.1016/j.matlet.2015.12.085
0167-577X/

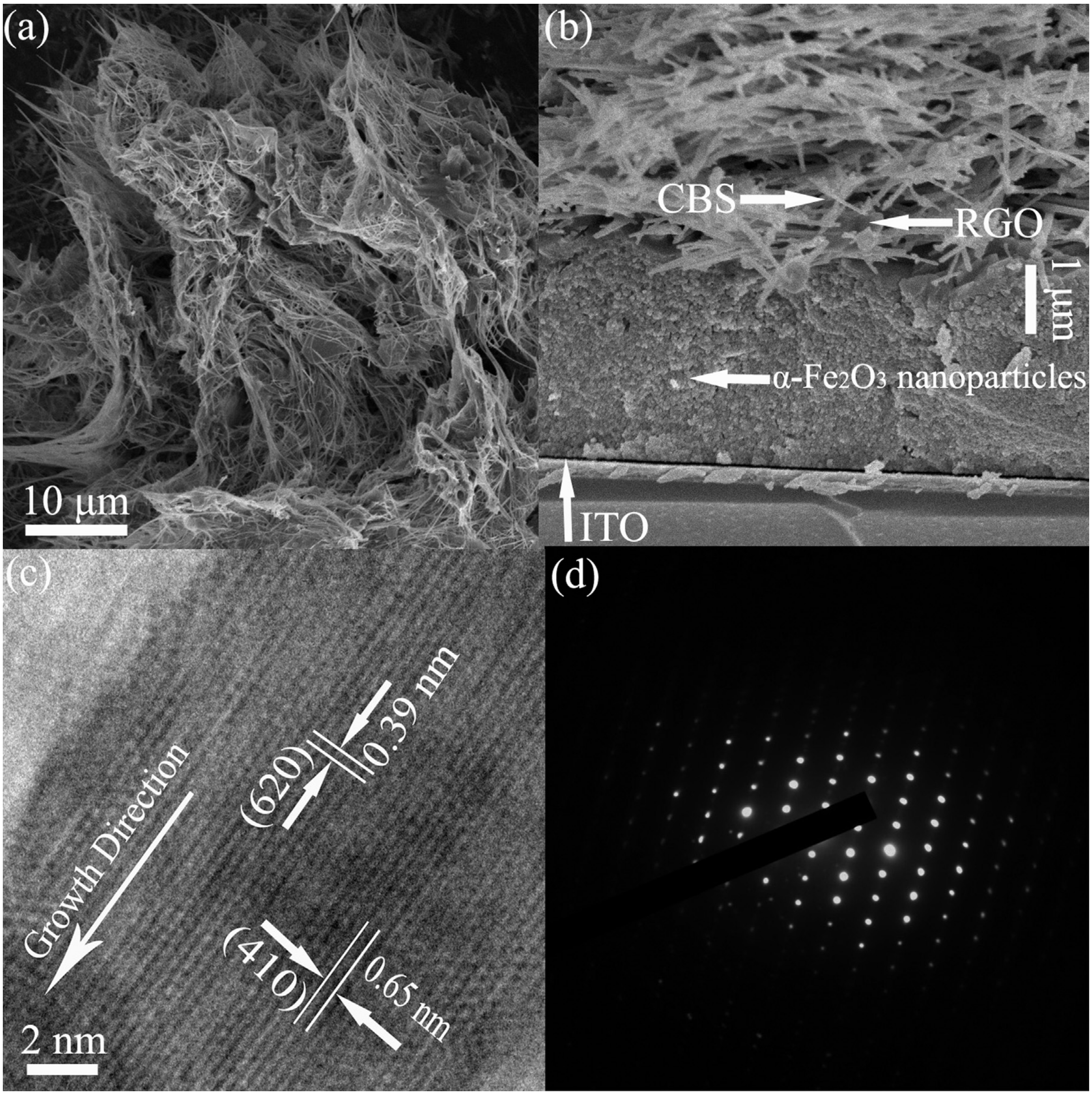

Fig. 1. (a) SEM image of CBS–RGO, (b) cross-section of SEM image of α-Fe_2O_3/RGO–CBS, (c) HRTEM image and (d) SAED image of CBS.

hundreds of micrometers and widths of 20–150 nm. From the cross-section of SEM image as shown in Fig. 1(b), α-Fe_2O_3/CBS–RGO is formed by spin-coating CBS–RGO onto α-Fe_2O_3 film, and CBS–RGO protrudes clearly above α-Fe_2O_3. For the high-resolution TEM image of CBS nanoribbons as seen in Fig. 1(c), the measured lattice spacing of 0.65 nm corresponds to the D-spacing of (410) planes and the vertical-direction lattice spacing of 0.39 nm is consistent with the D-spacing of (620) planes. Besides, Fig. 1 (d) presents the selected area electron diffraction (SAED) image of CBS nanoribbons. The excellent single-crystalline structure of CBS can be demonstrated.

The surface photovoltage (SPV) of CBS nanoribbons with 6.5 μm is shown in Fig. 2(a). As seen, there are two photovoltaic regions, one region from 300–780 nm and the other from 780–1400 nm. However, the SPV is very low and there is a high recombination rate of photogenerated charges in pure CBS film [8,9]. The surface photovoltaic spectra (phase (θ)=180°) of α-Fe_2O_3/CBS and α-Fe_2O_3/CBS–RGO (RGO 1.6 wt%) with different thicknesses are not provided. Here, the SPVs of heterojunctions increased linearly with thickness changing from 3.0 to 6.5 μm. Above 6.5 μm, the SPVs decreased slowly. In our work, CBS and CBS–RGO as donor were spin-coated onto α-Fe_2O_3 layer (thickness of 3 μm) with increasing the times. The optical absorption and photogenerated charges can be improved by adding the donor, inducing the higher SPVs. Above 6.5 μm, the photogenerated carriers can not be collected effectively by current collectors due to the long distance and the short-circuit current density will decrease gradually with the low SPV.

For different RGO wt%, the SPVs of CBS–RGO are shown in Fig. 2 (a). With the same thickness, the SPV increased gradually with RGO from 0.4 to 1.6 wt%. Above 1.6 wt%, the photovoltaic response decreased continuously and the separation between two response regions becomes clearly as pure CBS. For 1.6 wt% RGO, there is the highest SPV (330 μV at 483 nm) and the two SPV response regions have nearly joined together relative to pure CBS. As shown in Fig. 3, the conduction band edge of CBS is higher than the Fermi level of RGO. The excitons diffuse to the interface of α-Fe_2O_3 and CBS where they are split, forming charge carriers; holes in the donor side of CBS and electrons in the acceptor side of RGO. Then the electrons and holes transport to bilateral current collectors, inducing the true separation and SPV signal. With RGO increasing, more photogenerated electrons can transport from CBS to RGO. Due to the markedly high electron mobility of RGO [5], the accumulated electrons in RGO will quickly transfer to ITO electrode, which can improve the separation efficiency of photogenerated