Arabian Journal of Chemistry (2014) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Optical and morphological studies of transition metal doped ZnO nanorods and their applications in hybrid bulk heterojunction solar cells

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Received 18 September 2013; accepted 1 October 2014

KEYWORDS

Transition metals;
Doping;
Defect emission;
Photofunctional material;
Solar cells;
Oxygen vacancy

Abstract One of the challenges in improving the efficiency of hybrid solar cells is to remove crystal defects from the semiconducting nanoparticles. Here we report the synthesis, characterization and applications of transition metal doped ZnO nanorods in hybrid bulk heterojunction solar cells. $Mn_xZn_{1-x}O$ and $Ni_xZn_{1-x}O$ with dopant concentrations ranging from $x = 0.01$–0.10 were successfully synthesized by a novel facile solution-processed wet chemical method, which gave better yield at low cost and temperature. The morphological and optical properties of the material were investigated by Transmission electron microscopy (TEM), UV–Visible and Fluorescence spectroscopies. TEM measurements confirmed the reduction in size of nanorods upon doping. UV–Visible spectra of doped nanorods showed blue shift with respect to the reference undoped ZnO. The defect emissions were completely disappeared from the fluorescence spectra upon doping at high concentrations. These doped nanorods in combination with P3HT were employed in the hybrid solar cells which gave better current densities than their corresponding undoped counterparts.

1. Introduction

ZnO is an important II–VI compound semiconductor which finds wide applications in sunlight harvesting, sensors, spintronics, piezoelectric and optoelectronic devices (Wang and Song, 2006; Zhiyong et al., 2004). In order to be useful for these applications, one of the key requirements is to dope it with certain elements so as to control and regulate its optical and electrical properties (Zheng et al., 2004; Wen et al., 2003). ZnO has been the focus of research in solar cells in various morphological forms and orientations but little or no attention has been paid to the use of its doped form for harvesting solar energy

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2014.10.001
1878-5352

Please cite this article in press as: Shah, S.M. et al., Optical and morphological studies of transition metal doped ZnO nanorods and their applications in hybrid bulk heterojunction solar cells. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.10.001

(Law et al., 2005). Zhong et al. reported that the n-type conductivity of ZnO could be controlled by growing it in an inert atmosphere or doping with elements of group III (Zhong et al., 2003; Kohiki et al., 1994). Similarly Gang Xiong et al. demonstrated that reactive sputtering can produce intrinsic P-type ZnO, controlled by adjusting the partial pressure of oxygen in the sputtering plasma (Xiong et al., 2002). P-type conductivity in ZnO has also been reported by doping the semiconductor with arsenic (Ryu et al., 2000) or phosphorus (Xiang et al., 2006). Nitrogen doping of ZnO nanorods was reported to show strong UV-emission and negligible defect emission (Ishizumi and Kanemitsu, 2005; Lin et al., 2005). But the problem with P-type doping is that it is not as straightforward as n-type. P-type conductivity is difficult to achieve due to the presence of native defects (Djurišić and Leunh, 2006).

Presence of the 3d transition metal ions in the ZnO matrix can lead to phonon scattering, thereby improving thermoelectric efficiency (Lo et al., 2012). Using transition metal ions having the same valence state as Zn, the differences in ionic radii are minimized and hence defects are suppressed (Mohan Kumar et al., 2013). Cr-doping affects the defects and oxygen vacancies and thus helps in the bandgap tuning of ZnO nanorods for applications in nano-optoelectronic devices, charge storage and nanoscale memory devices (Gupta et al., 2012). Mn, Ni and Co have been found effective in the red/blue shift and hence bandgap tuning of ZnO nanorods (Fukumura et al., 1999; Bhat and Deepak, 2005).

Oxygen atoms are tetrahedrally arranged around Zn in the hexagonal structure of ZnO. Substitution of Zn atoms by selected transition metals impregnates ZnO with interesting physical and optical properties (Herng et al., 2011).

The electrical and optical properties of transition metal doped ZnO nanostructures have been studied for several years (He et al., 2005) using different methods of synthesis. These techniques for the growth of doped and undoped ZnO nanorods include metal–organic chemical vapour deposition (MOCVD), metal–organic vapour phase epitaxy (VPE), pulsed laser deposition (PLD), Carbo-thermal evaporation (CTE), aqueous chemical growth (ACG) electro deposition (ED) and hydrothermal deposition (HD) (Wu and Liu, 2002; Bakin et al., 2007; Nobis et al., 2004; Czekalla et al., 2008; Vayssieres et al., 2001; Illy et al., 2005; Park et al., 2002; Anthony et al., 2007; Damen et al., 1966). The route of synthesis reported in this paper is wet and solution based. It is cost effective, low temperature and large scale synthesis method which can be used for the productions of ZnO nanospheres as well as nanorods. The effect of selected transition metals doping on the optical properties, structural defects and the use of material in hybrid bulk heterojunction solar cells makes this study interesting and novel.

2. Experimental

All the chemicals for the synthesis of transition metal doped and undoped ZnO nanorods were used as received without further purification.

2.1. Synthesis of transition metal doped ZnO nanorods and nanoparticles

For the synthesis of transition metal doped ZnO nanoparticles, $Mn_xZn_{1-x}O$ and $Ni_xZn_{1-x}O$ wet chemical method, modified Pacholski method (Pacholski et al., 2002) was used. Absolute methanol was employed as a solvent because crystal growth is highly effected by the presence of water. The dopant concentration x ranged from 0.01 to 0.10, where $x = 0.01$ represents (1%), 0.05 (5%) and 0.10 (10%) doped samples, respectively. 4.15 g of zinc acetate and acetate salt of dopant material at a desired concentration were dissolved in 214.15 ml of purified distilled methanol by heating at appropriate temperature. 1.5 ml of distilled water was added to it. Next in a separate flask 1.40 g sodium hydroxide was dissolved in 117.5 ml of methanol by ultrasonification. This was added to the former solution (reaction mixture) drop by drop under an inert (Argon) atmosphere and constant magnetic stirring. Reaction mixture attained different colors with different dopants at different stages. In case of manganese acetate, by adding alkali it turned dark brown then went through a brownish transparent phase and after 2 h and 15 min the reaction mixture attained dark brownish white colour. When chromium acetate was used as dopant, the addition of alkali imparted grayish white colour to the reaction mixture which passed through a light grayish transparent phase and after a duration of 2 h and 15 min it attained milky grayish white color. In all the cases, precipitates were collected, thoroughly washed and then stored in the dark.

In order to grow the nanoparticles into nanorods, the solution of nanoparticles was concentrated using rotary evaporator under reduced pressure (75 torr at 55 °C) until its volume was reduced to almost one-tenth. This concentrated solution having transparent appearance was replaced over the oil bath at 60 °C for almost 48 h under constant stirring. The precipitate so obtained was washed thrice with freshly distilled methanol and stored in the dark.

2.2. Fabrication of hybrid bulk heterojunction solar cell

Doped semiconductor nanoparticles were synthesized and dissolved in methanol. This solution was termed as solution A. 20 mg/mL solution of P3HT was prepared in methanol by heating in argon atmosphere. This solution was termed as solution B. These two solutions were thoroughly mixed. A glass sheet of $3 \times 2\ cm^2$ dimensions covered with ITO (80 nm) was used as a substrate, a portion of which was etched with hydrochloric acid (32%). Thereafter it was properly washed in order to remove traces of HCl. This clean substrate was coated with a thin layer of PEDOT–PSS by spin coating. In the subsequent step, the photo-functional material which is a blend of doped ZnO nanorods and P3HT was spin coated over the top of PEDOT–PSS at a speed of 1500 rpm and acceleration of 2000 rpm/min for 20 s, and then at a rate of 500 rpm and 100 rpm/min for 20 s in order to remove the solvent completely. Finally Al was deposited by thermal evaporation under high vacuum conditions. This was done in the metal evaporator and 80 nm thick cathodic strips were made to extract and guide electrons to the external circuit. The device was annealed at 90 °C for 15 min under argon flow to attain nice morphological distribution of the active blend.

2.3. Characterization techniques

2.3.1. UV–Visible spectroscopy

Absorbance spectra were recorded with UV–Visible (Shimadzu 1601) spectrophotometer, using a quartz cuvette of 1 cm

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