Materials Letters 64 (2010) 1372–1375

Contents lists available at ScienceDirect

Materials Letters

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

Modification of ZnO nanorods through Au nanoparticles surface coating for dye-sensitized solar cells applications

C.K.N. Peh [a], L. KE [b], G.W. Ho [a,*]

[a] Department of Electrical and Computer Engineering, National University of Singapore, 117576, Singapore
[b] Institute of Materials Research and Engineering, 3 Research Link, 117602, Singapore

ARTICLE INFO

Article history:
Received 12 November 2009
Accepted 11 March 2010
Available online 20 March 2010

Keywords:
ZnO
Nanorods
Dye-sensitized solar cell
Plasmon
Au nanoparticles

ABSTRACT

Dye-sensitized solar cells (DSSC) based on ZnO nanorods were fabricated and modified through the addition of Au nanoparticles. The as-synthesized ZnO nanorods were well-dispersed and of high crystallinity quality leading to a high cell efficiency of 5.2%. On the other hand, thick layer of Au nanoparticles aggregation may have led to distortion of plasmonic effect. Also, the addition of Au nanoparticles have effectively decreased the surface area of ZnO nanorods with direct contact to the dye molecules, resulting in a lower amount of adhered dye molecules to convert sunlight. The electrons generated by the photo-absorption through thick aggregated Au nanoparticles layer may have a lower injection rate to ZnO nanorods as compared to those absorbed by the dye.

1. Introduction

Metal nanoparticles such as Au and Ag can exhibit strong localized surface plasmon resonances at UV, visible and near infrared wavelengths [1]. The optical properties of metal nanoparticles are highly dependent on their geometrical dimension [2]. By introducing the Au nanoparticles to the ZnO material, Schottky barrier is formed in the interfacial region of the Au and the ZnO semiconductor. Due to the formation of the Schottky barrier, electrons in the lowest unoccupied molecular orbital of the dye tunnel across the Au nanoparticles to the ZnO conduction band are not able to back transfer to either the dye or the electrolyte. Thus, electron injection efficiency of the cell is increased. However, it is noted that improving the efficiency of solar cells needs tight control of the properties of metal nanoparticles. Metal nanoparticles have been shown to affect the performance of solar cells [3–6]. In this paper, we have fabricated DSSC based on ZnO nanorods and carried out surface modification through Au nanoparticles coating. We have shown that the addition of aggregated Au nanoparticles to ZnO nanorods can lead to counter effect of suppressing the photocurrent in the device. The effectiveness of Au nanoparticle plasmon-enhanced bulk heterojunction solar cell depends on the dimension and monodispersivity of the metal nanoparticles.

2. Experimental procedures

The ZnO nanorods were synthesized from a precursor of zinc acetate dihydrate in an alcoholic solution [7–9]. The Au nanoparticles were synthesized based on the work of Suh et al. [10]. The ZnO nanorods suspension was dried at 50 °C and 0.025 g were weighed out and mixed with DI water or different amount (0.5 and 1 ml) of the Au nanoparticles. SEM images were obtained from a JEOL JSM 6700 scanning electron microscope with operating voltage of 5.0 kV and operating current of 10 μA. Energy dipersive X-ray (EDX) spectrum was obtained using Oxford Instrument and Inca software. The crystallography of the nanostructures were analyzed using transmission electron microscope (TEM, Phillips FEG CM300) and X-ray diffractometer (XRD, Philip X-ray diffractometer equipped with a graphite monochromator Cu Kα radiation $\lambda = 1.541$ Å). Absorption spectra of the sample were measured with a Shimadzu UV-1800 spectrophotometer.

The resulting suspensions were drop casted onto FTO coated glass and annealed at 450 °C for 30 min with active areas of 0.5×0.5 cm^2. Three devices were made namely the pure ZnO nanorods, ZnO nanorods with 0.5 ml and 1 ml of Au nanoparticle solutions. The resulting films were then immersed in a 0.5 mmol ethanol solution of N719 dye for 1 h at 50 °C, and then rinsed with ethanol and dried at 50 °C. Platinum was used as a counter electrode. A redox electrolyte solution, comprising of 0.1 M lithium iodide, 0.03 M iodine, 0.5 M 4-tert-butylpyridine and 0.6 M 1-propyl-2,3-dimethyl imidazolium iodide dissolved in acetonitrile was used. *I–V* characteristics of solar cells were measured with a sourcemeter (Keithley 2420). An AM1.5 solar simulator (Newport Inst., Model #:91160A) with a 150 W Xe lamp and an AM filter (#: 81088A) was used as the light source. The light intensity corresponding to AM 1.5

* Corresponding author. Tel.: +65 6516 8121; fax: +65 6775 4710.
E-mail address: elehgw@nus.edu.sg (G.W. Ho).

0167-577X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2010.03.022

(100 mW/cm^2) was calibrated using a standard silicon solar cell (Oriel, SRC-1000-TC).

3. Results and discussion

A dissolution–recrystallization growth method via simple and mild conditions was employed for the growth of ZnO nanorods. Fig. 1(a)–(b) show as-synthesized ZnO nanorods with lengths of 80–100 nm, and diameters of 15–20 nm. The ZnO nanorods are well-dispersed and rather uniform in dimension. Fig. 1(c) shows the TEM images of the ZnO nanorods. The dimension of the nanorods complements with the SEM results. The histogram of Fig. 1(d) shows the average length of the nanorods is 90 nm.

High purity of Au nanoparticles was synthesized using seed-mediated approach in aqueous solution. TEM images of the Au nanoparticles together with their histograms are shown in Fig. 2. The synthesized Au nanoparticles are not well-dispersed and of different shapes and sizes (Fig. 2(a)–(b)). High resolution TEM image (Fig. 2(c)) shows that the Au nanoparticles have a *d*-spacing of 0.25 nm corresponding to (111) lattice plane [11]. The {111} facet of fcc metal has the lowest surface energy compared to the other facets, thus the Au nanoparticle confers its tendency to nucleate and grow with their surfaces bounded by {111} facets. Fig. 2(d) shows that the size distribution of the Au nanoparticles is wide typically 2–14 nm.

Fig. 3(a)–(b) shows the TEM images of as-synthesized ZnO nanorods and ZnO nanorods with Au nanoparticles coating respectively. The ZnO nanorods with Au nanoparticles coated samples revealed aggregated Au nanoparticles on surfaces of the nanorods. The Au nanoparticles are coated uniformly on the entire length of the nanorods. At higher resolution (Fig. 3(c) inset), the ZnO nanorods shows well-oriented lattice fringes of interplanar distance of ~0.26 nm indicating a wurtzite ZnO high quality single-crystalline structure [7]. The crystallographic structures of the ZnO nanorods and Au nanocrystals are further characterized and confirmed by XRD (results not shown). The diffraction peaks of Au nanoparticles are assigned to the {111}, {200} and {220}{311} planes of face-centered cubic (fcc) Au, respectively [12]. Similarly, all the diffraction peaks of the ZnO nanorods can be indexed as the hexagonal wurtzite ZnO structure with the lattice constants $a = 3.249$, $c = 5.206$ Å. EDX spectra were obtained from ZnO nanorods and Au–ZnO hybrid nanorods samples. Fig. 3(c) shows that that the Au–ZnO hybrid nanorods spectrum has an additional Au peak at 2.12 keV other than the Zn peaks at 0.884, 0.906, 1.012 keV and O peak at 0.525 keV. The EDX results indicate that the Au nanoparticles were indeed coated on the ZnO nanorods.

Fig. 4(a) shows the UV–vis absorption spectra of the devices before dye loading. The Au nanoparticles coated ZnO nanorods show a higher absorbance. The absorbance is observed to improve with an increased amount of Au nanoparticles coating. Fig. 4 (b) shows the typical *I–V* curves for the three devices under the illumination while Table 1 shows the performance of the devices.

The ZnO nanorods device gives the highest performance of 5.2% conversion efficiency. The pure ZnO nanorods devices are well-dispersed and of high crystallinity quality (as shown in TEM results), thereby leading to a high cell efficiency. The consistent result is one of the highest cell efficiency reported from ZnO nanorods based solar cell. However, the Au–ZnO nanostructure devices have a lower cell performance. It is noted that the Au nanoparticles employed are highly aggregated which could distort the plasmonic effect by broadening their spectral enhancement [13]. It has been shown that Au nanoparticles aggregation can lead to suppression of photocurrent thereby reducing the cell efficiency [14]. Thus effectiveness of Au nanoparticle depends on nanoparticle monodispersivity to induce the collective electron oscillations at the surface. Also, the addition of Au nanoparticles have effectively decreased the surface area of ZnO nanorods with direct contact to the dye molecules, resulting in a lower amount of adhered dye molecules to convert sunlight leading to a lower I_{sc}. The electrons generated by the photo-absorption through thick aggregated Au nanoparticles layer may have a lower injection rate to ZnO nanorods as compared to those absorbed by the dye, hence leading to a decrease in I_{sc}. Finally, the introduction of Au nanoparticles may introduce more

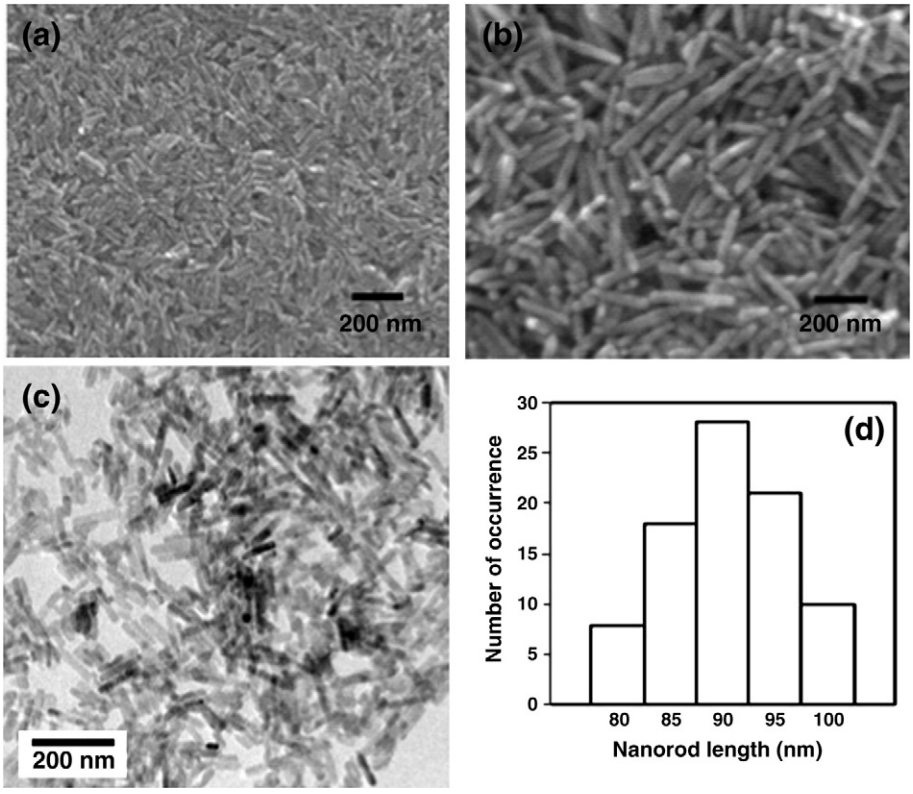

Fig. 1. (a–b) SEM and (c) TEM images of ZnO nanorods. (d) Histogram of the length of ZnO nanorods.

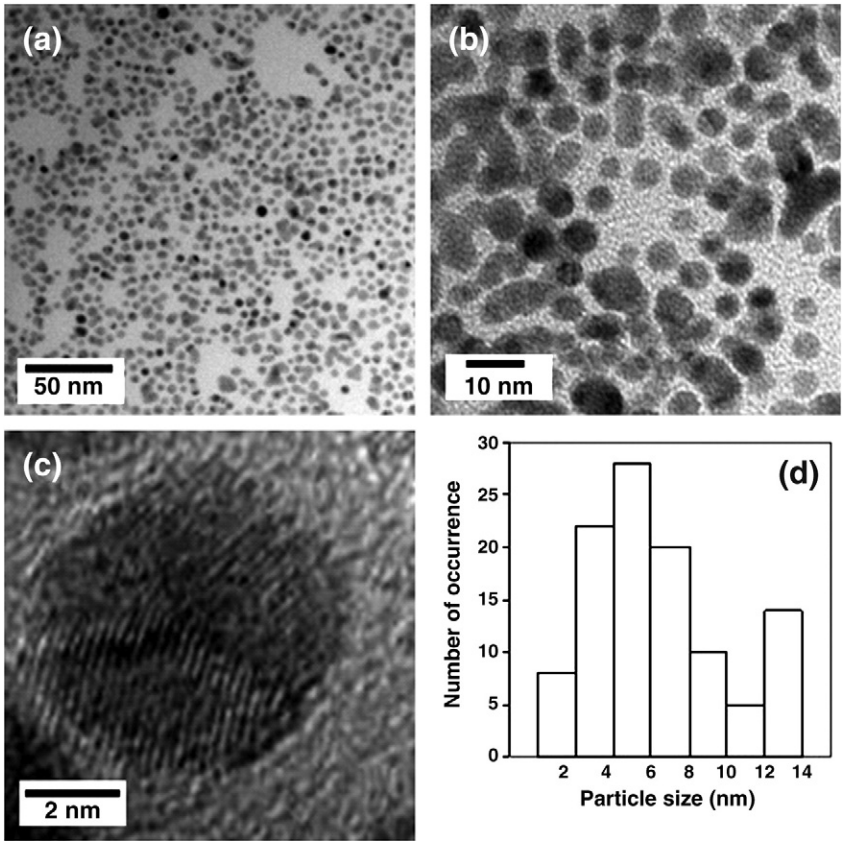

Fig. 2. TEM images of (a–c) low and high magnification and (d) histogram of the Au nanoparticles.

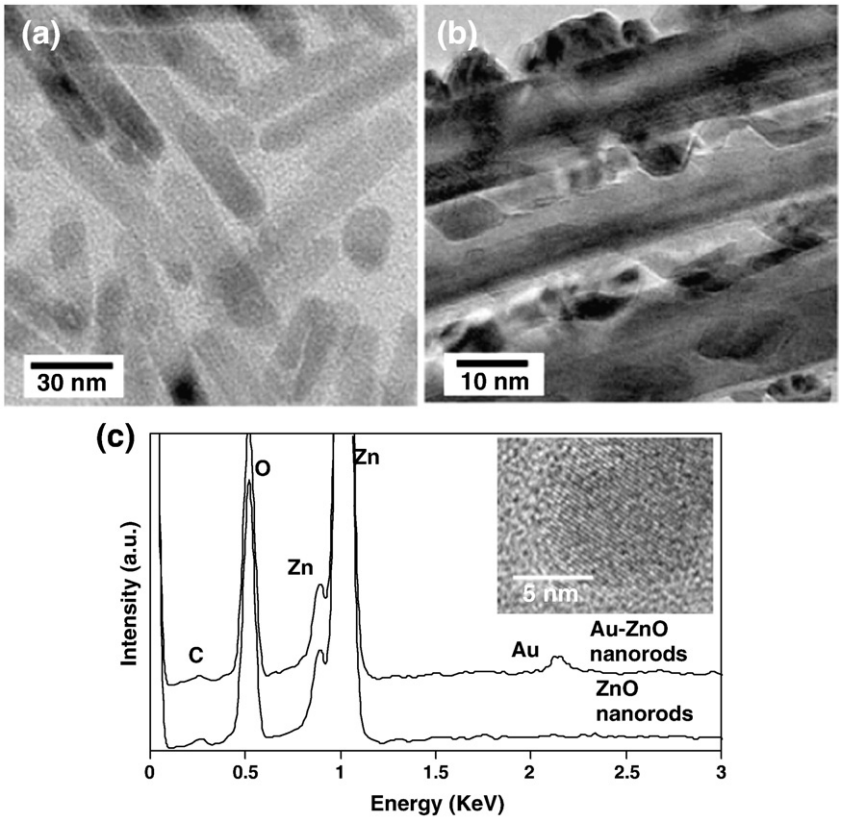

Fig. 3. TEM images of (a) as-synthesized ZnO nanorods and (b) ZnO nanorods with Au nanoparticles coating. (c) EDX spectra of pure ZnO nanorods and ZnO nanorods with Au nanoparticles coating (inset: High resolution image of the ZnO nanorod).

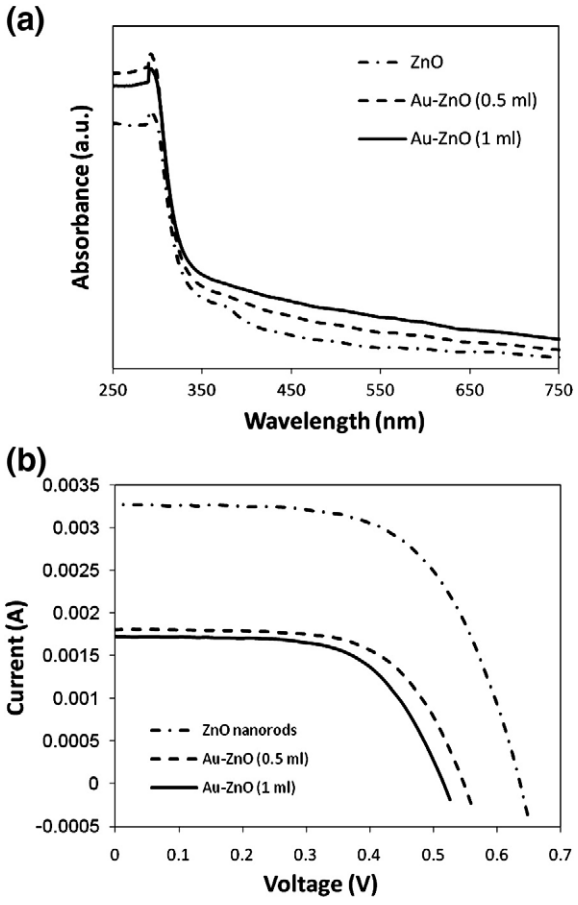

Fig. 4. (a) UV–vis absorption spectra and (b) *I–V* characteristics of DSSC using ZnO and Au–ZnO nanostructures.

interface defects to the whole nanostructure matrix, resulting in a lowering of the V_{oc}. Furthermore, we have noted that the increase in the amount of Au nanoparticles coating has a detrimental effect which has resulted in a decrease of the I_{sc}. The cell efficiency decreases from 2.5 to 2.2%. The thicker Au nanoparticles coating could have further increased the Au nanoparticles aggregation and defects density, thereby further degraded the cell performance.

Table 1
Summary of DSSC device performances.

Device	V_{oc} (V)	I_{sc} (mA)	FF (%)	η (%)
ZnO	0.63	3.27	61.9	5.2
Au–ZnO (0.5 ml)	0.55	1.80	63.4	2.5
Au–ZnO (1 ml)	0.51	1.72	63.0	2.2

4. Conclusion

DSSC based on ZnO nanorods were fabricated and modified through the addition of Au nanoparticles. A pure ZnO nanorod device has a higher efficiency as compared to the Au nanoparticles modified devices. The pure ZnO nanorods devices are well-dispersed and of high crystallinity quality, thereby leading to high cell efficiency. On the other hand, thick layer of Au nanoparticles aggregation may have led to distortion of plasmonic effect. Also, the addition of Au nanoparticles have effectively decreased the surface area of ZnO nanorods with direct contact to the dye molecules. The electrons generated by the photo-absorption through thick aggregated Au nanoparticles layer may have a lower injection rate to ZnO nanorods as compared to those absorbed by the dye.

References

[1] Hutter E, Fendler JH. Adv Mater 2004;16:1685–706.
[2] Kelly KL, Coronado E, Zhao LL, Schatz GC. J Phys Chem B 2003;107:668–77.
[3] Dhas V, Muduli S, Lee WJ, Han SH, Ogale S. Appl Phys Lett 2008;93:243108–200.
[4] Hayashi S, Kozaru K, Yamamoto K. Solid State Comm 1991;79:763–7.
[5] Chou CS, Yang RY, Yeh CK, Lin YJ. Powder Technol 2009;194:95–105.
[6] Derkacs D, Chen WV, Matheu PM, Lim SH, Yu PKL, Yu ET. Appl Phys Lett 2008;93:91107–9.
[7] Seow ZLS, Wong ASW, Thavasi V, Jose R, Ramakrishna S, Ho GW. Nanotechnology 2009;20:45604–9.
[8] Beek WJE, Wienk MM, Kemerink M, Yang XN, Janssen RAJ. J Phys Chem B 2005;109:9505–16.
[9] Pacholski C, Kornowski A, Weller H. Angew Chem Int Edn Engl 2002;41:1188–91.
[10] Suh KY, Kim YS, Lee HH. Adv Mat 2001;13:1389–93.
[11] Zhang JH, Liu HY, Wang ZL, Ming NB. Adv Func Mat 2007;17:3295–303.
[12] Zhang CX, Zhang JL, Han BX, Zhao YJ, Li W. Green Chem 2008;10:1094–8.
[13] Sosa IO, Noguez C, Barrera RG. J Phys Chem B 2003;107:6269–75.
[14] Sundararajan SP, Grady NK, Mirin N, Halas NJ. Nano Lett 2008;8:624–30.