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Plasmonic Effect in Au-Added TiO_2-Based Solar Cell

LE VAN HONG,[1,2,4] DO TRAN CAT,[2] LE HA CHI,[2] NGUYEN THI THUY,[2] TRAN VAN HUNG,[2] LY NGOC TAI,[3] and PHAM DUY LONG[2]

1.—Duy Tan University, Da Nang, Vietnam. 2.—Institute of Materials Science, VAST, Hanoi, Vietnam. 3.—Nha Trang Pedagogical College, Nha Trang, Khanh Hoa, Vietnam. 4.—e-mail: honglv.ims@gmail.com

TiO_2 nano thin films have been fabricated on fluoride tin oxide (FTO) film electrodes by hydrothermal synthesis at temperatures of 80°C, 120°C, 150°C, and 200°C for different synthesis times of 1 h, 2 h, and 3 h in 2.5 mol, 5 mol, and 7.5 mol NaOH solution. X-ray diffraction patterns and field-emission scanning electron microscopy (FESEM) images were recorded for all the film samples, and the results confirmed that TiO_2 anatase phase was generally formed in nanowire form. The influence of synthesis temperature, processing time, and NaOH content on the structure and morphology of the TiO_2 material was studied. Au nanoparticles with size of around 2×10^{-8} m were added into the TiO_2 thin films by thermal evaporation in vacuum combined with thermal annealing. Based on photocurrent–voltage (I–V) characteristics measured under irradiation with visible light, the short-circuit current, open-circuit voltage, and efficiency of solar cells with FTO/Au-added TiO_2/(I^-/I^{2-}) electrolyte/Pt configuration were evaluated. The short-circuit current and efficiency of the Au-added solar cell were greatly improved, which is supposed to be related to a contribution of the surface plasmon resonance effect.

Key words: TiO_2 nanotechnology, Au nanoparticles, surface plasmon resonance, dye-sensitized solar cells

INTRODUCTION

Gold metallic nanoparticles exhibit a peak wavelength of localized surface plasmon resonance (LSPR) of around 530 nm, which approaches the absorbance of N719, the sensitizer usually used in dye-sensitized solar cells (DSSCs). The wavelength with peak intensity depends on the refractive index of the surrounding medium.[1] It has been shown that composite films consisting of nanoparticles of noble metals such as Au and Ag embedded in dielectric oxide matrixes such as TiO_2 have various applications including photocatalysis, solar cells, and novel optoelectronic devices,[2] and particularly DSSCs. Titanium dioxide films are extensively used as the dielectric matrix for combination with noble-metal nanoparticles to obtain the surface plasmon resonance (SPR) effect, depending on the concentration, size, shape, and behavior of the metal nanoparticles as well as the dielectric properties of the medium.[3,4] Many recent investigations have indicated that noble metals embedded in nano-TiO_2 film can capture photoinduced electrons, separating electron–hole pairs effectively and extending the light absorption of TiO_2 into the visible light region.[5,6] Therefore, a TiO_2 matrix containing embedded noble-metal nanoparticles exhibits enhanced photocatalytic activity.[7] Zhao et al.[8] observed anodic photocurrents in response to visible-light irradiation of gold- and silver-added TiO_2 films. Zhou et al.[9] fabricated Au-TiO_2 by a simple spray hydrolysis method using a photoreduction technique at 90°C. They observed strong visible-light photocatalytic activity for degradation of rhodamine B (RhB) in water for the prepared Au-TiO_2 nanocomposites. This enhancement in the photocatalytic degradation of RhB in water was concluded to be related to improved interfacial charge transfer. Sheehan and coworkers[10] systematically studied the influence of SiO_2 and SiO_2@TiO_2 shells on the quantum

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efficiency of DSSCs using N719 dye as light sensitizer. They recorded enhanced efficiency of 5.3% for a DSSC using aggregated Au@SiO_2@TiO_2 in comparison with 2.8% for a DSSC without Au nanoparticles.

Herein, we report an enhancement in the photocurrent of a gold-added TiO_2-based solar cell manufactured using hydrothermal synthesis combined with evaporation in vacuum and thermal annealing.

EXPERIMENTAL PROCEDURES

Metallic Ti thin film with thickness of about 200 nm to 300 nm was deposited onto a cleaned FTO substrate by using an ULVAC S300 vacuum sputtering unit. Using the Ti thin film, TiO_2 thin film was synthesized by a hydrothermal method in NaOH solution with different concentrations of 2.5 mol, 5 mol, and 7.5 mol (M) at different temperatures of 80°C, 120°C, 150°C, and 200°C. The synthesized TiO_2 thin film was cleaned using 1.0 M HNO_3 solution and deionized water, then dried and annealed in atmosphere at 450°C for 1 h. Au nanoparticles were added into the TiO_2 thin films by the two following steps: Au thin film with thickness in the range from 3×10^{-9} m to 1×10^{-8} m was first deposited by thermal deposition in vacuum, then the obtained Au-embedded TiO_2 films were annealed at 450°C for 2 h. The phase structure and microstructure of the TiO_2 films were investigated by x-ray diffraction analysis and FESEM imaging, respectively. Ultraviolet–visible (UV–Vis) absorption spectra of the films were recorded using a Shimadzu UV-1800 spectrometer. Solar cell devices with FTO/Au-added TiO_2/(I^-/I^{2-}) electrolyte/Pt configuration were manufactured, and their photocurrent–voltage (I–V) characteristics recorded under irradiation by a 150-W xenon lamp equipped with a filter of air mass (AM) 1.5G coefficient (Newport) so that its light intensity was adjusted to 1-sun conditions (100 mW/cm^2), using a Keithley 2400 source meter.

RESULTS AND DISCUSSION

Manufacturing Au-Embedded TiO_2 Thin Films

With the aim of synthesizing TiO_2 nano thin films on FTO substrate, we first deposited Ti metallic thin film onto FTO substrate by sputtering in vacuum. The Ti films on FTO substrate with thickness of 2×10^{-7} m to 3×10^{-7} m were used to synthesize TiO_2 thin films by a hydrothermal technique in NaOH solution of various concentrations using different times and temperatures. Figure 1 presents the x-ray diffraction pattern of a typical TiO_2 thin film synthesized at 80°C in 2 h and annealed at 450°C for 1 h. It shows that anatase-phase TiO_2 was predominantly formed in the films.

In addition, other peaks identified as corresponding to rutile phase of TiO_2 and the FTO substrate

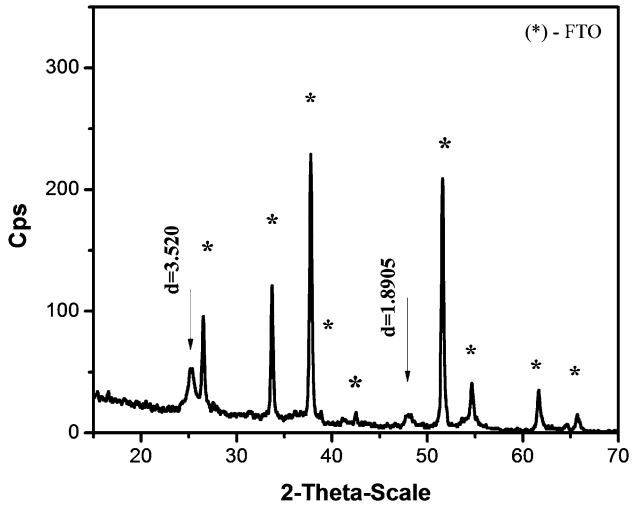

Fig. 1. X-ray pattern of TiO_2 thin film synthesized at 80°C for 2 h and annealed at 450°C.

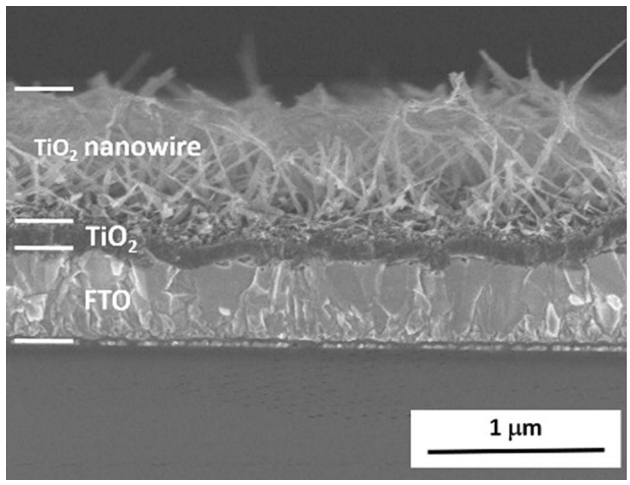

Fig. 2. Cross-sectional FESEM image of TiO_2 thin film deposited onto FTO substrate.

are observed. These identified material phases are again confirmed by the FESEM image presented in Fig. 2. It is known that the microstructure of TiO_2 films plays a very important role in DSSCs. Using FESEM images, we checked the microstructure of the synthesized TiO_2 films. Technological conditions such as the temperature and time of the hydrothermal process and NaOH concentration in solution influence the microstructure and properties of the TiO_2 thin film. First, we checked the influence of the NaOH concentration in solution on the microstructure of the TiO_2 thin film. Figure 3 shows FESEM images of TiO_2 thin films synthesized in solution containing NaOH concentration of 2.5 M, 5 M, and 7.5 M at 80°C in hydrothermal time of 2 h.

It is easy to see that the TiO_2 film was formed by accumulation of TiO_2 wires of different sizes. The size of the wires depended on the NaOH concentration in

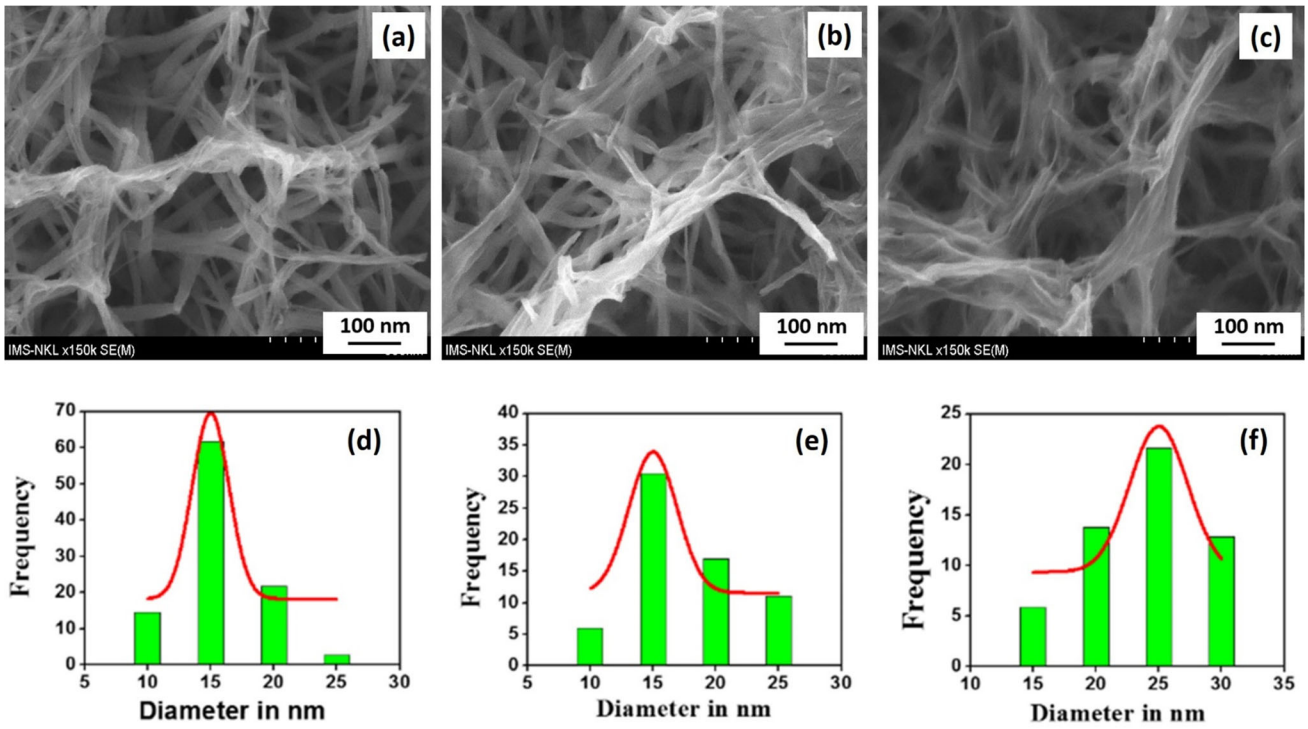

Fig. 3. FESEM images of TiO_2 thin films synthesized by hydrothermal processing in solution containing (a) 2.5 M, (b) 5 M, or (c) 7.5 M NaOH at 80°C in 2 h, and the grain size distribution with Gaussian fitting for (d) 2.5 M, (e) 5 M, or (f) 7.5 M NaOH.

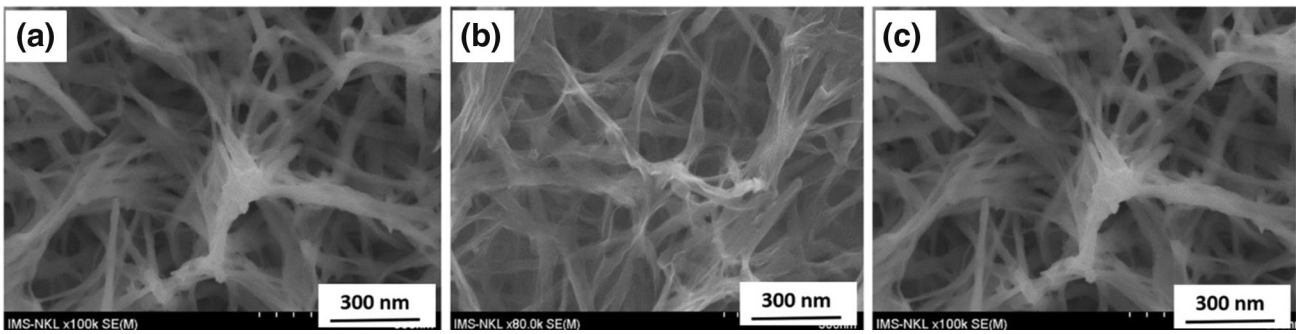

Fig. 4. FESEM images of TiO_2 thin films synthesized at 80°C in 1 h (a), 2 h (b), and 3 h (c) in solution containing 5 M NaOH.

solution as well as the temperature and time of the hydrothermal process (Figs. 4 and 5).

To prepare Au-embedded TiO_2 DSSCs, we deposited Au thin film with thickness of 3×10^{-9} m, 5×10^{-9} m, and 1×10^{-8} m onto TiO_2 thin films and annealed the films at 450°C. FESEM images of these Au-embedded TiO_2 films are presented in Fig. 6.

From the recorded FESEM images, the size of the Au nanoparticles was estimated to be about 16×10^{-9} m and 21×10^{-9} m for TiO_2 films coated with a Au layer of 5×10^{-9} m and 1×10^{-8} m, respectively. It is clear that Au nanoparticles were successfully created and embedded on the surface of the TiO_2 nanowires, and their size and concentration depended on the thickness of the Au layer.

Optical Properties

Figure 7 presents the absorption spectra of the TiO_2 thin films (without Au nanoparticles and Au-embedded films).

The absorption of the TiO_2 film without Au nanoparticles shows band-edge absorption at wavelength of about 380 nm, corresponding to a bandgap of 3.26 eV, slightly larger than that of bulk TiO_2. This is due to quantum confinement as the size of the material decreases to the nanometer region. It is clear that the surface plasmon resonance effect of Au nanoparticles contributed significantly to the absorption spectrum of the Au-embedded TiO_2 thin films. A wide SPR absorption band with peak around wavelength of 540 nm appears, and its intensity increases

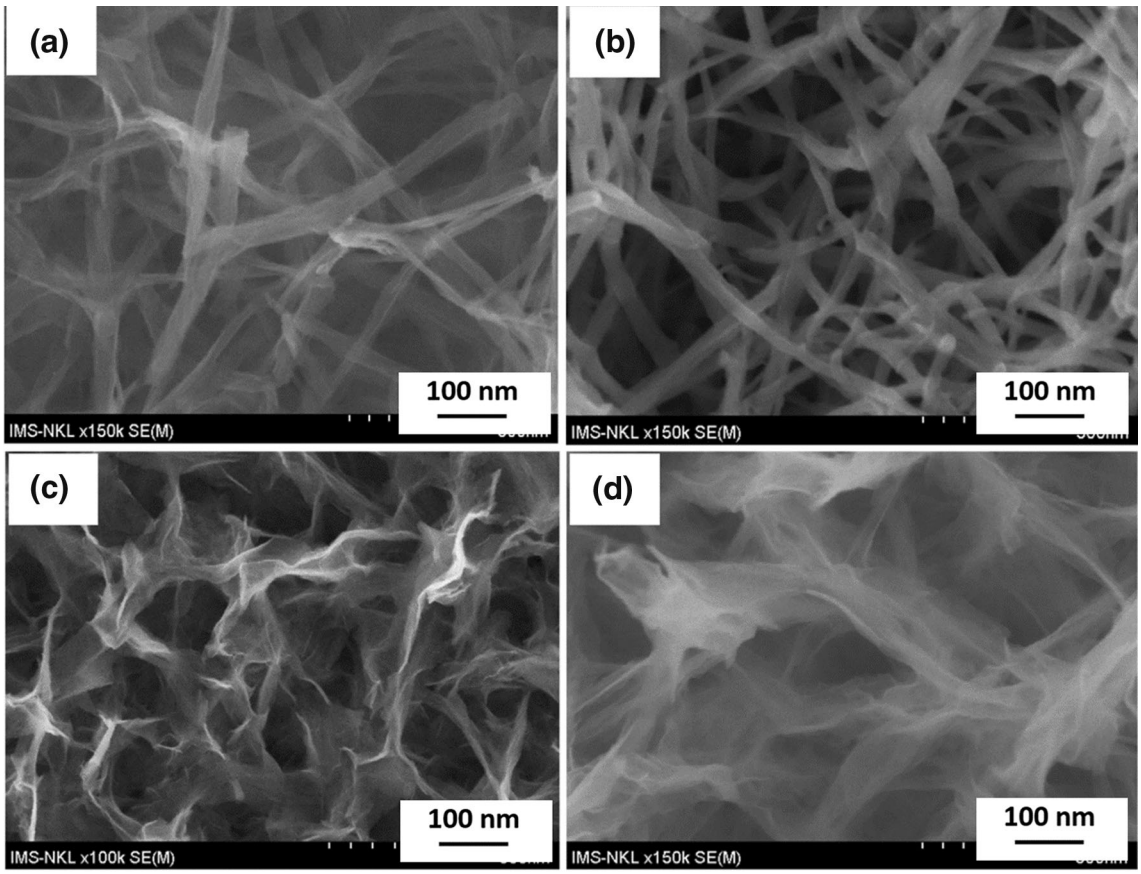

Fig. 5. FESEM images of TiO_2 thin films synthesized at 80°C (a), 120°C (b), 150°C (c), or 200°C (d) by hydrothermal process in solution containing 5 M NaOH in 2 h.

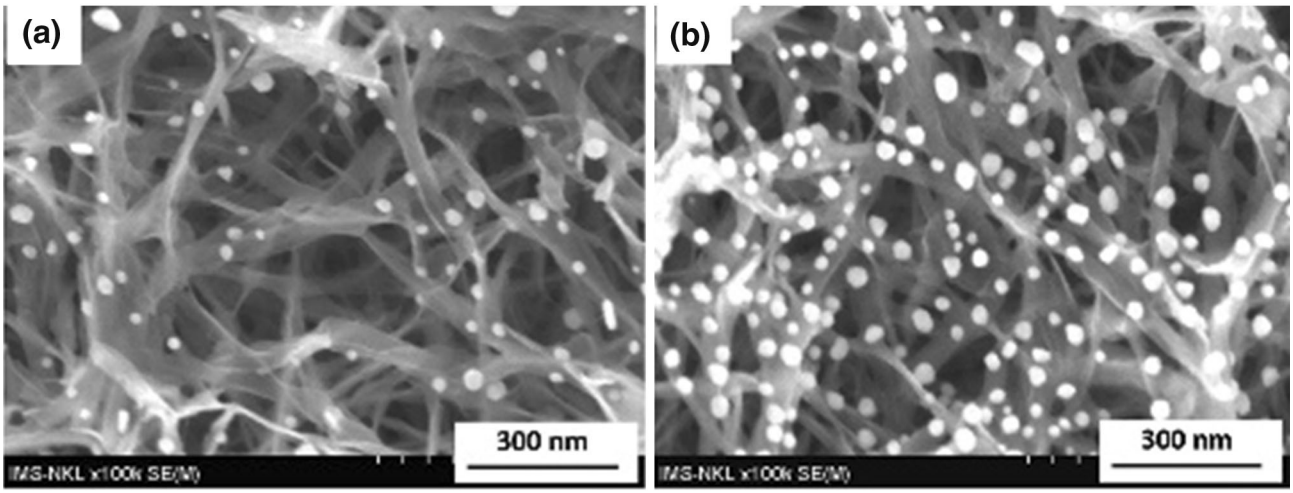

Fig. 6. FESEM images of TiO_2 thin films embedded with Au nanoparticles created by annealing TiO_2 thin film coated with Au layer with thickness of 5×10^{-9} m (a) and 1×10^{-8} m (b).

depending on the Au-coated layer. According to reports by Hutter and Shutthanandan, the intensity of SPR absorption depends on the concentration, size, shape, and behavior of the metal nanoparticles as well as the dielectric properties of the medium.[3,4] This SPR effect of Au-embedded nanoparticles simultaneously improved the optical absorption of the TiO_2 thin films in the visible light region and the charge transportation of the TiO_2 thin layer, being favorable for the efficiency of TiO_2-based DSSCs.

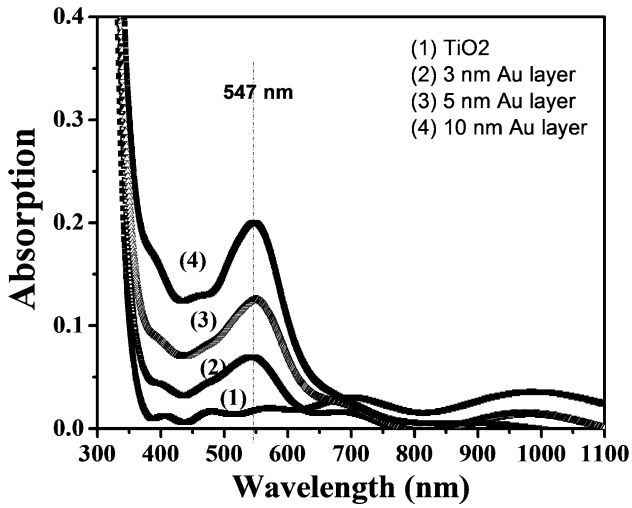

Fig. 7. UV–Vis absorption spectra of TiO_2 films Au-coated with different thickness.

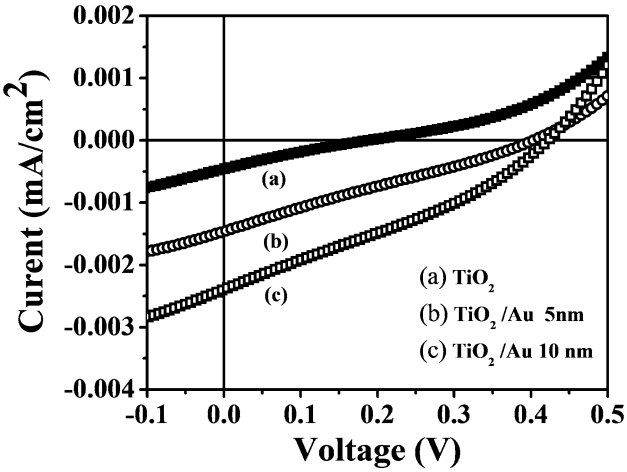

Fig. 8. *I–V* characteristics of TiO_2-based solar cells irradiated with a typical light source with power of 100 mW/cm^2 (AM 1.5G).

SPR Effect and Efficiency of DSSCs

TiO_2-based DSSCs with FTO/Au-embedded TiO_2/(I^-/I^{2-}) electrolyte/Pt configuration were constructed and manufactured. *I–V* characteristics of the cells were recorded under irradiation by a typical light source with power of 100 mW/cm^2 (equivalent to 1-sun AM 1.5G) at the surface of the cells (xenon lamp, Oriel 69907, Newport). To obtain the current–voltage characteristics of the cells, an external bias voltage was applied to the DSSC and the photocurrent was recorded using a digital source meter (model 2400, Keithley, USA). The obtained results are presented in Fig. 8. It is clear that both the open-circuit voltage V_{oc} and short-circuit current J_{sc} of the cells with Au-embedded TiO_2 nanoparticles were increased depending on the thickness of the Au-coated layer. In contact with TiO_2 nanoparticles, the plasmonic absorption of Au nanoparticles in the visible-light region increased the electron density in the conduction band of the TiO_2 nanoparticles. When the electron density in the conduction band increases, the effective Fermi level rises. This is related to the increase of V_{oc} and J_{sc} presented in Fig. 8. High electron density in the conduction band affects the charge-transfer process in the cell, as reported by Zhou,[9] increasing the J_{sc} of the cells. Increase of both V_{oc} and J_{sc} is favorable to improve the efficiency of the solar cell. The TiO_2/Au-embedded cell using a coated Au layer of 1×10^{-8} m showed almost 10 times larger efficiency than that of the TiO_2-based DSSC solar cell.

CONCLUSIONS

Au-embedded TiO_2 DSSCs were successfully manufactured by a hydrothermal technique from metal Ti thin film in NaOH solution combined with embedding Au nanoparticles by annealing the TiO_2 film coated with a thin layer of Au. Plasmonic absorption of the Au nanoparticles in the visible-light region improved both the open-circuit voltage V_{oc} and short-circuit current J_{sc} of the cells. Consequently, the efficiency of the Au-embedded TiO_2 solar cell increased, depending on the concentration of Au nanoparticles. The best efficiency value was achieved for the case of the TiO_2 thin film coated with a Au layer with thickness of 1×10^{-8} m. The efficiency enhancement is considered to be related to the SPR effect.

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REFERENCES

1. H.J. Chen, X.S. Kou, Z. Yang, U.H. Ni, and J.F. Wang, *Langmuir* 24, 5233 (2008).
2. M.G. Manera, J. Spadavecchia, D. Busoc, C. de Julian Fernandez, G. Mattei, A. Martucci, P. Mulvaney, J. Perez-Juste, R. Rella, L. Vasanelli, and P. Mazzoldi, *Sensors Actuators B* 132, 107 (2008).
3. E. Hutter and J.H. Fendler, *Adv. Mater.* 16, 1685 (2004).
4. V. Shutthanandan, Y. Zhang, S. Thevuthasan, L.E. Thomas, W.J. Weber, G. Duscher, and C.M. Wang, *Nucl. Instrum. Method B* 242, 448 (2006).
5. H.Y. Chuang and D.H. Chen, *Nanotechnology* 20, 105704 (2009).
6. R.C. Adochite, M. Torrell, L. Cunha, E. Alves, N.P. Barradas, A. Cavaleiro, J.P. Riviere, D. Eyidii, and F. Vaz, *Optoelectron. Adv. Mater.* 5, 73 (2011).
7. N.P. Barradas, C. Jeynes, and R.P. Webb, *Appl. Phys. Lett.* 71, 291 (1997).
8. G. Zhao, H. Kozuka, and T. Yoko, *Thin Solid Films* 277, 147 (1996).
9. M. Zhou, J. Zhang, B. Cheng, and H. Yu, *Int. J. Photoenergy* (2012). doi:10.1155/2012/532843.
10. S.W. Sheehan, H. Noh, G.W. Brudvig, H. Cao, and C.A. Schmuttenmaer, *J. Phys. Chem. C* 117, 927 (2013).