Materials Letters 163 (2016) 266–269

Contents lists available at ScienceDirect

Materials Letters

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

Photovoltaic characteristics of titania photoanodes modified with silver nanoparticles by pulsed laser deposition

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ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form
17 October 2015
Accepted 20 October 2015
Available online 21 October 2015

Keywords:
Pulsed laser deposition
Nanoparticles
Optical materials and properties
Semiconductors
Solar energy materials

ABSTRACT

Plasmonic metals such as gold, silver and copper are optically attractive photosensitizers owing to its unique optical properties at nano-scaled level, where the unique surface plasmon resonance (SPR) phenomenon becomes operative. These photosensitizers are usually deposited by immersion techniques which impart poor control on density of these photosensitizers dispersed on semiconductors. Herein, we report the deposition of silver NPs on TiO_2 semiconductor by employing pulsed laser deposition (PLD). PLD efficiently deposits Ag NPs on TiO_2 with effective control on NPs distribution on photoanodes which, ultimately, tune the photovoltaic (PV) characteristics of the resultant NPs sensitized solar cells, since the formed NPs sizes and morphology, and their spatial distribution on semiconductor have a significant influence on the PEC performance.

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1. Introduction

Nanoparticles-sensitized solar cells can be recognized as an extension to a well-known dye-sensitized solar cells (DSSCs), where plasmonic metal NPs function as photosensitizers on account of its enhanced visible light absorption because of SPR phenomena [1,2]. Organic compounds, metal complexes and compounds [3,4] have widely been explored as photosensitizers. Gold clusters (CLs) [5] and ruthenium based complexes are very expensive, whereas, metal halides complexes, though highly efficient, may pose environmental concerns, predominately, owing to the presence of Lead [4]. These cost and environmental problems call for alternative photosensitizers to be explored. Ligand-protected metal CLs are becoming promising photosensitizers [5,6]. During synthesis of metal CLs and NPs, in salt reduction methods, ligands in conjunction with reductant form metal ions complexes which change reaction kinetics, and ultimately, control the NPs morphology [7]. Glutathione-protected silver CLs [6], and gold CLs [5,8] as photosensitizers have thoroughly been investigated. Photosensitizers are deposited on semiconductors by immersion techniques where photoanodes are immersed in solvents containing desired dye complexes. These immersion techniques provides limited control on densities and distribution of photosensitizers, especially with metal NPs and CLs. We are exploring an efficient, cost-effective, scalable, and versatile techniques for deposition of metallic photosensitizers on semiconductors. We, previously, have shown that spray-coating of metal CLs on TiO_2 results in an efficient and viable route to deposit metal NPs and CLs [9]. We, herein, demonstrate PLD to deposit silver NPs on TiO_2. PLD, being a fast and controllable technique, can efficiently be employed to deposit metal NPs on TiO_2.

2. Experimental section

All reagents were used as analytical grades without any further purification. Synthesis of mesoporous TiO_2 and glutathione-protected Ag NPs has been carried out according to the literature [9]. Device-1 (based on photoanode-1 formed by depositing silver NPs on TiO_2 by immersion technique) and Device-2 (based on photoanodes-2 formed by depositing silver NPs on TiO_2 by PLD) are different only in photoanodes, and for comparison, the same fabrication procedure has been followed for both devices according to the literature [5]. Optical absorption spectra were obtained using Zolix Omni-λ 300 Spectrograph and DCS103 Data Acquisition System. The surface morphology, and crystallite size and crystal phase of TiO_2 photoanodes were characterized by SEM (JSM, 6390A) and XRD (Xpert-PRO diffractometer), respectively. TEM (TECNAI instrument) and selected area electron diffraction (SAED) were conducted to characterize the NPs. Silver NPs were deposited by PLD in a vacuum chamber with a base pressure of 2×10^{-4} Pa. The 99.99% pure silver was used as a target in PLD. The targets

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http://dx.doi.org/10.1016/j.matlet.2015.10.096
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were irradiated with a nanosecond Q-switched Nd: YAG laser beam (Lithuania EKSPLA NL303HT), wavelength 266 nm, pulse duration 3–6 ns. The laser beam diameter was ~1 mm, with an energy density of ~200 mJ/pulse. Both target and substrate rotated at the speed of 5 rpm during deposition. The photoanodes were placed 5 cm away from the target in the chamber. The laser was operated at the frequency of 10 Hz. All the depositions were conducted at room temperature for 20 min irradiation time. PV characteristics were determined using visible light generated through 300 W Xenon lamp with 100 mW/cm^2 incident power using CHI660C electrochemical workstation. EIS, and Mott–Schottky (M–S) analysis were performed on assembled devices having active area 0.14 cm^2. M–S plots were obtained at amplitude of 10 mV with voltage in the range of $+1$ to -1 V. EIS was conducted under dark conditions at 10 mV amplitude and frequency in the range of 1 Hz to 100 KHz. The resultant spectra were fitted by using ZView software according to the equivalent circuit.

3. Results and discussion

TiO_2 coated on FTO shows the anatase phase marked by the peaks (A) in accordance with JCPDS # 21-1272, and the peaks (F) are assigned to FTO substrate according to JCPDS # 46-1088, as shown in Fig. 1a. No appreciable Ag peaks are observed in XRD patterns of TiO_2 modified with Ag NPs (not shown here), likely owing to the small amount of NPs and its uniform distribution on TiO_2. The crystallite size of anatase TiO_2 is 17.9 nm as calculated from well-known Scherer's equation. In immersion technique, the pH value of NPs dispersion should be between 2 and 6. In this pH range, the –COO$^-$ group of glutathione is electrostatically coupled with the positive charge of TiO_2 [8]. In our experiment, the adjustment in pH has been made through the addition of NaOH and acetic acid. The concentration of silver NPs in DI water and pH were 0.60–0.70 wt% and 5, respectively. Fig. 1b displays the optical absorbance spectra of all types of photoanodes under observation. No distinct SPR peaks are observed, since the absorbance spectra have been conducted on TiO_2 coated FTO assembly containing low concentration of Ag NPs. Photoanode-2 distinctly shows comparatively higher optical absorbance.

Thickness of TiO_2 coated on FTO is estimated to be 5 microns (Fig. 2a), whereas, Fig. 2(b–d) show SEM images of all types of photoanodes. The compact morphology of photoanode-2 might be responsible for the increased optical absorption. Fig. 2(e–f) are the TEM images of Ag NPs synthesized by salt reduction method and PLD, respectively. It can be noted that Ag NPs deposited by PLD have uniform morphology and narrow size distribution with an average NP size of 5 nm. NPs in Fig. 2e have large size distribution with slight agglomeration, thus, creating difficulty to estimate average NP sizes. The formed Ag NPs are polycrystalline as indicated by the SAED patterns shown in the insets of corresponding figures. The different density of spatially dispersed metal NPs and varied morphology in photoanode-1 and 2 can have significant influence on photo-sensitization of these metal NPs.

The higher short circuit photocurrent density (J_{sc}) in device-2 as shown in Fig. 3a might be attributed to its higher light absorption and uniform distribution of Ag NPs on TiO_2 compared with that of device-1. Ag NPs loaded by immersion technique have some agglomeration which might be responsible for its lower PEC response. Fig. 3b manifests the photocurrent stability with time. The response of PV cells under illumination on/off cycle indicates the decay of J_{sc}. PV characteristics of both devices are summarized in Table 1. From literature [9], for comparison, the devices based on TiO_2 photoanodes modified with Ag CLs by spray-coating technique have also been included in the Table 1. If optimum conditions are applied to perform PLD; the loading of metal NPs, their distribution and morphology can be changed significantly, which ultimately, influence PV characteristics.

From Fig. 4a, it can be seen that the series resistance (R_s) of device-2 is slightly lower which gives rise to higher fill factor (FF). The longer electron recombination lifetime (τ_r) in device-2 results from the lower characteristic frequency, since the characteristic frequency at intermediate frequency range in Bode phase plots (Fig. 4b) is normally related to τ_r [10]. From Fig. 4c, the slope of the linear region and the x-intercept of that linear region are described as donor density (N_D) and flat band potential (E_{FB}) of photoanodes, respectively. Parameters evaluated from EIS and M–S analysis have also been included in Table 1. Larger J_{sc} obtained in device-2 is likely due to its higher N_D, resulting from its higher optical absorbance and longer τ_r. Carrier concentration is lower in the device-1, largely, due to its lower light absorbance and a bit higher expected electron recombination rate resulting from slight NPs agglomerating effect.

From the mechanism viewpoints, photoelectrons are excited from the Fermi level of Ag NPs by SPR and injected into TiO_2 conduction band followed by its transportation towards current collector. The V_{oc}, being the difference between qusai-Fermi level of TiO_2 and the redox-couple potential, should be larger if N_D is

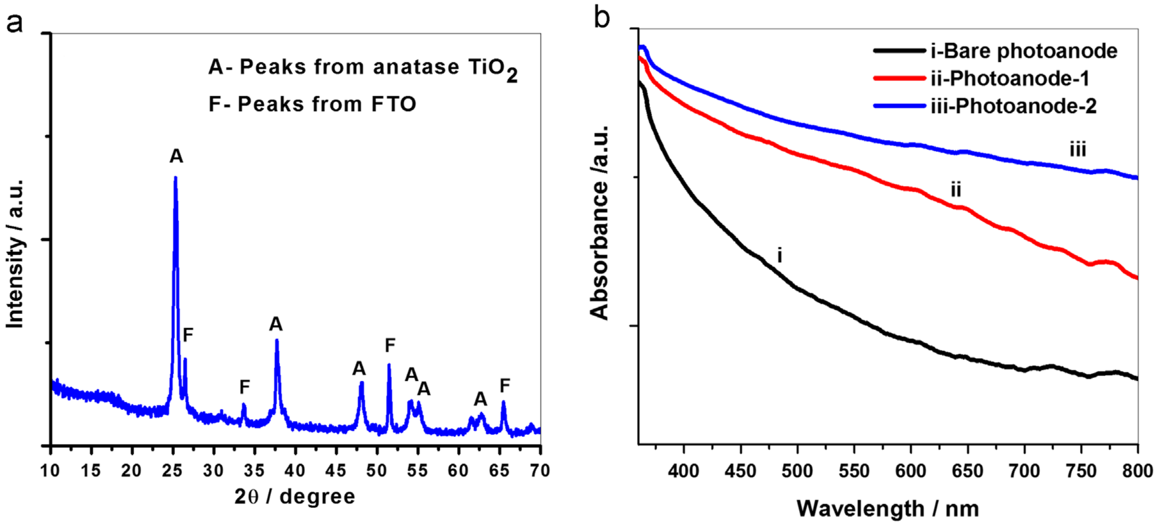

Fig. 1. (a) XRD pattern of anatase TiO_2 and (b) optical absorbance spectra.

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