



Enhanced photoelectrochemical property of gold nanoparticle sensitized TiO₂ nanotube: A crucial investigation at electrode–electrolyte interface



S.K. Jana ^{*}, T. Majumder, S. Banerjee

Surface Physics & Material Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Salt Lake, Kolkata 700064, India

ARTICLE INFO

Article history:

Received 6 March 2014

Received in revised form 19 May 2014

Accepted 26 May 2014

Available online 14 June 2014

Keywords:

Electrodeposition

Interfaces

TiO₂ nanotube

Gold nanoparticle

Photoelectrochemical

ABSTRACT

We have reported for the first time a simple one step electrodeposition of gold nanoparticle (GNP) on TiO₂ nanotube (TNT) structure and GNP sensitized TNT shows enhanced photoelectrochemical property than pristine TNT in visible region. GNP loaded TNT array photoelectrode has a broad visible light absorption (450–700 nm) observed by UV–Vis spectroscopy. The GNPs are photoexcited due to plasmon resonance and facilitates the photogenerated electron–hole pair separation under visible illumination. Electrochemical impedance spectroscopy measurement ensures efficient electron transfer from nanoparticle to TNT. Charge transfer mechanism at electrode–electrolyte has also been investigated using Mott–Schottky analysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Photoelectrochemical (PEC) device is very promising to be used in solar to electrochemical energy generation at lower cost than other renewable devices [1–5]. PEC devices work on the basis of water splitting into hydrogen and oxygen gases by means of solar energy [1]. Electrode of the PEC cells absorbs sunlight and generates charges which split water into hydrogen at the cathode and oxygen at anode. The main challenge would be to find out the proper electrode material with sufficient light absorption in the visible region and low cost of active material. In last decades different materials have been studied, among them mostly studied (ZnO, TiO₂ etc.) are wide band gap materials which use higher energy photons (ultra violet) for activation in PEC performance, this limitation of these materials hinders the efficiency of PEC devices. Hence discovering new materials and tuning the absorption of visible light for the active electrode material is of much interest to the researchers. TiO₂ based PEC devices have been studied mostly because of their high chemical stability or reactivity [6]. Different groups have shown the improvement PEC property on mostly TiO₂ based electrode by coating with various low band gap materials [7–9]. Among them mostly studied are based on Cd based materials which are very toxic and hazardous. So non-toxic material should be the right choice for the PEC based devices. Metal nanoparticles (NPs) attached PEC device would be promising

because of their absorption at visible range. Visible light harvesting method in Si based photovoltaic devices using metal NPs has been reported early [10]. Catalytic study of semiconductor–metal NPs composite structure has been reported in some earlier publications [11–13]. Also charge transfer mechanism from the metal NPs to semiconducting host matrix has the key role for enhancement of the catalytic effect under light illumination.

The preparation method of Au/TiO₂ composite system reported in some earlier articles is mainly on sol–gel [14], dip coating [15], or co-sputtering technique [13] which are relatively prolonged process, requires a number of expensive organic or inorganic solvents. In this article we have reported for the first time a simple one step electrochemical fabrication of gold nanoparticles (GNPs) on TiO₂ electrodeposition method which is comparatively less cost process using single aqueous solvent. Also this process facilitates relatively high speed coating. Apart from the novel fabrication process of GNPs on TiO₂ nanostructure the main aspect of this manuscript is also study the surface plasmon effect on the enhancement of its PEC property under visible light by means of electrochemical impedance spectroscopy (EIS) measurements. Moreover, some crucial results have been investigated in this communication to study the charge transfer mechanism at metal–semiconductor and electrode–electrolyte interface under visible light.

2. Experimental

Ti foils (99.98%, from Sigma–Aldrich) of 0.3 mm thick and 1 cm² were anodized electrochemically in two electrode configuration (Ti

^{*} Corresponding author. Tel.: +91 7501272685; fax: +91 3323374637.

E-mail address: skj_ec@yahoo.co.in (S.K. Jana).

foil adopted as anode and platinum as cathode) at 30 V (DC) for 7 h. An aqueous solution of 0.4 wt% ammonium fluoride mixed with 15 wt% ethylene glycol was used as electrolyte. Ti foils were properly cleaned with ethanol and acetone successively in ultrasonic bath for 15 min prior to anodization process. The anodized samples were then ultrasonicated in water for 1 min in DI water to remove any post anodization deposits. The anodized samples were annealed at 500 °C in air for 5 h to obtain crystallization.

One step electrodeposition technique was employed further to decorate GNPs on TNT substrate using CHI 660 electrochemical workstation with conventional three electrode configuration adopted with Ag/AgCl as reference, Pt wire (0.5 mm) as counter electrode and previously prepared TNT on Ti substrate as working electrode. A mixture of 1 mM chloroauric acid (HAuCl₄) and 1 M phosphate buffer solution (PBS) was used as electrolyte. Deposition of NPs was carried out using cyclic voltammetry (CV) technique maintained between –1.4 and 0 V at scan rate of 20 mV/s for 7 cycles keeping temperature of the electrochemical cell at 50 °C. Finally all the samples were washed in DI water followed by heat treatment at 250 °C for 1.5 h in air prior to any measurements.

All photoelectrochemical measurements were performed in 1 M Na₂SO₄ electrolyte with illumination of 150 W mercury vapor lamp on the working electrode and data were recorded with CHI instrument.

3. Results and discussions

Gold nanoparticles have been grown on TNT substrate by using electrochemical deposition with the CV technique as mentioned above is shown in Fig. 1a. In the CV loop we observe two peaks, oxidation peak and reduction peak as indicated by arrows in Fig. 1a. GNP deposition on TNT surface occurs at reduction potential. This peak corresponds to the reduction of [AuCl₄][–] to Au. There is no change of oxidation peak observed in each cycle. Reduction peaks are getting more negative than oxidation peaks with increase of number of the cycles. Hence it indicates that reduction of gold increases with the cycle numbers, so gold particle density on TNT surface increases with the cycle numbers.

Surface morphology image shown in Fig. 1b of GNPs loaded TNT (GNP_TNT) sample was recorded by SEM (Quanta 200F). Highly ordered TNT is observed in Fig. 1b with the pore diameter of TNT is ~85 nm and the electrodeposited GNPs (size ~30 nm) can be recognized clearly on the periphery of TNT. Energy-dispersive X-ray spectroscopy analysis confirms the presence of GNPs on TNT surface as shown in the inset of Fig. 1b. During gold electrodeposition the current concentrates on the mouth of pore of TNT due to ionic transport through the tube to underneath Ti where the potential is applied. So the peripheral of the TNT mouth surface can act as active site for GNP nucleation. Hence we see GNP deposited mostly on the periphery of the tube.

X-ray diffraction (XRD, Bruker AXS D8 diffractometer) measurements plotted in Fig. 1c of both the samples were used to determine the phase structure of the GNP decorated TNT arrays. Apart from Ti (indicated as 'T'), two sets of diffraction peaks could be seen in GNP loaded TNT sample, corresponding to anatase TiO₂ (indicated as 'A' in XRD pattern) and gold, indicating that the as-synthesized products are composite materials. XRD pattern of bare TNT and GNP decorated TNT provides the information about the anatase TiO₂ prepared by electrochemical anodization technique. Inset of XRD figure clarifies the {220} of pure crystalline structure of face centered GNPs. Diffraction intensity at {004} is the main feature of anatase TNT with preferential growth along {001} direction which is also mentioned in an earlier report [16,17].

UV–Vis absorption spectrum was recorded using Perkin-Elmer spectrophotometer equipped with reflectance accessories. Diffuse

reflectance absorption spectra of as prepared pure and GNPs loaded TNT is shown in Fig. 2. One can easily see that each sample exhibits sharp absorption edge around 350 nm which is the characteristic peak of pure TiO₂ [18], also there is a broad peak with maxima at 530 nm which is actually plasmon resonance peak of individual GNPs decorated TNT heterostructure. Therefore, such GNPs sensitized TNT can absorb wide range (blue to red) of incident spectrum. Underlying dielectric medium (TiO₂) results to broadening of surface plasmon peak [10].

Fig. 3a shows the I–V characteristics of the two TNT samples (loaded and unloaded with GNPs) under the light illumination. For pure TNT sample we observed a very small current density while a pronounced photocurrent density is observed for gold loaded sample implying efficient charge generation and separation in visible light. In fact I–V curve denotes the flow of anodic and cathodic current at active electrode–electrolyte interface with variation of working electrode potential with and without light illumination as shown in Fig. 3b for TNT-gold sample. At lower biasing voltage the tendency of Na²⁺ (red-ox electrolyte Na₂SO₄ used in our experiment) get reduced and forms Helmholtz double layer on GNP_TNT structure. Thus cathodic current flows from electrolyte to the electrode. At some potential (below 0.2 V for both the cases) reduced species get oxidized and anodic current starts increased up to a point (indicated by dashed arrow both under dark and light) then decreases up to certain potential limit i.e. flat band potential (which is clearly explained in Mott–Schottky analysis in Fig. 3c) and remain constant in dark. Almost no anodic or cathodic current follows in each direction at this potential. But under illumination minority charge carrier induced current is attributed because of the depletion of the space charge layer of the electrode–electrolyte interface by the gold NPs induced free charge.

Mott–Schottky (M–S) analysis (variation of capacitance formed between active electrode and electrolyte interface with applied potential) [19] gives an important information about the intrinsic electronic properties of GNP_TNT heterostructure in contact with electrolyte. There are two types of layer formed between active electrode material and electrolyte; space charge layer and Helmholtz double layer which give two capacitances (named C_{sc} and C_{dl} respectively) in series. The double layer capacitance of TNT is much higher than space charge layer capacitance, so that the measured capacitance can be conveniently considered as due to space charge as shown schematically in the inset of Fig. 3c. Thus M–S equation can be expressed as

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\epsilon \epsilon_0 q N_d A^2} \right) \left[(V - V_{FB}) - \frac{KT}{q} \right]$$

where C_{sc} is the space charge capacitance, ϵ is the dielectric constant of TNT, ϵ_0 is the electric permittivity of vacuum, q is the electron charge, N_d is the donor density, A is the area of the active electrode, k is the Boltzmann constant, T is the absolute temperature of the electrochemical cell, V is the electrode applied potential, and V_{FB} is the flat band potential. M–S plot of both pure and GNP_TNT structure is shown in Fig. 3c. The data of this plot was extracted from impedance – potential technique. In this technique we have applied a small ac signal of amplitude 5 mV at 1 kHz frequency to WE with respect to CE. Positive slope of these curve proves TNT nanostructure is n-type. Increase (from –0.34 to –0.37 V) in V_{FB} of GNP_TNT structure over pristine TNT indicates higher carrier concentration in the hybrid system. The intercept of Mott–Schottky plot shows negative shift indicating a very efficient charge separation and transportation. Importantly, GNP_TNT shows substantially higher slopes in M–S plot compared to the pristine TNT sample indicating lower value of C_{sc} (low space charge capacitance) at the GNP_TNT/electrolyte interface than TNT/electrolyte interface. This also indicates that GNP_TNT is more favorable for charge separation and

Download English Version:

<https://daneshyari.com/en/article/218751>

Download Persian Version:

<https://daneshyari.com/article/218751>

[Daneshyari.com](https://daneshyari.com)