Enhanced Photo Electrochemical Performance of CeO$_2$ Functionalized TiO$_2$ Nanotube Arrays with Ag Coating

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Abstract. The photoelectrochemical performance of Ag coated CeO$_2$ functionalized TiO$_2$ nanotube arrays (AgCeTNT) is investigated here. The sample is prepared via three steps, such as synthesis of TiO$_2$ nanotube by electrochemical anodization, CeO$_2$ functionalization by hydrothermal and Ag coating by Successive Ionic Layer Adsorption and Reaction (SILAR) method. X-ray diffraction (XRD) analysis showed the anatase phase formation after annealing of TiO$_2$ nanotubes. Field Emission Scanning Electron Microscopic (FESEM) images showed the conformal coverage of CeO$_2$ and Ag nanoparticles on the surface of TiO$_2$ nanotubes. Energy Dispersive X-Ray (EDX) analysis confirmed the presence of Ce, Ag, Ti and O in the AgCeTNT sample. Diffuse Reflectance Spectroscopy (DRS) study revealed the enhancement in visible light sensitivity with CeO$_2$ functionalization and further with Ag coating. The photoelectrochemical measurement showed that the AgCeTNT sample exhibits improved photoelectrochemical performance compared to bare TiO$_2$ nanotubes (TNT), CeO$_2$ functionalized TiO$_2$ nanotubes (CeTNT) and Ag coated TiO$_2$ nanotubes (AgTNT) under the illumination of sunlight. This improvement in photoelectrochemical performance happened due to the combined effect of favorable band alignment of CeO$_2$ and TiO$_2$ and Surface Plasmon Resonance (SPR) effect of Ag nanoparticles, which lead to superior charge separation, efficient charge transport and enhanced visible light response.

INTRODUCTION

In recent decades, photoelectrochemical water splitting is considered to be one of the cleanest artificial techniques to promisingly address the global concerns related to energy shortage and environmental pollution. TiO$_2$ is an extensively used metal oxide semiconductor in this field owing to its high chemical and thermal stability, biocompatibility and low cost[1]. Among other nanostructures, one-dimensional (1D) nanostructure such as nanotubes, nanorods, nanowires, etc. have been given more interest for solar energy harvesting because of high specific surface area, unidirectional charge transport and unique beneficial properties [2]. However, the utmost utilization of TiO$_2$ in this field for practical applications is limited by its photoactivity in the ultraviolet (UV) region (only 5% of overall solar spectrum) caused by its wide bandgap (anatase phase 3.2 eV and rutile phase 3.0 eV) and fast recombination rate [3]. To date, heterojunction formation with suitable material has emerged to be one of the most efficient approaches to resolve these issues. In recent days, CeO$_2$ is gaining much attention as a companion semiconducting material for heterojunction formation with TiO$_2$ because of its favorable band positions responsible for efficient charge separation, high thermal stability and variable valences Ce$^{3+}$/Ce$^{4+}$ of Ce aided better charge transport [4,5].

On the other hand, in order to improve photocatalytic activity of metal oxide photocatalysts, noble metal nanoparticles such as silver (Ag), gold (Au), platinum (Pt) have been widely used as a coating layer on the surface [6,7,8]. More specifically, Ag has been used, coupled with metal oxides such as TiO$_2$, CeO$_2$ and ZnO to enhance the photoactivity of these materials assisted by SPR effect of noble metals [9,10].
However, there are few reports available on CeO$_2$ functionalization on TiO$_2$ nanotube arrays using several techniques such as electro-deposition[11], microwave homogeneous process[12] and impregnation method[13]. In this study, we synthesized CeO$_2$ functionalized TiO$_2$ nanotube arrays using a hydrothermal process. In addition, Ag nanoparticles were coated on CeO$_2$ functionalized TiO$_2$ nanotube arrays. The microscopic and optical studies were carried out for AgCeTNT in comparison with TNT, CeTNT and AgTNT samples. Their photoelectrochemical water splitting performance was investigated under illumination of solar light.

**EXPERIMENTAL DETAILS**

TiO$_2$ nanotubes (TNT) were fabricated on Titanium (Ti) foil (99.7% purity, Sigma-Aldrich) by electrochemical anodization method as reported to our earlier paper [14] with small change. Ti foil was used as an anode, where Pt was used as a cathode in the anodization set up. A mixture of 4 ml of de-ionized (DI) water, 96 ml of Di-ethylene glycol (DEG) and 0.6 wt% of Ammonium fluoride (NH$_4$F) was used as the electrolyte in the anodization process at a constant voltage of 60 V for 2 hr. Post anodization, the prepared sample was rinsed with isopropanol and DI water and left to dry. The as-prepared amorphous TNT samples were annealed at 450°C for 3 hr to obtain proper phase and crystallinity.

CeO$_2$ functionalization on TiO$_2$ nanotubes was carried out by the hydrothermal method following Han et al. report on TiO$_2$ nanorod functionalization with CeO$_2$ as a core/shell type structure[15]. In this process, the annealed TiO$_2$ nanotube sample was kept inside an autoclave containing a mixture solution of 0.02 mol Cerium nitrate dehydrate (Ce(NO$_3$)$_3$·6H$_2$O) and 0.01 mol hexamethylenetetramine (C$_6$H$_{12}$N$_4$) dissolved in 100 ml DI water and hydrothermally treated at 100°C for 2 hr. This CeO$_2$ functionalized TiO$_2$ nanotube sample is denoted as CeTNT.

Ag nanoparticles were deposited on CeTNT sample by simple SILAR method[16]. Briefly, the CeTNT sample was immersed into 0.01 M NaBH$_4$ ethanol solution and 0.01 M AgNO$_3$ aqueous solution successively for 5 sec in each solution. The cycle was repeated four times to obtain an effective coating of Ag nanoparticles on CeO$_2$ functionalized TiO$_2$ nanotube arrays. The sample was rinsed with DI water and dried under N$_2$ flow. Using the same technique Ag coated TNT sample was prepared. The Ag coated CeTNT and TNT samples are named as AgCeTNT and AgTNT respectively.

The surface morphological study of the samples was carried out by using FESEM (FEI Inspect F50) and elemental composition was investigated by EDX attached with it. The phase analysis was done by using X-ray diffractometer (Rigakusmartlab X-ray Diffretatomter) using CuKα (λ = 0.154 nm) radiation. Optical measurement was carried out in DRS mode by Perkin Elmer LAMBDA 950 UV-VIS-NIR spectrophotometer equipped with integrating sphere accessory.

Photocurrent and photoelectrochemical impedance measurement was done using Oriel Newport 300-Watt Xenon lamp with AM 1.5 G and CH (model CHI6054E) electrochemical instrument.

**RESULTS AND DISCUSSIONS**

Figure 1(a) shows the XRD patterns of as-prepared and annealed (450 °C for 3 hr) TNT samples. The peaks of the as-prepared sample are consistent with the peaks of Ti foil (ICSD reference code: 00-044-1294), whereas in annealed samples some extra peaks are observed at 25.27° and 47.95 which are corresponds to anatase phase of TiO$_2$ having space group I4/m amd [17,14]. There is no evidence of any secondary phase, which confirmed that TNT formed through anodization process is in the pure anatase phase. The surface morphology of TNT, CeTNT, AgTNT and AgCeTNT samples were investigated using FESEM images. Figure 1(b) shows a vertically grown tubular structure of bare TiO$_2$ sample (TNT) on Ti foil. It is observed that nanotubes have an average length of ~ (2.6 ± 0.1) μm with an average pore size of ~ (280 ± 40) nm and a wall thickness of ~ (24 ± 3) nm. The inset of figure 1(b) represents the cross-sectional view of TiO$_2$ nanotubes. The microscopic image of CeTNT sample (Figure 1(c)) showed that the hydrothermal process adopted for CeO$_2$ deposition on the surface of TiO$_2$ nanotubes does not affect the tubular morphology of TNT rather provides a uniform functionalization on TiO$_2$ nanotubes with CeO$_2$. The top view of AgTNT sample is presented in figure 1(d), which shows the uniform distribution of Ag nanoparticles throughout the TiO$_2$ nanotubes. Figure 1(e) shows a conformal coverage of CeO$_2$ and Ag nanoparticles on the surface of TiO$_2$ nanotubes. The elemental composition of AgCeTNT is estimated using EDX spectra (Figure 1(f)) and the table presented in the inset of it confirms the presence of O, Ag, Ti and Ce in the AgCeTNT sample.
FIGURE 1. (a) XRD pattern of as-prepared and annealed TNT, FESEM images of (b) TNT (inset represents the cross-sectional view of TNT), (c) CeTNT, (d) AgTNT, (e) AgCeTNT and (f) EDX spectra of AgCeTNT (inset presents the data table).

The absorbance spectra recorded for all samples using UV-Vis diffuse reflectance spectrometer is shown in figure 2(a). Kubelka-Munk function was calculated from the DRS data [18] and the plot is presented in figure 2(b). The absorption edge for bare TiO$_2$ nanotube appears at ~3.23 eV as observed from the KM plot. The functionalization with CeO$_2$ reduces the effective absorption edge to ~3.18 eV. Further, Ag coating on CeO$_2$ functionalized TiO$_2$ nanotube sample leads to a significant enhancement in overall absorption response in visible light region. This can be attributed to the combined impact of SPR effect of Ag nanoparticles [9] and visible light sensitivity of CeO$_2$ material [19].

FIGURE 2. (a) UV-Vis diffuse reflectance spectra and (b) Tauc plot of TNT, CeTNT, AgTNT and AgCeTNT samples.

Photocurrent for all samples was measured using 0.5 M Na$_2$SO$_4$ aqueous solution as an electrolyte, Ag/AgCl as a reference electrode and Pt as counter electrode under one sun (100 mW/cm$^2$) illumination. Figure 3(a) presents the
photocurrent response of all the samples. Photocurrent density of bare TiO$_2$ nanotube sample is ~0.20 mA/cm$^2$ at 0.6 V (vs. Ag/AgCl), which increases after deposition of CeO$_2$ and with a further coating of Ag nanoparticles. The photocurrent values obtained for CeTNT, AgTNT and AgCeTNT samples are ~ 0.22, 0.25 and 0.28 mA/cm$^2$ respectively. This enhancement of photocurrent with compare to that of bare TiO$_2$ nanotube sample happened due to electron-hole pair separation resulted from the suitable band alignment of CeO$_2$ and TiO$_2$ in CeO$_2$-TiO$_2$ heterojunction and SPR effect of Ag nanoparticles. Moreover, Ce having variable valences such as Ce$^{3+}$/Ce$^{4+}$ shows good electron transfer ability and reduces the recombination chances [20].

![Figure 3](image_url)

**FIGURE 3.** (a) Photocurrent density versus time plot, (b) EIS Nyquist plot for TNT, CeTNT, AgTNT and AgCeTNT samples.

In order to investigate the charge transfer kinetics inside the material and at the interfaces, Electrochemical Impedance Spectroscopy (EIS) measurement was carried out in a frequency range of 0.1 Hz to 1 MHz and presented in figure 3(b). It is observed that arc radius reduces after functionalization with CeO$_2$ on TiO$_2$ nanotube surface compared to that of bare TiO$_2$ nanotube sample. Coating with Ag nanoparticles results in a further decrement in arc radius, indicating the lower charge transfer resistance at the interfaces. The smallest arc radius for AgCeTNT sample compared to that of other samples suggests the faster charge transfer attributed to the synergetic effect of SPR phenomena of Ag nanoparticles and efficient charge separation aided by the favorable band alignment of CeO$_2$-TiO$_2$ heterojunction.

A schematic is presented in figure 4 to clearly understand the energy band alignment and electron transfer pathway inside the electrode and throughout the electrochemical circuit. In general, water molecules get adsorbed on the material's surface, which react with photogenerated charges in the presence of light. Under illumination of light on the exposed surface of CeO$_2$ nanoparticles and TiO$_2$ nanotubes, electron-hole pairs are generated. Due to favorable band alignment of CeO$_2$ and TiO$_2$, the photogenerated electrons are transferred from conduction band (CB) of CeO$_2$ to CB of TiO$_2$, while the holes move in reverse direction i.e., from valence band (VB) of TiO$_2$ to VB of CeO$_2$. Further, electrons are transferred from Ag nanoparticles towards the CeO$_2$-TiO$_2$ heterojunction as a result of SPR effect stimulated by illumination of light. This intern improves the charge separation phenomena. Meanwhile, the holes move towards the electrode surface and get involved in the oxidation reaction of water molecules at the electrode/electrolyte interface. On the other side, electrons move from anode towards the cathode through the outer circuit and interact with water molecules at the cathode surface.
CONCLUSION

In this study, we prepared Ag coated CeO$_2$ functionalized TiO$_2$ nanotube arrays on Ti foil via three-step processes such as electrochemical anodization, hydrothermal and SILAR technique. The AgCeTNT sample showed superior photocatalytic water splitting performance compared to that of TNT, CeTNT and AgTNT samples. This enhanced photo-activity is associated with the synergetic effect of perfect heterojunction formation between two suitable materials like CeO$_2$ and TiO$_2$, and further Ag coating aided SPR effect. This combined effect promotes the separation of photogenerated charges, with providing a feasible electron transfer pathway and extends the light sensitivity towards the visible light region. In addition, the base material being prepared by electrochemical etching method from the Ti foil, it shows high stability and good adhesion on the substrate, which is beneficial for using it as an electrode in practical applications. This study suggests the Ag coated CeO$_2$-TiO$_2$ heterojunction to be a potential photoelectrode material for photoelectrochemical water splitting application.

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