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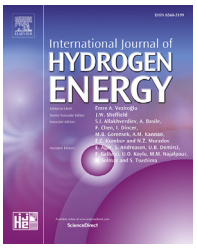

Plasmonic Ag nanoparticles decorated $NaNbO_3$ nanorods for efficient photoelectrochemical water splitting

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ABSTRACT

In the present work, photoanodes comprising of $NaNbO_3$ nanorods and Ag nanoparticles decorated $NaNbO_3$ nanorods have been fabricated by using hydrothermal and chemical solution method respectively. Photoelectrochemical water splitting performance of the fabricated photoanodes have been measured and it is found that Ag decorated $NaNbO_3$ nanorods exhibit ~4 fold enhancement in photocurrent as compared to bare $NaNbO_3$ nanorods. The enhancement in the photoelectrochemical water splitting activity of Ag decorated $NaNbO_3$ nanorods is attributed to efficient charge carrier separation and visible light sensitization due to Ag nanoparticles on $NaNbO_3$ nanorods.

Introduction

Hydrogen, due to its high-energy density and environment friendly nature is proven to be a potential energy carrier for future [1,2]. Photoelectrochemical (PEC) water splitting is a promising method for the generation of hydrogen (H_2) using the abundant solar energy and water [3]. In the PEC process, the photoelectrode comprising of semiconductor material absorbs photons with energy higher than its band gap resulting in the excitation of electrons from the valence band to the conduction band of the semiconductors. These photogenerated electron-hole pairs drive the reduction and oxidation reactions for the generation of H_2 and O_2, respectively [4–6]. The key requirements for achieving high efficiency in the photoelectrochemical process are the low recombination rate of the electron-hole pairs, chemical stability and efficient absorption of the solar spectra by the semiconductor [7–9]. Several semiconductor oxides such as ZnO [10], TiO_2 [11], WO_3 [12] and Cu_2O [13] have been studied for the generation of hydrogen using photoelectrochemical process.

Recently, complex metal oxides such as $BaTiO_3$, $SrTiO_3$ and $BiFeO_3$ have shown a lot of potential for photoelectrochemical activities due to their excellent stability in aqueous electrolytes [14–17]. Among the complex metal oxides, $NaNbO_3$ is also shown to possess high photoelectrochemical activity. But the major drawbacks of $NaNbO_3$ are its wide band gap of (~3.3 eV) and faster recombination rate of the photogenerated charge carriers [18,19]. Due to its wide band gap it absorbs only UV part of the solar spectrum, thereby limiting the use of remaining part [20]. Thus, for an efficient generation of

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hydrogen using $NaNbO_3$, the two main challenges are (i) to reduce the recombination rate of photogenerated charge carriers and (ii) to shift the photoresponse of $NaNbO_3$ to the visible light region to utilize maximum part of solar spectra. In the previous reports, the metal nanoparticles coupled with semiconductor have proved to be one of the most effective strategies to improve the photoelectrochemical activity of wide band gap semiconductors in the visible light region, due to their plasmonic effect [21,22]. The metal nanoparticles have been shown to act as photosensitizers, which absorb the visible light irradiation and transfer the charge carriers directly from excited states of metal nanoparticles to the semiconductor [23,24].

$NaNbO_3$ can be a direct replacement of widely used ZnO and TiO_2 semiconductor thus, to study its visible light responsive PEC activity is of great interest. To the best of our knowledge, there is no report in using Ag decorated $NaNbO_3$ nanorods for photoelectrochemical applications. In the present work, we have synthesized photoelectrode comprising of Ag nanoparticles decorated $NaNbO_3$ nanorods for photoelectrochemcial application. We have demonstrated that decoration of Ag nanoparticle on $NaNbO_3$ nanorods shift the optical response of $NaNbO_3$ nanorods from UV to visible light region result in substantial enhancement in the photoelectrochemical activity. The obtained photocurrent enhancement in Ag decorated $NaNbO_3$ is much higher compared to previously reported Ag decorated ZnO [25] and TiO_2 [26] semiconductors.

Experimental section

Synthesis of $NaNbO_3$ nanorods

$NaNbO_3$ nanorods were synthesized by using hydrothermal method. Initially, a 30 mM of niobium pentoxide (Nb_2O_5) was dispersed in 80 ml of deionized water and stirred for half an hour using a magnetic stirrer. Afterwards, a 3 M NaOH solution was added to the above mixture and stirred for further 2 h. Finally, the mixture was transferred to a 100 ml Teflon-lined stainless steel autoclave which was put into an oven at 150 °C for 48 h for the hydrothermal treatment. The resulting white colour paste was washed several times with deionized water and dried at 70 °C for 4 h.

Synthesis of Ag coupled $NaNbO_3$ nanorods

$NaNbO_3$ nanorods were decorated with silver (Ag) nanoparticles by using a facile chemical solution method. A 100 mg of $NaNbO_3$ nanorods was dispersed in 50 ml of deionized water and then 25 mM aqueous solution of trisodium citrate was added to the above solution and stirred for 30 min afterwards, 25 mM aqueous solutions of $AgNO_3$ were added to the above mixture. A 4 ml solution of $NaBH_4$ was added dropwise into the above mixture and stirred for 1 h. The resulting product was washed 3–4 times with deionized water and finally dried at 70 °C for 2 h. Fig. 1 shows the schematic diagram for the synthesis of $NaNbO_3$ nanorods and Ag decorated $NaNbO_3$ nanorods.

Fabrication of photoelectrodes

For the Photoelectrochemical (PEC) measurements, the photoelectrodes were prepared by coating thin films of $NaNbO_3$ nanorods or Ag decorated $NaNbO_3$ nanorods onto fluorine doped tin oxide (FTO) substrates by using the spray coating technique. The prepared photoelectrodes were covered with insulating epoxy and only a working area of ~0.9 cm^2 left open for photoelectrochemical water splitting reactions.

Characterization

X-ray diffraction patterns of nanostructures were taken by using Rigaku Ultima IV diffractometer equipped with Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range of 20–60° at a scanning rate of 4°/min. The morphological studies were carried out by using FEI Tecnai (accelerating voltage ~200 kV) transmission electron microscope. The compositional analysis was done by using an energy dispersive X-ray spectroscopy (EDX). Optical spectra were recorded by using Perkin Elmer Lambda 1050 spectrophotometer.

Photoelectrochemical measurements

Photoelectrochemical (PEC) measurements were performed in a conventional three electrode cell assembly, where nanostructured photoelectrode, Platinum wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively. A 0.5 M NaOH solution was used as an electrolyte. The photocurrent density, electrochemical impedance spectroscopy (EIS) and Mott-Schottky measurements were carried out using PEC workstation (Zahner Zennium, PP 211). A halogen lamp with intensity ~100 mW cm^{-2} was used as a light source.

Results and discussion

Structural analysis

Fig. 2 shows the XRD patterns of the $NaNbO_3$ nanorods and Ag decorated $NaNbO_3$ nanorods. The XRD patterns of $NaNbO_3$ show the respective peak positions at 2θ values of 22.8°, 23.0°, 32.3°, 32.6°, 39.9°, 40.2°, 46.4°, 46.9°, 52.1°, 52.6°, 57.6° and 57.9° corresponding to (101), (020), (200), (121), (031), (022), (202), (040), (301), (141), (321) and (123) diffraction which confirms the formation of the single phase orthorhombic $NaNbO_3$ (Matched with JCPDS no. 82-0606). For the Ag nanoparticles, peak positions at 2θ values of 38.1° and 44.3° corresponding to (111) and (200) diffraction planes confirmed the formation of cubic phase of Ag nanoparticles. The XRD pattern of Ag coupled $NaNbO_3$ nanocomposite exhibit peaks corresponding to both Ag and $NaNbO_3$, which indicates the presence of both the materials in the nanostructures.

Morphological studies

The morphological analysis of the $NaNbO_3$ nanorods and Ag decorated $NaNbO_3$ nanorods was carried out using

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