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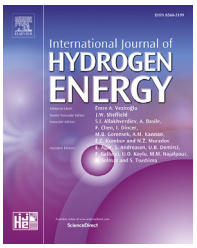

MWCNTs and Cu_2O sensitized Ti–Fe_2O_3 photoanode for improved water splitting performance

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ABSTRACT

Fe_2O_3 and Cu_2O, both earth abundant materials are used in functionalizing Ti doped Fe_2O_3 photoanodes with Cu_2O and MWCNTs for improving photoelectrochemical performance for hydrogen generation. Pristine Ti doped Fe_2O_3 are fabricated by spray pyrolysis deposition method on the conducting ITO coated glass substrate. Two different modifications are adopted to improve the photoelectrochemical performance of pristine sample by subsequent deposition of multi walled carbon nano tubes (MWCNTs) alone and also in combination with Cu_2O. Better photoresponse in modified samples is attributed to increase in conductivity and promotion of electron transport to Fe_2O_3 layer due to presence of MWCNTs while formation of heterojunction also promotes charge transfer kinetics by effective separation of charge carriers. Offering high photocurrent density of 5.17 mA cm^{-2} at 1 V vs SCE, high open circuit voltage (V_{oc}), least resistance, higher negative flat band potential (V_{fb}), Ti–Fe_2O_3/(MWCNTs + Cu_2O), emerges as the most photoactive sample. High applied bias photon to current conversion efficiency (*ABPE*) value of 4.6% is obtained for the modified sample against 0.07% ABPE for Ti–Fe_2O_3 photoanodes.

Introduction

Hydrogen is clean, sustainable and high energy density fuel. In the present scenario, hydrogen production is mainly based on the techniques which release gases like carbon dioxide contributing to global warming [1,2]. The production of hydrogen by the photoelectrochemical (PEC) water splitting is one of the efficient ways to fulfill the growing energy demand [3]. The PEC water splitting technology potentially provides a new insight to fulfill energy demands as it is based on solar energy and water, both of which are plentiful on earth. The

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development of PEC technology involves making suitable light harvesting material having following properties viz. photochemical stability, corrosion resistance, straddling band edge positions, ability to absorb visible portion of sunlight, low rate of recombination to yield high life time of charge carriers and low cost [4–7]. Significant efforts have been made to modify various metal oxide and non-oxide semiconductors to harness solar energy and making them a potential catalyst. Although there are several reports on numerous tactics to improve the PEC performance but the most popular approaches adopted include doping [8–10], heterojunction [11–13], nanostructuring [14–16], quantum dot sensitization [17,18], plasmons [19,20] and ion irradiation [21,22].

Hematite (α- Fe_2O_3) is a photoactive material with a high potential to be used as catalyst in PEC water splitting. Besides the appropriate band gap (1.9–2.2 eV) lying in visible region, other captivating characteristics include abundance, low cost, non-toxicity, photochemical stability and non corrosive nature. However, the drawback of using hematite lies in its poor water oxidation reaction kinetics which requires high applied bias for oxygen evolution reaction. The other issues involved are high recombination rate of photoexcited charge carriers, short diffusion length of minority charge carriers and poor electrical conductivity. Doping, formation of heterojunction and nanostructuring have been adopted to aggrandize the performance of hematite [23–25].

Cu_2O, a p-type semiconductor with band gap of 1.9–2.2 eV is yet another attractive metal oxide with more or less similar encouraging properties as that of hematite such as opulence, non toxic nature, ascendable and economical. Hydrogen production is feasible by Cu_2O even without the application of external bias due to its straddling band edges with water redox potential. But the application of Cu_2O as competent material for PEC water splitting is hampered by its susceptibility towards photocorrosion and inadequacy for collection of charge carriers [26–27].

Recent studies on carbon nanotubes (CNTs) suggest that they offer excellent electrical and mechanical properties, large surface area and ability to store electrons and also used as supporter for energy storage and conversion. CNTs render the conduction of photogenerated charge carriers and also increases charge injection and extraction [28–32]. The single walled carbon nano tubes (SWCNTs) can be used as channel for transporting electrons in PEC cell for improved PEC conversion efficiency due to their electron accepting properties has been recently demonstrated [33,34]. D. Das et al. investigated the role of CNTs in addressing the corrosion issues in Co_2P/CNT by acting as conductive support for the easy transportation of electrons [30]. E. Kecsenovity et al. studied the role of CNTs in overcoming instability and corrosion issues in special context to Cu_2O and their study revealed that CNTs help in rapid charge carrier separation and transport and in turn was responsible for higher photocurrent and stability. Long term PEC measurements were performed by Kecsenovity et al. with Cu_2O and CNT/Cu_2O and observed 25% of initial photoactivity was retained by Cu_2O alone while 66% was retained by CNT/Cu_2O. The increased stability of CNT/Cu_2O photocathode was attributed to the introduction of highly conductive nanostructured scaffold [35]. Ternary Ag/TiO_2/CNT photoanode was found to exhibit effective interfacial electron transfer which was attributed to the synergetic effect of Ag nanoparticles and CNTs [36]. Improved visible light photoactivity was found in CNTs/MnO_2–C_3N_4 ternary catalyst. CNTs induces evolution of hydrogen by facilitating electron capture from C_3N_4 and MnO_2 helps in oxygen evolution by the decomposition of hydrogen peroxide and this leads to effective separation of photogenerated electron-hole pairs [37]. CNT/g-C_3N_4 photocatalysts was synthesized by Song et al. and enhanced hydrogen production was observed due to synergistic effect between CNTs and g-C_3N_4. Photoelectrons attracted by the CNTs are rapidly transferred to the catalyst interface which resulted in better charge separation as well as effective use of photoelectrons by g-C_3N_4. The stability of g-C_3N_4 was also improved due to the presence of CNTs [38]. ZnO/MWCNT nanocomposite photoelectrode exhibited five times higher photocurrent density (1.14 mA/cm^2 at 1 V vs. Ag/AgCl) in comparison to bare ZnO (0.24 mA/cm^2 at 1 V vs. Ag/AgCl) and this enhanced response was attributed to the conducting CNT scaffolds which promotes charge collection and transport in the ZnO/MWCNT nanocomposite [39].

Fe_2O_3-CNT composite and Fe_2O_3 photoanode modified with MWCNTs have shown remarkably enhanced PEC water oxidation [40,41]. Liu et al. obtained improved PEC response by incorporating functionalized CNTs in Ti-doped Fe_2O_3 thin films showing improved absorption of visible portion of sunlight, reduced recombination of excitons and fast charge transfer [42]. For water purification, in terms of Rhodamine B degradation, enhanced photocatalytic activity of Fe_2O_3/MWCNTs/RGO composite was demonstrated by Pawar et al. [43]. Li et al. studied Co/Cu_2O nanomaterial based on carbon nano tubes which showed enhanced photocatalytic water splitting property [44].

Besides the modification of Fe_2O_3 and Cu_2O with CNTs, an efficient approach is formation of heterojunction between them owing to Z-scheme band alignment (staggered type). This type of band arrangement is of great importance due to their effective charge separation and transfer. Heterojunction α-Fe_2O_3/Cu_2O composite and Ti–Fe_2O_3/Cu_2O bilayered thin films for photoreduction of CO_2 and PEC water splitting for hydrogen generation respectively has been reported in the recent past. The photostability problem of Cu_2O can also be combated by forming type II band alignment with another semiconducting material [45,46].

Recent reports on hematite reveal that co-doping by Sn and Co resulted in photoelectrochemical response of 1.25 mA/cm^2 at 1.23 V/RHE [47]. Hydrothermally fabricated α-Fe_2O_3/CQDs heterojunction photoanode shows eight time increment in photocurrent density (0.35 mA/cm^2 at 1.23 V/RHE) in comparison to bare hematite [48]. Zhang et al. investigated the effects of Sn precursors on the morphology, surface characteristics and the PEC properties of hematite photoanode and maximum photocurrent achieved was 1.54 mA/cm^2 at 1.23 V/RHE [49].

In the present study, we have designed and developed Ti-doped Fe_2O_3based photoanodes modified with MWCNTs alone and MWCNTs-Cu_2O nanopowder composites. We schematically show here the various approaches taken in this study with the sole aim to improve the performance of α-Fe_2O_3 (Fig. 1). To enhance the electrical conductivity of hematite, Ti was used as dopant and this material was considered as pristine sample. MWCNTs as a layer was deposited over the Ti–

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