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Surface modification of aligned TiO_2 nanotubes by Cu_2O nanoparticles and their enhanced photo electrochemical properties and hydrogen generation application

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ABSTRACT

In this work, we report the synthesis of cuprous oxide (Cu_2O) nanoparticles modified vertically oriented aligned titanium dioxide (TiO_2) nanotube arrays through wet chemical treatment of TiO_2 nanotubes and their multi-functional application as enhanced photo electrochemical and hydrogen generation. The synthesized samples were characterized by X-ray diffraction, SEM, TEM, and UV–Vis spectroscopy. The structural characterization revealed that the admixed Cu_2O nanoparticles on the TiO_2 surface did not alter its crystalline structure of vertically oriented aligned TiO_2 nanotube. The photocatalytic performance and hydrogen generation of as synthesized Cu_2O nanoparticles modified aligned TiO_2 nanotube was found to highly depend on the Cu_2O content. The optical characterizations reveal that the presence of Cu_2O nanoparticles extends its absorption into the visible region which improves the photocurrent density in comparison to pristine aligned TiO_2 nanotubes electrodes due to enhanced photoactivity and better charge separation. The optimum photocurrent density and hydrogen generation rate has been found to be 3.4 mA cm^{-2} and 127.5 μmole cm^{-2} h^{-1} in 1 M Na_2SO_4 electrolyte solution under 1.5 AM solar irradiance of white light with illumination intensity of 100 mW cm^{-2}.

Introduction

In recent years, hydrogen as a fuel has attracted much attention for scientists and engineers from all over the world due to its promising and challenging issue in the conversion of solar energy into chemical energy. Hydrogen fuel is clean, climate friendly and renewable energy source, therefore, is attracting more and more research interests and large number

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of patents and scientific literature published on hydrogen generation for fuel using semiconductors as the photoactive components. Hydrogen produced from water, after use in fuel cell or internal combustion engine (ICE) burns back to water and can be produced from a variety of feedstocks. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (*e.g.* sunlight, wind, wave or hydro-power etc.). A variety of process technologies has been reported, including chemical, biological, electrolytic, photolytic and thermo-chemical. Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges.

The semiconducting material such as titanium dioxide (TiO_2) electrode in a photoelectrochemical solar cell was first used by Fujishima and Honda in 1972 [1] for hydrogen production through dissociation/splitting of water. Since then there has been enormous investigations of these for hydrogen production employing material tailored versions of TiO_2 electrodes [2–14]. One dimensional (1D) grown TiO_2 nanotubes have been employed extensively for hydrogen production [14–16]. The 1D TiO_2 nanotubes arrays gain much attention because of their high self-organization, superior chemical stability, structure controllability, good light-trapping properties and simple fabrication process [17–20]. The material tailoring has been done to lower the band gap of TiO_2 which is 3.2 eV and hence responds in ultraviolet region of the spectrum. The lowering of the band gap improves the solar response in the visible region.

In addition, the high recombination rate of photogenerated electron-hole pairs in TiO_2 nanotubes under UV light irradiation results in low quantum efficiency of photocatalytic reactions. To improve for high quantum efficiency, a variety of strategies have been attempted including doping with a metal or non-metal [21,22], and coupling with organic dye or suitable narrow-band semiconductor to obtain high and efficient photoelectrochemical (PEC) solar cells for hydrogen production [23–27]. For example, it has been reported previously that heterostructure electrodes consisting of narrow gap semiconductors as light absorbers and wide gap semiconductors as stabilizers can be prepared for applications in photoelectrolysis [28–30]. These studies involved single crystal Si, GaAs, GaP [28,29], CdS [28,29], CdSe, ZnTe [28], InP [29], and GaAlAs [30] as the absorbers and polycrystalline thin films TiO_2 [28–30], Al_2O_3; SnO_2 [28,30], $SrTiO_3$ [28] and Nb_2O_5; SiN_4 [30] for corrosion inhibition. The limitation of these studies originated from the fact that the light generated minority carriers in the narrow gap absorber were not efficiently transferred into the wide gap material and lost due to recombination. Different approaches have been pursued to harvest a larger portion of sunlight. Among them, sensitization of TiO_2 with narrow bandgap semiconductors, including CdS, CdSe, Fe_2O_3, SnO_2, etc, has been reported recently to reveal promising spectral response under visible light illumination [5,20,27,31–34].

The cuprous oxide (Cu_2O) is a p-type semiconductor with direct band gap containing comparatively low band gap (1.9–2.1 eV) [35,36] and exhibits a variety of interesting application and widely-used for solar cells [37], Li-ion battery systems (negative electrode material) [38], superconductors [39], magnetic storage systems [40], gas sensors [41], photothermal [41] and photoconductive systems [42] etc. The other important application of Cu_2O is that it is capable of absorbing and adsorbing a relatively large amount of oxygen both in bulk and on the surface. This excess oxygen on the surface or in the bulk leads to p-type semiconducting behaviour and unique oxidation catalytic properties of Cu_2O. When Cu_2O is illuminated with visible light radiation in an aqueous media/moisture, these excess oxygen species are released making it a unique material for photocatalytic splitting of H_2O into H_2 and O_2 [43].

It is worth stating that, the photovoltaic ability of Cu_2O was elucidated by researchers during the mid-seventies due to its high optical absorption properties in the visible region of the electromagnetic spectrum. The material was identified as a possible low cost material for solar cell applications. Cu_2O still remains an attractive alternative to silicon and other semiconductors for the fabrication of cheap solar cells for terrestrial applications. The advantage of the materials over others in the photovoltaic field include: (1) abundance, (2) easy preparation and (3) nontoxic nature. Cu_2O based solar cells are known to have a theoretical energy conversion efficiency of 22% in AM1 (Air Mass 1, i.e. on the earth surface at the equator) conditions [44]. So far, the highest actual (practical) efficiency obtained for Cu_2O cells is 2% [37]. This inability to reach a high efficiency could be attributed to the fact that light generated charge carriers in the micron-sized grains are not sufficiently transferred to the surface and are lost due to recombination effect.

In absence of suitable electron donor Cu_2O is prone to photo-degradation into Cu metal by the following pathway in aqueous electrolyte under illumination:

$$Cu_2O(s) + 2H^+ + 2e^- \rightarrow 2Cu(s) + H_2O \tag{1}$$

This degradation is a result of the fact that the copper redox potentials lie within the Cu_2O band gap [45]. Several schemes have been investigated to improve the stability of Cu_2O. Depositing a protective layer on Cu_2O or their composite with stable materials prevents the photocorrosion of Cu_2O. Paracchino et al. [45] and Segar et al. [46] have shown that depositing a protecting nanolayer of TiO_2 on Cu_2O can protect Cu_2O against photocorrosion. Teng et al. [47] reported that in presence of WO_3 electrodeposited Cu_2O powders shows stability against photocorrosion. Lin et al. [48] found that NiO_x modified Cu_2O electrode and later on Zhang et al. [49] reported the carbon layer on Cu_2O shows many fold photostability of the Cu_2O. Zhang et al. [50] reported that using electrochemically synthesized Cu_2O/CuO composite also prevents the photocorrosion of the electrodes.

The combined structure of two different semiconductor material (Cu_2O and TiO_2) are more beneficial for the electron transfer between their energy band structures and shows the improved application in various research areas. Recently, Hou and his co-workers showed the significant increase in the photocurrent by Cu_2O/TiO_2 heterojunction synthesized by photoreduction [51]. Siripala et al. prepared Cu_2O/TiO_2 heterojunction as a potential thin film photocathode with high activity for hydrogen production [52]. Detailed mechanism of interparticle electron transfer in xCu_yO_z/TiO_2 heterojunctions has been discussed by Helaïli et al. [53]. Tsui et al. reported the

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