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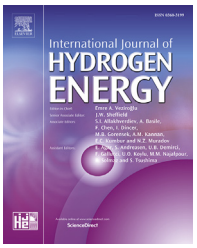

Influence of the morphology of ZnO nanowires on the photoelectrochemical water splitting efficiency

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ABSTRACT

Defect-free ZnO nanowire arrays were synthesized and assessed as photoanodes in photoelectrochemical cells. Several tens of samples classified into five different average diameters in the range 40–260 nm were prepared to explore the role of morphology and polar surfaces. The photoelectrochemical performance of the NWs was studied in basic aqueous electrolytes (pH 12.7). A non-monotonic behavior of the performance was demonstrated, which maximizes for nanowires with diameter ~120 nm. The maximum applied bias photoconversion efficiency is ~6.3% upon irradiation with 11.5 mW at 365 nm. The photoanodes exhibit a rather stable performance for ~10 h, while they stabilize at ~60% of the initial photocurrent after 20 h of continuous bias illumination. The degradation of their performance was attributed to partial detachment of the NWs from the supporting conductive film. The enhanced stability is attributed to the decrease of the pH at the electrochemical interface to values that inhibit the dissolution of ZnO.

Introduction

The low-cost supply of electricity using renewable energy sources, particularly solar, is today one of the pervasive challenges worldwide aimed at alleviating the quick depletion of natural resources and mitigating carbon dioxide emissions. Photocatalytic and photoelectrochemical (PEC) water splitting is a promising way for solar-driven hydrogen production, among various renewable energy technologies [1]. Hydrogen production by reforming natural gas with steam is accompanied by carbon dioxide emission, while electrolysis of water doesn't entail this shortcoming. A large number of investigations is currently underway to develop PEC cells with high stability and efficiency because the possibility of hydrogen use at large-scale as a transport fuel increases the potential for the above-mentioned renewable energy technology [2–7]. Metal oxide semiconductors possess a special placement in preparing anodes for photo-electro-catalytic water splitting. Apart from TiO_2 which stands as the most thoroughly explored material, other metal oxides have also been scrutinized as alternative solution to TiO_2. Despite the many advantages that these materials exhibit in photocatalytic water splitting, i.e. low cost, stability in harsh liquid environment, resistance to photocorrosion, the fact that are mostly wide bandgap semiconductors, i.e. absorb in the UV spectral region, poses serious limitations in the exploitation of direct sunlight for PEC cells operation. Therefore, sensitization of wide bandgap semiconductors (by doping) to enhance

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visible light absorption or use of other narrow band metal oxides, is a common approach to confront the decreased absorption of solar spectrum [6,7].

Besides optimizing the material's bandgap, rational strategies for highly efficient water splitting have also explored the role of the morphology of the nanostructured photoanode materials. For more than a decade efforts are concentrated on moving from nanoparticle-based films to one-dimensional (1-D) nanostructures, such as nanorods (NRs) or nanowires (NWs) and their derivatives. The advantage of 1-D structures for solar-based renewable energy sources have been discussed recently in terms of the benefits they offer in both the photogeneration and the separation of excitons by the built-in electric potential gradient [8]. Indeed, NWs have the advantage of fast electron conduction along the main axis of the wire. This advantage results in a more efficient collection of electrons in NWs owing to the decrease of collection time. On the contrary, in nano-particulate films the scattering of electrons across the particle grain boundaries leads to trap-limited diffusion with negative consequences in the performance of the device. Further, if NWs are prepared as single crystalline (defect-free) structures they offer fewer sites for electron trapping. Good crystallinity enhances fast electron transport towards the conductive glass electrode. Consequently, electron transport in single-crystalline NWs is expected to be several orders of magnitude faster than the transport in particulate films where diffusion is dictated by percolated-type random walk. Given this context, ZnO has attracted considerable interest over the last few years as an alternative to TiO_2 anode material for PEC water splitting as it exhibits a dazzling variety of nanostructure configurations, with 1-D structures being the dominant morphology. While both ZnO (~3.37 eV) and TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) have comparable optical bandgaps, the former exhibits much better electrical properties. The mobility of an individual ZnO NW has been measured to be 1–5 $cm^2 V^{-1} s^{-1}$; this translates to an electron diffusivity in the range 0.05–0.5 $cm^2 s^{-1}$ [9]. These values are three orders of magnitude larger than the best diffusivity measured for TiO_2 and ZnO nano-particulate films in solar cells [10].

Synthesis of ZnO nanostructures can take place using a variety of vapor phase and solution phase methods [11–15]. Among them, chemical bath deposition (CBD) has emerged as a promising method to grow NW arrays with a reproducible manner [16]. Usually CBD is a two stage method. In the first stage, a seed layer of ZnO nanocrystals is deposited on the substrate from the thermal decomposition of a zinc precursor [17]. Other methods for the formation of the seed layer include electrodeposition [18,19] and sputtering [20,21]. In the second stage, growth of the NWs inside an aqueous solution take place at temperature below 100 °C for several hours. Different growth solutions have been proposed in the literature, containing a zinc precursor, a source of OH^- ions and different substances in order to control the length and the diameter of the NWs [12,16].

In the current work we present a detailed study of the influence of the nanowire morphology on the PEC properties of ZnO NW arrays. A large number (several tens) of ZnO NW arrays with different average NW diameters in the range 40–260 nm were grown and characterized morphologically and optically. Their PEC properties are explored in detail demonstrating a non-monotonic behavior of the PEC activity against the average NW diameter and the total surface area. The role of the polar-to-nonpolar surface area on the PEC efficiency of the ZnO photoanodes is discussed in detail. Extensive stability tests under continuous bias illumination reveals that the prepared ZnO photoanodes exhibit much better stability than that reported up to now in the literature. The long term stability is attributed to the transient decrease of the pH at the electrochemical interface to values that inhibit the dissolution of the vulnerable to strongly basic media ZnO nanostructures.

Brief survey on the PEC performance of various ZnO nanostructures

Despite that the number of studies concerning the use of ZnO-based nanostructures in PEC processes is considerably lower than that related to TiO_2-based materials, a rather good deal of information has already been acquired over the last few years. The primary focus has been the assessment of the influence of the particular nanostructure morphology on the PEC efficiency, while doping – mainly by nitrogen – has also been contemplated to modify the photoanode material rendering absorption more efficient in the visible part of the spectrum. We briefly present in this section the progress in the field placing the emphasis on neat ZnO structures, as mixed crystals and heterostructures have been reviewed in recent articles and are beyond the scope of the current work.

Ahn et al. [22] have shown that alignment of ZnO NWs vertically oriented to the substrate provides much more efficient PEC response than that obtained by polycrystalline powders. Extending this exploration, the same group compared the PEC performance between various morphologies of ZnO reporting an appreciable increase (by a factor of 5) of the photocurrent in the order compact films → nanorods → nanocorals [23]. Wolcott et al. [24] prepared ZnO nanocrystals by pulsed laser deposition using different deposition geometries. They assigned the PEC efficiency improvement to differences such as film porosity, charge transport properties and defect concentration. Chen et al. [25] reported a threefold increase of PEC performance of ZnO NW arrays (4 μm long, 150 nm in diameter) upon sensitization to the visible spectrum by CdTe quantum dots.

The role of the nanocrystal morphology was explored by comparing the PEC properties and photoconversion of ZnO nanosheets and nanotubes [26]. The former (sheets) expose predominantly the polar (0001)-Zn and $(000\bar{1})$-O surfaces while the latter (tubes) expose the non-polar facets. The absence of the polar surfaces in ZnO nanotubes resulted in a decreased PEC efficiency by a factor of 3 in comparison to the nanosheets. Qiu et al. [27] compared the efficiency of ZnO nanotetrapods (NTs), branched NTs, and nitrogen-doped NTs observing a substantial increase in PEC performance between the first and the third structure by a factor of ~20. Hsu et al. [28] reported that the very low PEC efficiency of pure ZnO nanorods improves by an order of magnitude after hydrogen treatment or Al doping. Covering ZnO NW arrays by a thin TiO_2 shell was found not only to improve the material's stability against photodegradation but also results in an enhancement of

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