Protection of inorganic semiconductors for sustained, efficient photoelectrochemical water oxidation

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ABSTRACT

Small-band-gap ($E_g < 2$ eV) semiconductors must be stabilized for use in integrated devices that convert solar energy into the bonding energy of a reduced fuel, specifically $H_2(g)$ or a reduced-carbon species such as CH_3OH or CH_4. To sustainably and scalably complete the fuel cycle, electrons must be liberated through the oxidation of water to $O_2(g)$. Strongly acidic or strongly alkaline electrolytes are needed to enable efficient and intrinsically safe operation of a full solar-driven water-splitting system. However, under water-oxidation conditions, the small-band-gap semiconductors required for efficient cell operation are unstable, either dissolving or forming insulating surface oxides. We describe herein recent progress in the protection of semiconductor photoanodes under such operational conditions. We specifically describe the properties of two protective overlayers, TiO_2/Ni and NiO_x, both of which have demonstrated the ability to protect otherwise unstable semiconductors for >100 h of continuous solar-driven water oxidation when in contact with a highly alkaline aqueous electrolyte (1.0 M KOH(aq)). The stabilization of various semiconductor photoanodes is reviewed in the context of the electronic characteristics and a mechanistic analysis of the TiO_2 films, along with a discussion of the optical, catalytic, and electronic nature of NiO_x films for stabilization of semiconductor photoanodes for water oxidation.

1. Introduction

The efficient, sustained oxidation of water is a crucial component of a photoelectrosynthetic solar fuels generator [1,2]. Cathodic fuel-forming reactions such as the hydrogen-evolution reaction (HER) [3–5] or the carbon-dioxide-reduction reaction (CO_2RR) [6] both require the presence of electrons that must come from water oxidation (the oxygen-evolution reaction, OER) to ensure sustainability and global scalability. Since the pioneering work by Honda and Fujishima on TiO_2 in 1972, easily prepared, inexpensive, and earth-abundant semiconductor materials such as TiO_2 have been known to effect stable light-driven water oxidation [7]. Such materials generally have a large band gap (>3 eV) and

therefore can contribute significantly to the required voltage needed for sustained water splitting, ~1.5–1.7 eV, when highly active catalysts of the HER and OER are employed in a minimally resistive cell. Metal oxide photoanodes are however generally limited by either low maximum photocurrent densities and/or instability in relevant media [8–14].

Although only 1.23 V of potential difference is required to overcome the thermodynamic barrier for the simple process of water splitting, in practice, higher voltages are necessary to overcome solution losses and kinetic barriers to the reactions (Eq. (1)). In Eq. (1), η_{HER} is the overpotential for the HER, η_{OER} is the overpotential for the OER, and iR is the resistance loss through the solution.

$$V_{\text{water splitting}} = 1.23\,V + \eta_{HER} + \eta_{OER} + iR \tag{1}$$

Using a single light absorber [15], sustained water splitting is generally limited in the maximum attainable photocurrent density under 1 Sun illumination, because the band gap of the required light absorber is too large to effectively absorb most of the solar

spectrum. In contrast, a tandem-device architecture, in which two separate semiconductor materials each provide a substantial contribution toward the needed photovoltage, can produce much higher efficiencies [16–18]. Technologically important semiconductors such as silicon [19], Group III–V [20], and the Group II–VI [21] semiconductor families, which are generally regarded as 'small band-gap' materials with the appropriate band gaps of 1.1–1.7 eV for optimal efficiency [16,22], provide attractive materials options for the construction of such tandem structures.

However, small-band-gap semiconductors generally corrode under anodic operation, either by active dissolution or by the formation of insulating oxides [23]. The formation of insulating oxides leads to reduced performance or complete non-performance, whereas active corrosion by dissolution catastrophically destroys the semiconductor photoanode. The requirements for a protection layer thus include that it must be: Stable in the thermodynamic, kinetic, and mechanical senses when incorporated onto the semiconductor, immersed in the electrolyte, and operated at the potentials of interest; Active catalytically for the OER, either possessing intrinsic catalytic activity or integrating the activity of a co-catalyst; capable of providing Built-in electronic asymmetry to allow for the separation of electrons and holes, or to allow for a separate buried junction to perform efficiently; Optically transparent to provide optical properties that are optimized for the transmission of light; and, capable of providing low Resistance, to allow for charge-carrier conduction with minimal performance loss due to *iR* drops. These properties are collectively termed "SABOR".

Protective coatings have been investigated in detail, but with only secondary emphasis on operation in highly alkaline (pH 14) media. Thin metal films have been used for this purpose [24–26], although work has mostly focused on the behavior of photoanodes in buffered media at near-neutral pH. A thin layer of Ni has been shown to provide substantial stability for Si photoanodes in alkaline media [26]. TiO_2 has been investigated and used as a protective film in alkaline and acidic media, but coatings thicker than a few nm were observed to be highly electrically resistive [27]. Other conventional n-type transparent conductive oxides eventually failed due to corrosion or due to other effects [28] in alkaline media.

We describe herein recent progress in two approaches to enhance the stability of such semiconductor photoanodes while allowing for sustained, efficient water oxidation under conditions where intrinsically safe, efficient solar-driven water-splitting systems can be constructed. In one implementation, TiO_2 is used as a protection layer with a sputtered Ni OER catalyst. We additionally elucidate the applicability of the TiO_2/Ni layer in terms of morphologies, semiconductors, and electrolytes; the energetics at the semiconductor/TiO_2 and the TiO_2/liquid junctions; and mechanisms of charge conduction. For the second implementation, we describe the development of reactively sputtered protective layers of NiO_x onto various semiconductor surfaces, and also describe the optical, catalytic, and electrical properties of such NiO_x films.

2. Previous work

Materials such as $SrTiO_3$, $KTaO_3$, and TaON are stable as photoanodes for water oxidation, but necessarily have low solar-to-hydrogen efficiencies due to their large band gaps precluding absorption of much of the terrestrial solar spectrum [29]. Generally, a tandem structure or triple junction structure is necessary to produce sufficient voltage and current density for efficient water splitting [19,20,30]. In addition to use of semiconductor/liquid interfaces as the voltage-generating junction, buried-junction structures, including planar p-n homojunctions [31,32], semiconductor/metal Schottky barriers [33,34], spherical [35] and radial-junction microwire [36] electrodes,

heterojunctions [37,38], metal-insulator-semiconductor contacts [9,15], and emitters derived from in situ inversion layers [21] have all been investigated for use in photoelectrosynthetic or photovoltaic-biased electrosynthetic cells [39]. The efficiencies and main performance characteristics of various reported solar-driven water-splitting systems have been recently compiled [40].

Due to the instability of these small band-gap semiconductors toward photocorrosion, the semiconductors must be kinetically stabilized and/or protected by an overlayer in contact with aqueous electrolytes. The extensive historical efforts to stabilize photoanodes and photocathodes for water splitting, specifically focusing on the development of protection schemes, have been reviewed recently [41]. Some examples include work by Chen, McIntyre and coworkers demonstrating that TiO_2 as a tunnel oxide, with a sputtered Ir co-catalyst, can stabilize silicon as a photoanode in acidic, neutral, or basic media [27]. Kenney, Dai and coworkers demonstrated that a thin Ni film allowed for photoelectrochemical water oxidation in both alkaline (pH 14) and borate (pH 9.5) buffers, although these samples generally exhibited a decrease in stability after 24 h of operation [26]. An alternate approach by Mei, Chorkendorff, Vesborg and coworkers used thin Ir/IrO_x as a protection and catalytic layer for silicon in acidic (1 M H_2SO_4) media [42]. Amorphous Si:H triple junctions protected by transparent conductive oxides (TCOs), in conjunction with either Pt or with earth-abundant electrocatalysts, have produced solar-to-hydrogen efficiencies of up to 5% [43]. a-Si:H devices that are protected on one side by ZnO in conjunction with a Co-Mo HER catalyst, and protected on the other side by SnO_2 in conjunction with an Fe-NiO_x OER catalyst, have yielded $\eta_{STH} = 2.5$–3.0% in 1.0 M KOH(aq), with stability for >18 h of operation [44]. Operation in aqueous alkaline electrolytes allows the construction of efficient, intrinsically safe systems and allows use of highly active, low overpotential, earth-abundant electrocatalysts based on Ni and related alloys [45]. In accord with established properties of commercial electrolyzers, an intrinsically safe electrolysis or photoelectrolysis system does not produce a flammable, potentially explosive mixture of $H_2(g)$ and $O_2(g)$ in the reactor at any point in space or time. Common TCO's, such as indium tin oxide (ITO), are not stable in alkaline electrolytes [30,46], consequently prior solar-driven water-splitting devices and systems based on a-Si:H triple junctions in 1.0 M KOH(aq) failed due to the lack of a stable protective anode coating. In electrolytes buffered in the bulk to near-neutral pH values, Nocera and coworkers constructed both photoanodes [47] and integrated water-splitting devices [30] by use of a transparent conductive oxide as a conductive contact between the PV cell and Co-based electrocatalysts [48]. Electrolysis or photoelectrolysis systems that are operated in buffered or unbuffered bulk near-neutral pH electrolytes are inefficient and/or not intrinsically safe [17,48–50].

3. TiO_2

3.1. Background

TiO_2 was investigated as a photoanode for water splitting [7] before being used in dye-sensitized solar cells [51]. TiO_2 has also been used as a gate dielectric [52], with different deposition conditions producing markedly different conductivities and materials properties. TiO_2 has been used as a protection layer, but films thicker than a few nm were highly resistive [27].

3.2. Planar materials and ALD-TiO_2

TiO_2 deposited using atomic-layer deposition (ALD) at 150 °C from tetrakis dimethylamido titanium (TDMAT) is highly resistive as-deposited. Unless indicated otherwise, "ALD-TiO_2" generally refers to films produced in this manner from this precursor. These