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Growth of bismuth oxyhalide nanoplates on self-standing TiO$_2$ nanowire film exhibiting enhanced photoelectrochemical performances

Jun Wu[a,b], Xuebo Cao[c,*]

[a] Nanhu College, Jiaxing University, Jiaxing, Zhejiang 314001, China
[b] College of Chemistry, Chemical Engineering and Material Science, Soochow University, Suzhou, Jiangsu 215123, China
[c] School of Biological and Chemical Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, China

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ABSTRACT

We report the sequential modification of the free-standing TiO$_2$ nanowires film with Ag nanoparticles and BiOX (X = Cl, Br, and I) nanoplates, for a purpose of achieving an efficient photoelectrochemical cells (PECs). In the resulting BiOX-Ag-TiO$_2$ film, Ag nanoparticles densely coated on the broad and flat surfaces of TiO$_2$ nanowires increase the conductivity of TiO$_2$ by 10^7 and enable the film to propagate electrons rapidly. BiOX nanoplates obliquely grown on the Ag-coated TiO$_2$ nanowires can move the absorption edge of the film into the region of visible light and endow the film with the anti-reflection property. Especially, when the BiOCl-Ag-TiO$_2$, BiOBr-Ag-TiO$_2$, and BiOI-Ag-TiO$_2$ films are overlapped to form a laminated film, the anti-reflection response is further promoted. Besides the above optical and electronic metrics, the band alignment in the multi-component system favors the directed flow of photogenerated electrons from BiOX and TiO$_2$ to Ag, thus efficiently blocking the recombination of the e$^-$–h$^+$ pairs. Therefore, under the illumination of simulated solar light, the photoanode fabricated by the laminated BiOX-Ag-TiO$_2$ film could yield a small onset potential around 0.7 V vs RHE and a large photocurrent approaching 10 mA/cm^2 at 1.2 V vs RHE, which outperforms the state of the art photoanode based on IrO$_2$ modified hematite nanorod arrays.

1. Introduction

Current global energy demand is ∼5.3×10^{20} J/y, about 80% of which is provided by oil (32%), coal (27%), and natural gas (21%) [1]. Owing to the finite reserves and non-renewability of fossil fuels, alternative energies must be developed to sustain population growth. The solar energy received on the earth's surface is never exhaustible and may meet current and future human energy demand [2–5]. The available technique utilizing solar energy today is the photovoltaic cells, but the cells are usually expensive and the converted electricity is difficult to store and distribute over long distances [6,7]. Directly converting the solar energy into hydrogen with a photoelectrochemical cells (PECs) by splitting water seems to be a promising and appealing way to solve the problems [3,4,7]. The key to the success of hydrogen production with PECs is the development of high performance photoanodes made from earth-abundant materials for catalyzing the water oxidation reaction [8]. This is because water oxidation involves four electron transfer ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) and is complicated in kinetics when compared to water reduction reaction.

In principle, water oxidation on the photoanode is primarily composed of three sequential steps: (i) the light absorption by the photoanode to generate e$^-$–h$^+$ pairs; (ii) the transport of the holes (h$^+$) to the photoanode/electrolyte interface and the electrons (e$^-$) to the back contact; (iii) the transfer of the holes to water molecules to remove four protons to form an oxygen-oxygen bond [9]. Consequently, an efficient photoanode material should combine the features of broad light-harvesting range, high efficiency in separating the photogenerated charges, and rapid interfacial charge transfer rate. In fact, no single materials can meet all the demands so far [10]. For instance, intrinsic TiO$_2$ crystal, a benchmark of photoanode materials [11], suffers the narrow light absorption range ($E_g = 3.2$ eV for anatase TiO$_2$), low conductivity (ca. 10^{-9} S/cm at 25 °C) [12,13], and slow water oxidation kinetics closely connected to the slow charge transport [7,14–17]. It is well-known that the modification of TiO$_2$ surface with metal or

semiconductor nanoparticles can lead to the emergence of fascinating physical effects, such as the red shift of the absorption edge [18,19], the built-in field [14,16], the improved conductivity [20,21], or the surface plasmon resonance (SPR) [22], all of which are desired for PEC photoanodes. Another benefit from the modification of TiO_2 surface with the secondary nanoparticles is the formation of a relatively rough surface, which can diminish the reflection of the light, expand the electrode/electrolyte interface, and maximize PEC reaction sites.

However, current modification of TiO_2 photoanodes is still dictated by several constraints as follows: (i) most of the heterostructures are two-component and the light absorption range is only extended to a limited extent. Thereby, a substantial portion of solar energy has not been utilized by the photoanode in the PEC water splitting; (ii) the nanoparticles for modifying TiO_2 are usually fine and irregular, which does not yield the enough large light-harvesting surface; (iii) TiO_2 is a proton conductor at the low temperature and its low charge mobility and short excited state lifetime causes a large energy loss arising from the charge transport and transfer [7,13], but it has not been gotten sufficient attention yet.

Bismuth oxyhalides (BiOX, X = Cl, Br, or I) have been used as the pearl imitation by Egyptians as early as 5000 years ago. Recently, these ancient optical materials find new applications in the fields of energy and environment. For instance, nanostructured BiOX can serve as the earth-abundant photocatalysts for decomposing hazardous pollutants and the photoanodes for water splitting [23–25]. One characteristic of BiOX is the layered structure, where the covalently bonded $[Bi_2O_2]$ slabs are joined together by van der Waals interactions and the halogen atoms are located between the slabs. As a return, the single-crystal surfaces of BiOX are free of dangling bonds and self-passivating. This minimizes the influence of surface states and photo-corrosion and makes nanostructured BiOX particularly interesting for PEC applications [23]. The second characteristic of BiOX is the habit to develop into nanoplates with exposed {001} facet [26,27]. The thin nanoplates not only increase the photoreceptive area but also shorten the diffusion distance of photogenerated charges to the nanoplate/electrolyte interface. Moreover, along the direction perpendicular to the side faces of the nanoplates, there exist internal static electric fields established by the positively polar $[Bi_2O_2]$ slabs and the negatively halogen atoms [26], which are able to drive the photogenerated e^-–h^+ pairs to migrate oppositely. The third characteristic of BiOX is the band gap tunable over the wide range of $3.5 \sim 1.9$ eV by altering the species of the interlayer halogen atoms [27,28]. Consequently, the family of BiOX nanoplates should be the ideal candidates for modifying TiO_2.

To design an efficient TiO_2-based photoanode with the above factors in mind, herein, we first develop ternary BiOX-Ag-TiO_2 system through the sequential growth of Ag nanoparticles and BiOX nanoplates on the surface of a free-standing film self-assembled by ultralong TiO_2 nanowires. Subsequently, the BiOCl-Ag-TiO_2, BiOBr-Ag-TiO_2, and BiOI-Ag-TiO_2 films were overlapped to form a laminated photoanode. In this tandem configuration, photons with energies less than the band gap of BiOCl and TiO_2 are absorbed by the narrow band semiconductors of BiOBr and BiOI. Thereby, a large fraction of the solar spectrum (ca. 50%) is utilized by the laminated film. In the laminated film, Ag nanoparticles also play an important role, which transform the nanowire film into a highly conductive network, accelerate the surface electron transfer rate, and decrease the interfacial charge transfer resistance. Moreover, the band alignment in the system favors the directed flow of photogenerated electrons from BiOX and TiO_2 to Ag, which inhibits the recombination of the e^-–h^+ pairs. With the combination of the above metrics, the photoanode fabricated by the laminated BiOX-Ag-TiO_2 film shows a remarkably improved PEC performance.

2. Materials and Methods

2.1. Preparation of Ag-TiO$_2$ nanowire film

To a clean Teflon-lined autoclave with a volume of 50 ml, 0.04 g of Ti(O-Bu)$_4$ were added to 10 mol/L aqueous NaOH solution under violent stirring. Afterwards, the autoclave was heated at 200 °C for 48 h. White film was seen to grow around the inner wall of the Teflon liner after the reaction was finished. The solution was poured out and the film was remained in the autoclave, which was washed to neutral with excessive distilled water and then protonated in 0.1 mol/L HCl. The above autoclave was then filled by 40 mL of ethylene glycol dissolved by 0.1 mol/L AgNO$_3$ and then heated at 180 °C for 2 h. After that, a grey film was obtained, which is peeled off from the inner wall of the Teflon liner, rinsed with absolute ethanol to remove the ethylene glycol residue, and dried in air. The dried Ag-titanate film was annealed at 400 °C for 6 hours in nitrogen atmosphere. After the thermal treatment, Ag-TiO$_2$ nanowire film was formed.

2.2. Preparation of BiOX-Ag-TiO$_2$ nanowire film

The Ag-TiO$_2$ nanowire film was put back in the autoclave filled by 0.05 mol/L Bi(NO$_3$)$_3$ and 0.05 mol/L KCl, KBr, or KI dissolved in ethylene glycol. The autoclave was heated at 160 °C for 12 hours to form the desired BiOX-Ag-TiO$_2$ film. The films taken out from the autoclave was thoroughly washed with distilled water and dried in air. To fabricate the bi-layered film, BiOBr-Ag-TiO$_2$ film and BiOI-Ag-TiO$_2$ film with the size of 1×1 cm^2 were overlapped. To fabricate the tri-layered film, BiOCl-Ag-TiO$_2$ film, BiOBr-Ag-TiO$_2$ film, and BiOI-Ag-TiO$_2$ film with the same size were overlapped. For a comparison, we also prepared BiOX-TiO$_2$ films under the conditions identical to those for BiOX-Ag-TiO$_2$ films, except that the starting film was bare TiO$_2$ film.

2.3. Characterizations

Scanning electron microscopy (SEM) measurements were performed on a HITACHI S-4800 electron microscope equipped with energy dispersive X-ray (EDX) spectrometers. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were performed on an FEI Tecnai G20 electron microscope. XRD measurements were performed on a Panalytical X'Pert PRO diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB MK II X–ray photoelectron spectrometer using an Al Kα source. Diffusion reflection spectra were recorded on a Shimadzu 3150 UV-vis–near-infrared spectrophotometer equipped with an integrating sphere. Alternating current imped-ance measurements were performed on a Zahner Im6ex instru-ment under the following conditions: ac voltage amplitude 5 mV, frequency ranges 0.01 Hz to 100 kHz, and open circuit. The electrical conductivities of the films were measured by two-probe method. The electrodes were fabricated by sandwiching the edges of the films between two copper foils. Then, the electrodes were connected to a CHI 660c potentiostat-galvanostat (CHI Instru-ments Inc.) for conductivity measurements.

2.4. Photoelectrochemical measurements

The PEC measurements were performed in a standard three-electrode cell with a quartz window (CHI Instruments, model 660C, Shanghai Chenhua). The self-standing films, platinum wire, and Ag/AgCl were used as the working electrode, the counter electrode, and the reference electrode, respectively. A 0.5 M Na$_2$SO$_4$ aqueous solution was used as the electrolyte. The working