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Solar energy protects steels against corrosion: Enhanced protection capability achieved by NiFeO$_x$ decorated BiVO$_4$ photoanode

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ABSTRACT

Coupling *n*-type semiconductor photoelectrode with steels provides protection from corrosion for the latter by pumping electrons produced by water oxidation reaction in a sustainable way. Although the concept of the photocathodic protection of steels has been proposed for about two decades, this technique is still far away from practical applications due to the limited protection capability. In this work, we reported that the BiVO$_4$ photoanode significantly decreases the self-corrosion potential of 316 steel by 166 mV, and the decoration of NiFeO$_x$ films onto BiVO$_4$ further shifts the self-corrosion potential by ~90 mV negatively, which exhibits an excellent protection capability. The protection capability of the photoelectrode to steel is limited by the relative position of the Fermi level of the semiconducting material, and confined by the thermodynamics of the surface reactions on the semiconductor-electrolyte interface.

1. Introduction

Steels, which are the most widely used bulk metal materials in industrial and engineering structures due to their high strength and ductility, have a strong tendency to decay into rust compounds via corrosion [1] driven by the reduction in the free energy of system. To prevent or retard the corrosion, strategies have been developed by considering either the corrosion kinetics or the thermodynamics, or both [2]. Various barrier layers are used to isolate steels from direct exposing to aggressive environments and to block the diffusion of atoms, in the intellectual way [3,4] or not [5,6]. The other anti-corrosion route for steels is cathodic protection either by sacrificial anodes [7], such as Zn and Mg, or impressed current [8] which polarizes the steel to the corrosion stable region. A common feature to both the technologies above is that massive energy is consumed to keep steels at the metallic state. No matter which protection technology is adopted, an astonishing amount of materials and energies are consumed annually to maintain steels at the metastable metallic state, causing massive economic losses in most countries [9].

Mimicking the natural photosynthesis, artificial photoelectrochemical (PEC) cells harvest solar energy and store it in the chemical bonds using light-absorbing semiconductors [10–14]. Similarly, by coupling to light illuminated *n*-type semiconductor electrode, steels receive electrons from the photoelectrode when the conduction band is higher than the Fermi level of the steel, and thus the promoted electrons can be used to suppress or prevent the corrosion of steels. Those electrons compensate the corrosion current and shift the potential of the protected metal to the stable region [15,16]. Accordingly, the energy required to maintain the metastable metallic condition of steels could be provided by the sun through a sustainable way. Although the concept of the photocathodic protection of steels has been proposed for about two decades [15], the practical applications are still waiting due to the limited protection capability of photoanodes, even feasibilities have been demonstrated on photoanode materials such as TiO$_2$ [15,17], ZnO [18], and WO$_3$ [19]. One principal challenge is that the protection capabilities of photoanode are limited and below the predicted values. Because the protecting electrons are derived from the oxygen evolution reaction (OER) over the photoanode surface, the protection ability of photoanodes is determined by relative position between the open circuit potential (OCP) of photoanode and the corrosion potential of the protected metal [16]. Comparison investigations have also confirmed that only metals with relative high corrosion potential can be protected [18]. However, large overpotentials of the OER due to its sluggish kinetics and complex mechanism [20] constrain the protecting capability of the photoanode. To overcome this problem, one alternative strategy is that photoanodes are immersed in electrolyte containing hole

scavengers such as Na_2S [18,21] which shift the OCP of the photo-anodes to lower levels. Despite of the effectiveness, obviously, the usage of hole scavengers is not compatible with large-scale employment. Accordingly, how to understand the relationship between the anti-corrosion performance of steels and physiochemical nature of semi-conducting photoanodes, and thus to maximize the protection power for metal anti-corrosion is becoming an important issue in the field of corrosion.

2. Results and discussion

In the present study, we utilized the porous $BiVO_4$ photoanode to protect ASAI 316 austenitic stainless steels against corrosion. $BiVO_4$ is a *n*-type semiconductor with a relatively high conduction band edge position [22]. By modifying the semiconductor with OER catalyst, the obvious enhancement in photocathodic protection has been achieved. The suppression effect is correlated to the electronic states of $BiVO_4$ surface. Porous $BiVO_4$ films of highly crystallizing without intentional doping were fabricated by a two-step process: the BiOI nanoflakes were firstly electrodeposited on the FTO and then chemically converted to $BiVO_4$ with drops of $VO(acac)_2$ DMSO solution by heating treatment [23]. As shown in Fig. 1, the BiOI nanoflakes changed into wormlike porous structures composed of $BiVO_4$ nanoparticles with heating temperature dependent sizes ranging from 80 nm at 400 °C to 300 nm at 500 °C. The phase structures of the films were confirmed by XRD pattern (Figure S1). The bandgap of the as-synthesized $BiVO_4$ films were estimated between 2.3∼2.4 eV from the Tauc plots by assuming a di-recttransition [24] (Figure S2). In this case, solar irradiation with wavelength below 516 nm could be absorbed to pump the electrons generated from the water oxidation into the steels for protection.

The photocurrent density-potential (J–V) curves for $BiVO_4$ porous structures prepared at different temperatures, which are believed as a measure of oxygen evolution by oxidizing water, are given in Fig. 2. The $BiVO_4$ film prepared at 450 °C exhibits the highest photoelectrochemical activity for water oxidation. For photoanode with porous structure, the photocurrent density which represents the OER rate is influenced by the specific surface area, electron-hole separation efficiency on the surface layer and charge transport in the bulk [25]. Samples prepared at 450 °C have a porous structure with ligament diameter matching the sum of the diffusion length and depletion layer thickness which favors the charge collection at the interface. Coarsening of the structure at higher temperature decreases the charge transport in the bulk of $BiVO_4$ and results in a decreased PEC performance. Therefore, we use the $BiVO_4$ prepared at 450 °C for providing
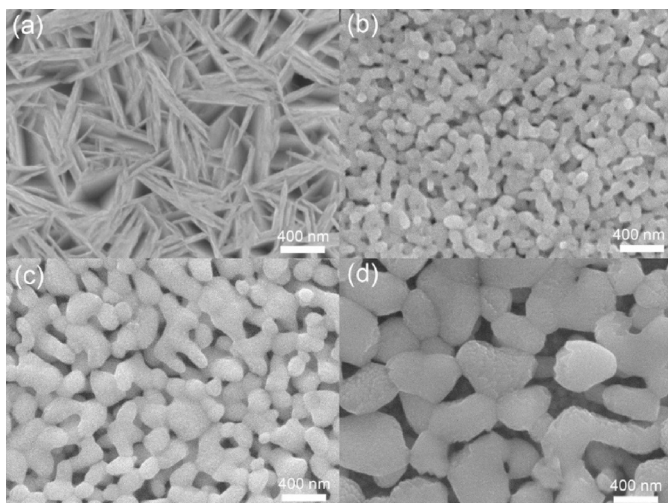

Fig. 1. SEM images of BiOI precursor film (a) and $BiVO_4$ films obtained after heating treatment at 400 °C (b), 450 °C (c), and 500 °C (d).
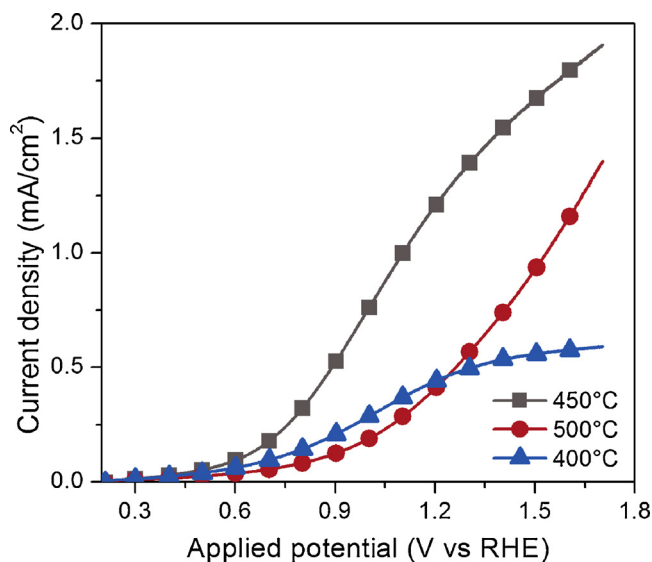

Fig. 2. Photoelectrochemical properties of $BiVO_4$ films obtained at different heating temperatures under 1 Sun illumination. The measurements were conducted in 0.5 M phosphate buffer at pH 7.0. The solid lines are the measured data, while the symbols on the line are presented for clarity.

cathodic protection for steels.

Fig. 3(a) depicts the cathodic and anodic curves of the paired steel-photoanode system in 3.5% NaCl at room temperature. The corrosion potential of the bare 316 steel is at −0.19 V *vs* SCE. When connected to the illuminated $BiVO_4$ electrode, a negative shift of 166 mV in the self-corrosion potential occurs. Though the reported currents in Fig. 3 are normalized by the exposed area of the steel plate, these currents are actually the sum of the reaction currents on both the steel plate and the photoanode, *i.e.*

$$i_{measure} = i_{C, Steel} + i_{A, Steel} + i_{C, PA} + i_{A, PA}$$

where C and A represent the cathodic and anodic half-reaction, respectively, over the steel or the photoanode (PA).

In the potential range below −0.19 V, cathodic current is expected on the steel by noting that the coupling with photoanode does not change the surface chemistry or electrochemistry. However, if the anodic half-reaction, namely the OER, on the photoanode overrides the cathodic reaction on the steel, an anodic current of the paired steel-$BiVO_4$ system is measured, as shown on the red Tafel curve in Fig. 3(a) at potential −0.19 V ∼ −0.35 V. In this region, the corrosion of the steel is inhibited by the cathodic polarization, and electrons are injected from the photoanode to the protected steel. At -0.35 V, namely the apparent- corrosion potential of the paired system, the anodic current on the $BiVO_4$ surface is balanced by the cathodic current on the steel surface. More interestingly, there is a further negative shift of the corrosion potential (about 90 mV) when the $BiVO_4$ film is decorated with electrodeposited $NiFeO_x$. $NiFeO_x$ films with proper Ni:Fe ratio [26] prepared by different methods have been proven effective to catalyze the photoelectrochemical OER either by shifting the photocurrent onset potential close to the theoretical values or increasing the photocurrent [27,28], although the detailed mechanism on how the surface $NiFeO_x$ improves the PEC performance of the modified photoanode is still under debate [28,29]. IMPS (Intensity Modulated Photocurrent Spectroscopy) studies showed that the charge collection efficiency of $BiVO_4$ is limited mainly by surface recombination [30]. The enhanced OER on the photoanode results an increased electron injection to the steel plate at a fixed potential, which well explains the negative shift in corrosion potential after $NiFeO_x$ deposition.

This improvement in the photocathodic protection capability of $BiVO_4$ photoanode on steel anti-corrosion can be further confirmed, as