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Research Paper

# Characteristics of elemental carbon overlayers over hematite electrodes prepared by electrodeposition with organic acid additives

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ABSTRACT

We report that inducing elemental carbon overlayers on hematite electrodes is a universal case that can be achieved by electrodeposition with addition of a wide range of organic acid following by thermal treatment. The thickness of elemental carbon ovrelayers directly affects the photocurrent density of as-obtained samples, which can be adjusted by selection of organic acid and electrodeposition pH. An optimal carbon overlayer of approximately 2–5 nm enhanced a 10 times higher photocurrent density (2.0 mA/cm$^2$ at 0.4 V$_{SCE}$) in comparison with those without carbon overlayers. While carbon overlayers were effective in passivating surface states, a capacitor was formed at the hematite/carbon overlayer interface upon illumination for 90 min. Our results clearly demonstrated the characteristics of effective carbon overlayers include (i) passivating surface states to reduce the onset photocurrent potential, (ii) injecting additional charges to enhance the photocurrent plateau, and (iii) the durability to sustain a long period of sunlight illumination.

## 1. Introduction

Sunlight harvesting is one of the most promising alternatives in curtailing globe warming through the use of low carbon footprint energy such as hydrogen by photoelectrochemical (PEC) water splitting. To this end, semiconductor catalysts are the key components necessary for harvesting sunlight through the generation, separation, and transport of charge carriers at semiconductor/aqueous interfaces. Among all photocatalysts, material abundance, chemical stability over a wide pH range, and narrow band gap structure enabling the efficient utilization of a significant portion of visible light make hematite an attractive material selection. Several methods have been proposed to prepare hematite electrode for PEC applications [1]. Among all of these methods, electrodeposition has received the most attention due to its simplicity, particularly for large scale manufacturing [2]. For instance, granular and compact nanocrystalline hematite electrodes prepared by pulse reverse electrodeposition method has exhibited a photocurrent density of 0.5 mA/cm$^2$ at 1.23 V vs. RHE [3]. Zeng et al. reported that a hematite electrode could generate a photocurrent density of 1.35 mA/cm$^2$ at 1.23 V vs. RHE by controlling the thickness and crystallinity of the electrode carefully by electrodeosition time and annealing conditions [4]. The variations in the crystallographic properties will enhance hole transport and collection and bring about high current intensity [5]. Furthermore, Zandi et al. reported that cobalt-phosphate (Co-Pi) cocatalysts greatly enhanced the photocurrent density by 70% over electrodeposited dendritic type hematite electrodes due to increase in the suppression of the photogenerated electron–hole recombination [6]. Chemelewski et al. reported photocurrent density of 10 mA/cm$^2$ by doping oxygen evolution reaction (OER) catalysts with metals, such as Ni-doped goethite (Ni:FeOOH) via electrodeposition [7]. Passivating surface trapping states with a thin layer of $Al_2O_3$, $In_2O_3$ or $Ga_2O_3$ was also reported to greatly enhance photocatalytic performance [8]. Passivation layers could effectively improve the charge-separation and charge-transfer processes across semiconductor–liquid interfaces as evidenced by significant changes in surface capacitance and radiative recombination [8]. One of the most important characteristics of passivation overlayers is the cathodic (negative) shift of the overpotential due to suppression of the electron-hole recombination, which increases the photovoltage and band bending [9]. Recently, a thin elemental carbon overlayer has been successfully synthesized by pyrolysis of ferrocene over hematite using crucible

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which center region was less accessible to atmospheric oxygen and therefore carbon overlayers were formed readily during sintering. Results of X-ray absorption spectroscopy analyses revealed that a significant amount of oxygen vacancy was concurrently introduced by the carbon overlayers [10]. We have also discovered that the addition of citric acid to the electrolyte will form elemental carbon overlayers on the electrodeposited hematite electrodes that yielded a photocurrent density of around 2.1 mA/cm$^2$ at 0.4 V versus SCE under standard illumination [11]. Although organic acids are frequently added in electrolyte to stabilize metal ions, induced carbon overlayers have bared discussed in the literature. Importantly, the PEC performance was closely related to the thickness of surface carbon layer [11]. We have speculated that the enhanced PEC performance is due to the passivation effect that reduces the hole-electron recombination loss at surface states. Despite a lack of understanding the functionality of the carbon overlayer, it is clear that the elemental carbon overlayer will greatly enhance the photocatalytic activity of hematite electrodes. Two important questions arise: first, is cirtic acid the only organic additive capable of creating carbon overlayers?; second, what are the typical characteristics of carbon overlayer effectively enhancing PEC activity and how to characterize them?

In order to answer the above questions, a series of hematite electrodes were prepared by electrodeposition in electrolyte containing 0.1 M of five different organic acids, namely, acetate (Ace), citrate (Cit), EDTA, salicylate (Sal), and ascorbate (Asc) as a function of pH. Based on MINEQL software [12], the formation constants (logK) are 9.59, 13.10, 29.20, 29.30, and 11.57, for the Fe(III) complexes of Ace, Cit, EDTA, Sal, and Asc [13], respectively. The organic acids selected have a wide range of affinity toward $Fe^{3+}$, which will affect their adsorption onto iron oxyhydroxide (FeOOH) at different pH and the subsequent formation of carbon layers. Therefore it will address the first question of the specificity of the formation of carbon overlayers. That is, is citric acid the only organic acid forming carbon ovelayers? Then, the characteristics for an effective carbon overlayer were investigated and suggested for the perspective of manufacturing high photocatalytic hematite electrodes in the future.

## 2. Experimental section

### 2.1. Preparation of α-$Fe_2O_3$ photoelectrodes via electrodeposition

All chemicals used in this study were of ACS grade purchased from Sigma-Aldrich and Merck and used as-received without any further purification. To prepare electrodeposited α-$Fe_2O_3$ electrodes, FTO glass substrates (2 × 1 cm, working electrode) were immersed in an electrodeposition bath with a Pt plate (1 × 1 cm) as a counter electrode and a saturated calomel electrode (SCE) as a reference. The electrolyte was consisted of 0.1 M of iron(III) chloride hexahydrate and 1.0 M of sodium nitrate with/without 0.1 M citric acid additives in different pH values. The electrodeposition was conducted in chronopotentiometry mode (at 50 mA for 5 min, CH Instrument, CHI 608E). At the end of electrodeposition, the samples were first gently rinsed with deionized water and then air-dried followed by a two-step heating treatment (500 °C for 1 h than 750 °C for 10 min) at a heating rate of 10 °C/min in air. Six samples were prepared for each condition and the one exhibited the photocurrent density closest to the average value (the relative standard deviation, RSD, about 15%) was chosen for further characterization.

### 2.2. PEC measurements

For PEC measurements, hematite electrodes were covered by a stripe of nonconductive Teflon by leaving a working area (1 × 1 cm) for exposing to simulated sunlight (AM 1.5 G with the light power density of 100 mW/cm$^2$). All PEC measurements were conducted using a CHI 608E electrochemical workstation in a three-electrode configuration as mentioned above in an electrolyte containing 1.0 M of NaOH (pH 13.6). The measured potential was swept from −0.5 V to 1.0 V vs. SCE at a scan rate of 50 mV/s. To determine the charge carrier density of the hematite samples, Mott–Schottky (MS) plots were derived from the electrochemical impedance obtained in the potential between −0.5–0.7 V vs. SCE at a frequency of 10 kHz in dark and the capacitance was extracted according to Eq. (1) [11]:

$$Z'' = 1/2\pi fC \tag{1}$$

where the Z” stands for the imaginary impedance, *f* is the scan frequency and *C* refers to the capacitance of the sample measured. Note that the validity of using only one frequency point to extract capacitance for MS plots is built on the following assumption: two capacitances are to be considered, namely, the space charge region and the double layer, respectively. Since the space charge capacitance is much smaller than that of the double layer (by 2–3 orders of magnitude) and they are in series, the contribution of the double layer capacitance to the total capacitance is negligible due to that the total capacitance is the sum of their reciprocals. This means the capacitance value calculated from this model is assumed to be the value of the space charge capacitance (capacitance of hematite bulk in this study) and therefore a high frequency on the order of kHz is required. Electrochemical impedance spectroscopy (EIS) measurement was carried out under illumination with +0.1 V applied voltage by the same workstation in the frequency range of 1 Hz–100 kHz. Obtained data were fitted by an equivalent circuit using the Zview software.

### 2.3. Characterization of electrode

The scanning electron microscopy (SEM) images of hematite nanostructures were obtained using JSM700F, JEOL scanning electron microscope with acceleration voltage of 20 kV. High-Resolution transmission electron microscopy (HRTEM) images and energy dispersive X-ray analysis (EDX) were recorded using JEOL JEM-2100 HRTEM. To prepare HRTEM specimens, electrodeposited hematite samples were scratched from the surface of FTO substrates into 5 mL deionized water using a razor blade. After 10 min of sonication, the suspensions were transferred onto a holey carbon thin film supported by a copper grid. X-Ray Diffractometer (XRD, D2 Phaser diffractometer, Brucker) and X-ray photoelectron Spectrometer (XPS, PHI Quantera SXM/Auger) were utilized for the structure and the oxidation state characterization. Batch adsorption experiments were performed by dispersing 1.0 g FeOOH (Sigma-Aldrich) in 100 mL solution containing 10 mg/L of studied organic species with 10 mM of NaCl as the background electrolyte. The pH adjustment was conducted using either 0.1 N HCl or NaOH. In the end of 24 h reaction under vigorously stirring, the equilibrated pH was recorded and 1.0 mL mixture was collected and filtrated using a 0.25 μm PTFE filter. The concentration of organic acid remaining in the solution was determined using total organic carbon analyzer (Aurora 1030WOI Analytical TOC analyzer) and the difference in the concentration is assumed the amount of organic acid adsorbed on FeOOH particles.

## 3. Results and discussions

Fig. S1 shows typical J-V curves of hematite electrodes electrodeposited with 0.1 M of ascorbic acid additives at different pH values. Observed photocurrent density at 0.4 $V_{SCE}$ was recorded and arranged in Fig. 1a. As shown in Fig. 1a, it is noted that the photocurrent density of the different hematite electrodes was sensitive