Electronic Supplementary Information for

A Novel In-situ Preparation Method of Nanostructured α-Fe$_2$O$_3$ Films from Electrodeposited Fe Films for Efficient Photoelectrocatalytic Water Splitting and Organic Pollutant Degradation

Qingyi Zeng, Jing Bai, Jinhua Li, Ligang Xia, Ke Huang, Xuejin Li and Baoxue Zhou*[a]

School of Environmental Science and Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Rd, Shanghai 200240 PR China.

E-mail: zhoubaoxue@sjtu.edu.cn; Fax: (+86)21-54747351
Fig. S1 A photograph of the electrodeposition system.

Fig. S2 XRD patterns of the deposited film from the electrolyte: (a) 5 g FeSO$_4$•7H$_2$O and 2.75 g Na$_2$SO$_4$ dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH; (b) 5 g FeSO$_4$•7H$_2$O dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH. The electrodeposition duration was 30 s.
**Fig. S3** The surface SEM image of the prepared Fe film (the electrodeposition duration was 30 s).

**Fig. S4** The relationship of the thickness of $\alpha$-Fe$_2$O$_3$ film and the electrodeposition time.

**Fig. S5** The relationship of the resistance of the FTO glass and the annealing temperature.
Fig. S6 The EDX measurement of the 600s Co–Pi/α-Fe₂O₃ film.
The mechanism of electrodeposition of Fe film in the electrolyte with ammonia

In order to reveal the mechanism of ammonia content in the electrolyte crucial to preparing the uniform Fe film, the difference between the electrolyte with NaOH and the electrolyte with ammonia has been studied via their centrifugate. The electrolyte with NaOH was prepared by 5 g FeSO₄•7H₂O dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH; the electrolyte with ammonia was prepared by 5 g FeSO₄•7H₂O and 30 mL ammonia (27 %) dissolved in 150 mL deionized water (pH=10.8). The electrolytes were centrifuged at 3000 rpm for 5 min.

Under the alkaline condition (pH=10.8), a series of reactions would occur in the FeSO₄ solution, at least including:

\[
\begin{align*}
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \quad (1) \\
\text{Fe}^{2+} + 3\text{OH}^- & \rightarrow \text{Fe(OH)}_3^- \quad (2)
\end{align*}
\]

Colloidal particles, such as Fe(OH)₂/Fe(OH)₃⁻ colloidal particles, or precipitations, should suspend or deposit in the solution.¹

In ammonia solution, NH₄⁺ ions can be adsorbed on the surface of the Fe(OH)₂/Fe(OH)₃⁻ colloidal particles because of the large specific area of colloidal particles, and NH₄⁺ ions also can be adsorbed on the surface of FTO cathode under the charged condition. The adsorbed NH₄⁺ ions should facilitate the following reaction occurring on the surface of colloidal particles and cathode.

\[
\begin{align*}
\text{Fe(OH)}_2 + \text{NH}_4^+ & \rightleftharpoons \text{FeOH}^+ + \text{NH}_3\cdot\text{H}_2\text{O} \quad (3) \\
\text{Fe(OH)}_2 + 2\text{NH}_4^+ & \rightleftharpoons \text{Fe}^{2+} + 2\text{NH}_3\cdot\text{H}_2\text{O} \quad (4) \\
\text{FeOH}^+ + \text{NH}_4^+ + 2\text{e}^- & \rightarrow \text{Fe} + \text{NH}_3\cdot\text{H}_2\text{O} \quad (5) \\
\text{Fe(OH)}_2 + 2\text{NH}_4^+ + 2\text{e}^- & \rightarrow \text{Fe} + 2\text{NH}_3\cdot\text{H}_2\text{O} \quad (6) \\
\text{Fe}^{2+} + 2\text{e}^- & \rightarrow \text{Fe} \quad (7)
\end{align*}
\]
NH\textsubscript{4}\textsuperscript{+} ions may be a crucial factor for the reduction of Fe\textsuperscript{2+} on the surface of cathode, and the existence of NH\textsubscript{4}\textsuperscript{+} ions would make the reduction rate of Fe\textsuperscript{2+} moderately, which should facilitate the formation of uniform Fe film.

However, in NaOH solution, without the effect of NH\textsubscript{4}\textsuperscript{+} ions, Na\textsuperscript{+} ions and only a few amount of H\textsuperscript{+} ions should not be able to reduce Fe(OH)\textsubscript{2}/Fe(OH)\textsubscript{3}\textsuperscript{-} to Fe. Instead, the tin dioxide (SnO\textsubscript{2}) of the FTO substrate would be reduced into Sn under a reduction potential of -2 V, which should be accounted for the formation of Sn film with the NaOH content electrolyte.

\[\text{SnO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Sn} + 4\text{OH}^-\] (8)

**Fig. S7** The photograph of the centrifugate of (a) the FeSO\textsubscript{4} solution with NaOH and (b) the FeSO\textsubscript{4} solution with ammonia.

Fig. S7 showed the centrifugal solutions of the FeSO\textsubscript{4} solution with NaOH and the FeSO\textsubscript{4} solution with ammonia, respectively. The centrifugal solution of the FeSO\textsubscript{4} with NaOH was clear and transparent, while it was grayish green for ammonia, which means that, after centrifugation, ferrous species still existed in ammonia solution while should not exist in NaOH solution. This phenomenon indicates that colloidal particles of Fe(OH)\textsubscript{2}/Fe(OH)\textsubscript{3}\textsuperscript{-} should be more stable in ammonia solution. According to reaction (3) and (4), the absorbed NH\textsubscript{4}\textsuperscript{+} ions on the colloidal particles of Fe(OH)\textsubscript{2}/Fe(OH)\textsubscript{3}\textsuperscript{-} should make the colloidal particles positively charged and would restrict their coacervation, which should facilitate the
electrodeposition of Fe films. However, in NaOH solution, without the effect of NH$_4^+$ ions, the electrodeposition process of Fe films would be difficult to occur. Therefore, the ammonia in the electrolyte should be a crucial factor for the electrodeposition of Fe film in the alkaline condition.
Preparation of α-Fe₂O₃ films from traditional electrodeposition of FeOOH films

The anodic α-Fe₂O₃ films have been prepared via anodic electrodeposition according to the literature.² Briefly, the electrodeposition was carried out in an aqueous solution (pH 4.1) containing 0.02 M FeCl₂ at 75 ºC with a standard three-electrode setup as the FTO glass worked as the working electrode, platinum foil worked as the counter electrode, and an Ag/AgCl electrode in 4 M KCl solution worked as the reference electrode, under 1.2 V potentiostatically for 8 min. The as-deposited films were dried at 50 ºC for 5 h and then annealed in atmosphere at 520 ºC for 30 min after heating at a rate of 2 ºC/min.

Fig. S8 The XRD patterns of the (a) as-deposited and (b) annealed films.

Fig. S9 The SEM images of (A) the as-deposited FeOOH film and (B) the anodic α-Fe₂O₃ film (insert: cross-section SEM image of the anodic α-Fe₂O₃ film).
References
