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Electronic Supplementary Information
for

A Novel In-situ Preparation Method of Nanostructured α-Fe_2O_3 Films from Electrodeposited Fe Films for Efficient Photoelectrocatalytic Water Splitting and Organic Pollutant Degradation

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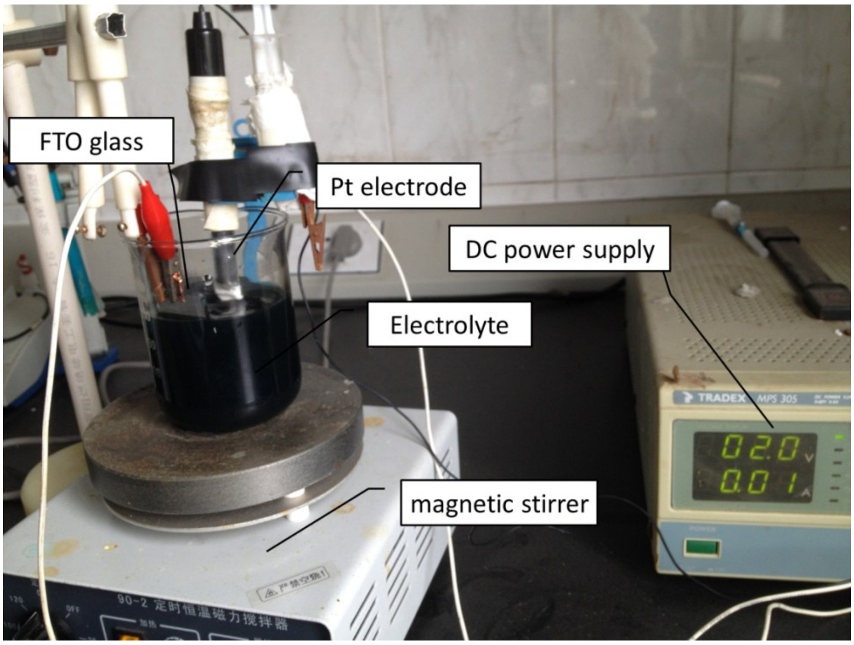


Fig. S1 A photograph of the electrodeposition system.

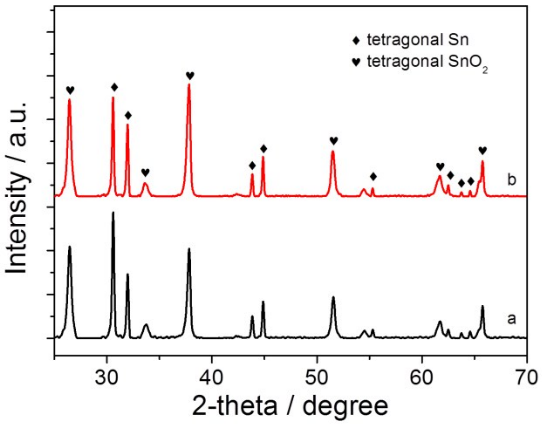


Fig. S2 XRD patterns of the deposited film from the electrolyte: (a) 5 g $FeSO_4\bullet 7H_2O$ and 2.75 g Na_2SO_4 dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH; (b) 5 g $FeSO_4\bullet 7H_2O$ dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH. The electrodeposition duration was 30 s.

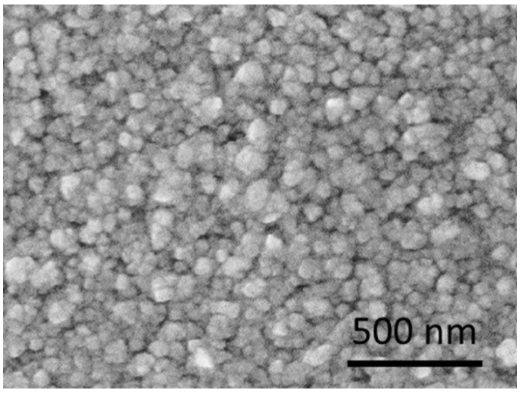


Fig. S3 The surface SEM image of the prepared Fe film (the electrodeposition duration was 30 s).

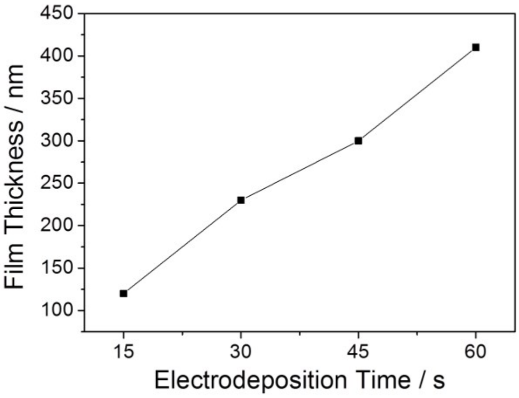


Fig. S4 The relationship of the thickness of α-Fe_2O_3 film and the electrodeposition time.

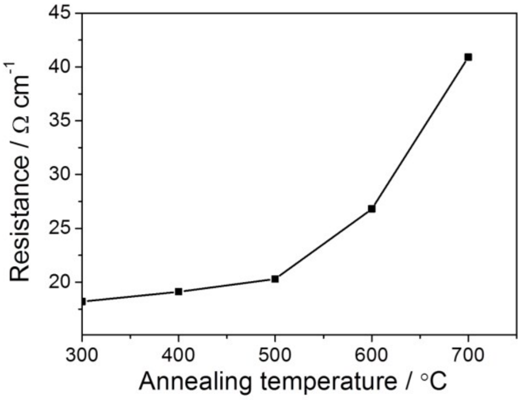
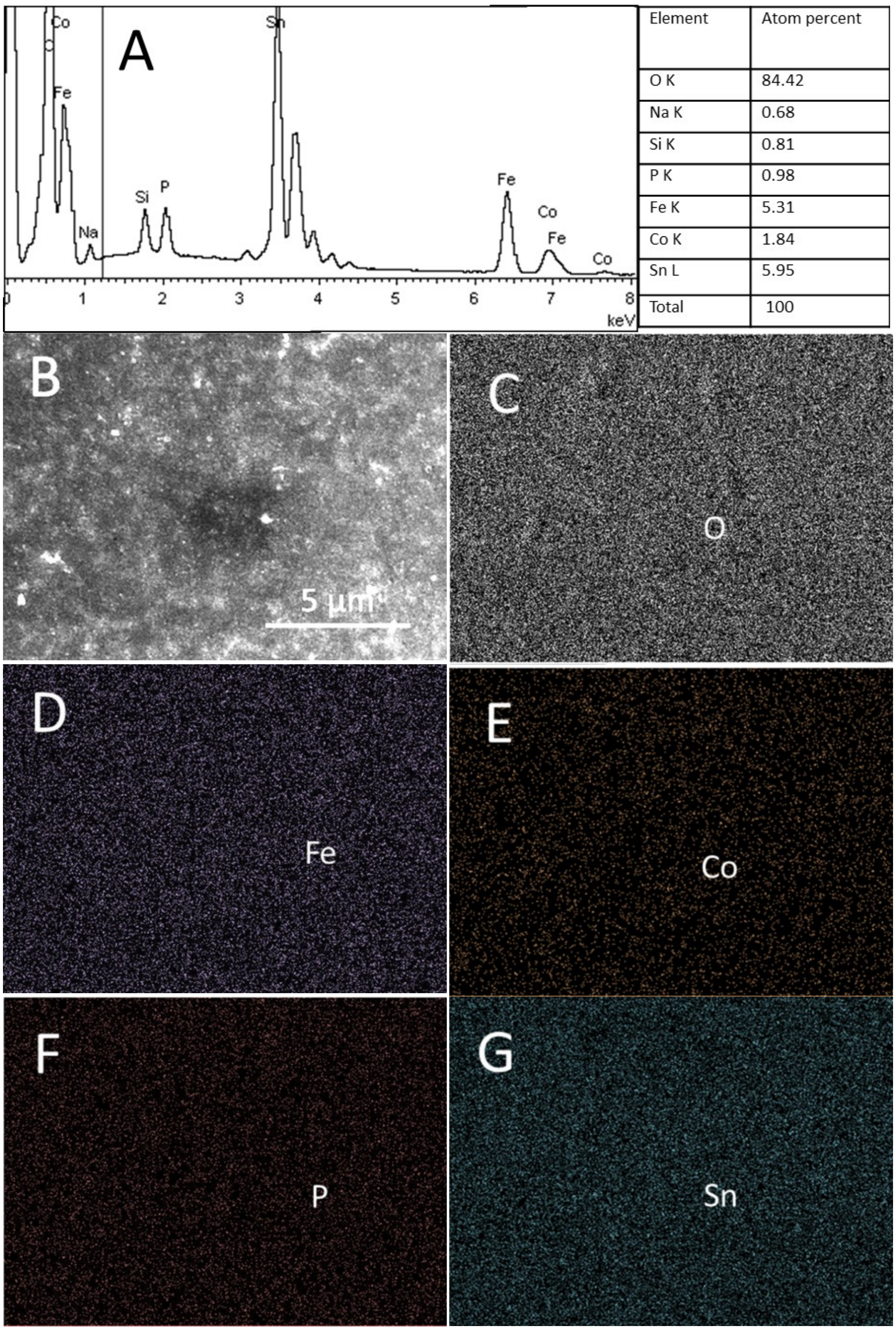


Fig. S5 The relationship of the resistance of the FTO glass and the annealing temperature.



Element	Atom percent
O K	84.42
Na K	0.68
Si K	0.81
P K	0.98
Fe K	5.31
Co K	1.84
Sn L	5.95
Total	100

Fig. S6 The EDX measurement of the 600s Co–Pi/α-Fe_2O_3 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 $FeSO_4 \cdot 7H_2O$ dissolved in 180 mL deionized water with the pH adjusted to 10.8 by NaOH; the electrolyte with ammonia was prepared by 5 g $FeSO_4 \cdot 7H_2O$ 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 $FeSO_4$ solution, at least including:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (1)$$

$$Fe^{2+} + 3OH^- \rightarrow Fe(OH)_3^- \qquad (2)$$

. 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, NH_4^+ 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 NH_4^+ ions also can be adsorbed on the surface of FTO cathode under the charged condition. The adsorbed NH_4^+ ions should facilitate the following reaction occurring on the surface of colloidal particles and cathode.

$$Fe(OH)_2 + NH_4^+ \rightleftharpoons FeOH^+ + NH_3 \cdot H_2O \qquad (3)$$

$$Fe(OH)_2 + 2NH_4^+ \rightleftharpoons Fe^{2+} + 2NH_3 \cdot H_2O \qquad (4)$$

$$FeOH^+ + NH_4^+ + 2e^- \rightarrow Fe + NH_3 \cdot H_2O \qquad (5)$$

$$Fe(OH)_2 + 2NH_4^+ + 2e^- \rightarrow Fe + 2NH_3 \cdot H_2O \qquad (6)$$

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad (7)$$

NH_4^+ ions may be a crucial factor for the reduction of Fe^{2+} on the surface of cathode, and the existence of NH_4^+ ions would make the reduction rate of Fe^{2+} moderately, which should facilitate the formation of uniform Fe film.

However, in NaOH solution, without the effect of NH_4^+ ions， Na^+ ions and only a few amount of H^+ ions should not be able to reduce $Fe(OH)_2/Fe(OH)_3^-$ to Fe. Instead, the tin dioxide (SnO_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.

$$SnO_2 + 2H_2O + 4e^- \rightarrow Sn + 4OH^- \qquad (8)$$

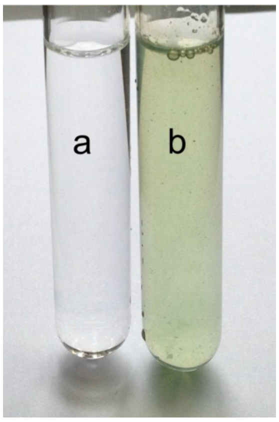


Fig. S7 The photograph of the centrifugate of (a) the $FeSO_4$ solution with NaOH and (b) the $FeSO_4$ solution with ammonia.

Fig. S7 showed the centrifugal solutions of the $FeSO_4$ solution with NaOH and the $FeSO_4$ solution with ammonia, respectively. The centrifugal solution of the $FeSO_4$ 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 $Fe(OH)_2/Fe(OH)_3^-$ should be more stable in ammonia solution. According to reaction (3) and (4), the absorbed NH_4^+ ions on the colloidal particles of $Fe(OH)_2/Fe(OH)_3^-$ 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-Fe_2O_3 films from traditional electrodeposition of FeOOH films

The anodic α-Fe_2O_3 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 $FeCl_2$ 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.

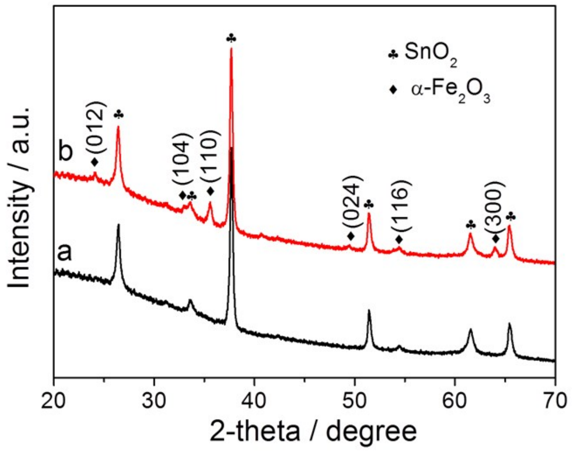


Fig. S8 The XRD patterns of the (a) as-deposited and (b) annealed films.

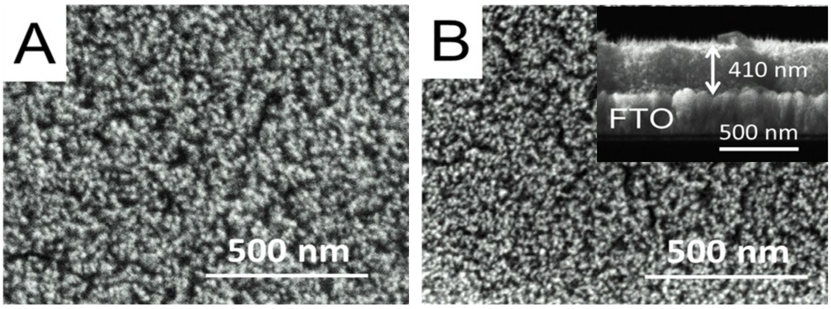


Fig. S9 The SEM images of (A) the as-deposited FeOOH film and (B) the anodic α-Fe_2O_3 film (insert: cross-section SEM image of the anodic α-Fe_2O_3 film).

References

1 M. Pourbai, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd ed.; National Association of Corrosion Engineers: Houston, 1974.

2 R. L. Spray and K.-S. Choi, *Chem. Mater.*, 2009, **21**, 3701–3709.