Supplementary Information

Facile growth of hierarchical hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) nanopetals on FTO by pulse reverse electrodeposition for photoelectrochemical water splitting

Pravin S. Shinde, Geun Ho Go and Won Jae Lee*

Battery Research Center, Korea Electrotechnology Research Institute (KERI), Changwon 641-120, Republic of Korea.
Fax: +82 55 280 1590; Tel: +82 55 280 1643;
*E-mail: wjlee@keri.re.kr
X-diffraction study

Fig. S1 shows the XRD patterns of Fe$_2$O$_3$ photoanodes prepared by pulse reverse and normal electrodeposition methods in the diffraction angle (20) range of 20-100° (step size: 0.013° s$^{-1}$, dwelling time: 24 s). Both the samples are polycrystalline with hematite crystal structure. However, Fe$_2$O$_3$ prepared by pulse reverse electrodeposition is more crystalline since the intensity of hematite peaks at 24.152, 33.164, 35.636° is enhanced as compared to that of Fe$_2$O$_3$ prepared by normal electrodeposition method.

**Fig. S1** X-ray diffraction (XRD) patterns of Fe$_2$O$_3$/FTO photoanodes prepared by (a) pulse reverse electrodeposition (PRED) and (b) normal electrodeposition (ED).
Scanning electron microscopy study

Fig. S2 shows the low magnification SEM images of Fe$_2$O$_3$/FTO photoanode prepared by normal electrodeposition. The Fe$_2$O$_3$ film shows agglomerated morphology. Some white impurity overgrowths are seen.

Fig. S2 SEM images of Fe$_2$O$_3$/FTO photoanode prepared by normal electrodeposition. Magnification, Scale bar: (a) 10K, 5 μm; (b) 30K, 1 μm;
**UV-Vis absorption study**

The band gap energy was calculated from the absorbance (αt) data of Fe₂O₃ recorded in the wavelength range of 350-800 nm using Tauc relation (1):

\[ a(h\nu) = A_0 (h\nu - E_g)^n \]

where, \[ A_0 = \frac{e^2}{nch^2m^*_e} \] (2)

Here, α is the measured absorption coefficient (cm⁻¹) near the absorption edge, t is the film thickness, \( A_0 \) is a constant, \( h\nu \) is photon energy (eV), \( E_g \) is optical band gap (eV), n is a constant. The value of n is determined from the nature of optical transition. n=2 or 3 for indirect allowed and indirect forbidden transition, respectively and n=1/2 or 3/2 for direct allowed and direct forbidden transition, respectively. \( m_e^* \) and \( m_r \) are the effective and reduced masses of charge carriers, respectively.

**Fig. S3** Tauc plot i.e. plot of \((αh\nu)^{0.5}\) and \((αh\nu)^2\) vs. photon energy (hv) for the Fe₂O₃ film synthesized with +6V/-4V pulse deposition condition, revealing indirect and direct band gap energies of 2.1 and 2.2 eV, respectively.
The optical band gap of semiconductor can be estimated from the intercept of the extrapolated linear fit for the plotted experimental data of $(\alpha h\nu)^n$ versus incident photon energy $(h\nu)$ near the absorption edge. Although, hematite has an indirect band gap [R1, R2], a direct band gap for oriented hematite nanorods is also reported [R3]. Therefore, we determined both indirect and direct band gap energies for $\text{Fe}_2\text{O}_3$ by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ versus photon energy, respectively. The indirect allowed and direct allowed band gap energies for $\text{Fe}_2\text{O}_3$ film prepared by pulse reverse electrodeposition are 2.1 and 2.2 eV, respectively. The estimated band gap values are in good agreement with the earlier reported values for hematite films [R2].

**Electrochemical Impedance Spectroscopy (EIS) study**

Potentiostatic electrochemical impedance study of the $\text{Fe}_2\text{O}_3$/FTO photoanode was performed with a conventional three-electrode configuration in 1M NaOH electrolyte in dark and under simulated 1 SUN (100 mW cm$^{-2}$) illumination. The obtained data were fitted using ZView program with equivalent circuit elements such as $R_s$ and three parallel RC circuits (See Fig. S4 and S5). Their physical significance is mentioned as follows:

- The $R_s$ represents series resistance (sheet resistance of the FTO and the external contact resistance of the cell such as wire connections).
- First RC circuit comprising $R_1$ and CPE1 (constant phase element) represent $\text{Fe}_2\text{O}_3$/FTO contact. CPE is used instead of capacity C if the films are porous in nature.
- Second RC circuit comprising $R_2$ and CPE2 represent interface inside the $\text{Fe}_2\text{O}_3$ layer.
- Third RC comprising $R_3$ and CPE3 represent $\text{Fe}_2\text{O}_3$/Electrolyte system
### Circuit Element Values

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs (Ω)</td>
<td>12.08</td>
<td>0.0054701</td>
<td>0.045282</td>
</tr>
<tr>
<td>R1 (Ω)</td>
<td>2.324</td>
<td>0.016949</td>
<td>0.7293</td>
</tr>
<tr>
<td>CPE1-T (F)</td>
<td>0.0066136</td>
<td>0.000069839</td>
<td>1.056</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>0.54989</td>
<td>0.0012602</td>
<td>0.22917</td>
</tr>
<tr>
<td>R2 (Ω)</td>
<td>1018</td>
<td>3.9432</td>
<td>0.38735</td>
</tr>
<tr>
<td>CPE2-T (F)</td>
<td>0.0014851</td>
<td>1.2372E-06</td>
<td>0.083308</td>
</tr>
<tr>
<td>CPE2-P</td>
<td>0.83031</td>
<td>0.0002208</td>
<td>0.026592</td>
</tr>
<tr>
<td>R3 (Ω)</td>
<td>3245</td>
<td>27.265</td>
<td>0.84022</td>
</tr>
<tr>
<td>CPE3-T (F)</td>
<td>0.0015608</td>
<td>1.7139E-06</td>
<td>0.10981</td>
</tr>
<tr>
<td>CPE3-P</td>
<td>1</td>
<td>0.00040598</td>
<td>0.040598</td>
</tr>
</tbody>
</table>

**Fig. S4** Nyquists plot for Fe$_2$O$_3$/FTO photoanode in 1M NaOH electrolyte under dark recorded in the frequency range of 0.1-10,000 Hz. Inset shows the magnified curve in the high frequency region depicting a small semicircle.
Circuit Model File: C:\Users\SONY\Desktop\Pravin DOCs\JPB\Work IREK\Paper Communication Fe2O3-FTO pulsed deposition\EIS and Mott Schottky\Jae Sung Lee Light.mdl

Fig. S5 Nyquits plot for Fe2O3/FTO photoanode in 1M NaOH electrolyte under 1 SUN illumination recorded in the frequency range of 0.1-10,000 Hz. Inset shows the magnified curve in the high frequency region depicting a small semicircle.
Mott-Schottky study

Mott-Schottky study of Fe₂O₃ prepared by pulse reverse electrodeposition was carried out in 1M NaOH electrolyte (pH=13.6) with a three-electrode setup. DC potential from -0.6–0.4V vs. Ag/AgCl was applied at the AC frequency of 30000 Hz and AC amplitude of 0.023 V. Space charge layer capacitance values were obtained at each potential (ΔV=0.1V vs. Ag/AgCl). A higher frequency was selected to minimize the contribution of Helmholtz capacitance, which results from the charge redistributions within the solution at the surface.

Fig. S6 Mott-Schottky (1/Cₛ² vs. potential) plot for Fe₂O₃ film measured at an AC frequency of 30 kHz under dark condition in 1M NaOH solution (pH 13.6) and with AC amplitude of 0.023 V. The reference electrode was Ag/AgCl.

Flat band potential (V_fb) can be calculated using Mott-Schottky relation (3),

\[
\frac{1}{C_s^2} = \frac{1}{e_0 N_D e_r e_A^2} \left( |V - V_{fb}| - \frac{kT}{e} \right)
\]

… (3)

where, Cₛ is space charge capacitance (F cm⁻²), e₀ is the electron charge (1.602177×10⁻¹⁹ C), eᵣ is the dielectric constant (eᵣ=80 for α-Fe₂O₃) [R4], e₀ is the permittivity of vacuum (8.8542×10⁻¹⁴ F cm⁻¹), N_D is donor density (cm⁻³), V is the applied potential (V), T is the absolute temperature, k is Boltzmann’s constant and A is the surface area of the photoanode. At room temperature, Value of V_fb determined by extrapolating the linear fit of 1/Cₛ² versus
V plot to C=0 is -0.4V vs. Ag/AgCl. The positive slope of the plot indicates that Fe$_2$O$_3$ is n-type semiconductor with electrons as majority charge carriers. At room temperature, the value of kT/e is negligibly small (0.025V) and can be omitted. According to relation (3), the slope determined from the Mott-Schottky plot can be used to estimate the carrier density using following relation,

$$N_D = \frac{2}{\varepsilon_0 \varepsilon_r A^2} \left[ \frac{d(1/C^2)}{dV} \right]^{-1}$$

... (4)

References