

Supporting Information

Ethylene Glycol Adjusted Nanorod Hematite Film for Active Photoelectrochemical Water Splitting

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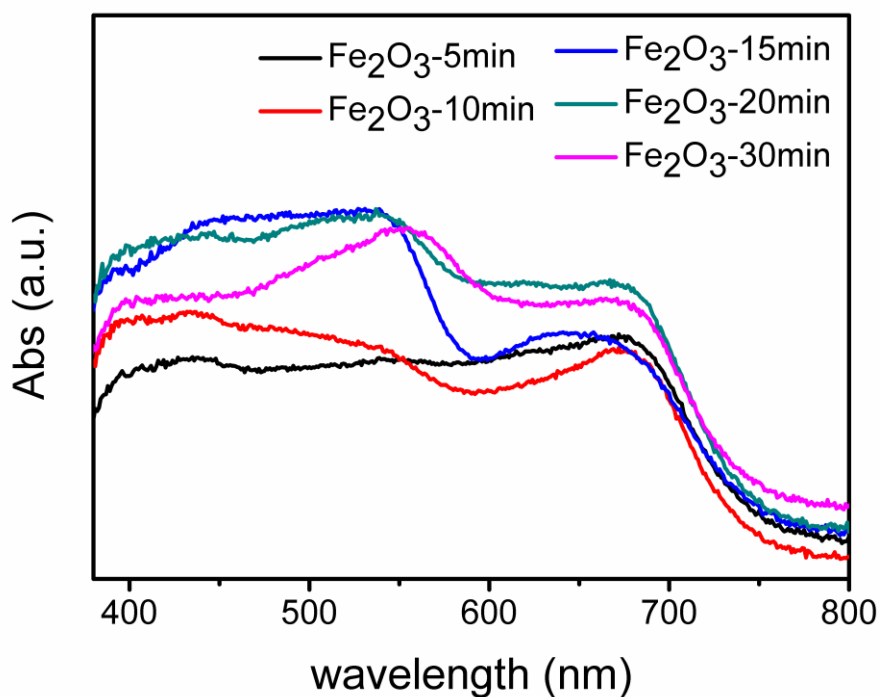


Figure S1 UV-Vis spectra of the hematite film from 380 nm to 800nm at different deposition time of 0 min, 5 min, 10 min, and 15min, 20 min, 30 min under heat treatment of 600 °C.

Fig. S1 exhibits the UV-visible spectra for hematite films from 380 nm to 800nm at different deposition time of 0min, 5min, 10min, and 15min, 20 min, 30 min under heat treatment of 600 °C. Compared all the above samples, the photoabsorption in the visible regions are enhanced along with deposition time as a result of the increased optical absorption thickness.

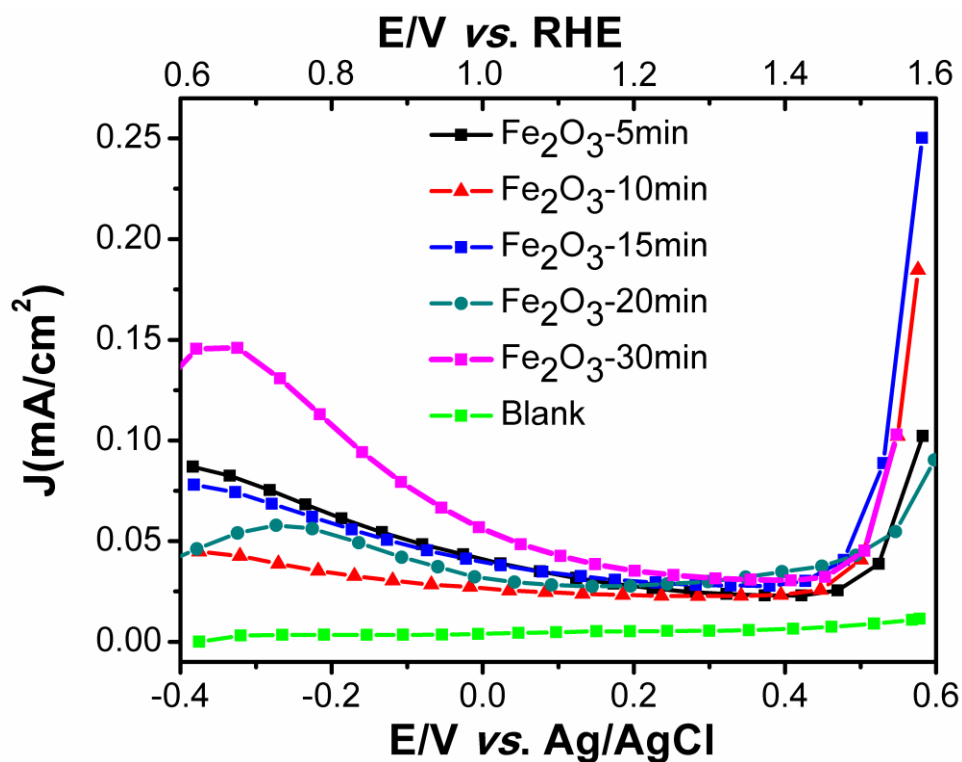


Figure S2 *J-V* curve of the hematite film on the FTO under different deposition time measured at 0.4V (vs. Ag/AgCl), 100mW/cm², 1M KOH (pH=13.6): a, different deposition time of 0min, 5min, 10min, and 15min, 20 min, 30min.

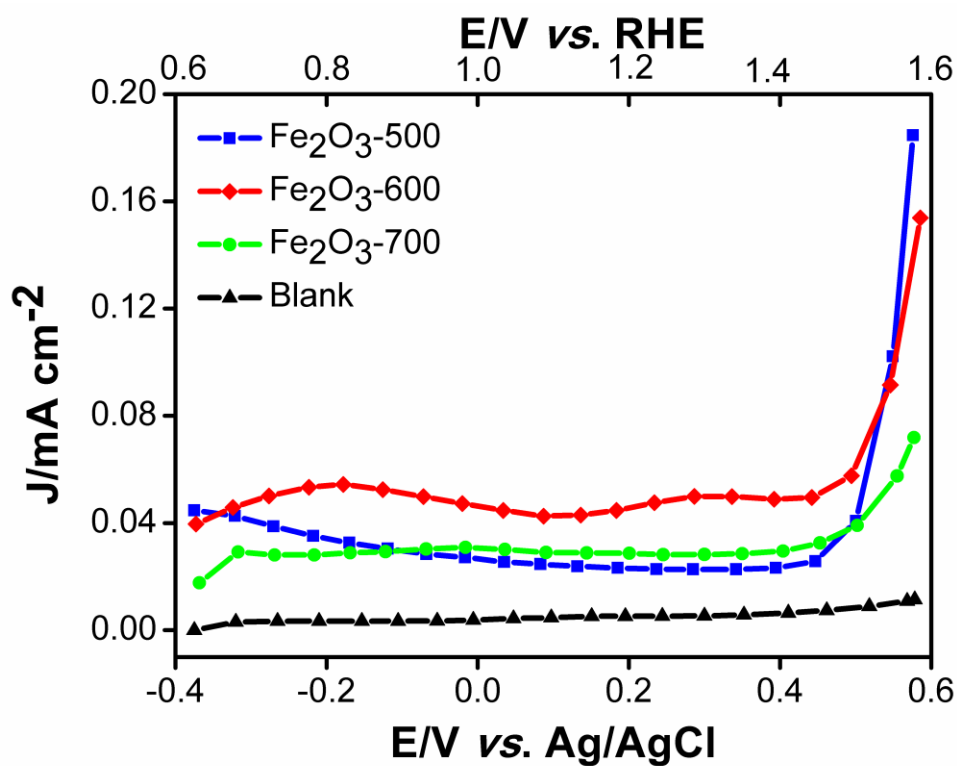


Figure S3 *J-V* curve of the hematite film on the FTO under different annealing temperature measured at 0.4V (vs. Ag/AgCl), 100mW/cm², 1M KOH (pH=13.6): blank sample (black UpTriangle), 500 °C (Blue Square), 600 °C (Red circle) and 700 °C (Green diamond).

Compared the J - V curve of the hematite film on the FTO under different deposition time in Fig. S2, it can be concluded that the photocurrent of the α - Fe_2O_3 photoanode is increased from 0.01 mA cm^{-2} of 5 min deposition sample to 0.05 mA cm^{-2} at the 20 min deposition then getting down to 0.03 mA cm^{-2} of 30 min deposition α - Fe_2O_3 (0.4 V, 100 mW, visible light). It is proved that there is an optimization in deposition time which could make sure a better photocurrent density in water splitting. There are some reports [1] have explained the reason as below. The initial increase of PEC performance is mainly due to the increased amount of photoactive α - Fe_2O_3 nanoparticles, which improves the light absorption as well as the number of photoexcited charge carriers. When the deposition time extends, the thickness of this film keeps increasing and reaches to the certain threshold which exceeds the combine between the film and the substrate. The recombination rate of the electrons and holes becomes the major factor in the water splitting process. It is known the compact and thick film takes the carrier more time to reach the top, leading to the reduction in separation efficiency of the photogenerated carriers and the photocurrent. Considering all the factor in the PEC water splitting, the best deposition time is around 15 - 20 min under 1.2 V, 70 °C, pH = 4.1. The J - V curves of the hematite film on the FTO under different annealing temperatures were shown Fig. S3. Clearly, it can be seen that the PEC has a better photocurrent density at the 600 °C in Figure SI-3. Shown in this experiment, the resistance of the α - Fe_2O_3 photoanode would increase with the annealing temperature. However, there are some reports shown that with high

temperature annealing Sn can be induced from FTO to the α - Fe_2O_3 film with the consequential enhancement of the photo activity [2, 3]. When the impedance rises into the value that hampers the transport of charge carriers it will decrease the photocurrent of the α - Fe_2O_3 semiconductor. Therefore, to get a good PEC property, it is necessary to take all the parameters into consideration. In this experiment, the sample annealing at 600 °C for 20 min has a better PEC performance.

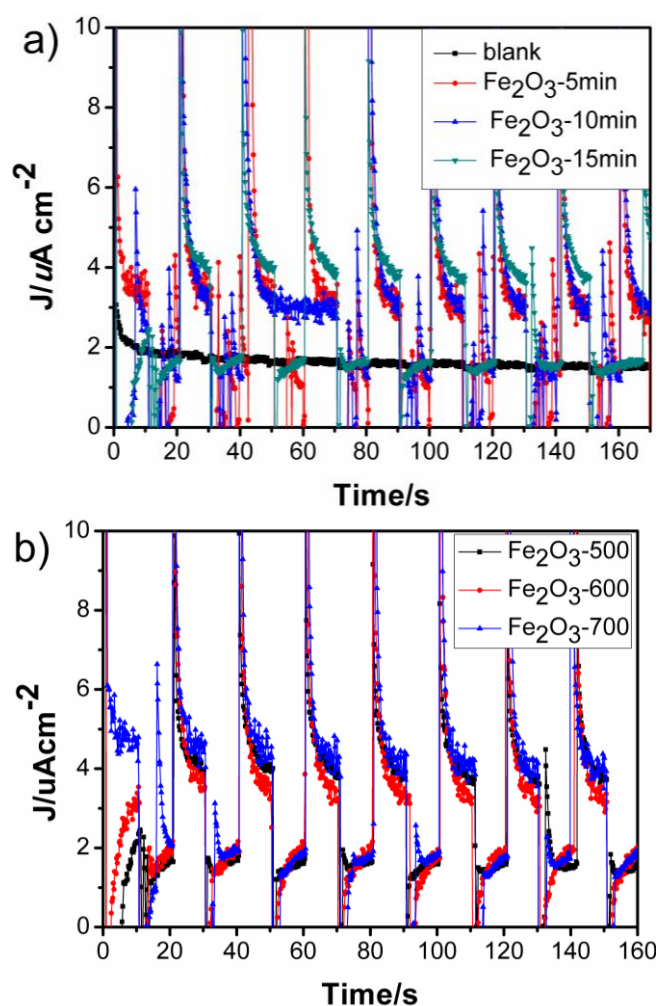


Figure S4 Chopped-light photocurrent of the hematite film at 0.4V (vs. Ag/AgCl), 100mW/cm², 1M KOH (pH=13.6): a, different deposition time of 0min, 5min, 10min, and 15min; b, various annealing temperature of 500 °C, 600 °C, and 700 °C for 10 min.

And it is also verified by the measured instantaneous photocurrent vs voltage (chopped light J - V , Fig. S4) during the J - V testing at the positive potential of 0.4 V in

1M KOH. The chopped-light photocurrent obviously indicated that the Fe_2O_3 showed photoactivity when the light illuminated and turned to $10^{-7} \text{ A cm}^{-2}$ in darkness which is negligible.

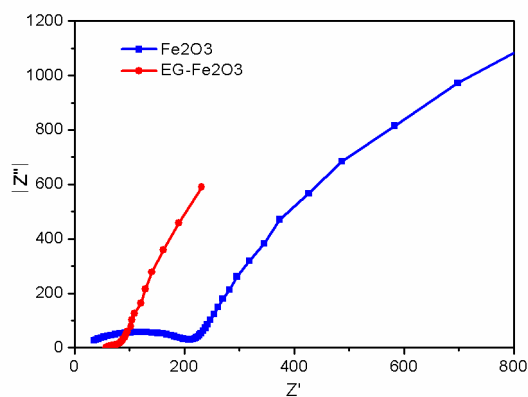
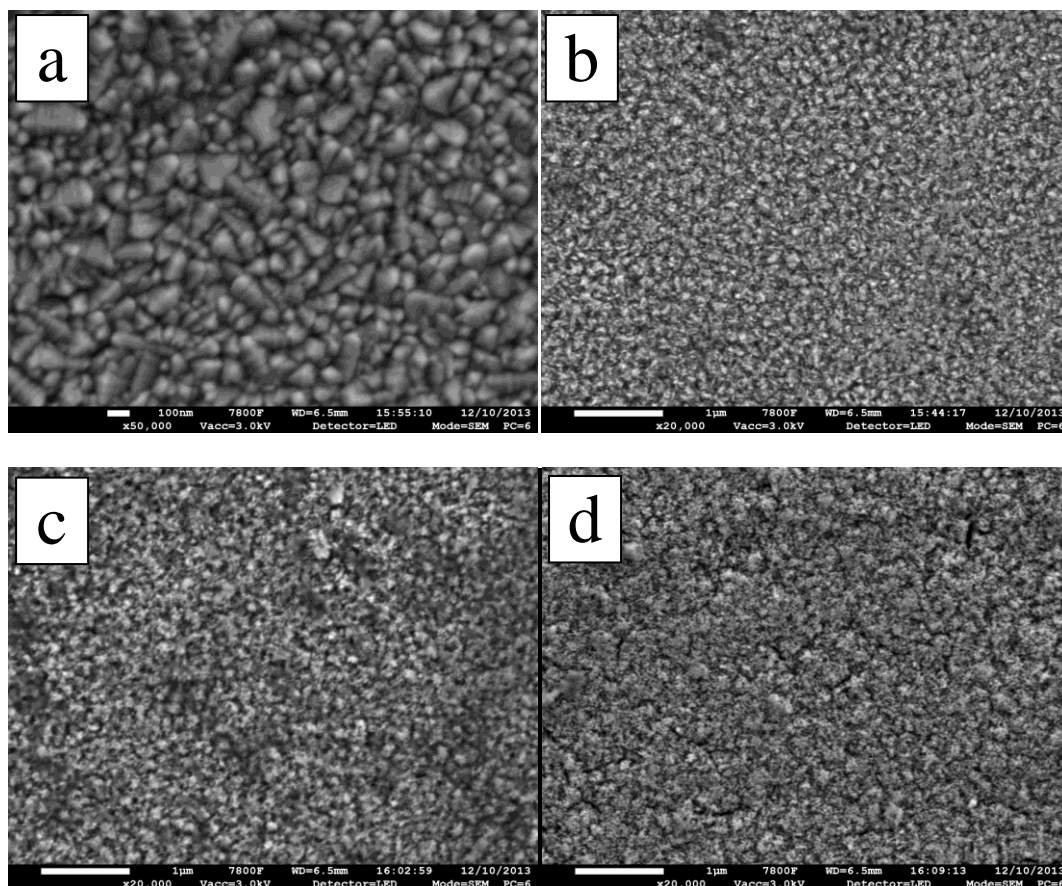


Figure S5 electrochemical impedance spectra of $\alpha\text{-Fe}_2\text{O}_3$ and EG- $\alpha\text{-Fe}_2\text{O}_3$

The semicircles of the $\alpha\text{-Fe}_2\text{O}_3$ are much larger than the EG- $\alpha\text{-Fe}_2\text{O}_3$, indicating that the photogenerated charge carriers of EG- $\alpha\text{-Fe}_2\text{O}_3$ substantially lower the charge transfer resistance.



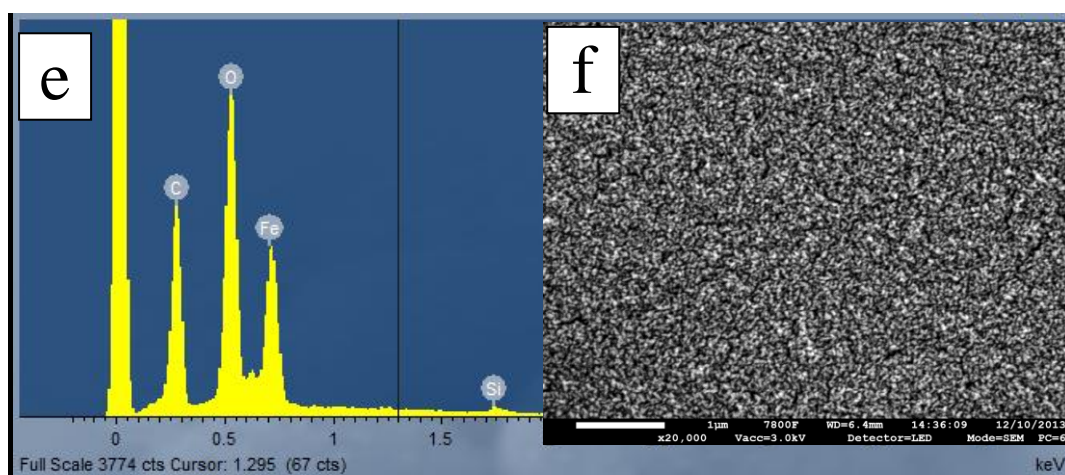


Figure S6 FESEM and EDS of electrodeposited hematite samples in the aqueous solution (a), top view of FTO substrate; (b), top view of α -Fe₂O₃ nanostructure with 5 min deposition; (c), top view of α -Fe₂O₃ nanostructure with 10 min deposition; (d), top view of α -Fe₂O₃ nanostructure with 15 min deposition; (e) EDS spectra for α -Fe₂O₃ nanostructure with 20 min deposition. (f), top view of α -Fe₂O₃ nanostructure with 20 min deposition

References

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