Supporting Information

Efficient Photoelectrochemical Water Splitting of Nanostructured Hematite on Three-dimensional (3D) Nanoporous Metal Electrode

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Experimental:

Preparation of 3D nanoporous gold (3D-NG) electrode

All chemicals in this study were used as-received without further purification. Electrochemical deposition was performed in a traditional three-electrode system for the growth of the Au/Ag alloy films. We used an Ag/AgCl electrode as the reference electrode, a Pt plate as the counter electrode, and a gold substrate as the working electrode. The electrolyte was aqueous solution containing 0.02 M $KAu(CN)_2$, 0.06 M $KAg(CN)_2$, and 0.25 M Na_2CO_3. The potential for Au/Ag alloy deposition was −1.2 V. To prepare the 3D-NG structure, Au/Ag alloy films were prepared first and the Ag part was selectively etched by concentrated nitric acid for 1 hour at room temperature. The deposition time was found to affect the growth of the 3D-NG films. (see Fig. S2).

Preparation of the hematite thin film photoanodes

Hematite photoanodes were prepared via a simple solution-based method and one-step annealing. Pristine α-Fe_2O_3 from β-FeOOH NPs was prepared following recently reported procedures.[1] For the synthesis of α-Fe_2O_3/3D-NG, the 3D-NG electrode was immersed in 20 ml of a $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution and kept in a convection oven at 75 ^{o}C with a ramp rate of 1 ^{o}C/min for 3 hours. The iron hydroxide with various NPs size can be prepared by varying the initial concentration of $Fe(NO_3)_3 \cdot 9H_2O$ aqueous solution from 5 mM to 50 mM. The samples were washed with DI water and EtOH. Finally, β-FeOOH/3D-NG was annealed at 750 ^{o}C for 3 min and was naturally cooled to room temperature.

Characterization

The morphology of the structures was examined by SEM (Hitachi model S-4800) and TEM (FEI Tecnai G^2 F30). The variation of the chemical composition was analyzed by X-ray diffraction (Rigaku D/MAX-2500) and XPS (Thermo Fisher, UK). Photoconversion efficiency was confirmed using the IPCE measurement system (QEX10, PV measurements).

Photoelectrochemical measurement

The PEC performance of the α-Fe_2O_3/3D-NG electrodes was explored in a three-cell electrode system under front-side illumination of AM 1.5 G (Newport solar simulator) using a potentiostat (Princeton Applied research VersaSTAT3, AMETEK). The power of the solar simulator was measured to be 100 mW/cm^2. An Ag/AgCl electrode and a Pt mesh were used as reference and counter electrodes, respectively. A solution of 1 M NaOH was used as an electrolyte. The exposed area of the working electrode was 0.393 cm^2. Photocurrent stability tests were carried out by measuring the photocurrent produced under chopped light irradiation (light/dark cycles of 10 s) at a bias of 1.5 V vs. RHE. Electrochemical impedance spectroscopy (EIS) in the dark was carried out at a frequency range from 100 kHz to 0.1 Hz using a potentiostat. Mott-Schottky plots were obtained at a 10 kHz frequency in the dark conditions

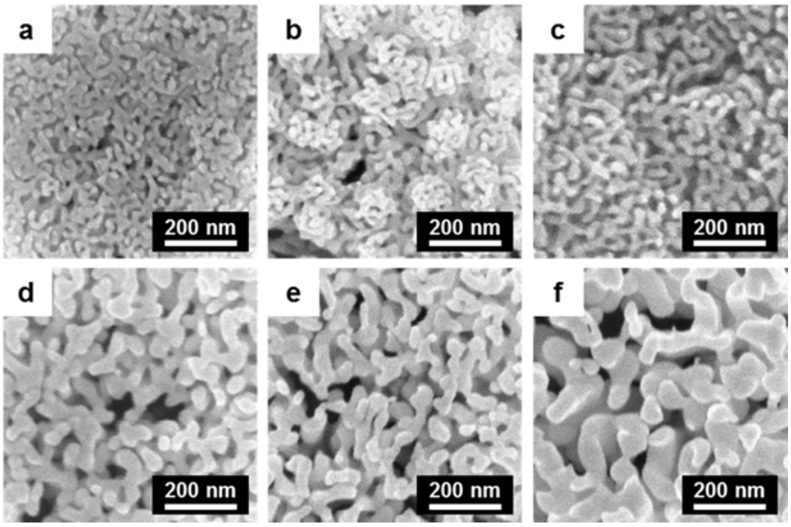


Fig. S1 SEM images of 3D-NG films which show the variations in the size of nanopore at chemical de-alloying in 70 vol% HNO_3 for (a) 10 min, (b) 30 min, (c) 1 h, (d) 2 h, (e) 4 h, and (f) 24 h.

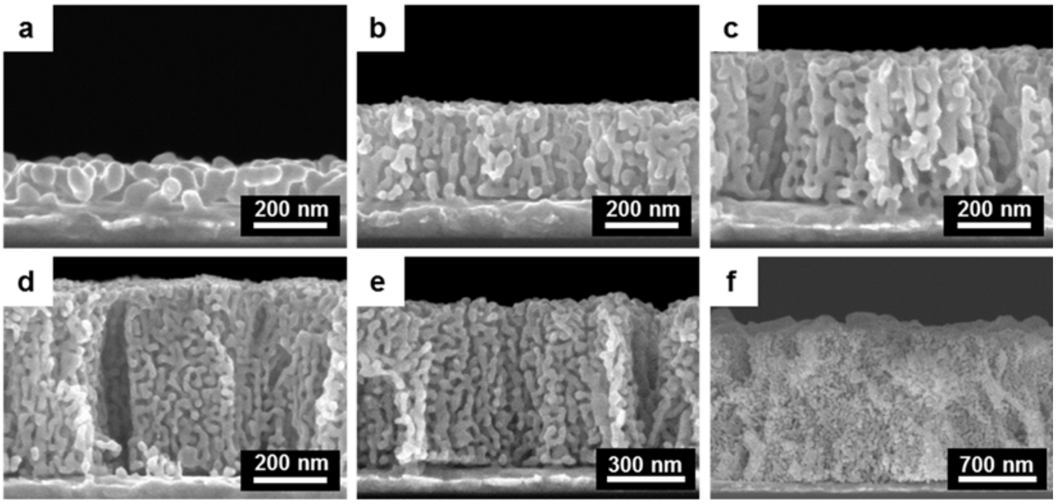


Fig. S2 SEM images of 3D-NG films with different deposition times for (a) 60 s, (b) 120 s, (c) 180 s, (d) 240 s, (e) 300 s, and (f) 600 s.

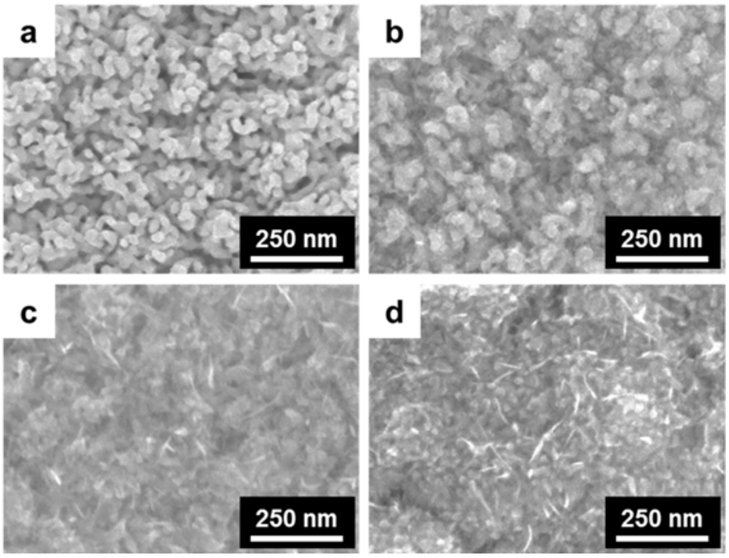
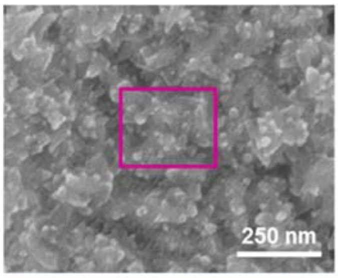


Fig. S3 SEM images of β-FeOOH/3D-NG which show the variations in the size of nanoparticles at various concentrations of $Fe(NO_3)_3 \cdot 9H_2O$ solution: (a) 5 mM, (b) 10 mM, (c) 25 mM and (d) 50 mM.



Element	Weight %	Atomic %
O K	23.57	70.55
Fe K	17.68	15.16
Au M	58.75	14.28
Totals	100.00	100.00

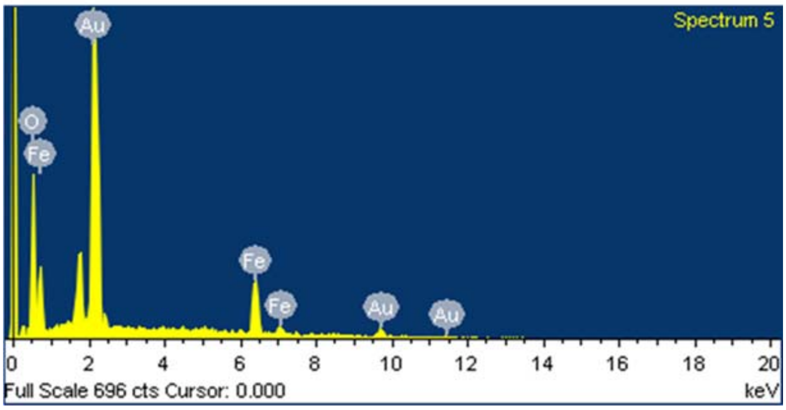


Fig. S4 SEM-EDS results of α-Fe_2O_3/3D-NG thin film prepared from an aqueous solution of 50 mM $Fe(NO_3)_3 \cdot 9H_2O$.

Resistivity (10^{-7} Ω·m)	(A) Bare gold film	(B) 3D-NG film	(C) Fe_2O_3/3D-NG at 750 ºC
1	2.505	1.475	2.488
2	2.139	1.329	2.547
3	2.551	1.392	2.944
4	2.207	1.408	3.14
5	2.342	1.361	2.413
6	2.381	1.429	3.025

Bare gold film	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
A	6	2.354	0.16144	14.125	2.139	2.3615	2.551

3D-NG film	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
B	6	1.399	0.05128	8.394	1.329	1.4	1.475

Fe_2O_3 /3D-NG	N total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
C	6	2.759	0.31248	16.557	2.413	2.7455	3.14

Fig. S5 Electrical conductivity measured for the *α*-Fe_2O_3/3D-NG annealed at 750 °C.

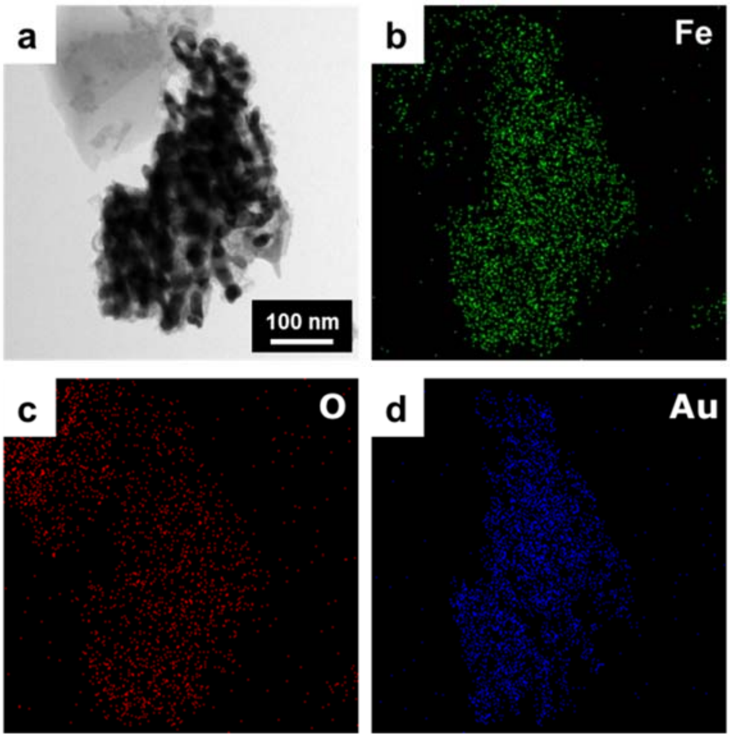


Fig. S6 EDS elemental maps of α-Fe_2O_3/3D-NG: (a) TEM images; (b) iron (Fe Kα1); (c) oxygen (O Kα1); (d) gold (Au Lα1).

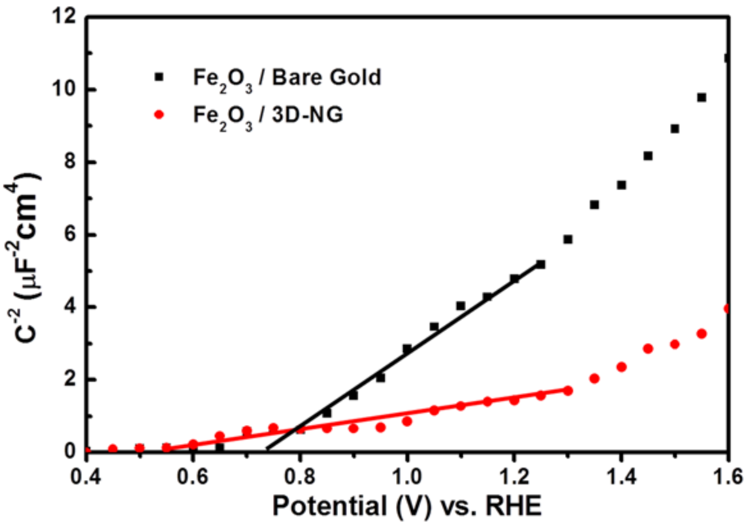
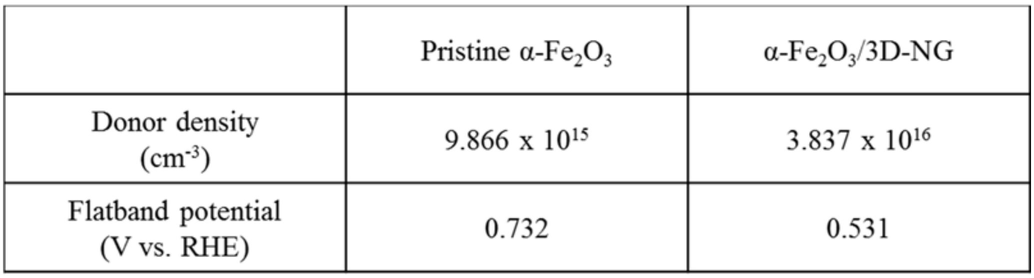


Fig. S7 Mott-Schottky plot of pristine *α*-Fe_2O_3 and *α*-Fe_2O_3/3D-NG.

A Mott–Schottky analysis was performed to estimate the donor density (N_d) and flat band potential (E_{FB}), as shown in Fig S7. We can check the donor density and flat band potential through the simple calculation of the following equation by the slope and intercept with the potential axis, respectively.

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 e N_d A^2}(E - E_{FB} - \frac{k_B T}{e})$$

, where ε is the dielectric constant, ε_0 is the permittivity of the vacuum, e is the electron charge, A is the active area, E is the applied potential, k_B is the Boltzmann constant and T is the absolute temperature. The result of the calculation is in Table S1. They all have positive slopes which indicate that hematite on a gold substrate is an n-type semiconductor with electrons as the major charge carriers. The calculated donor density confirms the enhanced efficient electron transfer of 3D-NG over that of the pristine one. The onset potential indicates that reduction reactions were well-matched with the calculated flat band potential from Mott-Schottky plots.



	Pristine α-Fe_2O_3	α-Fe_2O_3/3D-NG
Donor density (cm^{-3})	9.866×10^{15}	3.837×10^{16}
Flatband potential (V vs. RHE)	0.732	0.531

Table S1 Donor density and flat band potential obtained from the Mott-Schottky plot.

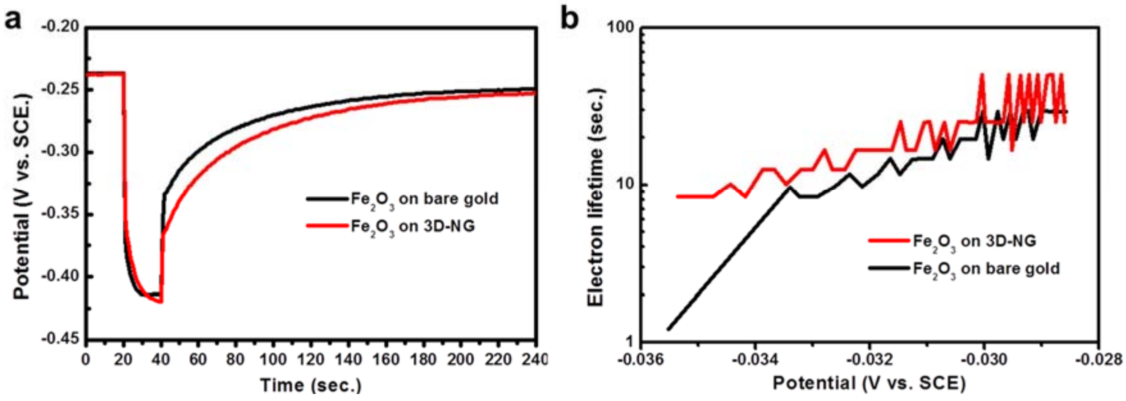


Fig. S8 (a) Open circuit potential vs. time profile of pristine α-Fe_2O_3 and α-Fe_2O_3/3D-NG. (b) The corresponding electron lifetime measurements determined from the V_{oc} decay.

To better understanding of the electron recombination kinetics of pristine α-Fe_2O_3 and α-Fe_2O_3/3D-NG, we investigated the decay of photovoltage, V_{oc} as a function of time upon turning off the illumination shown in Fig. S8a. The open circuit photovoltage decay under dark conditions can be exploited for the evaluation of photoelectron lifetime by measuring V_{oc} with time.[2] The calculated electron lifetime is plotted in Fig. S8b as a function of V_{oc} for pristine α-Fe_2O_3 and α-Fe_2O_3/3D-NG, which confirms the longer lifetime of photoexcited electrons in α-Fe_2O_3/3D-NG than in α-Fe_2O_3. This again confirms that the 3D-NG current collector can drive facile electron transport and thus suppress charge recombination.

References

1. J. Y. Kim, G. Magesh, D. H. Youn, J.-W. Jang, J. Kubota, K. Domen, and J. S. Lee, *Sci. Rep.*, 2013, **3**, 2681.

2. K. Kim, M.-J. Kim, S.-I. Kim, and J.-H. Jang, *Sci. Rep.*, 2013,**3**,3330.