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Supporting Information

Nanoporous hematite structures to overcome short diffusion lengths in water splitting

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Experimental

Chemicals used

Iron (III) chloride hexahydrate (Kanto chemical, > 97.0%), Sodium Hydroxide (Samchun, extra pure), Ethanol(SK chemical, > 95%), Boric acid (Sigma-Aldrich, > 99.5%), Methylene blue (Sigma-Aldrich, > 82%). All chemicals were used without further purification.

Preparation of pristine α -Fe₂O₃ and boric acid treated α -Fe₂O₃

For the synthesis of P-H, B5-H, B10-H and B20-H, the FTO substrate was immersed in a mixture of 0 wt%, 5 wt%, 10 wt% and 20 wt% of H₃BO₃, respectively, and 40 ml of FeCl₃•6H₂O and kept in a convection oven at 100 °C with a ramp rate of 1 °C/min for 4 hrs. The samples were washed

with DI water and EtOH. Finally β -FeOOH was annealed at 550 °C for 1 h and 800 °C for 20 min in the furnace.

Photoelectrochemical measurement

The PEC performance of the α -Fe₂O₃ electrodes was explored in a three-cell electrode system under front-side illumination of AM 1.5 G. 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 fabricated to have an exact value of 0.25 cm² using scotch tape. 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 versus RHE. Electrochemical impedance spectroscopy (EIS) was carried out at a frequency range from 100 kHz to 0.1 Hz using a potentiostat. The photodegradation of methylene blue (MB) was measured by separately immersing P-H and B5-H in 100ml of the MB solution (50mg/l in water) under illumination. After the given exposure period, the absorbance change of MB was tracked by a UVvisible spectrophotometer to compare the photocatalytic activity.



Figure S1. Raman spectroscopy of pure β -FeOOH and 5 wt% of boric-acid treated β -FeOOH.

Table S1. The summary of relation between the concentration of boric acid and the thickness of FeOOH.

| | P-H | B-5H | B-10H | В-20Н |
|--------------------|------|------|-------|-------|
| Thickness of FeOOH | 80nm | 35nm | 60nm | 160nm |



Figure S2. (a) TEM image of FeOOH as a precursor of α -Fe₂O₃: (a) pristine FeOOH, (b) 5wt% boricacid treated FeOOH, (c)10wt% boric-acid treated FeOOH and, (d) 20wt% boric-acid treated FeOOH.



Figure S3. TEM image of α -Fe₂O₃: (a) pristine α -Fe₂O₃ (b) 5wt% boric-acid treated α -Fe₂O₃ (B5-H), (c)10wt% boric-acid treated α -Fe₂O₃ (B10-H), and (d) 20wt% boric-acid treated α -Fe₂O₃. All TEM images are taken after 550 °C treatment.



Figure S4. BET analysis of α - Fe_2O_3 : (a) P-H, (b) B5-H, (c) B10-H and (d) B20-H. The image below is the table for the BET value.



Figure S5. (a) TEM image of 5wt% boric-acid treated β -FeOOH. (b) High magnification TEM image of 5wt% boric-acid treated β -FeOOH. (c) TEM image of 550 °C treated B5-H (5wt% boric-acid treated α -Fe₂O₃). (d) TEM image of 800 °C treated B5-H. (e) TEM image of pure β -FeOOH. (f) High magnification TEM image of pure β -FeOOH. (g) TEM image of 550 °C treated P-H (pristine α -Fe₂O₃) and (h) TEM image of 800 °C treated P-H



Figure S6. SEM images of α -Fe₂O₃ before and after 800°C heat-treatment.: (a) SEM image of pristine hematite (P-H). (b) SEM image of P-H after 800°C heat-treatment. (c) SEM image of boric acid 5wt% treated hematite (B5-H). (d) SEM image of B5-H after 800°C heat-treatment.



Figure S7. Cross sectional SEM images of (a) 550 °C treated P-H, (b) 550 °C treated B5-H, (c) 800 °C treated P-H and (d) 800 °C treated B5-H.



Figure S8. (a) Open circuit potential of the P-H, B5-H, B10-H and B20-H under light irradiation. (b) The corresponding electron lifetimes as a function of open circuit voltage.

To understand the charge-transport properties of P-H and B5-H more clearly, we measured the electron lifetimes (τ n) by monitoring the decay of open circuit voltage (V_{oc}) after short-time illumination in Fig. S8. After photoexcited electrons are accumulated in α -Fe₂O₃ by the initial illumination, the electron density in the conduction band of the α -Fe₂O₃ is reduced due to the recombination of electrons and holes under the non-illumination conditions. Therefore, the rate of V_{oc} decay can be considered to be the rate of recombination. A much lower rate of V_{oc} decay was observed in the B5-H sample relative to that of P-H, as shown in Fig. S8 a. The calculated electron life time of B5-H was higher than that of P-H, suggesting smaller α -Fe₂O₃ particles enhance charge transport and reduce electron recombination, as shown in Fig. S8 b. The electron lifetime was calculated from the following equation

$$\tau_n = -(\frac{k_B T}{e})(\frac{dV_{OC}}{dt})^{-1}$$

Where k_B is the Boltzmann's constant, T is the temperature, e is the elementary charge, and V_{oc} is the open-circuit voltage at time t.



Figure S9. The TEM image of the B5-H nanorod with 3 domains. Each domain is marked by the dotted line of star, circle, and triangle. They have the same directional plane along the [110] direction.

There is a typical and inevitable drawback when we increase the surface area of nanoparticles. The increased portion of the grain boundary in the metal oxide nanoparticles deteriorates the charge transport properties at the interface of the adjacent nanoparticles. However, our structures show somewhat different behavior because most particles preferentially have the same directional plane of (110) along which the electrons have 4 order higher transport properties than in the other plane in hematite. The TEM image of B5-H in Figure S9 reflects the area of the grain boundary created

by overlapping of three nanodomains in the hierarchical hematite nanorods. Importantly, as can be seen in the TEM image of the boric acid-treated nanoporous structures below, even though the nanorods are composed a number of separated domains, each domain has the same (110) plane, which implies that the overall conductivity of a hierarchical nanostructure is not inferior to that of the comb-shaped pristine hematite, which can also be confirmed by our recently updated conductivity measurement data in Figure S10. Therefore, the charge is transferred to the FTO glass with a similar rate along the [110] direction in both pristine and hierarchical nanostructures. We believe the TEM image and the conductivity data give the evidence that the transport properties of our boric acid treated hematite samples (B-5H), which are composed many hematite nanodomains, are rarely affected by the grain boundary in hierarchical nanorods.



Figure S10. (a) Schematic illustration of electrode which composed of hematite and au to test the conductivity. The 100nm of au was deposited on the hematite and FTO substrate, respectively. (b) The current-voltage curve of the hematite.



Figure S11. The absorption spectra of P-H, B5-H, B10-H and B20-H with same height of hematite film.



Figure S12. XPS spectra of P-H and B5-H.



Figure S13. Photocatalytic degradation of MB under light irradiation using P-H and B5-H.