Electronic Supplementary Information (ESI) for

Facet-Dependent Activity of Hematite Nanocrystals toward Oxygen Evolution Reaction

Toshihiro Takashima,*[a,b,c] Shota Hemmi,[b] Qingyu Liu [c] and Hiroshi Irie [a,b,c]

[a.] *Clean Energy Research Center, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan*
[b.] *Integrated Graduate School of Medicine, Engineering and Agricultural Sciences, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan*
[c.] *Department of Applied Chemistry, Faculty of Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu, Yamanashi 400-8511, Japan*

Contents

ESI-1) HRTEM images of α-Fe_2O_3 nanocrystals. (Fig. S1).

α-Fe_2O_3 cube

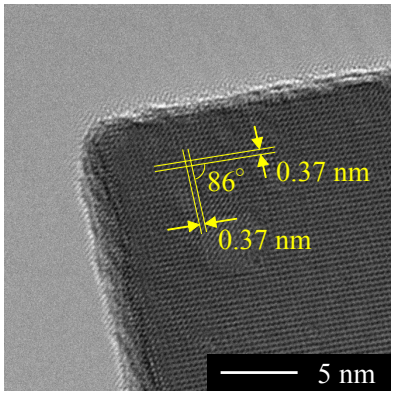

Fig. S1 High-resolution TEM (HRTEM) image of α-Fe_2O_3 cube.

The HRTEM image of α-Fe_2O_3 cube shows an interlaced two-dimension lattice fringes with a dihedral angle of 86° and an interplanar spacing of 0.37 nm, corresponding to the (012) and (10-2) lattice planes, respectively [1,2]. Because both planes belong to the (012) plane class, the α-Fe_2O_3 cube was revealed to be enclosed by the (012) facet.

α-Fe_2O_3 bipyramid

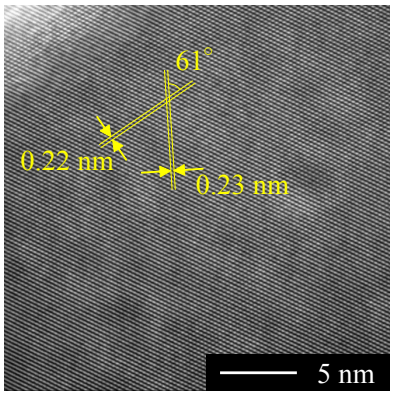

Fig. S2 High-resolution TEM (HRTEM) image of α-Fe_2O_3 bipyramid.

From the HRTEM image of α-Fe_2O_3 bipyramid, the lattice fringes with spacings of 0.22 and 0.23 nm and a dihedral angle of 61° were observed. These are assigned to the (113) and (006) planes,

respectively, and matches well with the ideal geometrical model of α-Fe_2O_3 hexagonal bipyramid enclosed by the (113) facets [3,4].

α-Fe_2O_3 plate

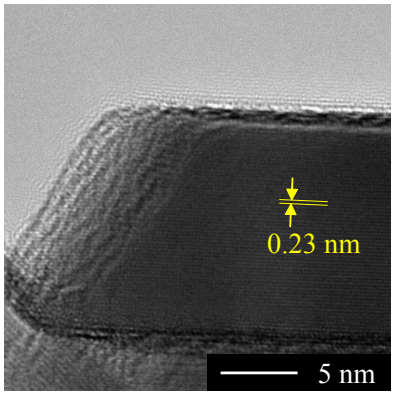

Fig. S3 High-resolution TEM (HRTEM) image of α-Fe_2O_3 plate.

The above HRTEM image is the side view of α-Fe_2O_3 plate. A spacing of the lattice parallel to the top surface was found to be 0.23 nm, corresponding to the distance between the (006) planes [5]. Therefore, the exposed basal plane can be indexed to the (001) facet.

ESI-2) Polarization curves at pH 13 normalized by ECSAs. (Fig. S4).

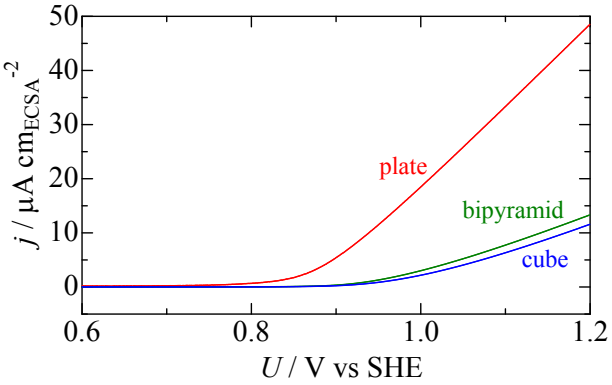

Fig. S4 ECSA-normalized polarization curves of α-Fe_2O_3 nanocrystals measured at pH 13.

ESI-3) Tafel plots of α-Fe_2O_3 nanocrystals. (Fig. S5).

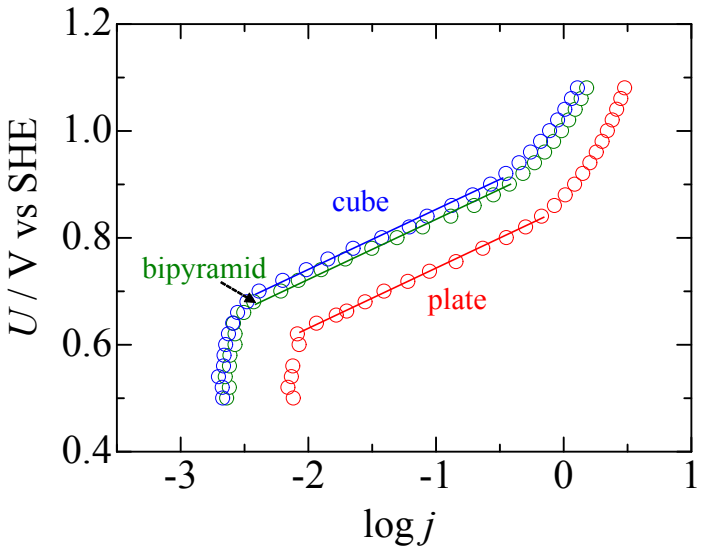

Fig. S5 Tafel plots of α-Fe_2O_3 cube, bipyramid and plate.

ESI-4) Polarization curves at pH 7 normalized by ECSAs. (Fig. S6).

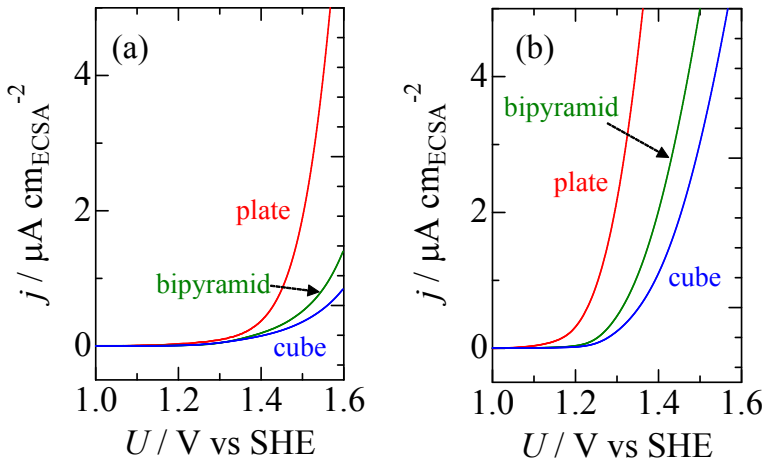

Fig. S6 ECSA-normalized polarization curves of α-Fe_2O_3 nanocrystals measured at pH 7. The measurements were conducted in (a) 0.5 M Na_2SO_4 and (b) the mixture of 0.5 M Na_2SO_4 and 0.05 M lutidine.

ESI-5) Results of kinetic isotope effect experiments. (Fig. S7).

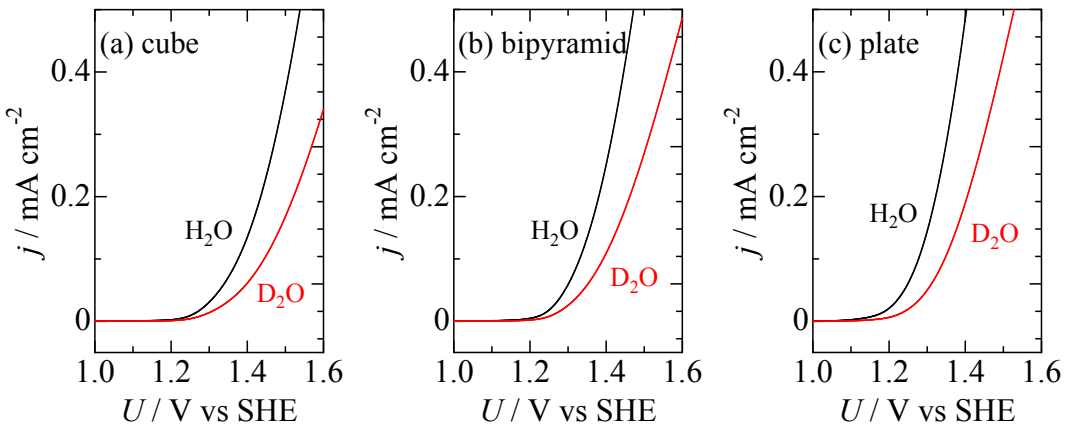

Fig. S7 Polarization curves of α-Fe_2O_3 with different morphologies ((a) cube, (b) bipyramid and (c) plate) measured to examine the kinetic isotope effect (black line: H_2O, red line: D_2O). The measurements were conducted at pH (pD) 7 in the presence of lutidine.

When the electrolyte prepared using D_2O instead of H_2O was used, decreases in current density were observed for all the samples, indicating that the kinetic isotope effect appeared. Because the kinetic isotope effect is observed when concerted PCET proceeds, these results indicates that concerted PCET was induced on the surfaces of α-Fe_2O_3 cube, bipyramid and plate in the presence of lutidine.

References

[1] C. Wang, C. Zhu, X. Ren, J. Shi, L. Wang and B. Lv, *CrystEngComm*, 2019, **21**, 6390–6395.

[2] H. Wan, T. Liu, X. Liu, J. Pan, N. Zhang, R. Ma, S. Liang, H. Wang and G. Qiu, *RSC Adv.*, 2016, **6**, 66879–66883.

[3] M. Lin, L. Tng, T. Lim, M. Choo, J. Zhang, H. R. Tan and S. Bai, *J. Phys. Chem. C*, 2014, **118**, 10903−10910.

[4] M. Chen, H. Yin, X. Li, Y. Qiu, G. Cao, J. Wang, X. Yang and P. Wang, *J. Hazard. Mater.*, 2020, **395**, 122628.

[5] M. Zong, X. Zhang, Y. Wang, X. Huang, J. Zhou, Z. Wang, J. J. De Yoreo, X. Lu and K. M. Rosso, *Inorg. Chem.*, 2019, **58**, 16727−16735.