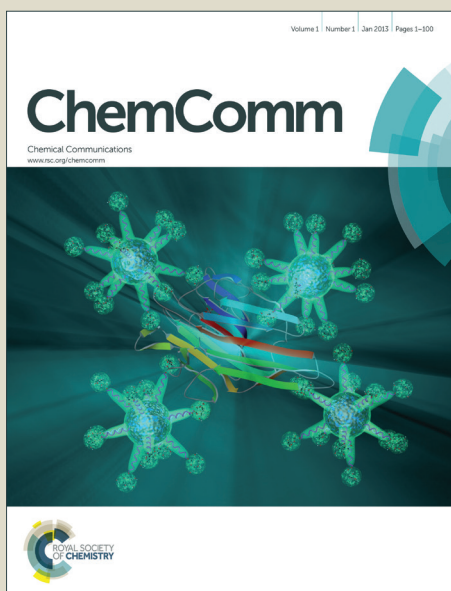


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COMMUNICATION

Manual Assembly of Nanocrystals for Enhanced Photoelectrochemical Efficiency of Hematite Film

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H. G. Cha, M. J. Kang, I. C. Hwang, H. Kim, K. B. Yoon and Y. S. Kang *†

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To improve the optoelectronic properties of hematite film as photoanode, hematite film was orientated on (012) plane using secondary growth of organized microcrystal and showed promising photoelectrochemical effects comparing with random oriented one with maximum photocurrent of 0.8 mA/cm² at 1.23 V vs. RHE under the 1 sun.

The design for morphology or exposed facet of photocatalyst crystal has been received the intensive interesting from theoretical prediction that high energy facet of photocatalytic crystals have shown high photocatalytic activity than low surface energy facets of ones. Several groups have substantiated above theoretical prediction by successful synthesis of particular facet-exposed photocatalytic crystals and realized to evaluate of the role of crystal facet in real photocatalyst reaction.¹ In this regard, morphology and controlled crystal-facet synthesis of semiconductor for photocatalysts are becoming attracted issue because of enhanced or optimized photocatalytic properties by tailoring the surface atomic structures.^{2,3} Several studies have extended this route to controlled crystal-facet without capping agent. For example, G. Lu *et al.* investigated that {001} facets of anatase TiO₂ are much more reactive than {101} facets for the H₂ production⁴ and L. Zhi *et al.* demonstrated that hematite nanorods with {110} facets are much more photo-reactive than other facets such as {001} and {012} for photodegradation of organic dye.⁵ From the viewpoint of photoelectrochemical cell (PEC) for utilizing solar light, the photoanode or photocathode exposed with photoactive a particular facet is highly desired. Although specific element doping has shown great potential in achieving high solar-energy conversion efficiency, oriented thin film as photoelectrode with certain photoactive facet can be alternative way to improve PEC efficiency by facilitating transport/collecting of photo-generated electrons and holes based on anisotropic charge carrier mobility in hematite.

Hematite (α -Fe₂O₃)⁶ is the most stable iron oxide, n-type semiconducting properties under ambient conditions, non-toxic, abundant, low-cost, and low band gap (~ 2.1 eV)⁷ that allows for the absorption of a significant portion of the incident visible solar spectrum as well as sufficient chemical and photo-electrochemical (PEC) stability in alkaline aqueous electrolyte.⁸ Therefore, it is a potentially viable photoanode for use in solar water splitting, thereby producing oxygen. However, reported efficiencies of hematite photoanode are significantly lower than the predicted value due to low conductivity, short excited-state lifetime (<10 ps)⁹, poor oxygen evolution reaction kinetics, and short hole diffusion length (2–4 nm).¹⁰ In this work, we report methods for the assembly of nano- and micro-sized crystals with plane orientation using straightforward manual assembly (rubbing method)¹¹ and secondary growth¹² of seed layer in the hydrothermal reaction via oriented attachment¹³ for the fabrication of transparent and plane oriented hematite film in FTO glass (F:SnO₂ glass) (Figure S1).

Significantly, an unprecedented (012) plane oriented hematite film showed high PEC performance compared to random oriented one without doping. The photocurrent on-set potential of (012) plane orientated hematite film is shifted ca. 0.1 V to cathodic shift compared with random orientated one and achieves the maximum photocurrent density of 0.8 mA/cm² at 1.23 V vs RHE.

Theoretical calculations suggest that Fe₂O₃(001) and (012) surfaces have similar surface energies, with the surface energy of the (012) slightly lower by ~ 0.1 J/m² in hematite, which can contribute to select synthetic method to get the largest exposure surface area of the highest photoactive facet.¹⁴

Monodisperse hematite pseudocubes (Figure 1(a-1) and S2) with diameter of ~ 550 nm were prepared as the building blocks for the orientated crystals by simple hydrothermal reaction according to the modified previous reports.¹⁵ From cross-sectional TEM image and SAED pattern in Figure S2(b-c), hematite crystal was bounded entirely by {012} facets because it was consisted with rod-shaped subunits by

orientated attachment along in both longitudinal and lateral directions of rod-shaped subunits. The crystal structure of synthesized hematite crystals has been characterized to be pure $\alpha\text{-Fe}_2\text{O}_3$ phase (JCPDS card no. 33-0664) by analysis of X-ray diffraction pattern (XRD) in Figure 1(a). FTO glass was spin-coated with polyethyleneimine (PEI) in ethanol; hematite crystals were then rubbed gently by finger on the PEI coated substrate. Hematite crystals were formed by hydrogen bonding among the two layers of hematite hydroxyl groups and PEI on the FTO glass.

PEI should be removed by calcination at 500°C for 3 h¹⁶ in order to not only to improve adhesion between hematite crystal and FTO glass but also to remove ineffective one to hinder charge transportation.¹⁷ After rubbing process, the diffraction lines only appeared at 24.15° and 49.46° of 2θ corresponding to (012) and (012) plane of the crystals as shown by analysis of the XRD pattern in Figure 1(b). This means that the film was orientated along with (012) plane. Calcined hematite crystals on FTO glass readily allows continuous (012) plane growth with gaps filling between crystals and the surface of FTO glass by secondary growth through orientated attachment.¹⁵ The SEM image and XRD pattern of hematite films after secondary growth are shown in Figure 1(c,c-1). XRD patterns of secondary grown hematite film with different reaction times show that (012) and (024) peaks intensity gradually increases from 1.1 to 2.85 times higher with increasing reaction time (Figure S3 (a)), compared with respect to the dominant peak intensity at 26.60° from FTO glass substrate, although other peaks from hematite were shown due to roughness of FTO glass. This implies that the gaps filling among hematite crystals and increasing the thickness occurs with keeping (012) plane orientation after secondary growth. The thickness of hematite film after secondary growth for 4 h was $\sim 750\text{--}800\text{ nm}$ as shown in Figure 2(a).

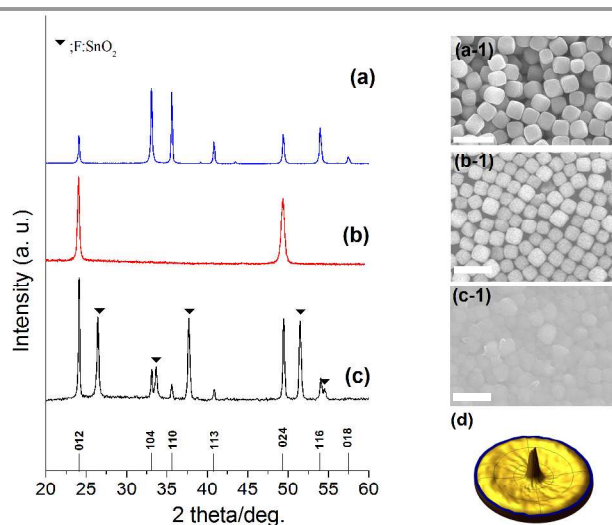


Figure 1. XRD patterns and SEM images of hematite crystals (a, a-1), arranged hematite crystal on amorphous glass substrate (b, b-1) and secondary grown hematite continuous film on the FTO glass (c, c-1) at 150°C for 4 h and annealed 500°C for 3 h. (d) (012) XRD pole figure of secondary grown hematite continuous film. All scale bars are $1\text{ }\mu\text{m}$.

XRD pole figure is a well-established technique to provide crystal growth orientation on the surface (Figure 1 (d) and S4). The (012) XRD pole figure reveals maximum intensity at 0° tilt angle. This indicates

that most of (012) planes are parallel to the substrate. In the case of the (104) pole figure, no definite features are observed, indicating absence of the (104) plane parallel to the substrate. As expected, plane without one axis growth orientation gives the off-peak intensity, which is invariant of the tilt angle. On the other hand, a ring pattern is observed at around 46.7° , which is attributed to the planes with the interfacial angle between (012) and (104) plane. Therefore, pole figure results have manifested that the obtained secondary grown hematite film has (012) plane orientation. Random oriented hematite film showed a dominant orientation along (104) plane. (Figure S5)

A detailed crystallographic relationship was revealed by HRTEM and related fast-Fourier transformation (FFT) electron diffraction patterns (EDP). A TEM image showed a piece of hematite continuous film with individual (012) plane orientated crystals, which was located at different position on the rough FTO glass (Figure 2(a)). The HRTEM images shown in Figure 2 (b), taken from the red, yellow, and blue square areas and by the analysis of the individual SAED patterns, contain parts along [1-12] (L), [10-2] (M), and [104] (R) zone axis, respectively (Figure 2(b), 2(c)). The discontinuous lattice plane with left and right side present among lattice fringes suggest the growth of film initiated arranged hematite crystals, which located on the rough surface of FTO glass. The growth direction of all positions is along their $\langle 012 \rangle$ axis.

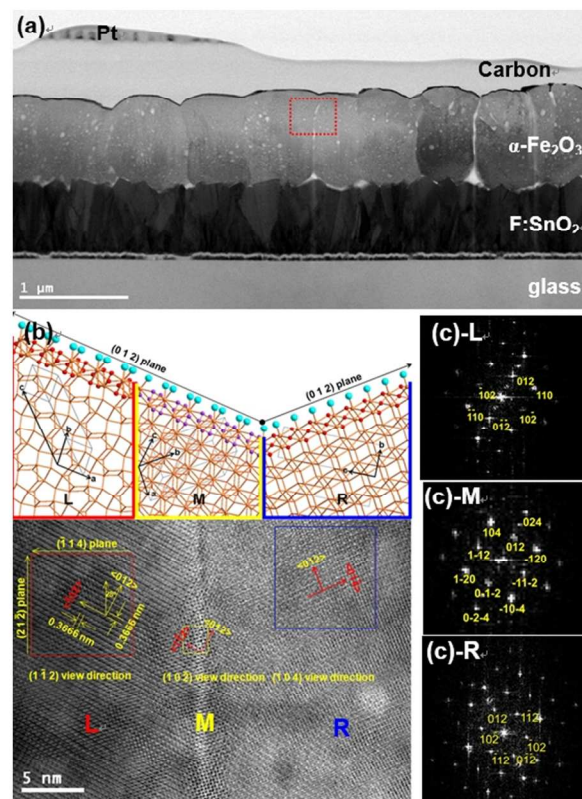


Figure 2. (a) Cross-sectional TEM image of a piece of (012) plane orientated hematite film on the FTO, (b) HRTEM image and FFT diffraction patterns of selected square areas L, M, and R-zone (L; left; M; middle; R; right). Inserted atomic network structure is the introduced lattice structure and orientation from (b) and demonstrated hydroxyl groups on the (012)-plane surface in hematite film. The yellow, red, and blue ones are representative of iron atoms, oxygen atoms, and hydroxyl group, respectively.

The (012) plane orientated film consisted with short bond length (Fe-O), ~ 0.19 nm (Figure 2(b)), which results in the improvement of charge transport along the (012) plane.¹⁸ Also well-connected continuous crystal film enhanced inter-particle electrical transportation and crystal structure deformation.¹⁹ Otherwise, random orientated hematite film with ca. 750 nm in thickness shown in Figure S6. SAED patterns of crystal and interface between crystals of random film consistent with single and poly-crystal features, respectively. It is direct indication for recombination loss of photogenerated electron in photoanode to hinder electron transportation from electrode to back contact because recombination was mainly occurred by mismatched interface in film like internal defects.

In the Fe 2p and O 1s core-level X-ray photoelectron spectroscopy (XPS) spectra of the hematite crystals and oriented hematite film (Figure S7 (a and b)), the Fe 2p_{3/2} peaks appear at a binding energy of about 711.4 eV, which is the typical value for Fe³⁺ in α -Fe₂O₃. Instead of this, we observed 708.54 eV, corresponding to the peak intensity of the difference between the oriented hematite film and the randomly oriented hematite crystals. This revealed that there is evidence for an additional Fe species, which has oxygen deficiencies at a binding energy of ~ 708 eV, on the (012) plane oriented hematite continuous film.²⁰ This is also reflected in the O1s spectra of both samples (Figure S12(c)), which show three different types of peaks, corresponding to structural O²⁻, water (H₂O), and a broad peak consisting of OH or O-C groups. We observed surface OH groups on the (012) oriented continuous film at ~ 299 eV that bonded with the oxygen deficient Fe species with relatively short bond lengths between the Fe and O atoms.

A UV-vis study is a facile method to characterize the thickness of a hematite film. So random and (012) plane orientation hematite films were measured and the results are shown in Figure S8. The absorption is similar on the samples random and (012) plane orientation, which suggests that the thickness of hematite have similar obviously. Moreover, higher magnification TEM images were also measured and showed the continuous film formation (see Figure S6).

in a 1 M NaOH (pH 13.6). Figure 3a shows that both random and (012) plane orientated hematite electrodes are n-type and generate anodic photocurrents by the consumption of photoinduced holes for water oxidation serving as photoanodes. While the random orientated hematite photoanode shows a photocurrent density of less than 0.2 mA/cm² at 1.23 V vs. RHE, the (012) plane orientated hematite film drastically enhances the performance and generated photocurrent densities of almost 1 mA/cm² at a potential 1.23 V vs. RHE in Figure 3 (b). Compared to random orientated electrode, (012) plane orientated hematite film has shown significantly shifted cathodic potential value about 0.1 V_{RHE}. Also the photocurrent density was increased about 4 times. J-V curves of the films grown at different secondary growth times under light illumination were recorded (Figure S9). The photocurrent values were enhanced with increasing growth times which are related to the extent of gap filling among crystals. This enhancement can be attributed to the increased charge transport in plane orientated film. We note that the arranged hematite crystal photoelectrodes without secondary growth did not show any photovoltaic effect (Figure S9). The highest photocurrent density was obtained from the secondary grown hematite film for 4 h as 0.8 mA/cm² at 1.23 V_{RHE} and this photocurrent density value lasted over 2 hours (Figure 3 and Figure S10). When the secondary growth time exceeds 4 h, photocurrent density decreases more than 50% of maximum value due to small particle formation of mismatched crystals on the hematite film. The junction of main hematite crystal and these small particles possibly generate electron trap sites and results in reducing the photovoltaic effect (Figure S11).

Electrochemical impedance spectroscopy (EIS) in Figure S12 was used to investigate the charge transfer process at the semiconductor-electrolyte interface. We measure the EIS spectra at near to onset potential of (012) plane orientation hematite film for water oxidation. From the results of EIS spectra at -0.2 V_{Ag/AgCl} under dark and light illumination in Figure S12, the radii of low frequency response become smaller after (012) orientation in hematite film comparing with random orientated film in dark condition and light illumination condition. It means that the interface charge transfer rate increase in (012) orientated hematite film. The enhanced charge transfer rate comes from one-axis orientated crystalline due to enhanced electron mobility, inter-particle electric connectivity, and low recombination loss of electrons for water oxidation.

Conclusions

In summary, a novel process for the formation of (012) plane-oriented hematite film has been achieved by the assembly of pseudocubes with {012} facets and a secondary growth process. Compared with the pristine hematite photoanode, the obtained (012) plane-oriented continuous hematite film shows an increased photocurrent density of 0.8 mA/cm² at 1.23 Vs. RHE without the incorporation of dopants or an oxygen evolution catalyst. The enhancement of photocurrent density attributed to a high electron/hole diffusivity between the Fe and O atoms and interparticle electronic connectivity. This allows low energy consumption for water oxidation. This work demonstrates a simple and effective method for the largest exposure of the highest photoactive (012) plane as a photoanode for use in PEC water oxidation.

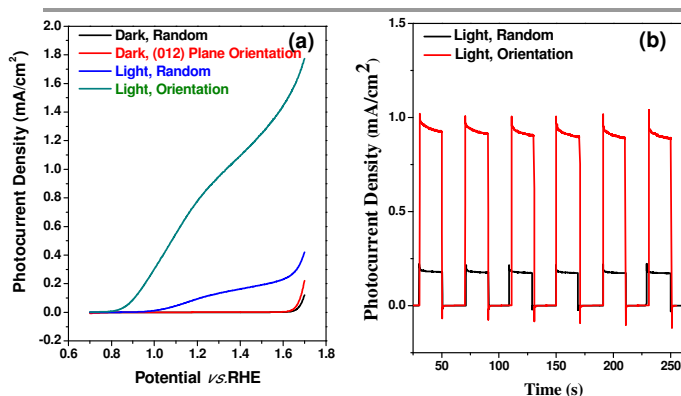


Figure 3. Photocurrent vs. Potential curves and transient photocurrent of (012) plane and random orientated hematite continuous films in 1 M NaOH (pH 13.6) when the light is on and off at potential 1.23 V_{RHE}

The photoelectrochemical performances of random and (012) plane orientated hematite were first compared by measuring photocurrent density-potential (J-V) plot under AM 1.5G (100 mW/cm²) illumination

Notes and references

Korea Center for Artificial Photosynthesis and Department of Chemistry, Sogang University, Seoul, 121-742, Korea.

† Electronic Supplementary Information (ESI) available: Experiment details, TEM images, X-ray diffraction patterns, X-ray photoelectron spectroscopy, UV-Vis spectroscopy and Nyquist plots are provided. See DOI: 10.1039/c000000x/

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