Hematite Dodecahedron Crystals with High-index Facets Grown and Grafted on One Dimensional Structures for Efficient Photoelectrochemical H₂ Generation

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Fe₂O₃ polyhedrons are one of the most promising morphologies for photoelectrochemical water splitting. In spite of recent reports on the successful synthesis of various Fe₂O₃ polyhedrons, the fabrication of defined photoelectrodes by anchoring the polyhedron in a suitable configuration remains a great challenge. Herein, we introduce a synthetic strategy to prepare Fe₂O₃ dodecahedrons with high-index {112} facets directly anchored on a one dimensional Fe₂O₃ nanoflake ({110} facets) electrode. Key is that the Fe₂O₃ nanoflakes act as seeds for the initiation of the growth of dodecahedral nanocrystals from an iron nitrate solution. The initial single crystals consist of Fe₃O₄ with exposed {110} basal surfaces that then in a thermal step can be converted to hematite with {112} facets. The resulting single crystal (bi-crystal) hematite photoanode demonstrates a high efficiency for solar water splitting with an excellent photoresponse due to the synergistic effect of direct grafting of the light harvesting and reactive polyhedron and the 1D transport geometry. Under optimized conditions the hematite polyhedrons on nanoflake-structure show photocurrent densities of 2.4 mA cm⁻² at 1.23 V_{RHE} and 3.5 mA cm⁻² at 1.5 V_{RHE} under AM 1.5G simulated sunlight.

1. Introduction

Photoelectrochemical (PEC) water splitting reactions have been regarded as one of the most promising approaches to convert solar energy into chemical energy, by direct hydrogen production from natural water and sunlight.^[1-5] Hematite (α -Fe₂O₃), one of the interesting n-type metal oxide semiconductors, has been extensively applied for PEC photoelectrodes due to its chemical stability, abundance in the earth, and favorable optical bandgap (~2.1 eV) that allows for light harvesting of approximate 40% of the solar spectrum. However, its performance has been severely limited by the conflict between light absorption (α^{-1} =0.12 μ m at 550 nm) and charge separation (short hole diffusion length of 2-4 nm).^[6-10] Therefore, it is necessary to tackle these issues by an optimized design of photoanode structures and taking advantage of some intrinsic Fe₂O₃ properties.

Recently the rational design and synthesis of α -Fe₂O₃ nanocrystals with tunable morphology and properties has drawn considerable research interest.^[11-14] It has been shown that the precise fabrication of crystals with a specific shape and orientation at the nanoscale level can enhance the performance of hematite in many applications, e.g. catalysis, solar conversion et al. Such shape effects inherently result from the atomic arrangement, electronic structure, and chemical reactivity of different exposed crystal facets.^[15,16] For instance, the energy levels of conduction and valence bands of different crystal facets on hematite are different due to the atomic arrangements characteristic at these facets, and these differences may serve as the driving force for the separation of electron and hole or may provide states that promote charge transfer across the interface, factors that are essential for the photocatalytic activity and reactivity.^[17] Recently the application of α -Fe₂O₃ polyhedrons to the photoelectrochemical field has demonstrated these structures to be highly promising for enhanced PEC water oxidation.^[18-20] For instance, dodecahedral and octodecahedral α -Fe₂O₃ particles prepared via a hydrothermal method in the presence of iron chloride and F⁻ anions showed a better photoelectrochemical and photocatalytic performance and a high stability.^[18,19] This beneficial effect has been ascribed to the higher activity of facets of the surface structure (namely (104) planes) of polyhedron nanocrystals that facilitate charge transfer.

Despite the successful synthesis of such α -Fe₂O₃ polyhedron structures, the relatively low specific surface area of the single crystals (typically micrometer size scale) strongly limits its PEC performance. Furthermore, sintered nanoparticle films suffer from a drastic decrease in electron mobility, due to abundant grain boundaries and associated defects, combined with a lack of directional charge transfer to the back contact.^[20] Work of Fang and coworkers^[21] has recently shown the successful fabrication of tetrakaidecahedral α -Fe₂O₃ particles coupled with graphene oxide. The high PEC performance of α -Fe₂O₃/graphene composite has been ascribed to the coupling of graphene, facilitating the charge separation and transfer and

hindering the charge recombination of photogenerated electron-hole pairs. Alternatively, one-dimensional (1D) nanostructures, e.g. nanotubes and nanorods, provide a directional charge transport for electrons and short holes transport distances, which lead to an improved charge separation and reduced bulk recombination.^[22] Therefore, an approach to combine α -Fe₂O₃ polyhedrons with reactive facets onto one dimensional structures is a promising route for taking advantages of both structures to achieve activity and transport improvement of hematite photoanodes.

In this work, we show that Fe₂O₃ 1D-nanoflake layers grown on a metallic Fe substrate can act very effectively as seeds for the initiation and growth of dodecahedral Fe₃O₄ with defined facets (exposing the {110} basal surfaces). As a result, on the 1D nanoflake, inter-grown crystals are formed that after a suitable annealing treatment become hematite polyhedrons with reactive high-index planes namely {112}. These α -Fe₂O₃ polyhedrons anchored on the NF-structure provide an excellent photoanode. The dodecahedral α -Fe₂O₃ provides hole transfer reactivity, while the 1D NFs serve not only as a seeding layer inducing the formation of polyhedrons but also act as an efficient electron transport medium, to the back side. Additionally, the combined polyhedron on NF structure can provide an efficient geometry for an increased light absorption, and finally Sn doping of the dodecahedral α -Fe₂O₃ anchored on 1D NFs can be used to achieve further enhancement in PEC water splitting due to a combined effect of three-dimensional structure and the Sn doping.

2. Results and discussion

Scheme 1 illustrates the synthesis process of dodecahedral α -Fe₂O₃ crystals on the hematite NFs. First we formed an ordered layer of α -Fe₂O₃ NFs by a facile thermal oxidation of iron foil at 400 °C for 2-3 h (**Scheme 1a**), as described in the SI. Then, the as-grown NF samples were immersed in an iron nitrate solution for various times at room temperature to induce the initiation and growth of Fe₃O₄ crystallites on the NFs (see experimental for details). At early

reaction stages, the primary nuclei are formed (**Scheme 1b**). The primary nuclei then grow further into irregular nanocrystals (**Scheme 1c**) that gradually evolve into 3D a polyhedron structure (**Scheme 1d**). The dodecahedral Fe_3O_4 can finally be completely transformed to $\alpha\text{-Fe}_2\text{O}_3$ dodecahedron by a thermal treatment in air at 600 °C (**Scheme 1e**). Remarkably the dodecahedrons show a high density of exposed {112} facets.

Figure 1a shows the scanning electron microscopy (SEM) image of as-grown $\alpha\text{-Fe}_2\text{O}_3$ NFs. The geometry of these flakes is crucial to initiate dodecahedral nanocrystal growth. The individual flakes with sharp apexes are 1.0-2.5 μm in length, 100-400 nm thick at the base, and the thickness tapers down to ~10 nm at the tip. The X-ray diffraction (XRD) pattern (**Figure 1h**) matches well with the crystal structure of hematite (JCPDS No. 33-0664) and magnetite (JCPDS No. 19-0629). The magnetite is observable in the SEM image underneath the NFs (**inset of Figure 1a**). Raman spectroscopy (**Figure 1i**) exhibits peaks at 222, 245, 289, 407, 495, and 609 cm^{-1} that can be assigned to hematite for the NFs sample.^[23,24] After immersion in the $\text{Fe}(\text{NO}_3)_3$ aqueous solution for the NFs sample, nanopolyhedron particles have been successfully formed with an average particle size of 150 nm (**Figures 1b and c**). The XRD pattern (**Figure 1h**) displays a small peak at 37.1° during the synthetic process, which can be attributed to the (222) crystal planes of the Fe_3O_4 nanopolyhedrons.^[11] Except for the hematite, the Raman bands (**Figures 1i**) at 275, 387, and 663 cm^{-1} can be clearly resolved, corresponding to the spectral characteristics of magnetite.^[23] Additionally, together with the XRD and Raman results, transmission electron microscopy (TEM) images (**Figure 1e and f**) and the corresponding selected area electron diffraction (SAED) pattern (**inset of Figure 1f**) confirm that the iron oxide is mainly hematite with the presence of a secondary magnetite phase. The lattice spacing of 0.29 nm in the polyhedron corresponds to the (220) plane of magnetite in **Figure 1f**. After the thermal transformation (annealed at 600 °C) of the polyhedron Fe_3O_4 to $\alpha\text{-Fe}_2\text{O}_3$, the polyhedron shape and morphology remain intact, *i.e.* no change is observed for the polyhedron $\alpha\text{-Fe}_2\text{O}_3$ on the NFs (**Figure 1d**). The TEM image

given in **Figure 1g** exhibits a lattice spacing of 0.37 nm, and the value can be assigned to the lattice fringe of {112} planes confirming a hematite crystal structure for the converted polyhedrons. Moreover, the Raman peaks (**Figures 1i**) at 275, 387, and 663 cm^{-1} corresponding to the magnetite decrease significantly after the second thermal annealing treatment, accompanied with an increased intensity of hematite. Furthermore, Sn treated polyhedron nanoparticles were obtained by dropping a 0.2 M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ethanol solution on the dodecahedral Fe_3O_4 on NFs followed by the thermal treatment at 600 °C (**Figures S1 and S2**). The presence of Sn in polyhedron nanoparticles anchored on NFs was confirmed by X-ray photoelectron spectra (XPS), in which two peaks at 486.8 eV (Sn 3d_{5/2}) and 495.2 eV (Sn 3d_{3/2}) assigned to Sn⁴⁺ appear for the Sn doped hematite (**Figure S2**). The Raman spectrum at peak of ~660 cm^{-1} shows a slightly increased and broadened peak compared to the un-doped sample (**Figure S3b**).

To further understand the formation process of Fe_3O_4 polyhedrons on the flakes, a series of time- and concentration-dependent experiments were conducted. Time and concentration (as shown in **Figures S4-S7**) play an important role in tuning the particle shape. **Figure S4** shows SEM images of the polyhedrons on the NFs after different growth steps. This sequence suggests that during the reaction iron hydroxides ($\text{Fe}(\text{OH})_3$ or FeOOH) are transformed to crystalized iron oxide,^[24] and the sizes of the as-synthesized Fe_3O_4 polyhedrons are dependent mainly on the reaction time. Moreover due to the acid solution, the iron substrate corrodes and causes additional Fe^{3+} and Fe^{2+} release into the NO_3^- solution. At the beginning (~10 h), small-sized nanoparticles initiate on the NFs orientation by the hydrolysis of iron nitrate (**Figure S4c**). After a synthesis time for 16-20 h, we obtain cubic shapes of nanocrystals with 6 faces, 8 vertices and 12 edges (**Figure S4d and e**). The size of these irregular shaped nanocrystals is in the range of 50-150 nm. After a reaction time of 24 h, nanocrystals of dodecahedron shape are obtained containing 12 faces with 20 vertices and 30 edges (**Figure S4f**) dominated by {110} facets – the crystal facet distribution increasingly becomes more

uniform (see NFs after 48 h reaction time in **Figure S4g**). After 72 h (**Figure S4h**), the polyhedron particles reach their final features. The formation of single crystals with different facets can be attributed to the surface energies of different facets and the relative growth rates of different facets.^[11,25,26] As a result, the facet with a slower growth rate will be exposed more on the nanocrystal surface. The preferential growth at a specific face leads to the final formation of Fe₃O₄ enclosed by {110} facets. Moreover, the three-dimensional nanocrystals comply with Euler's formula,^[27] which links the number the vertices (V), faces (F), and edges (E) of a polyhedron as $V+F-E=2$. Therefore, the synthesized nanocrystals after the longest growth are geometrically most stable. These {110} faceted Fe₃O₄ polyhedrons after thermal treatment convert to {112} faceted Fe₂O₃.

For comparison, various precursor concentrations for a synthesis time of 24 h were examined (**Figure S7**). Lower Fe(NO₃)₃ concentrations (1 and 2.5 mM) only induce the nanoparticles grafted on the NFs orientation. For Fe(NO₃)₃ concentrations increased to 5 mM, regular polyhedron nanoparticles with a typical size of ~150 nm and a straight edge are formed on the NFs. To further understand the role of NO₃⁻ ions on the phase transition process, the precursor of Fe(NO₃)₃ was substituted by FeCl₃ under the same immersion conditions. This did not lead to any crystallite initiation but only a uniform 1-2 nm amorphous FeOOH layer was formed on the NFs (**Figure S8**).^[28] Alternatively, a fluorine-doped SnO₂ (FTO) substrate was used, replacing α -Fe₂O₃ NFs on iron substrate, and was exposed to the same condition of Fe(NO₃)₃ solution. On this substrate only a filiform FeOOH layer is obtained (**Figure S9**). These results reveal that for the formation of a polyhedron morphology, hematite NFs as a seeding layer are essential to successfully grow dodecahedrons that are crystallographically grafted to the substrate.

Interestingly the inter-grown Fe₂O₃ bi-crystal structures also provide an improved light absorption morphology as apparent from ultraviolet-visible (UV-vis) absorption spectra (**Figures 1j and S10**). The light absorption of polyhedron hematite with {112} facets

anchored on NFs is significantly higher in comparison with pristine NFs with {110} facets over the entire wavelength range, but especially for longer wavelength (600-700 nm). This can be ascribed to a higher degree of light scattering within these structures, especially high-index facets.^[29,30] Also the band gap energy (E_g) can be elucidated by extrapolating the linear portion of $(\alpha h\nu)^{1/2}$ versus the $(h\nu)$ plot. On the basis of the results (**inset of Figure 1j**), the band gaps for the hematite NFs and polyhedron on NFs are 2.1 eV and 1.95 V, respectively. This is in line with the indirect (phonon-assisted) band gap of hematite, reported to be 1.9 eV to 2.3 eV dependent on crystal orientation.^[31-34]

The performance of corresponding photoanodes for water photoelectrolysis characterized under simulated AM 1.5G sunlight irradiation (100 mW cm^{-2}) in 1 M KOH electrolyte is shown in **Figure 2a**. For the pristine $\alpha\text{-Fe}_2\text{O}_3$ NFs photoanode under illumination, upon sweeping the potential from 0.6 to 1.7 V_{RHE} , a water oxidation onset potential of 0.6 V_{RHE} is obtained and the photocurrent density is approximately 0.24 mA cm^{-2} at 1.23 V_{RHE} and 0.58 mA cm^{-2} at 1.50 V_{RHE} . For the dodecahedral $\alpha\text{-Fe}_2\text{O}_3$ on the NFs, the photocurrent is more than doubled up to 0.57 mA cm^{-2} at 1.23 V_{RHE} . After Sn doping the onset potential slightly shifts to a more positive value, 0.73 V_{RHE} , while the photocurrent over the potential range from 0.8 V_{RHE} to 1.7 V_{RHE} is significantly increased to 2.4 mA cm^{-2} and 3.5 mA cm^{-2} at 1.23 V_{RHE} and 1.5 V_{RHE} , respectively. The calculated applied bias photon to current efficiency (ABPE) is determined to be 0.27% at 1.0 V_{RHE} (**Figure 2c**). The superior performance obtained from the dodecahedral $\alpha\text{-Fe}_2\text{O}_3$ photoanode with {112} facets on the NFs structure can be attributed to kinetic and light harvesting effects. Various polyhedron particle sizes and amounts were obtained by adjusting the immersion time, and the solar water splitting performance was examined (**Figures 2b and S11**). It can be seen that for the Sn doped $\alpha\text{-Fe}_2\text{O}_3$ polyhedron on the NFs for 48 h, the photocurrent density is distinctly increased over the whole potential range, while for the shorter (24 h) or longer (72 h) growth times, the photoanodes exhibit a lower photoresponse but still show a higher value compared to the Sn

doped Fe₂O₃ NFs (**Figures 2b**). Especially, for the longer growth time of sample (72 h), even though it shows a much better light absorption (**Figure S10**), the lower photoresponse indicates a hampered water oxidation kinetics in compared to the optimum sample, most likely due to the aggregation of polyhedron particles that cover the whole NFs structure (**Figure S4h**).

For further enhancement in PEC performance, a FeOOH cocatalyst was decorated on the surface of the α -Fe₂O₃ polyhedron. **Figure 2a** displays the PEC water splitting performance for a FeOOH-decorated Sn/ α -Fe₂O₃ polyhedron photoanode on NFs. Compared to the case of Sn doped α -Fe₂O₃ polyhedron on NFs, the photocurrent density reaches up to 2.9 mA cm⁻² at 1.23 V_{RHE}, and a maximum photocurrent density of 4.5 mA cm⁻² at 1.5 V_{RHE} is obtained with a cathodic shift of onset potential to 0.67 V_{RHE}. To the best of our knowledge, this is the highest value ever reported for polyhedron hematite photoanodes. Moreover, the photocurrent transient ratio values ($i_{\text{steady}}/i_{\text{initial}}$) reach 0.65-0.80 for the NFs or polyhedron hematite photoanodes, which even can be improved using Sn-doping or FeOOH decoration; here the $i_{\text{steady}}/i_{\text{initial}}$ values close to one are obtained (**Figure 2d**). Therefore, it can be deduced that the combination of polyhedron with {112} facets anchored on the 1D flake structure and Sn doping are particularly effective in reducing/eliminating the decay of the photocurrent due to charge accumulation effects – *i.e.* charge transfer is strongly enhanced.

Figure 3a shows the results of incident photon-to-current conversion efficiencies (IPCEs) as a function of wavelength measured at 1.5 V_{RHE} in 1 M KOH. The IPCE values are in line with the measurements using AM 1.5G sun light irradiation (**Figure 2a**). The Sn doped α -Fe₂O₃ polyhedron anchored on NFs photoanode with the decoration of FeOOH (Sn-D-NFs/FeOOH) shows a drastic improvement for all photon wavelengths compared to the pristine hematite. More specifically, over the entire spectral range from 350 nm to 600 nm (**Figure 3a**), this photoanode shows the highest IPCE value, and a maximum IPCE value around 340 nm reaching 66%. Moreover, in the range from 500 to 750 nm (**inset of Figure**

3a), all the α -Fe₂O₃ polyhedron on NFs, without and with doping or cocatalyst treatment, exhibit a higher IPCE than the pristine hematite NFs. This result indicates that the polyhedron exposed to {112} facets on 1D structure is more efficient at long wavelength, consistent with the enhanced light absorption seen in UV-vis spectra (**Figure 1j**).

To further elucidate the correlation between the unique structure and the higher photoresponse, electrochemical impedance spectroscopy (EIS) measurements of corresponding photoanodes were carried out (**Figure 3b**). The semiconductor-electrolyte charge resistance (R_{ct}) is a key parameter in characterizing the semiconductor-electrolyte charge-transfer process. In a Nyquist plot of the AC impedance data, the diameter of the semicircle reflects R_{ct} . In our case, R_{ct} was calculated by fitting an equivalent circuit as shown in the **inset of Figure S12** to the impedance data. In **Figures 3b and S12**, the R_{ct} for the D-NFs (2735 Ω) is obviously lower than that of the pristine NFs sample (16037 Ω). This may be attributed to the enhanced charge transfer provided by the D-{112} planes. Further treatment with Sn doping and FeOOH cocatalyst, the R_{ct} for the Sn-D-NFs/FeOOH (508 Ω) is clearly smaller than that of the D-NFs sample (2735 Ω). To further clarify the role on the enhanced charge electronic properties upon Sn doping and polyhedrons on 1D structure in Fe₂O₃, Mott-Schottky measurements were performed for the different samples (**Figure S13**). The obtained values for the Sn-D-NFs photoanodes without ($2.42 \times 10^{21} \text{ cm}^{-3}$) and with ($3.08 \times 10^{21} \text{ cm}^{-3}$) FeOOH decoration are twice around higher than that of the polyhedron on NFs ($4.47 \times 10^{20} \text{ cm}^{-3}$), in line with an increased carrier density created by Sn doping. In accord with above observations photoluminescence measurements showed the decay of photoluminescence intensity for the Sn-D-NFs sample to be slowed by Sn doping compared with that of the pristine α -Fe₂O₃ NFs (**Figure S14**), *i.e.* intrinsically a longer carrier life-time is provided.

Regarding the growth of high index plane polyhedron it should be noted that hematite single crystals during the growth processes usually expose low-index facets, such as {110} and {012}.^[35] The high-index faceted nanocrystals are produced typically under specific

energetic or seeding conditions.^[36,37] In this NF seed, a dodecahedral Fe₃O₄ crystal formed on the {110} basal surfaces (**Figure S4i**). In general, the facet growth rate is governed by the intrinsic surface energy. As a face-centered cubic (FCC) crystal, a general sequence of surface energies may hold, $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$ in a spinel oxide.^[38] The different terminated planes are composed of different Fe(III)/Fe(II) ratios.^[39] Therefore, the generating rate of Fe(II) reduced from Fe(III) likely affects the growth speed along different facets, which further determines the shapes of the polyhedrons. At a low concentration of [Fe³⁺]=1 mM and 2.5 mM, the irregular polyhedrons and many small particles are found (**Figure S7**), which indicates that there are two different shape determining routes in the process. Irregular polyhedrons as a result of Ostwald ripening, and the many small particles are generated due to irregular fast nucleation. Furthermore, in contrast to the Fe(NO₃)₃ solution, FeCl₃ solutions do not lead to the formation of polyhedron particles but a uniform amorphous layer on the NFs (**Figure S8**). This can be attributed to Cl⁻ that shows a strong coordination with Fe³⁺ and forms stable complexes, that reduce the nucleation probability of Fe₃O₄ crystals.^[40] A second key factor is the need of hematite NFs as a seeding layer that is essential to grow dodecahedrons that are crystallographically attached to the substrate.

These Fe₃O₄ dodecahedrons then can be transformed to Fe₂O₃ with {112} facets during annealing in air. The hematite polyhedrons with {112} facets represent a high surface energy state.^[41] The EIS and Mott-Schottky results (**Figures 3b and S13**) indicate that this faceting and the unique structure – polyhedron on 1D NFs – are a major factor in the improvement of PEC performance. The low charge resistance and high charge carrier density can be attributed to the {112} facets which have a lower energy barriers for water oxidation, and due to active sites provided by low-coordinated atoms located on step edges.^[42,43] According to literature it is also remarkable that a hole hopping along the [112] direction crosses less O²⁻ ions than that along the other directions (e.g. [104]), and thus the hole can transfer to the surface at lower energy (faster) when more {112} facets are exposed.^[44,45]

In addition, the 1D support further improves the electron transfer from the polyhedrons to and across the back contact. The implementation of Sn doping and FeOOH decoration as a cocatalyst further increase the charge-transfer rate across the semiconductor-electrolyte interface, and facilitate the hole transfer at this interface. The photoluminescence decay spectra give additional support to the general finding that recombination of photogenerated carriers can be inhibited by Sn doping and is further reduced by the fast transfer at high-index faceted crystals. Above results thus demonstrate the advantage of high-index {112} faceted nanocrystals grafted on a 1D structure as a photoelectrode and show that a suitable faceted polyhedron anchored on 1D structure leads to a remarkable improvement in PEC water oxidation.

Conclusion

In summary, we have demonstrated that the dodecahedral nanoparticles anchored on a one dimensional nanoflake structure represent a highly beneficial architecture for PEC water splitting. The photoanodes can be assembled by a sequence of simple thermal oxidation and precipitation methods. Fe_2O_3 nanoflakes act as seeds for the initiation of the growth of dodecahedral nanocrystals from an iron nitrate solution. These initial single crystals consist of Fe_3O_4 that then in a thermal step can be converted to hematite with high-index {112} planes. The resulting single crystal (bi-crystal) hematite photoanode demonstrates a high efficiency for solar water splitting with an excellent photoresponse due to the direct grafting of the light harvesting and reactive sites to the transport geometry. We expect that the concept to graft functional single crystals with high-index crystal facets grafted on a 1D structure opens up new approaches for the assembly highly efficient PEC devices.

Experimental Section

For the preparation of dodecahedral α -Fe₂O₃ anchored on NFs.

Iron foils (Alfa Aesar, 99.99%) were degreased by sonicating in acetone and ethanol for 10-20 minutes, followed by drying in a nitrogen stream. The samples then were thermally annealed in a furnace (Heraeus Furnace, ZEW 1451-4) in air at 400 °C for 2-3 h with a heating rate of 10 °C min⁻¹. For the dodecahedral Fe₃O₄ anchored on NFs (**D-NFs-1**), the α -Fe₂O₃ NFs samples were immersed in a 1~5 mM Fe(NO₃)₃·9H₂O (Sigma-Aldrich, 98%) aqueous solution for various times by a facile “top-down” method (The front sides of NFs were faced to the bottom), following by rinsing with distilled water and drying in a N₂ stream. Then, the dodecahedral Fe₃O₄ anchored on NFs (**D-NFs-1**) were transformed to the dodecahedral α -Fe₂O₃ on NFs (**D-NFs**) by an annealing treatment at 600 °C for several minutes. For the Sn doped dodecahedral α -Fe₂O₃ on NFs (**Sn-D-NFs**), a 0.2 M SnCl₄·5H₂O (Sigma-Aldrich, 99%) ethanol solution was dropped on the dodecahedral Fe₃O₄ on NFs (**D-NFs-1**). Then the samples were dried in a N₂ stream. The samples were further annealed at 600 °C for several minutes. For the further decoration of FeOOH cocatalyst (**Sn-D-NFs/FeOOH**), the samples (**Sn-D-NFs**) were immersed in a 5 mM FeCl₃ (Sigma-Aldrich, 99%) solution for 12 h, following by rinsing with distilled water and drying in a N₂ stream. For comparison, the α -Fe₂O₃ NFs samples were immersed in the 5 mM FeCl₃ (Sigma-Aldrich, 99%) aqueous solutions for various times.¹ Meanwhile, the FTO substrates were treated in the 5 mM Fe(NO₃)₃ aqueous solutions at room temperature, following by rinsing with distilled water and drying in a N₂ stream.

Characterization.

X-ray diffraction (X'pert Philips PRO with a Panalytical X'celerator detector, Germany) was carried out using graphite monochromized Cu K α radiation (Wavelength 1.54056 Å). Chemical characterization was carried out by a X-ray photoelectron spectroscopy (ESCALAB 250Xi, ThermoFisher Scientific). A field-emission scanning electrode microscope (Hitachi SU8020, Japan) was used for the morphological characterization of the

electrodes. TEM analysis was performed on a TECNAI G² TF20 microscope operated at 200 kV. UV-vis diffuse reflectance spectra were taken on an UV-2550 (Shimadzu) spectrometer by using BaSO₄ as the reference. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulse sat 454 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel in 4096 effective channels.

Photoelectrochemical performance.

The photoelectrochemical experiments were carried out under simulated AM 1.5 (100 mW cm⁻²) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight; RT). The 1 M KOH aqueous solution was used as an electrolyte after saturation with N₂ gas for 30 min. A three-electrode configuration was used in the measurement, with the α -Fe₂O₃ electrode serving as the working electrode (photoanode), an Ag/AgCl (3 M KCl) as the reference electrode, and a platinum foil as the counter electrode. Photocurrent vs. voltage (*I*-*V*) characteristics were recorded by scanning the potential from -0.4 to 0.7 V (vs. Ag/AgCl (3 M KCl)) with a scan rate of 10 mV s⁻¹ using a Jaissle IMP 88 PC potentiostat. The measured potentials vs. Ag/AgCl (3 M KCl) were converted to the reversible hydrogen electrode (RHE) scale using the relationship $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{0\text{Ag/AgCl}}$, where $E_{\text{Ag/AgCl}}$ is the experimentally measured potential and $E_{0\text{Ag/AgCl}} = 0.209$ V at 25 °C for an Ag/AgCl electrode in 3 M KCl. The applied bias photon-to-current efficiency (ABPE) was caclulated by following equation:

$$ABPE(\%) = \frac{I(\text{mA/cm}^2) \times (1.23 - V_{\text{bias}}) (\text{V})}{P_{\text{light}}(\text{mW/cm}^2)} \times 100 \quad (1)$$

where *I* is the photocurrent density, *V*_{bias} is the applied potential, *P*_{light} is the incident illumination power density (100 mW cm⁻²). Photocurrent spectra were acquired at an applied

potential of 1.5 V_{RHE} in 1 M KOH recorded with 20 nm steps in the range of 300-750 nm using an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator. IPCE was calculated as follow:

$$IPCE(\%) = \frac{1240 \times I(\text{mA}/\text{cm}^2)}{P_{\text{light}}(\text{mW}/\text{cm}^2) \times \lambda(\text{nm})} \times 100 \quad (2)$$

where I is the measured photocurrent density at specific wavelength, λ is the wavelength of incident light, and P_{light} is the measured light power density at that wavelength. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Chi760e electrochemical workstation (Huakeputian Technology Beijing). EIS measurements were performed by applying 1.23 V_{RHE} at a frequency range of 10⁵ Hz to 0.01 Hz with an amplitude of 10 mV under AM 1.5G (100 mW cm⁻²) illumination. The Mott-Schottky curves were obtained by using the Chi760e electrochemical workstation. Measurements were obtained in 1 M KOH under AM 1.5G illumination at a frequency of 1000 Hz, amplitude +/- 10 mV.

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Scheme 1 Schematic illustration of synthesis process of dodecahedron Fe_2O_3 on NFs. (a) Fe_2O_3 NFs formed on iron foil by thermal oxidation method (400 °C); (b) step 1: Fe_3O_4 nanoparticles grown on Fe_2O_3 NFs by immersion synthesis; (c) step 2: Fe_3O_4 nanopolyhedrons grown on Fe_2O_3 NFs; (d) step 3: Fe_3O_4 dodecahedrons grown on Fe_2O_3 NFs; (e) step 4: Fe_2O_3 dodecahedrons grown on Fe_2O_3 NFs after thermal treatment (600 °C).

Figure 1 (a-d) SEM top and cross-sectional images of (a) Fe_2O_3 NFs, (b,c) dodecahedron Fe_3O_4 on NFs; (d) dodecahedron Fe_2O_3 on NFs; (e-g) TEM images of (e,f) dodecahedron Fe_3O_4 on NFs and (g) dodecahedron Fe_2O_3 on NFs. Insets of (f) and (g) show SAD patterns of corresponding samples; (h) XRD patterns, (i) Raman spectra, and (j) UV-Vis absorption spectra of corresponding samples. Inset of (j) shows band gaps of samples from reflectance data, and optical images of samples. Fe_2O_3 NFs: NFs; D-NFs-1: dodecahedron Fe_3O_4 on NFs; D-NF: dodecahedron Fe_2O_3 on NFs (dodecahedron Fe_3O_4 on NFs was annealed at 600 °C); Sn-D-NFs: Sn treated dodecahedron Fe_2O_3 on NFs (Sn treated dodecahedron Fe_3O_4 on NFs was annealed at 600 °C).

Figure 2 (a) Linear-sweep voltammogram (LSV) curves of NFs, D-NFs, Sn-D-NFs, and Sn-D-NFs/FeOOH; (b) LSV curves of Sn-D-NFs for various immersion times in $\text{Fe}(\text{NO}_3)_3$ solutions. The Sn doped NFs (Sn-NFs) was examined for comparison. Line-in light; Dash dot-in dark; (c) applied bias photon-to-current efficiencies (ABPEs), (d) $i-t$ curves at $1.5 \text{ V}_{\text{RHE}}$ of NFs, D-NFs, Sn-D-NFs, and Sn-D-NFs/FeOOH. The solar water splitting experiments were carried out in 1 M KOH electrolyte under AM 1.5 G (100 mW cm^{-2}) illumination.

Figure 3 (a) Incident photon-to-current conversion efficiencies (IPCEs), (b) electrochemical impedance spectroscopy (EIS) of NFs, D-NFs, Sn-D-NFs, and Sn-D-NFs/FeOOH. The EIS measurements were carried out in 1 M KOH at 1.23 V_{RHE} under AM 1.5 G illumination.