Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Hierarchically three-dimensional branched hematite nanorod arrays with enhanced mid-visible light absorption for high-efficiency photoelectrochemical water splitting

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Experimental section

Materials: Ferric chloride ($FeCl_3\cdot 6H_2O$), $NaNO_3$, acetone, and anhydrous ethanol were all A.R. grade and purchased from Sinopharm Chemical Reagent Co. Ltd. at Shanghai. All aqueous solutions were prepared with deionized (DI) water from Milli-Q-Water (Millipore Corp, 18.2 MΩ/cm at 25 °C). Fluorine-doped tin oxide coated glasses (FTO, TEC-15) were purchased from NGS glass, and each piece of FTO glass was cleaned ultrasonically in acetone, pure water and ethanol, respectively. The atomic layer deposition (ALD) source of $TiCl_4$ (99.99%) is provided by Shanghai Ruihong material company.

Synthesis of 3D branched hematite NAs: $TiCl_4$ and water were utilized as the precursors and held in a customized bubbler at the room temperature. The typical pulse time for the Titanium precursors and water were 0.05 s and 0.025 s, respectively. Ti_yO_x ultrathin films were deposited on bare FTO substrates in a thermal ALD reactor (Kemin T-200L) at 150 °C. After an annealing treatment at 550 °C for 30 min, the as-prepared TiO_2 modified FTO substrates were used for growing vertically aligned hematite nanorod arrays using chemical bath deposition (CBD) in the literature.[1, 2] Typically, a piece of FTO glass with was placed up-side down in an autoclave which was filled with 20 mL aqueous solutions containing $FeCl_3$ (0.15 M) and $NaNO_3$ (1 M). Subsequently, the autoclave was put into a box oven and heated 95 °C for 6 h and a uniform yellow β-FeOOH film was formed on FTO substrate, and then it transformed to red α-Fe_2O_3 film after a further high-temperature annealing treatment at 550 °C for 30 min in the furnace. The β-FeOOH branches were then synthesized from hematite NAs after the similar CBD process except reducing to 3 h, and hematite branches were then formed after an additional annealing treatment at 600 °C for 30 min.

Structural characterization: The morphology of all samples was characterized by scanning electron microscope (SEM, JME2011, JEOL, Japan) and high-resolution transmission electron microscope (HRTEM, FEI TECNAI G^2 F20). TEM samples were scrapped from photoanodes with a new blade and then carefully dispersed in methanol (HPLC class) in EP tube. X-ray diffraction spectra (XRD) were collected by X-ray diffractometer (Bruker AXS, D8 Advanced) using Cu Kα radiation (λ=1.5418 Å).

Electrochemical characterization: all the photoanodes were first fabricated by sealing a part of the hematite-covered FTO electrode (including the edges) with epoxy resin except for the 0.25 cm^2 unsealed area left for photo-excitation, an external Cu wire was connected to FTO surface using a 63/37 Sn/Pb solder from Youbang soldering company, Hangzhou, China. Autolab® electrochemical station (Metrohm AG, Switzerland) with Nova® electrochemical software were then employed to study the electrochemical properties and stability of the as-fabricated photoanodes within a three-electrode electrochemical system. Impedance spectra were collected using a 10 mV amplitude perturbation of between 100 KHz and 0.01 Hz and Z-view software was adopted to fit these data. All of the photoanodes were tested under the illumination on FTO side.

PEC measurements: The PEC activity was measured using the line scan voltammetry in a standard three-electrode setup. The as-fabricated photoanodes were regarded as work electrode, a platinum plate as the counter electrode and the Ag/AgCl as the reference electrode. All measurements were conducted in the 1 M NaOH electrolyte (pH 13.6). The photocurrent density of each photoanode was recorded by the Autolab® electrochemical station under 100 mW/cm^2 provide by a 500 W Xe-lamp (Newport, Model SP 94023A) with an AM1.5 G filter (AM 1.5G), and the light intensity was standardized using a calibrated silicon photodiode (Newport, 91150V) before measurement. Incident-photon-to-current efficiency (IPCE) spectra were measured at 1.23 V vs. reversible hydrogen electrode (RHE) as a function of the wavelength of the incident light by an electrochemical station (CHI 650b) with a solar simulator (Newport 66902, 500 W Xe-lamp), coupled to an aligned monochromator (Newport 74125) and a Si detector (Newport 71675). The IPCE values are calculated by $IPCE=(1240I)/(\lambda J_{light})$, where I is the photocurrent density (mA/cm^2), λ is the incident light wavelength (nm), and J_{light} is the power density of monochromatic light at a specific wavelength.

References:

[1] P. Wang, D. G. Wang, J. Lin, X. L. Li, C. Peng, X. Y. Gao, Q. Huang, J. Q. Wang, H. J. Xu, C. H. Fan, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2295-2302.

[2] L. Vayssieres, A. Hagfeldt, S. E. Lindquist, *Pure Appl. Chem.*, 2000, **72**, 47-52.

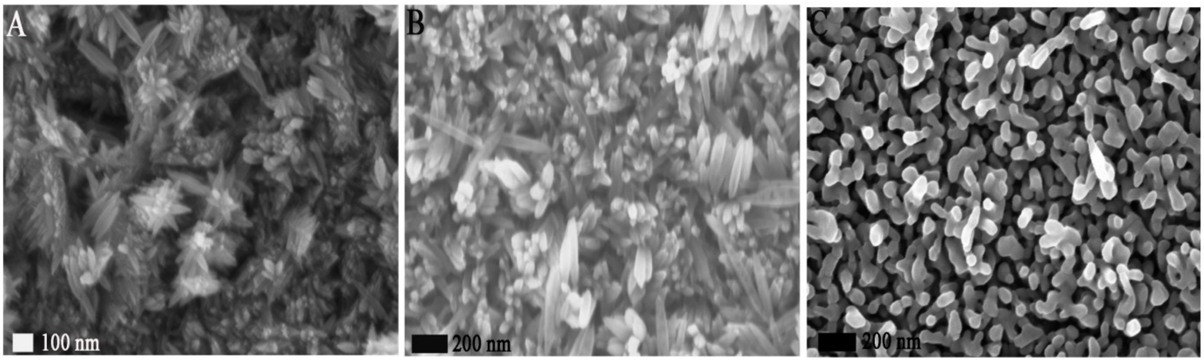

Figure S1. SEM images of (a) T-NAs, (b) H-NAs and (c) H-NAs annealing at 800 °C, respectively.

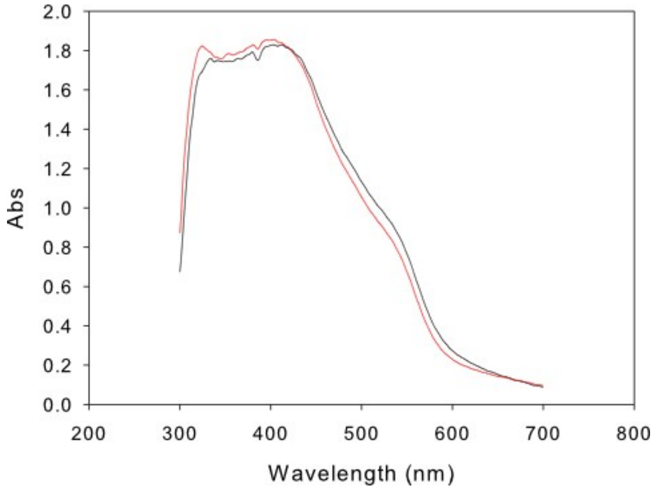

Figure S2. UV-vis spectra of T-NAs (red) and H-NAs (black), respectively.

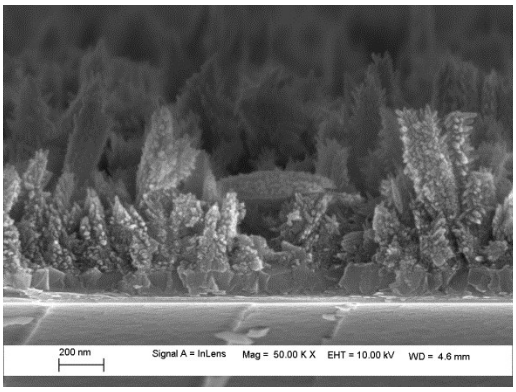

Figure S3. High-magnification cross-sectional SEM image of 3DB-NAs grew on the TiO_2-decorated FTO substrate.

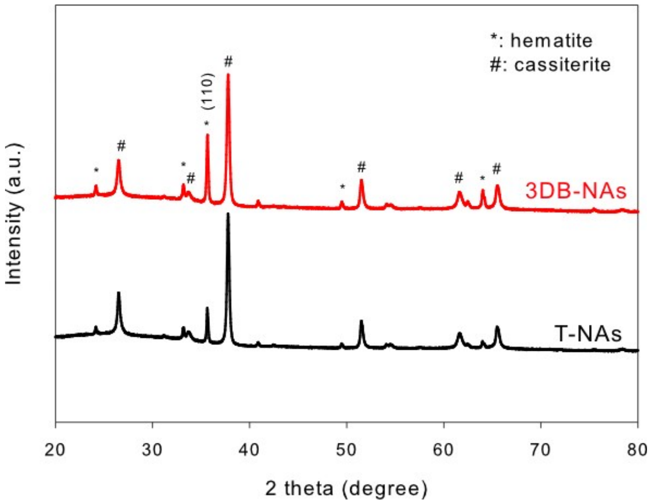

Figure S4. XRD patterns of 3D-NAs (red) and T-NAs (black), respectively.

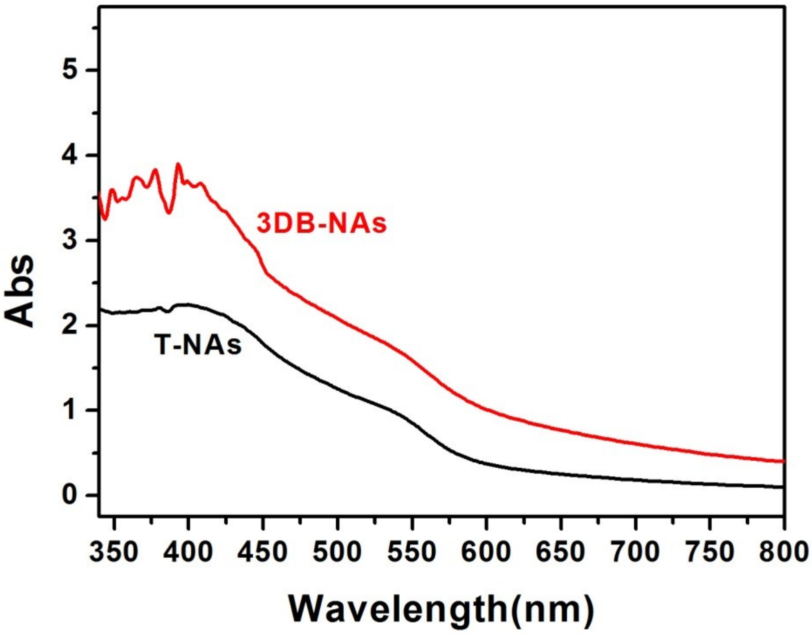

Figure S5. UV-vis spectra of 3DB-NAs (red) and T-NAs (black), respectively.

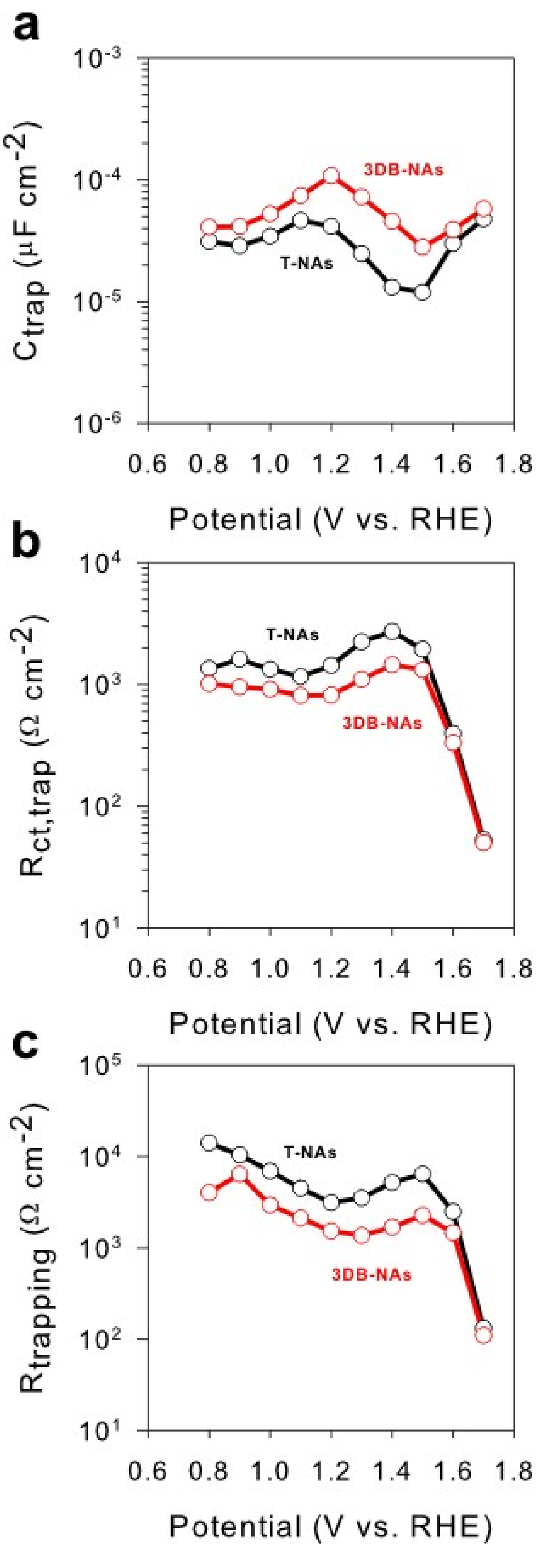

Figure S6 The fitting EIS results of 3D NAs and T-NAs, respectively.

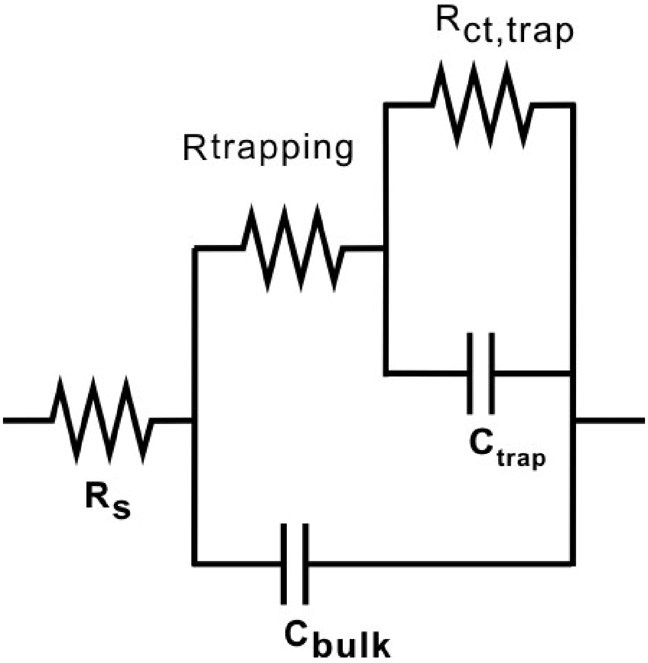

Figure S7 Equivalent circuit for fitting EIS data.