Supporting Information

Promoted water splitting by efficient electron transfer between Au nanoparticles and hematite nanoplates: a theoretical and experimental study

Fengcai Lei,[†,a] Huimin Liu,[†,a] Jing Yu,[*,b] Zhao Tang,[a] Junfeng Xie,[a] Pin Hao,[a]

Guanwei Cui,[a] and Bo Tang[*,a]

[a.] *College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Institute of Biomedical Sciences, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Shandong Normal University, Jinan, 250014, P. R. China. E-mail: tangb@sdnu.edu.cn.*

[b.] *School of Physics and Electronics, Institute of Materials and Clean Energy, Shandong Normal University, Jinan, 250014, P.R. China. E-mail: yujing1608@126.com.*

[†] *These authors contributed equally to this work.*

S1. Methods

Synthesis of Fe$_2$O$_3$ nanoplates: 300 mg FeCl$_3$·6H$_2$O and 24 mL ethylene glycol were added into 16 mL deionized water, after vigorous string for 30 min at the room temperature. Then 300 mg urea was added into the above mixed solution with another 30 min stirring. After that the mixed solution was moved into a 50 mL Teflon-lined stainless autoclave, sealed up and maintained at 180 ℃ for 15 h. After that, the autoclave was natural cooling down to room temperature, the final sample was collected by centrifuging, and washed with deionized water and ethanol for several times, then dried at 50 ℃ under vacuum.

Synthesis of Fe$_2$O$_3$ nanocrystals: the Fe$_2$O$_3$ nanocrystals was prepared via a similar procedure except for 40 mL deionized water instead of ethylene glycol/deionized water mixed solvents.

Fe$_2$O$_3$-based photoelectrode: FTO glasses were cut into regular pieces with 2 cm × 4 cm area and washed in acetone and ethanol mixed solution with a 1:1 volume, then rinsed by deionized water for several times. 100 mg as-synthesized hematite were dispersed into 20 mL absolute ethanol to form a homogeneous solution. Then 1 mL solution was uniformly coated on the conductive surface of a transparent FTO glass at 300 rpm for 30 s by spin coating. Afterwards, the FTO/Fe$_2$O$_3$ photoelectrodes were heated at 60 ℃ for 30 min to evaporate the absolute ethanol and then raised to 550 ℃ in an hour and maintained for 2 hours. After cooling down to room temperature, and the FTO/Fe$_2$O$_3$ photoelectrodes were obtained for future measurements.

Au/Fe$_2$O$_3$ nanoplates, Au/Fe$_2$O$_3$ nanocrystals-based photoelectrodes: The Au NPs were deposited on Fe$_2$O$_3$-based photoelectrodes by ion sputtering (HITACHI). The time of sputtering Au NPs on the Fe$_2$O$_3$-based electrodes was 4 s with a discharge current of 20 mA under an argon pressure at room temperature. Then the obtained Au/Fe$_2$O$_3$-based photoelectrodes was heated at 550 ℃ for 2 hours. After cooling down to room temperature, the Au/Fe$_2$O$_3$ nanoplates, Au/Fe$_2$O$_3$ nanocrystals-based photoelectrodes were obtained for future measurements.

Characterization: Powder X-ray diffraction (XRD) data were performed on a D8 Advance diffractometer (Bruker, Germany) with Cu Kα radiation (λ=1.5406 Å). Transmission electron microscopy (TEM) images and were performed by using a JEOL-2100F TEM at an acceleration voltage of 200 kV. The high-resolution TEM image were performed by JEOL-2010F TEM and the acceleration voltage is 200 kV. X-ray photoelectron spectra (XPS) were conducted on an ESCALAB 250xi (Thermo Fisher, USA). All of the peak's energy obtained in the XPS analysis were calibrate by referencing C 1s to 284.8 eV. Photoluminescent (PL) spectra were performed on an FLS-920 Edinburgh fluorescence spectrometer by using excitation wavelength of 385 nm. The UV/vis absorption spectra were measured on Lambda 950 UV/Vis-NIR spectrophotometer (Perkin Elmer).

Photoelectrochemical performance: Photoelectrochemical tests were performed in a conventional three-electrode configuration filled with 1 M KOH electrolyte, which was purged with N_2 for 20 min before use. The as-prepared Au/Fe_2O_3 nanoplates, Au/Fe_2O_3 nanocrystals, pristine Fe_2O_3 nanoplates-based photoelectrodes were used as the working electrodes. A platinum gauze and Ag/AgCl electrode were used as the counter electrodes and the reference electrodes, respectively. The photoelectrochemical performance were tested on an electrochemical work station (CHI 660d Shanghai, China) under irradiation of a 300 W Xe lamp with a power density of 100 mW/cm^2 (PLS-SXE300C, Trusttech Co., Ltd. Beijing). The LSV was swept at the applied potential from 0.7 to 1.5 vs. RHE with a sweep rate of 50 mV/s. The IPCE spectra were conducted at the applied potential of 1.23 V versus RHE on a Zahner CIMPS-QE/IPCE. Mott–Schottky plots were carried out in the dark from 0 V to 1.4 V vs. RHE. The electrochemical impedance spectroscopy was measured at a bias potential of 1.23 V versus RHE under irradiation.

Theoretical calculations details:

All of the first-principles calculations were performed with the Vienna ab initio simulation package (VASP).[1] The interaction between core electrons and nuclei of each atom was represent by the use of projector augmented wave (PAW) potentials, and the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof

(PBE) form functional was used to describe the exchange–correlation between electrons.[2] A parameter of U = 4.3 eV for Fe atoms was applied to treat the onsite repulsion. The slab model along the [001] projection of four stoichiometric units were built from the optimized bulk crystal structure to mimic Fe_2O_3 (001) surface. To obtain the accurate density of states, the plane wave cutoff energy was set as 700 eV and a 3×3×1 Monkhorst-Pack points mesh were used for (001) surface. Ionic relaxations were carried out under a force convergence criterion of 0.01 eV/Å.

The finite-difference time domain (FDTD) simulation was introduced in this paper to calculate the electric field distributions: The Au dimers with gap of 3 nm is placed on the surface of a Fe_2O_3 hexangular nanoplate to mimic the Au/Fe_2O_3 nanoplates hybrid. The sizes of Au nanoparticles and Fe_2O_3 nanoplate were set as 10 nm and 50 nm respectively according to the experimental results, and the incident and monitored lights were both set as 532 nm, which corresponds to the UV-vis absorption peak. Perfectly matched layer boundary condition was used for all the boundary in x-, y- and z-direction, and the refractive index data for Au and Fe_2O_3 were obtained from the reported papers.[3, 4]

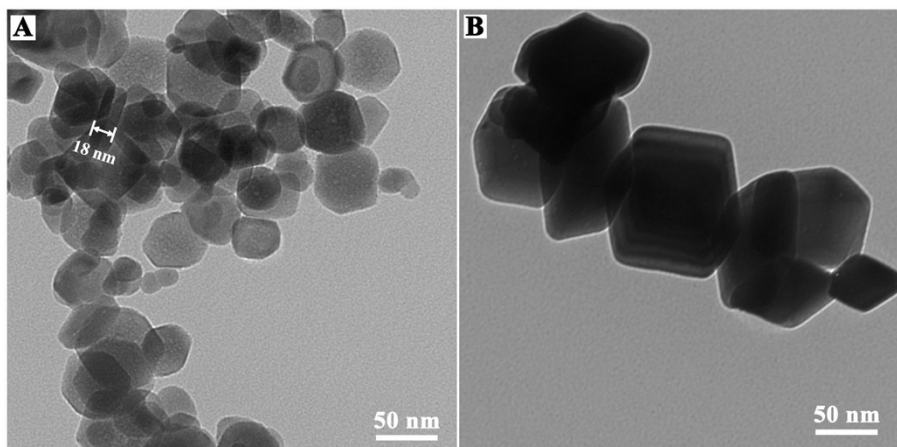## S2. Characterizations of the Fe_2O_3 nanoplates and Fe_2O_3 nanocrystals.

Figure S1. TEM of (A) Fe_2O_3 nanoplates and (B) Fe_2O_3 nanocrystals.

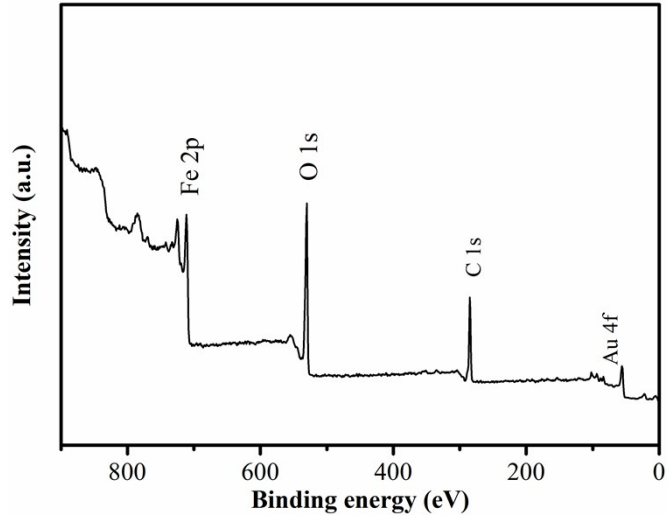## S3. Characterizations of the Au/Fe_2O_3 nanoplates.

Figure S2. XPS survey spectra for the Au/Fe$_2$O$_3$ nanoplates.
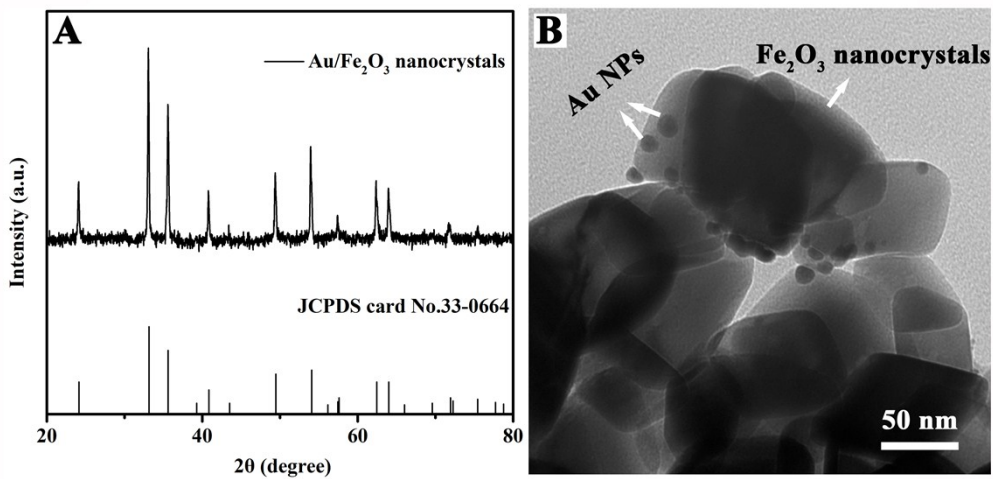
S4. Characterizations of the Au/Fe$_2$O$_3$ hybrid.

Figure S3. (A) XRD and (B) TEM of Au/Fe$_2$O$_3$ nanocrystals.
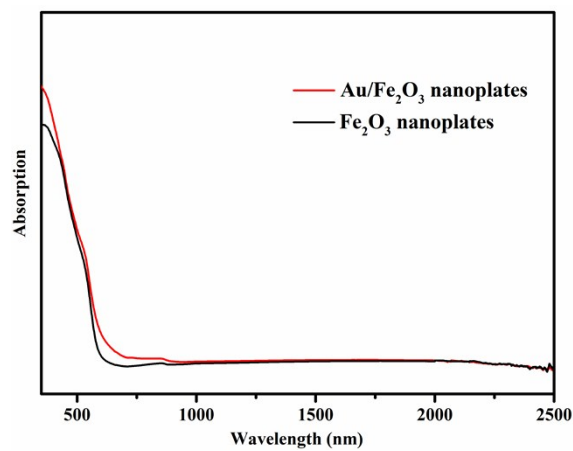

Figure S4. UV/Vis-NIR diffuse reflectance spectra for the Au/Fe$_2$O$_3$ nanoplates and pristine Fe$_2$O$_3$ nanoplates.
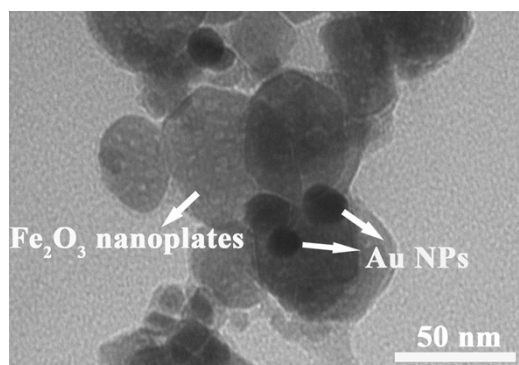
Figure S5. TEM image of Au/Fe_2O_3 nanoplates after photoelectrochemical stability test for 5 h, confirming the structural stability of the Au/Fe_2O_3 nanoplates-based photoelectrode.
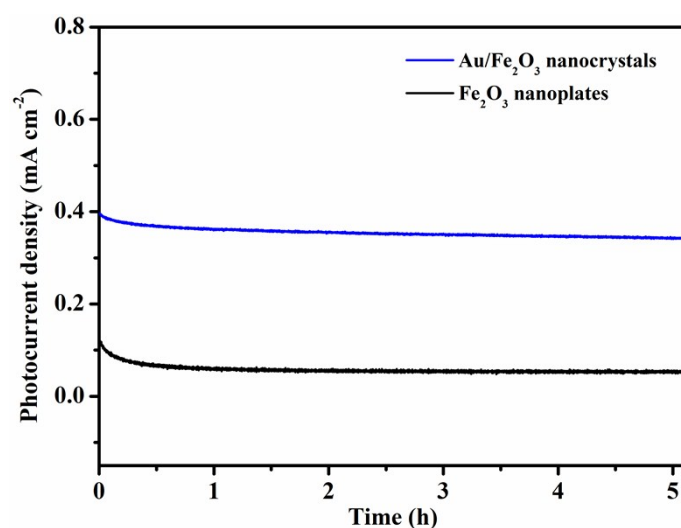

Figure S6. Photoelectrochemical stability curve at 1.23 V vs. RHE under light irradiation for the Au/Fe_2O_3 nanocrystals and pristine Fe_2O_3 nanoplates.

REFERENCES

1   G. Kresse and J. Furthmuller, *Comp. Mater. Sci.*, 1996, **6**, 15-50.

2   P. E. Blochl, *Phys. Rev. B*, 1994, **50**, 17953-17979.

3   P. B. Johnson and R. W. Christy, *Phys. Rev. B*, 1972, **6**, 4370-4379.

4   M. R. Querry, *Contractor Report CRDCCR-85034*, 1985.