Supporting Information

Plasmon-Enhanced Electrocatalytic Hydrogen/ Oxygen Evolution by Pt/Fe-Au Nanorods

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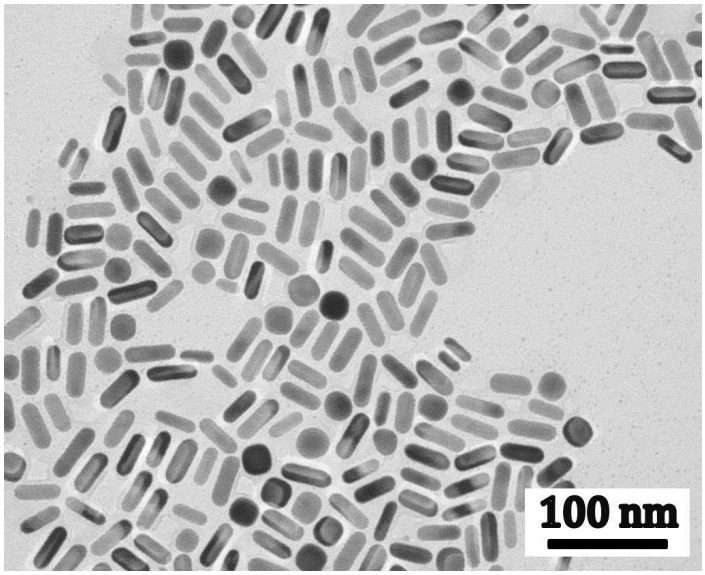

Fig. S1 TEM image of the original Au nanorods.

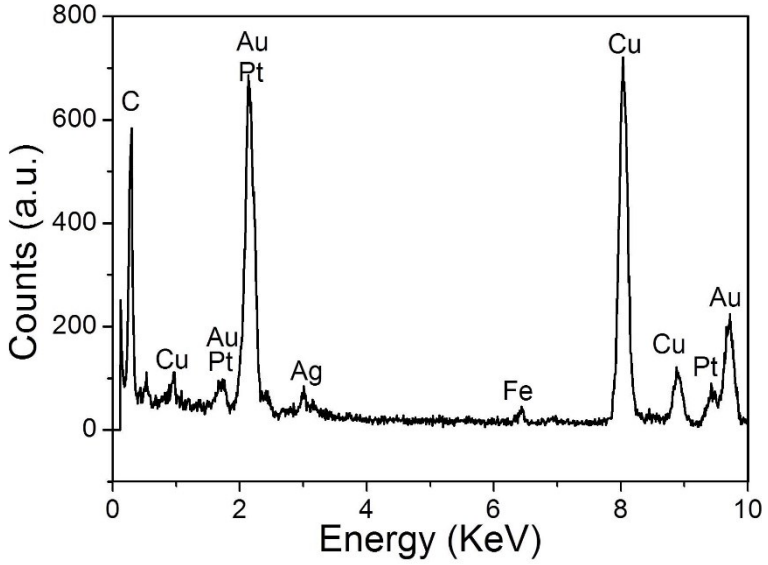

Fig. S2 EDS spectrum of the dumbbell-like Pt/Fe-Au nanorods.

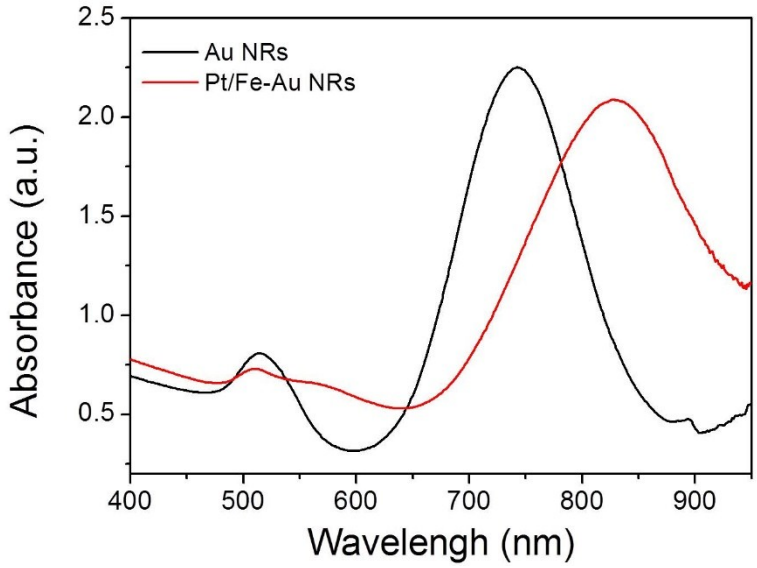

Fig. S3 UV-vis absorption spectra of the original Au nanorods and dumbbell-like Pt/Fe-Au nanorods.

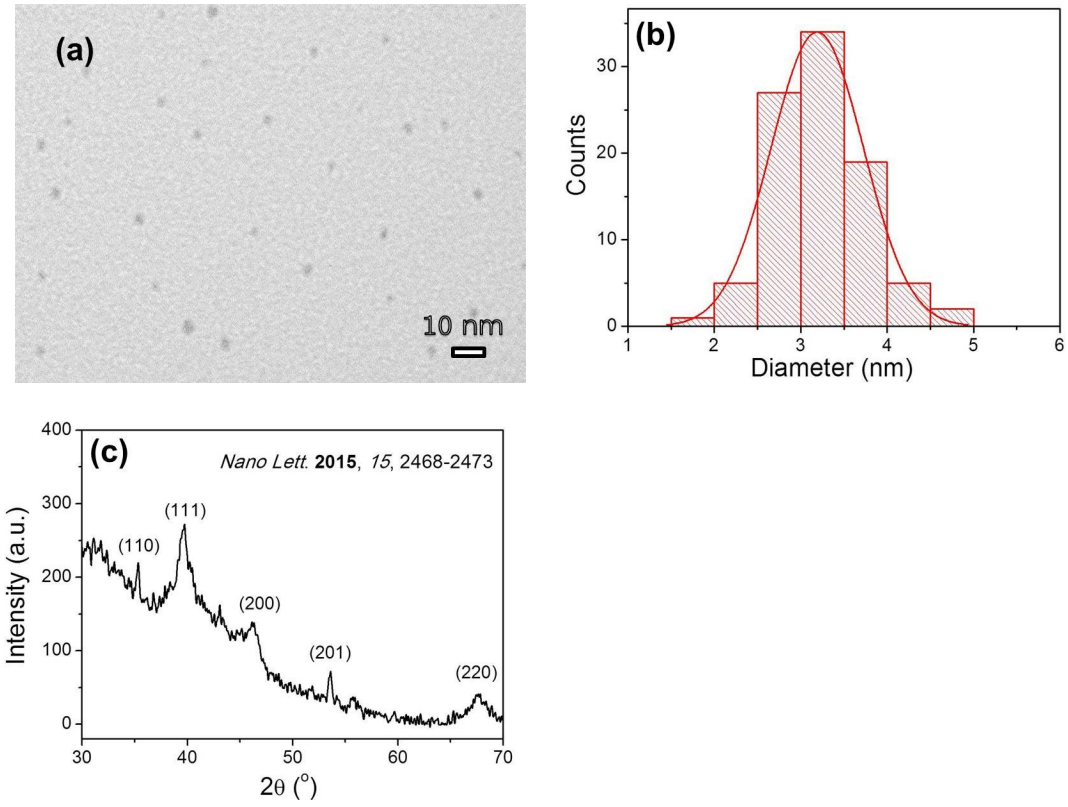

Fig. S4 TEM image, size distribution and XRD pattern of the obtained Pt/Fe nanoparticles. The average size of the obtained Pt/Fe nanoparticles is 3.21 ± 0.57 nm.

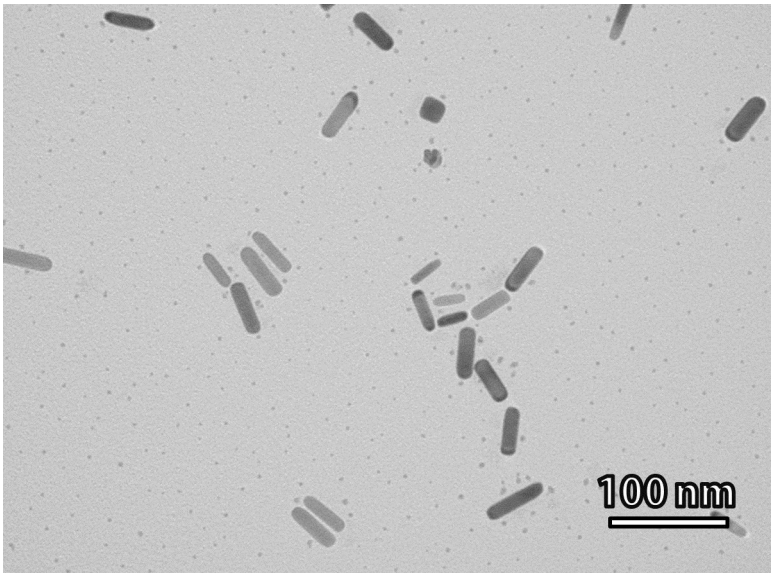

Fig. S5 TEM image of the mixture of Pt/Fe nanoparticles and Au nanorods.

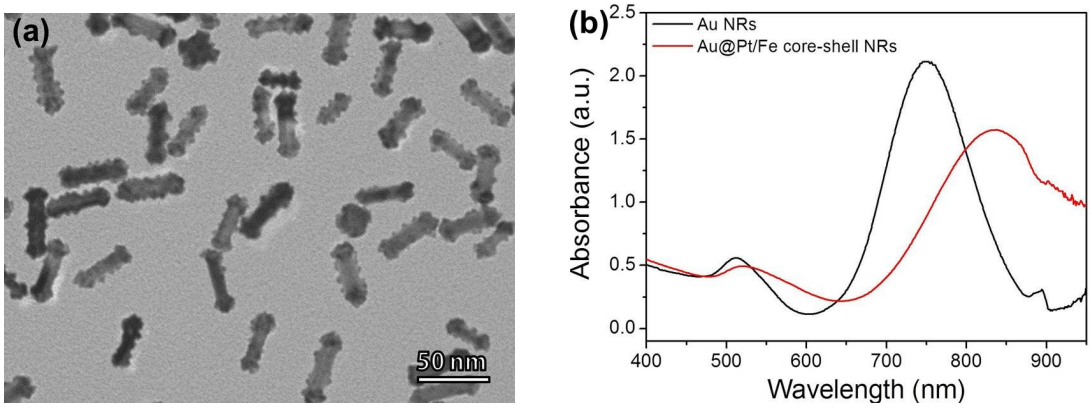

Fig. S6 (a) TEM image of Au@Pt/Fe core-shell nanorods and (b) UV-vis absorption spectra of the original Au nanorods and Au@Pt/Fe core-shell nanorods.

Table S1. Onset potential, η@ j = 10 mA cm^{-2}, Tafel slope, exchange current density (j_0) and TOF @ 50 mV vs RHE of different catalysts.

Catalysts	Onset potential (mV)	η@ j = 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Exchange current density (mA cm^{-2})	TOF@ 50 mV vs RHE (H_2 s^{-1})
Au	-211	357	114.7	0.011	-----
Irradiated Au	-210	336	113.8	0.015	-----
Pt/Fe	-10	39	27.3	0.41	0.66
Irradiated Pt/Fe	-10	39	27.3	0.45	0.73
Au + Pt/Fe	-12	41	29.1	0.34	0.58
Irradiated Au + Pt/Fe	-12	40	29.1	0.42	0.61
Au@Pt/Fe	-13	38	29.4	0.57	0.42
Irradiated Au@Pt/Fe	-7	32	28.6	0.83	0.69
Pt/Fe- Au	-13	43	30.6	0.31	0.44
Irradiated Pt/Fe-Au	0	18	29.3	3.16	2.28

The TOF was calculated by using an equation of TOF = jN_A/nFN, where j is the current density (A cm^{-2}), N_A is the avogadro number, n=2 is the number of electrons consumed in the electrode reaction, F is the Faraday constant and N is the number of active sites in an unit area.

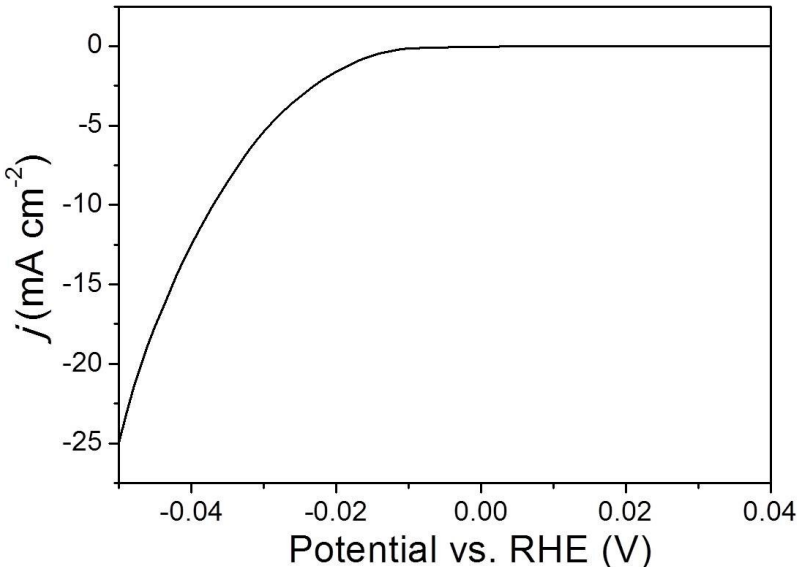

Fig. S7. HER polarization curves (with iR-correction) of commercial Pt/C in 0.5 M H_2SO_4. The scan rate is 2 mV s^{-1}.

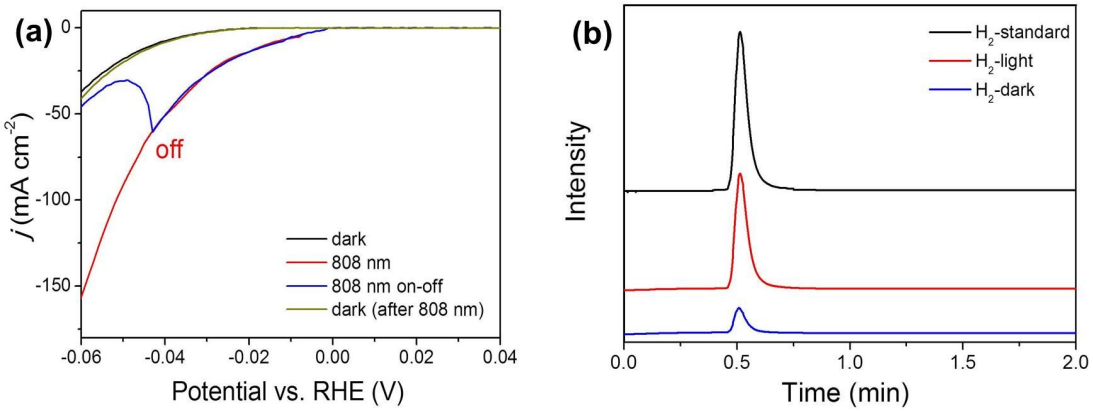

Fig. S8 (a) Polarization curves of Pt/Fe-Au nanorods without (black line), with (red line) light irradiation , with (blue line) light on and off (808 nm) and the electrocatalytic HER behavior of the Pt/Fe-Au nanorods in the dark after one irradiation cycle (yellow line) and (b) gas chromatography (GC) measurements of various samples but keep the same reaction time. Black line: pure H_2 collected from the gas cylinder; red line: gas collected from the catalysts under 808 nm laser irradiation; and blue line: gas collected from the catalysts in the dark.

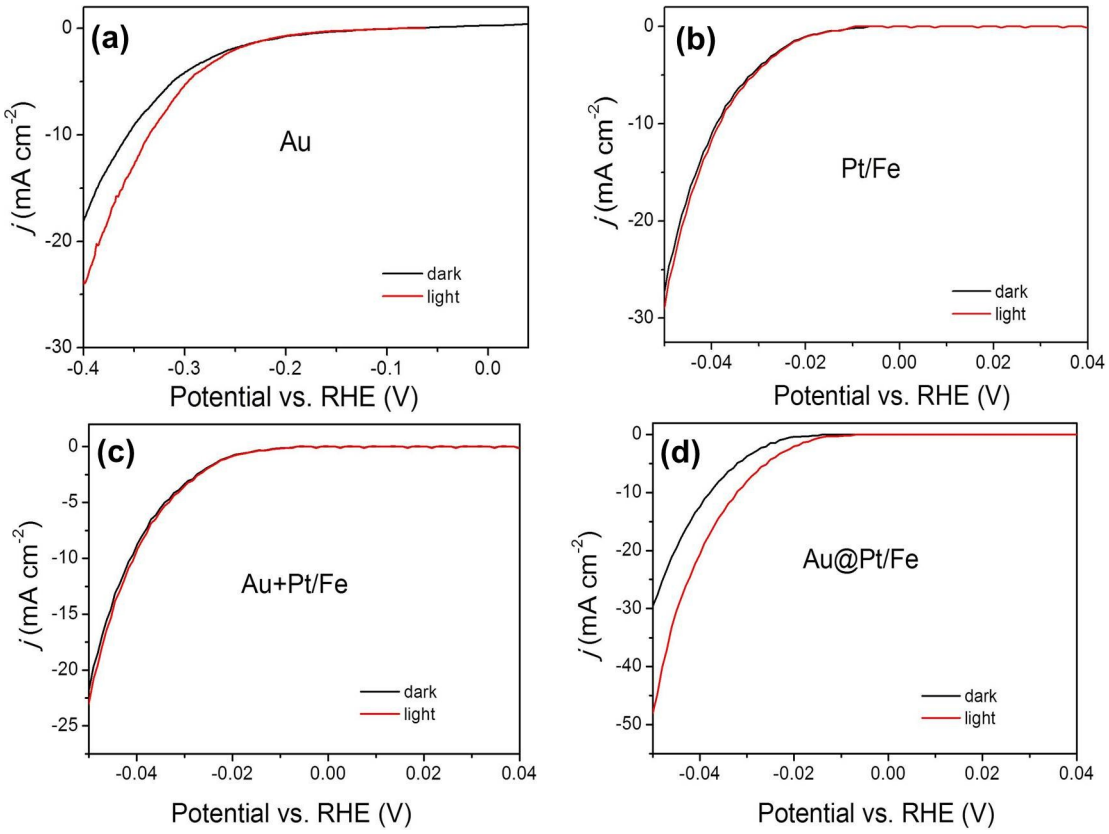

Fig. S9 Polarization curves (with iR-correction) of different catalysts with and without light irradiation (808 nm). (a) Au; (b) Pt/Fe; (c) Au+Pt/Fe; and (d) Au@Pt/Fe. The scan rate is 2 mV s^{-1}.

HER in acidic media starts with a discharge reaction, three possible reaction steps are as following:

Equ. S1 $H_{(aq)} + e^- \rightarrow H_{ads}$ (Volmer reaction)

Equ. S2 $H_{ads} + H_{(aq)} + e^- \rightarrow H_{2(g)}$ (Heyrovsky reaction)

Equ. S3 $H_{ads} + H_{ads} \rightarrow H_{2(g)}$ (Tafel reaction)

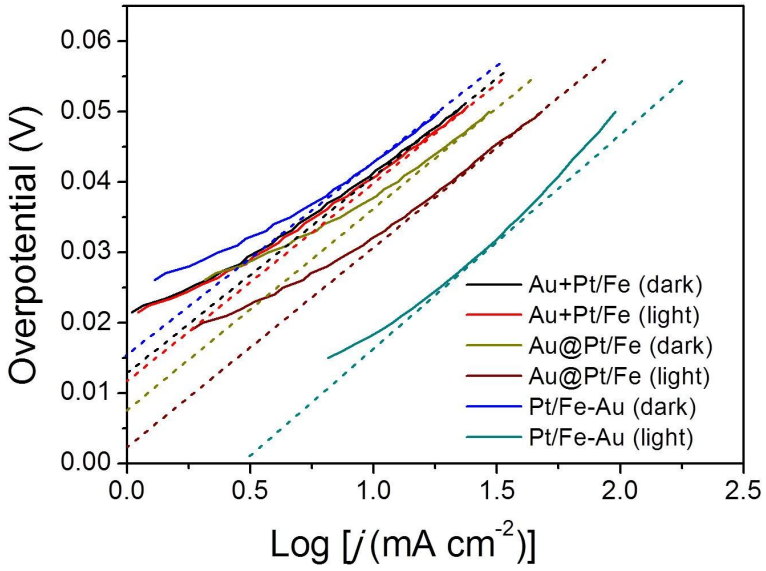

Fig. S10 The Tafel plots of Pt/Fe, Au+Pt/Fe, Au@Pt/Fe and Pt/Fe-Au with and without light excitation (808 nm).

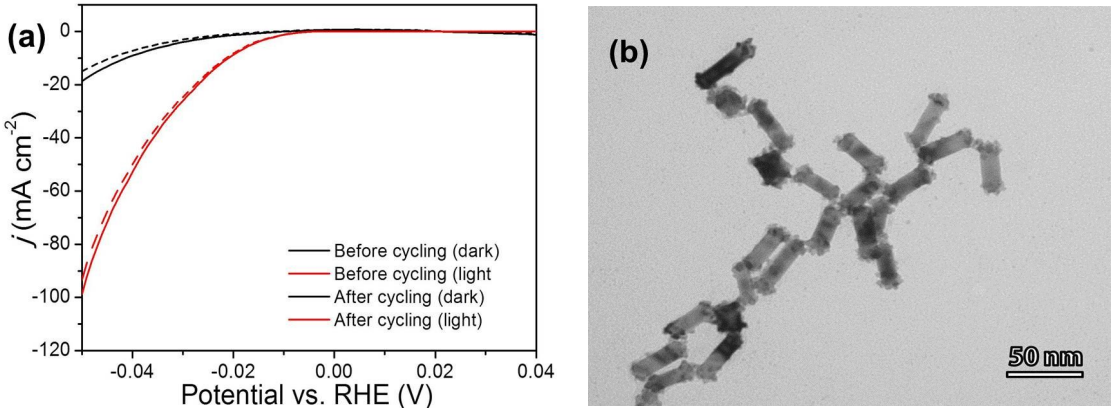

Fig. S11 (a) HER polarization curves of Pt/Fe-Au nanorods measured in 0.5 M H_2SO_4 before and after 1000 cycles of cyclic voltammetry and (b) TEM image of Pt/Fe-Au nanorods after repeated cycles. The scan rate is 2 mV s^{-1}.

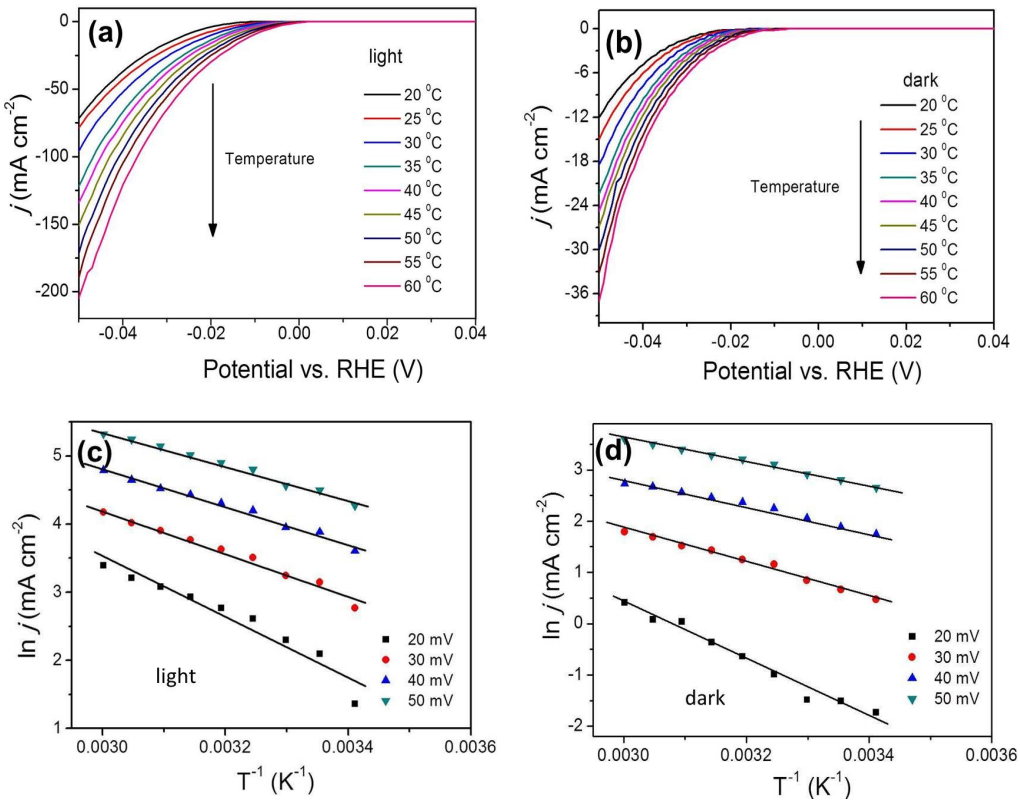

Fig. S12 HER polarization curves of Pt/Fe-Au nanorods with (a) and without (b) light excitation (808 nm) at different temperature and (c,d) Arrhenius plots of ln *j versus* inverse temperature for Pt/Fe-Au nanorods with (c) and without (d) light excitation (808nm) at various overpotentials. Overpotentials are taken from 20 to 50 mV at an interval of 10 mV.

The E_a for Pt/Fe-Au nanorods with and without 808 nm laser excitation were calculated from the slope of the Arrhenius plot. The Arrhenius equation is described as: $j = Ae^{-Ea/RT}$, and can be written equivalently as: $\ln j = \ln A - (E_a/R)(1/T)$, where A is pre-exponential factor, E_a is activation energy, R is gas constant and T is reaction temperature.

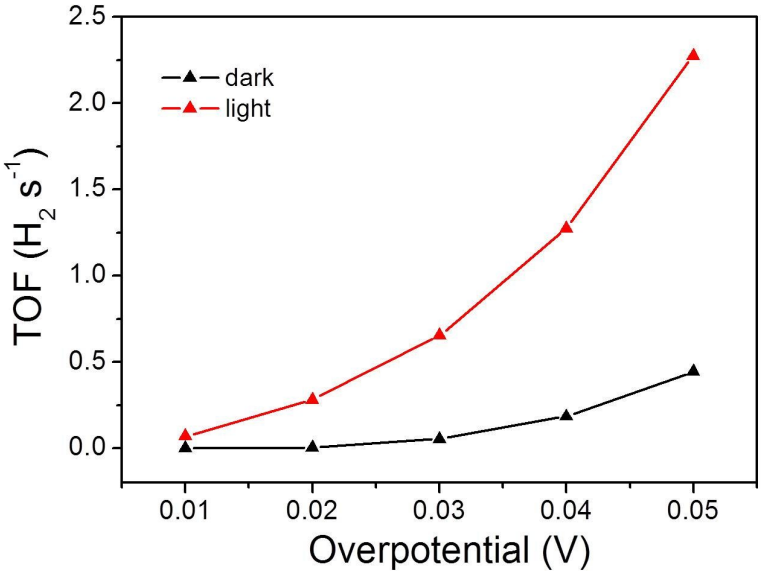

Fig. S13 TOF values of Pt/Fe-Au nanorods with and without light excitation (808 nm) at different overpotentials.

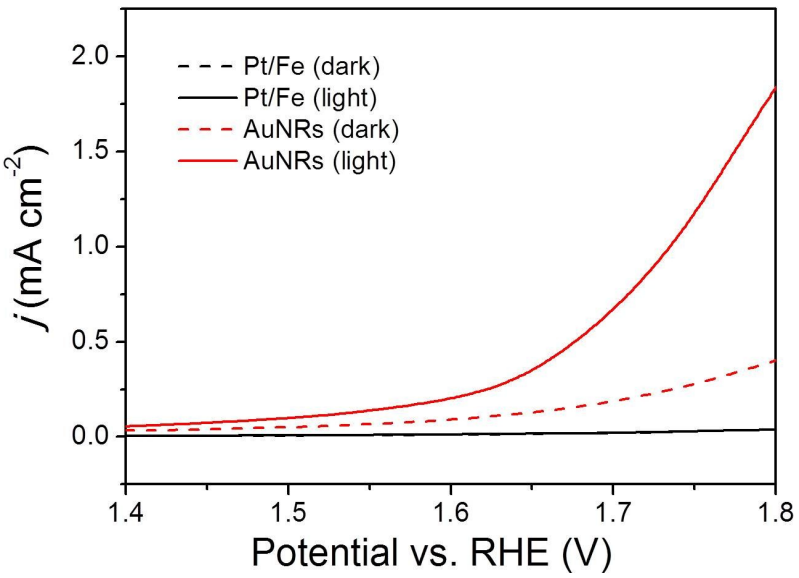

Fig. S14 OER polarization curves (with iR-correction) of Pt/Fe nanoparticle and gold nanorods with and without light excitation (808 nm). The scan rate is 5 mV s^{-1}.