Supporting information

Precise control of TiO_2 overlayer on hematite nanorod arrays by ALD for the photoelectrochemical water splitting

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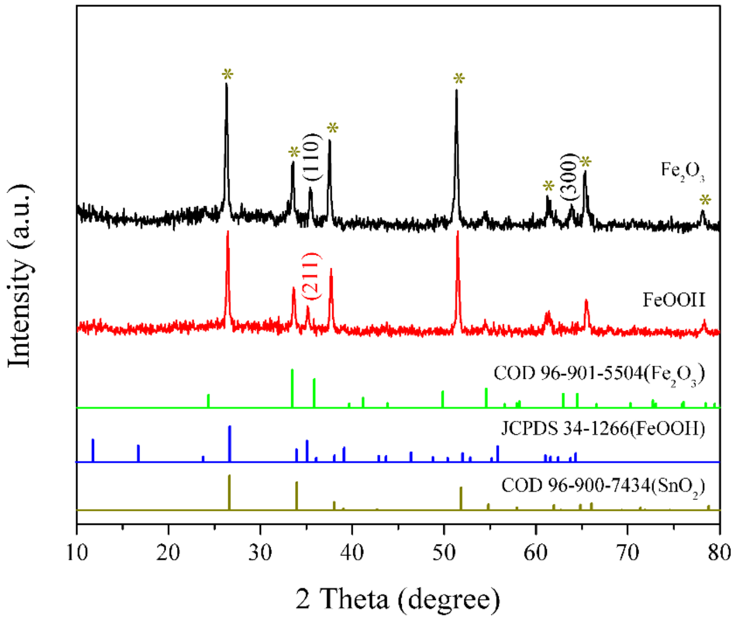

Figure S1. XRD patterns of pristine β-FeOOH and α-Fe_2O_3.

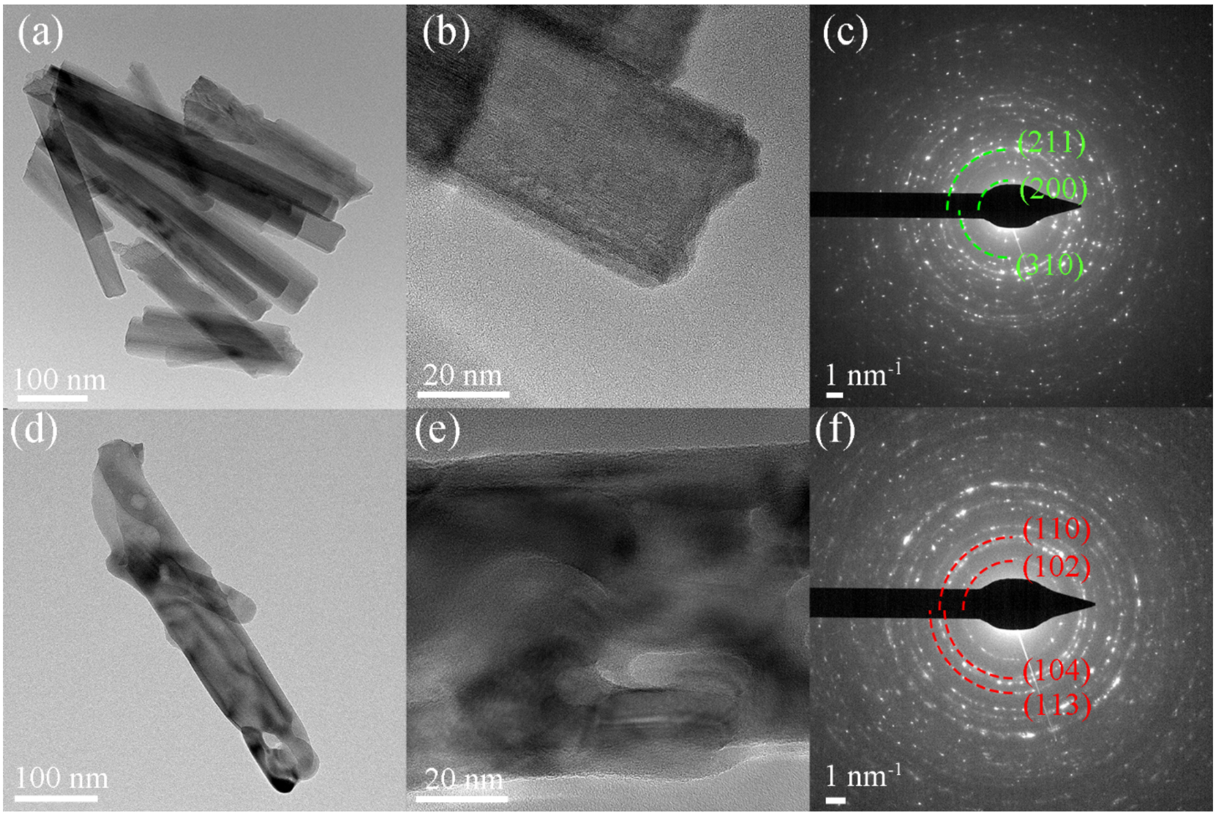

Figure S2. (a,b) TEM images of β-FeOOH nanorods. (c) Corresponding SAED pattern of β-FeOOH nanorods. (d,e) HRTEM images of α-Fe_2O_3 nanorods. (f) Corresponding SAED pattern of α-Fe_2O_3 nanorods.

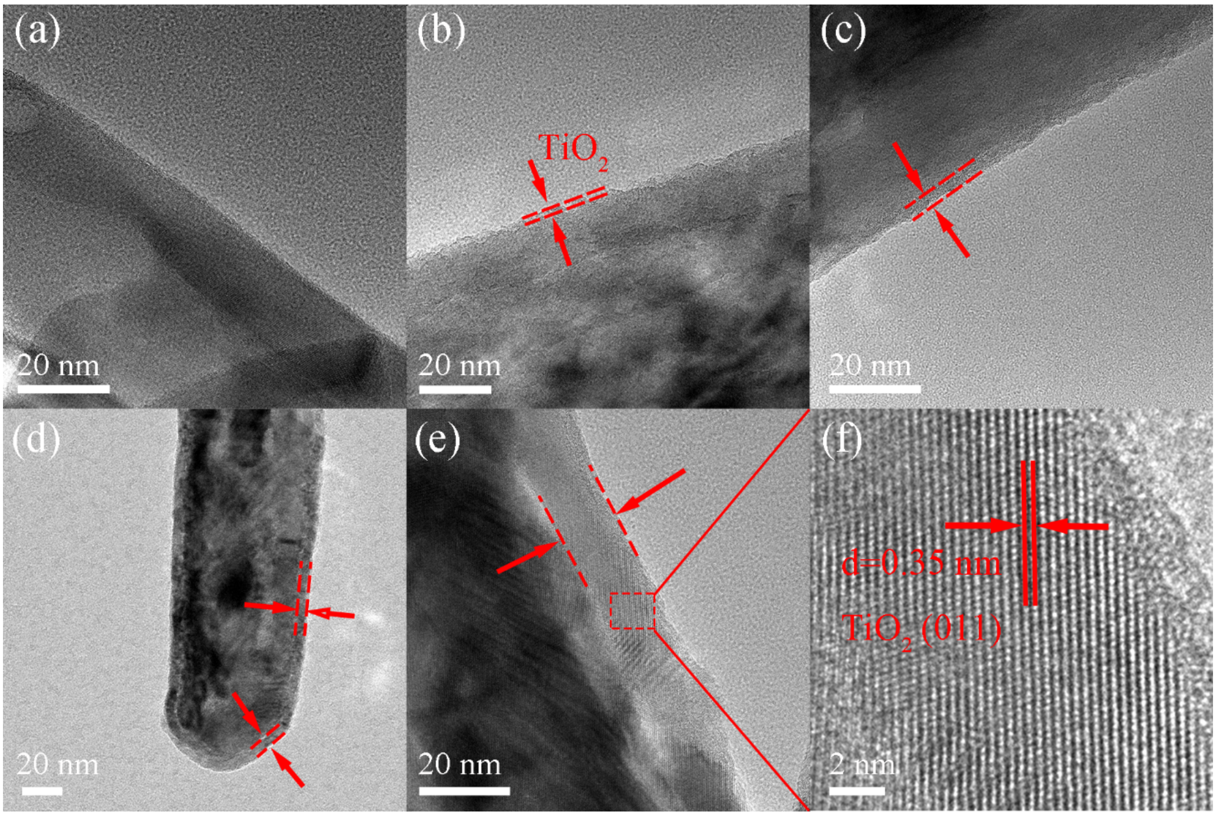

Figure S3. HRTEM images of TiO_2 deposited on pristine hematite with different ALD cycles: (a)TiO_2-10/Fe_2O_3, (b) TiO_2-20/Fe_2O_3, (c) TiO_2-40/Fe_2O_3, (d) TiO_2-80/Fe_2O_3, (e) TiO_2-150/Fe_2O_3, (f) The magnified view of the lattice fringes of TiO_2-150/Fe_2O_3.

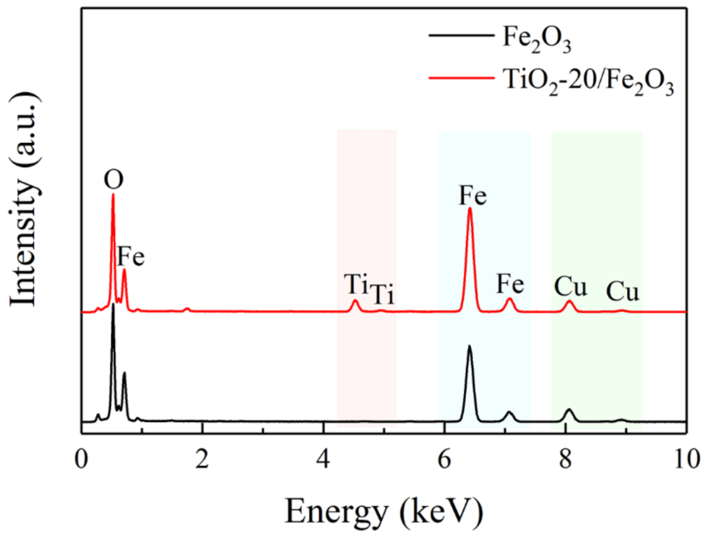

Figure S4. EDX spectra for pristine Fe_2O_3 and TiO_2-20/Fe_2O_3 analyzed on a copper TEM grid.

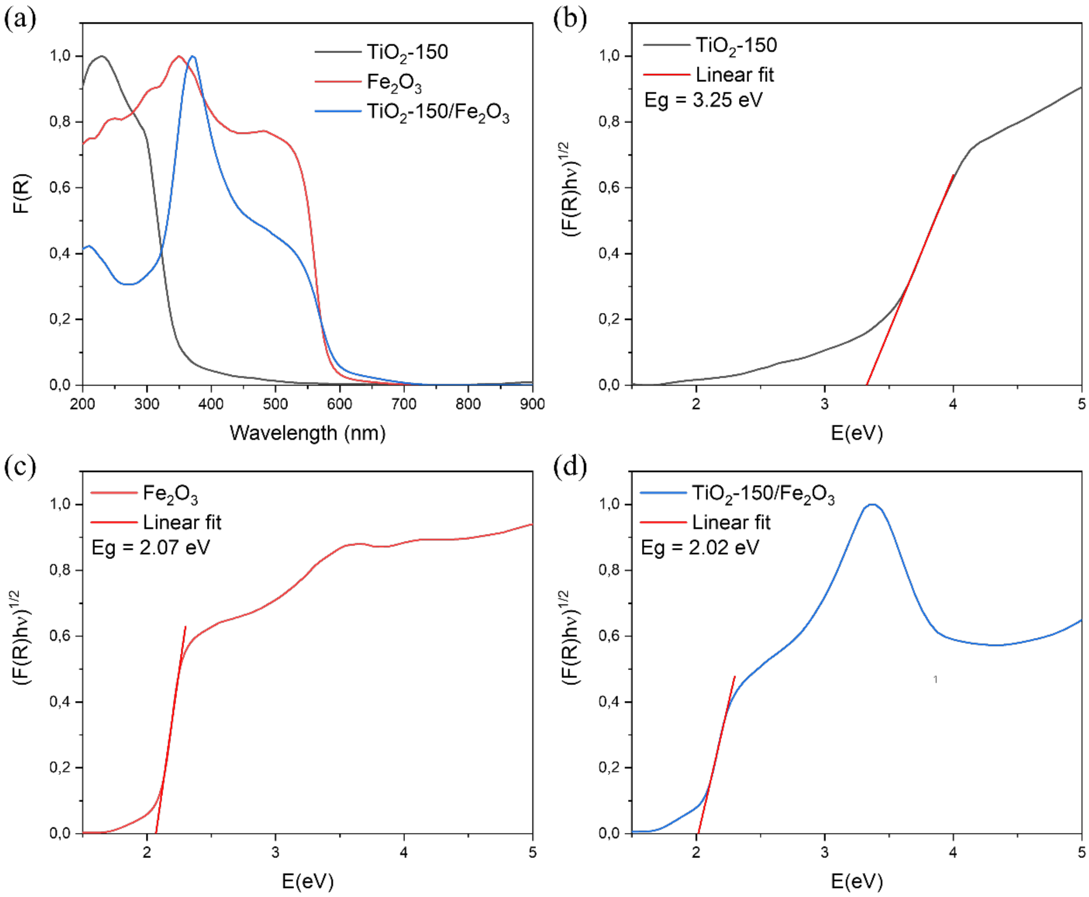

Figure S5. (a) Plots of F(R) versus wavelength of the pristine Fe_2O_3, pristine TiO_2 and TiO_2/Fe_2O_3 nanocomposites from the UV-vis diffuse reflectance spectra. Plots of $(F(R)h\nu)^{1/2}$ versus photon energy for the (b) pristine TiO_2 (c) pristine Fe_2O_3 and (d) TiO_2/Fe_2O_3 heterojunction.

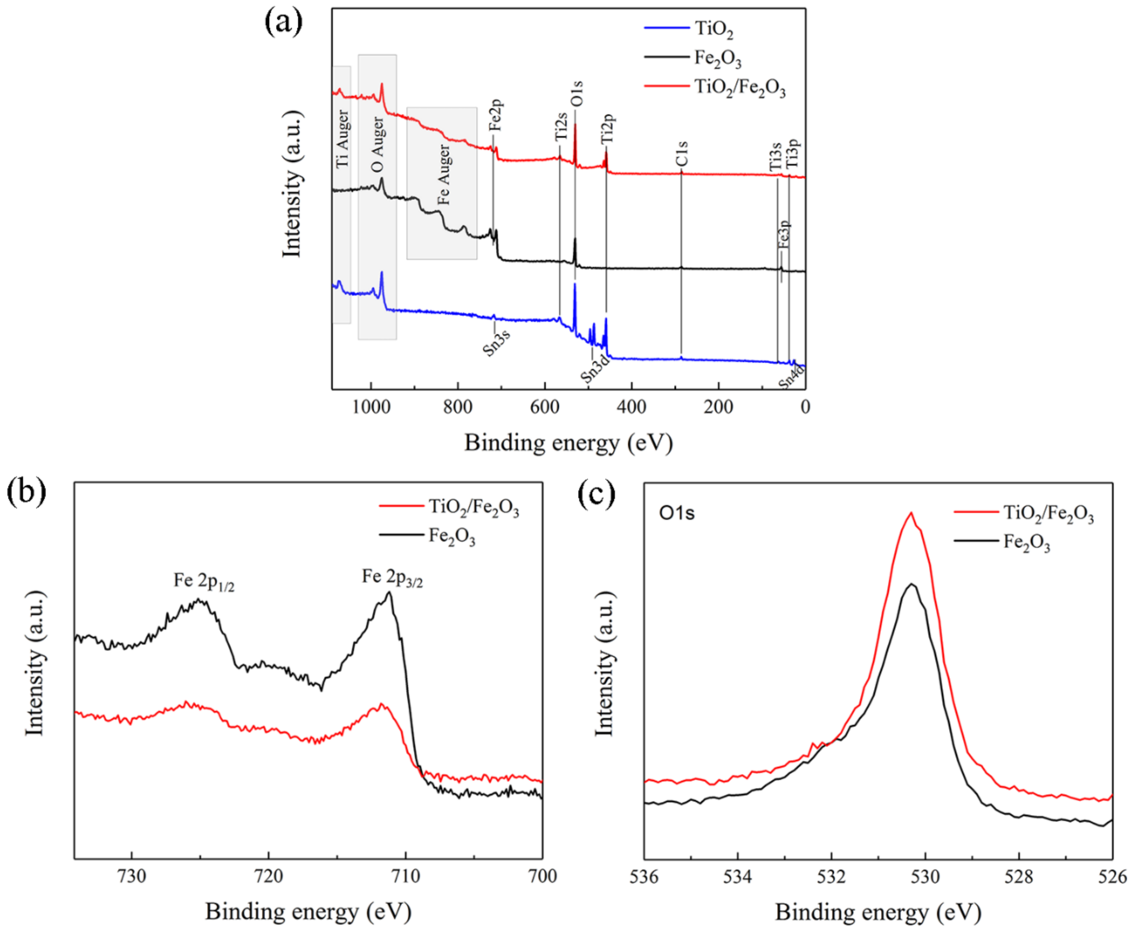

Figure S6. (a) XPS survey spectra of the pristine Fe_2O_3, pristine TiO_2 with 20ALD cycles and Fe_2O_3 coated with 20 ALD cycles of TiO_2 overlayer. For the TiO_2 sample, the tin signal from the FTO substrate is visible due to the small thickness of the TiO_2 layer. (b) High-resolution Fe2p photoelectron spectrum of the pristine Fe_2O_3 and TiO_2-20/Fe_2O_3. (c) High-resolution O1s photoelectron spectrum of pristine Fe_2O_3 and TiO_2-20/Fe_2O_3.

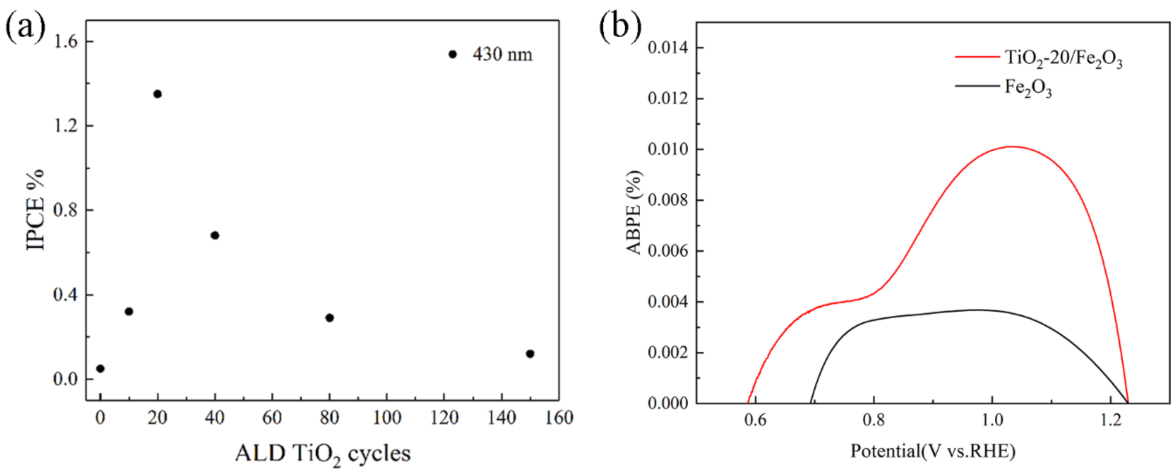

Figure S7. (a) IPCE spectra of pristine Fe_2O_3 and TiO_2/Fe_2O_3 photoanodes measured in 1M KOH at 0.5 V bias vs. Hg/HgO under 430 nm light irradiation. (b) ABPE of pristine Fe_2O_3 and TiO_2-20/Fe_2O_3 photoanodes.

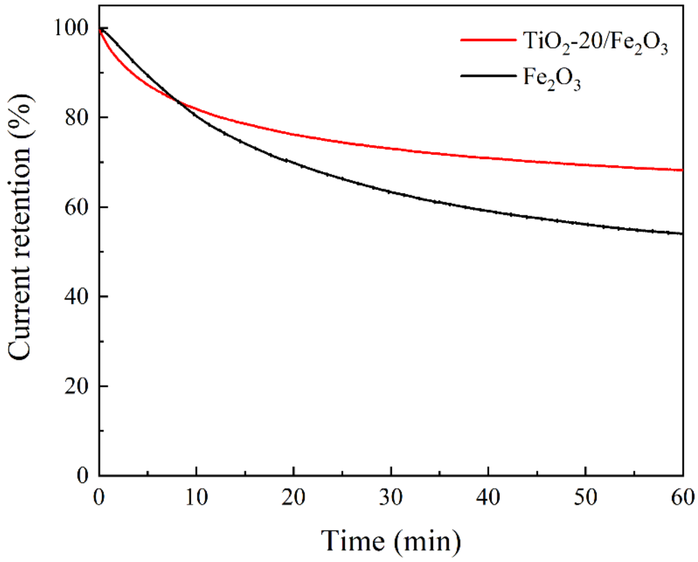

Figure S8. Stability test of pristine Fe_2O_3 and TiO_2-20/Fe_2O_3 photoanodes.

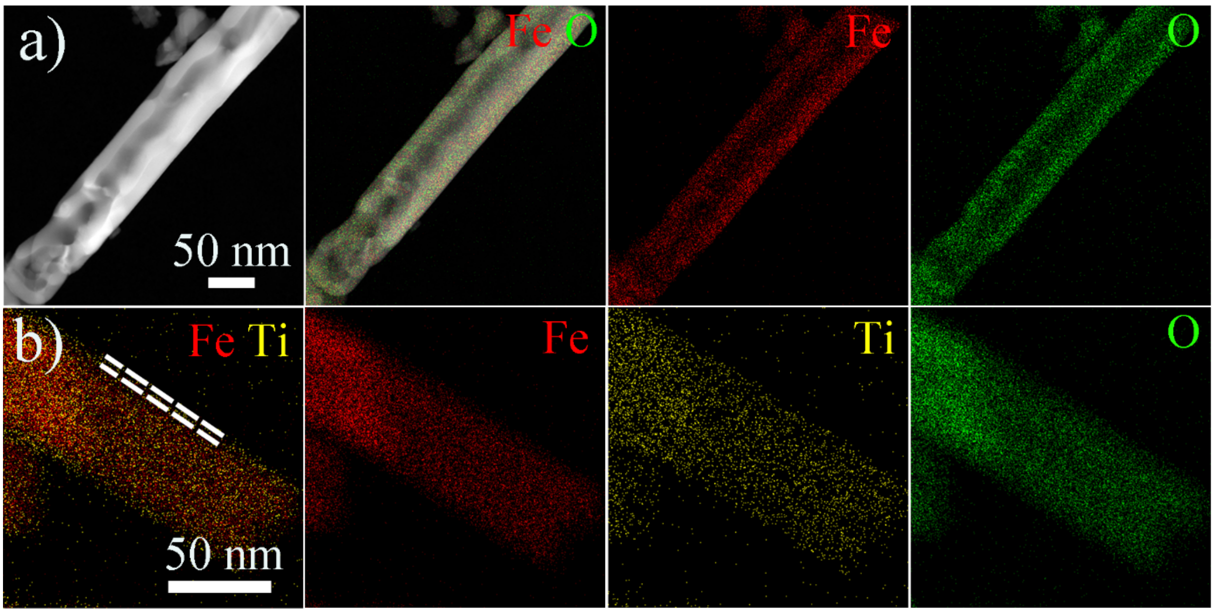

Figure S9. The morphology of the synthesized photocatalyst after stability test: a) pristine Fe_2O_3, b) TiO_2-20/Fe_2O_3.

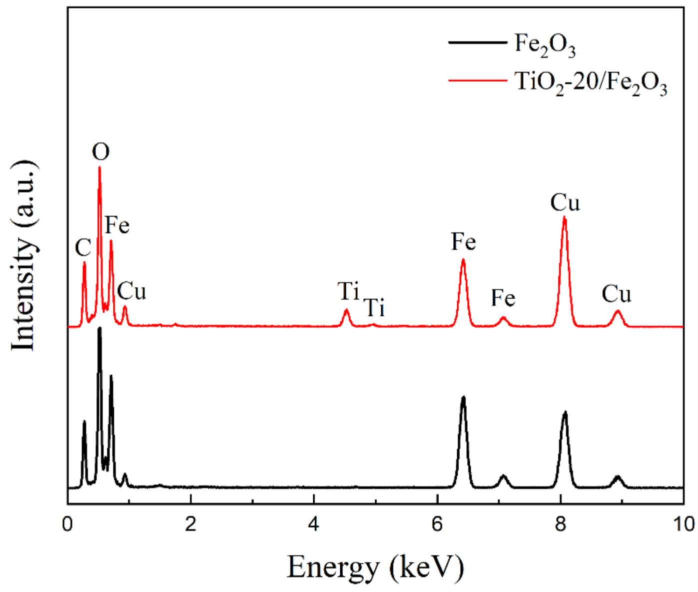

Figure S10. The composition of the pristine Fe_2O_3 and TiO_2-20/Fe_2O_3 after stability test.

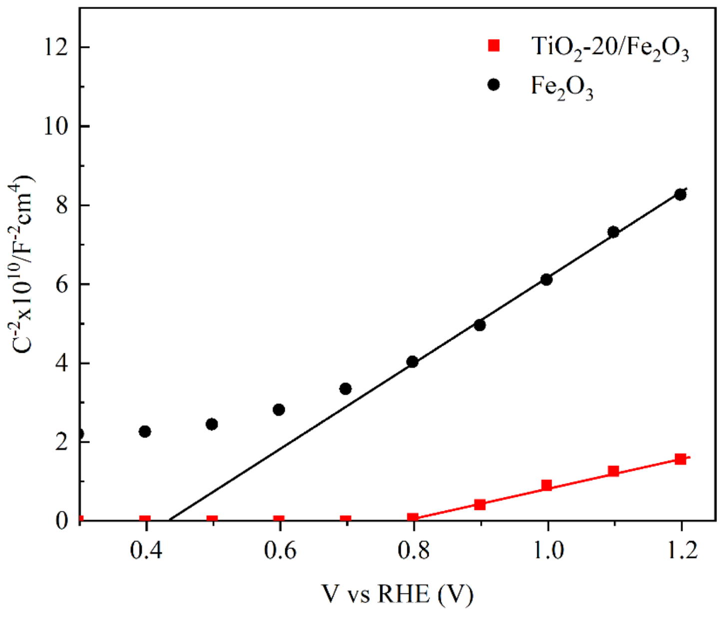

Figure S11. Mott-Schottky plots of pristine Fe_2O_3 and TiO_2-20/Fe_2O_3 heterostructure.

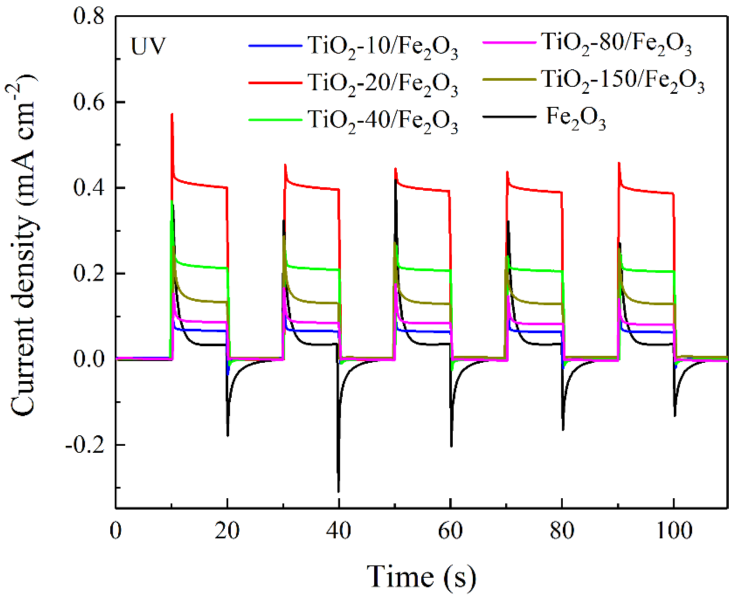

Figure S12. Time-based photocurrent density for pristine and TiO_2-coated hematite photoanodes at 0.5 V bias vs. Hg/HgO under UV light irradiation.

Table S1. Average TiO_2 overlayer thickness and the GPC calculated from TEM micrographs and spectroscopic ellipsometry.

Samples	Transmission electron microscopy		Spectroscopic ellipsometry	
	Thickness (nm)	Slope of line fit (GPC)	Thickness (nm)	Slope of line fit (GPC)
TiO_2-10/Fe_2O_3	---		2.2	
TiO_2-20/Fe_2O_3	1.7		3.5	
TiO_2-40/Fe_2O_3	3.5	0.88 Å	5.0	0.96 Å
TiO_2-80/Fe_2O_3	6.8		9.0	
TiO_2-150/Fe_2O_3	13.2		15.1	

Table S2. The atomic/weight percentage of all the samples with different ALD cycles.

Samples	Atom fraction (%)		Mass fraction (%)	
	Ti	Fe	Ti	Fe
TiO_2-10/Fe_2O_3	1.28	28.2	2.21	57.0
TiO_2-20/Fe_2O_3	3.89	39.9	5.62	67.2
TiO_2-40/Fe_2O_3	6.59	24.7	11.3	49.3
TiO_2-80/Fe_2O_3	9.88	22.1	16.9	44.1
TiO_2-150/Fe_2O_3	18.4	22.7	28.5	41.0