Supporting Information

MoS_x Supported Hematite with Enhanced Photoelectrochemical Performance

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Experimental section

Chemicals used

Iron (III) chloride hexahydrate ($FeCl_3$•$6H_2O$, Kanto chemical, > 97.0%), Titanium(III) chloride solution ($TiCl_3$, Sigma Aldrich, >12%), Ammonium tetrathiomolybdate ($(NH_4)MoS_4$, Sigma Aldrich, 99.97%), N,N-Dimethylformamide (DMF, Junsei, 99.5%), Sodium Hydroxide (NaOH, Samchun, extra pure), Ethanol (SK chemical, > 95%), Methylene blue (Sigma-Aldrich,>82%). All chemicals were used without further purification.

Preparation of Ti-Fe_2O_3 and MoSx/Ti-Fe_2O_3

For the synthesis of Ti doped Fe_2O_3 (Ti-Fe_2O_3), the FTO substrate was immersed in a mixture of 2.4 μl of $TiCl_3$ and 40 ml of $FeCl_3$•$6H_2O$ and kept in a convection oven at 100 °C with a ramp rate of 1 °C/min for 4 hrs. The samples were washed with DI water and EtOH. Finally β-FeOOH was annealed at 550 °C for 1 h and 800 °C for 20 min in the furnace.

To fabricate precursors of MoS_x, 0.1 wt% of $(NH_4)MoS_4$ in DMF was diluted to the proper concentration. The 10 μwt%, 100 μwt% and 1000 μwt% of $(NH_4)MoS_4$ solution was drop-casted on Ti-Fe_2O_3 for 10-MoS_x/Ti-Fe_2O_3, 100-MoS_x/Ti-Fe_2O_3 and 1000-MoS_x/Ti-Fe_2O_3,

respectively, and annealing at 100 ^{o}C for 10 min. To fabricate MoS_x/Ti-Fe_2O_3, the $(NH_4)MoS_4$ treated Ti-Fe_2O_3 was placed in a quartz tube with an outer diameter of 2 inch, heated at 700 ^{o}C under Ar (200 sccm) atmosphere with sulfur powder in alumina boat for 1 h.

Characterization.

The structures was examined by SEM (S-4800 Hitachi, 10kV), TEM (JEM-2100, 200kV). The XRD data were obtained using a Rigaku Co. High Power X-Ray Diffractometer D/MAZX 2500V/PC from 20^{o} to 80^{o}. The XPS data were obtained using k-alpha (Thermo Fisher, UK), The PL data were measured using a Cary Eclipse (Agilent, USA) at 400 nm excitation, The UV-visible extinction spectra were measured using a Cary-100 corns spectrophotometer (Varian).

Photoelectrochemical measurement

The PEC performance of the Ti-Fe_2O_3 and MoS_x/Ti-Fe_2O_3 electrodes was explored in a three-cell electrode system under front-side illumination of AM 1.5 G. An Ag/AgCl electrode and a Pt mesh were used as reference and counter electrodes, respectively. A solution of 1 M NaOH was used as an electrolyte. The exposed area of the working electrode was an exact value of 0.287 cm^2. Photocurrent stability tests were carried out by measuring the photocurrent produced under chopped light irradiation (light/dark cycles of 30 s) at a bias of 1.50 V versus RHE.). IPCE measurements were also conducted using an EQE system (Model QEX7) by PV Measurements Inc. (Boulder, Colorado) with 3 electrode system. Electrochemical impedance spectroscopy (EIS) was carried out at a frequency range from 100 kHz to 0.1 Hz using a potentiostat at 1.50 V_{RHE}. The photodegradation of methylene blue (MB) was measured by separately immersing Ti-Fe_2O_3 and MoS_x/Ti-Fe_2O_3 in 100ml of the MB solution (50mg/l in

water) under illumination. After the given exposure period, the absorbance change of MB was tracked by a UV-visible spectrophotometer to compare the photocatalytic activity.

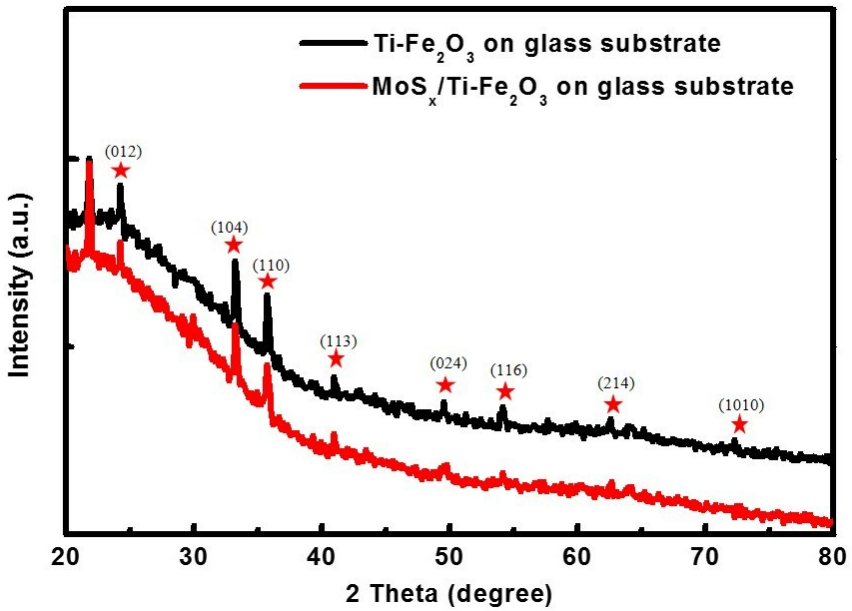

Figure S1. XRD patterns of the $Ti\text{-}Fe_2O_3$ and $MoS_x/Ti\text{-}Fe_2O_3$ on the glass substrate.

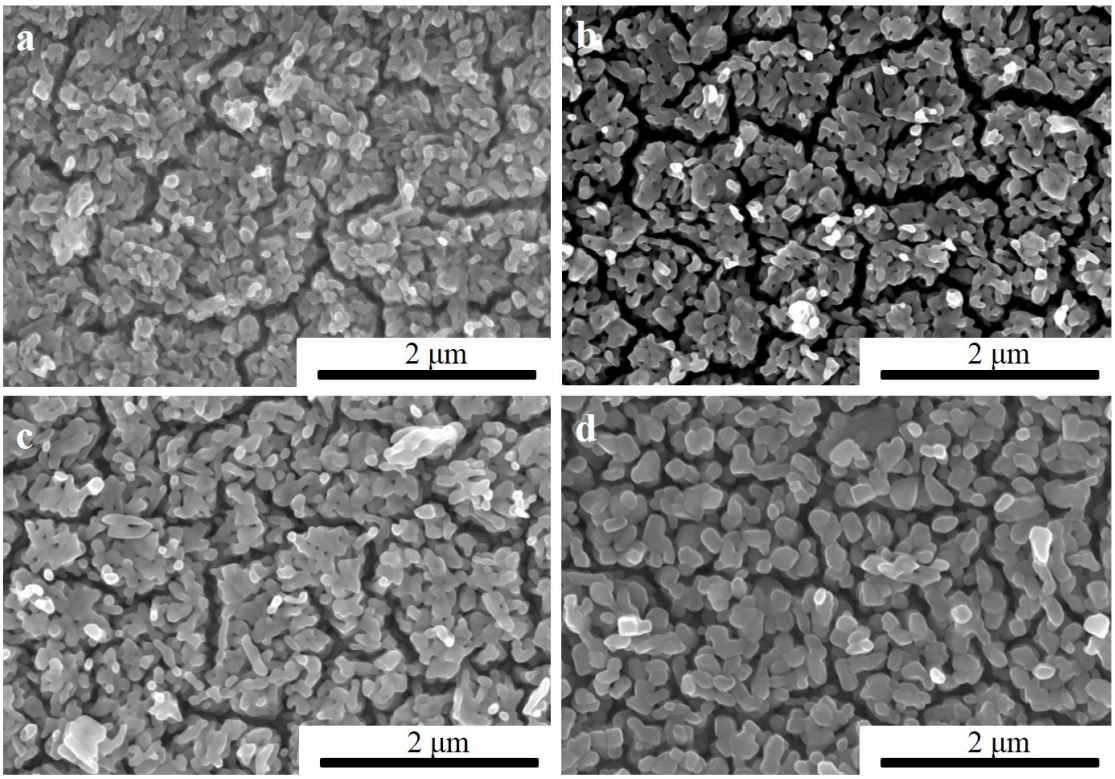

Figure S2. SEM images of (a) $Ti\text{-}Fe_2O_3$, (b) $10\text{-}MoS_x/Ti\text{-}Fe_2O_3$, (c) $100\text{-}MoS_x/Ti\text{-}Fe_2O_3$ and (d) $1000\text{-}MoS_x/Ti\text{-}Fe_2O_3$.

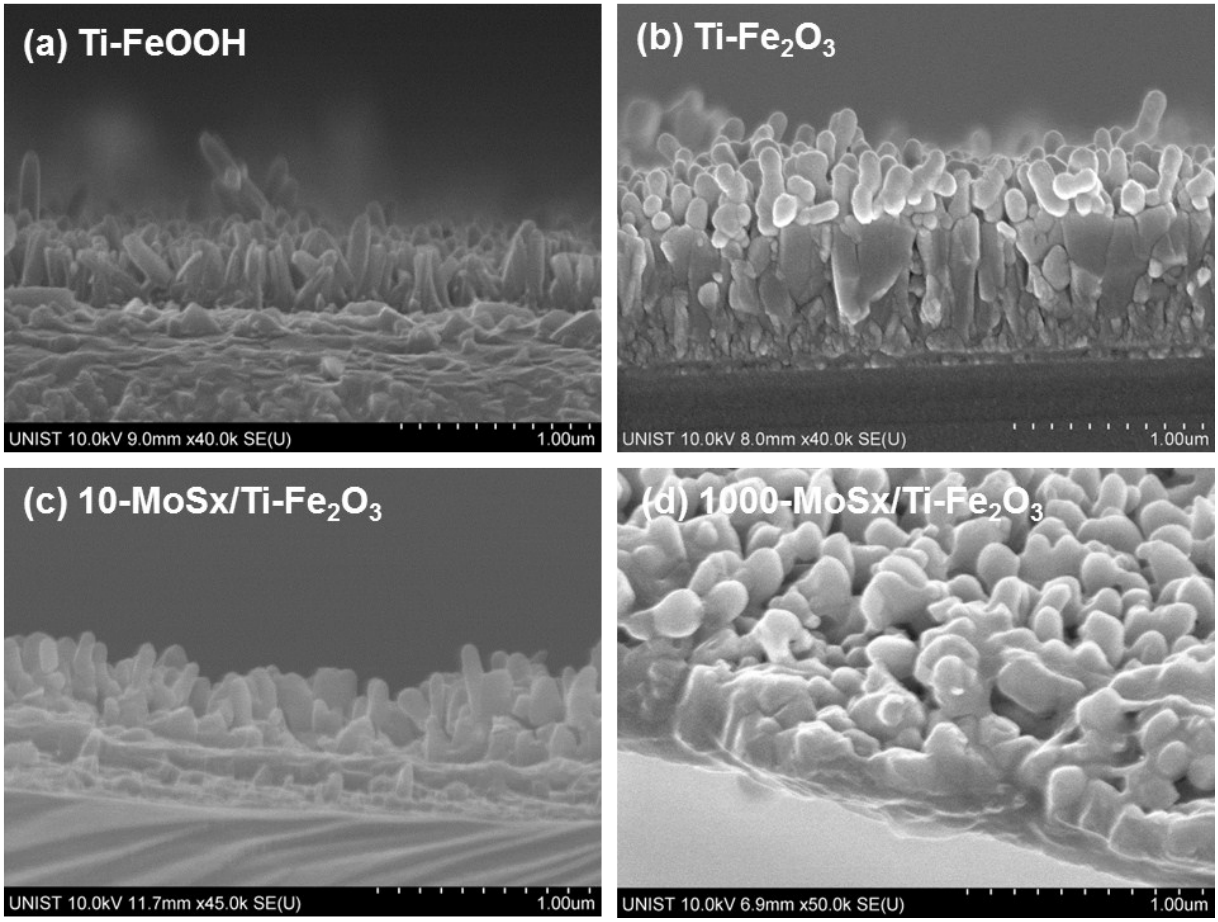

Figure S3. The cross-sectional SEM images of (a) Ti-FeOOH, (b) Ti-Fe_2O_3, (c) 10-MoSx/ Ti-Fe_2O_3 and (d) 1000-MoSx/ Ti-Fe_2O_3.

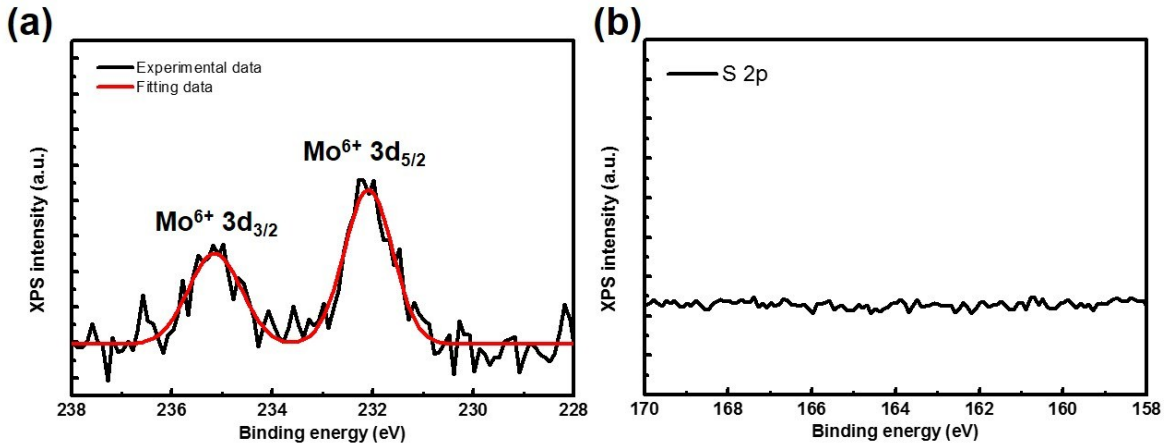

Figure S4. The XPS spectra of (a) Mo 3d and (b) S 2P. The sample was prepared from $(NH_4)_2MoS_4$/Ti-Fe_2O_3 precursors without sulfur powder.

It is known that MoS_x is easily converted to the MoO_3 with the oxygen components at high temperature.[1] The annealing of MoS_x without sulfur powder treatment resulted in the creation of MoO_3 as shown in XPS data.

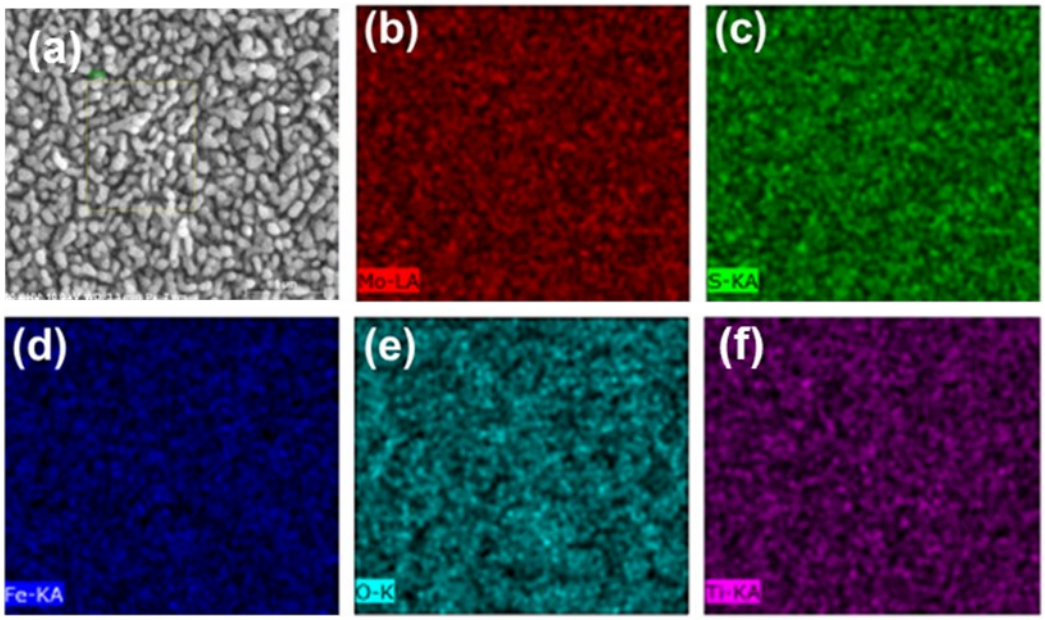

Figure S5. (a) SEM image and EDX mapping of (b) Mo, (c) S, (d) Fe, (e) O and (f) Ti in MoS_x/Ti-Fe_2O_3.

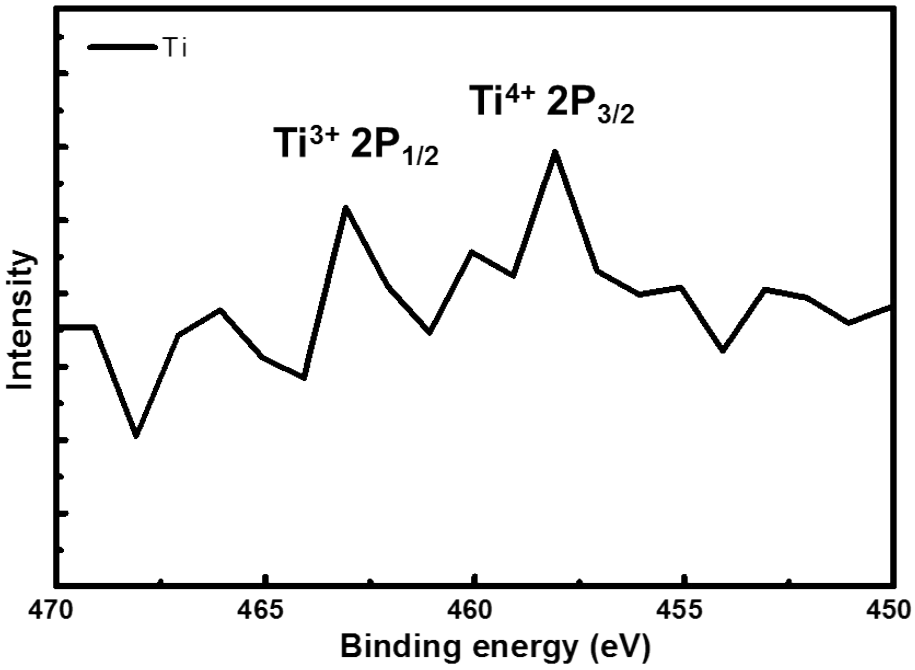

Figure S6. XPS of Ti ions of Ti-Fe_2O_3.

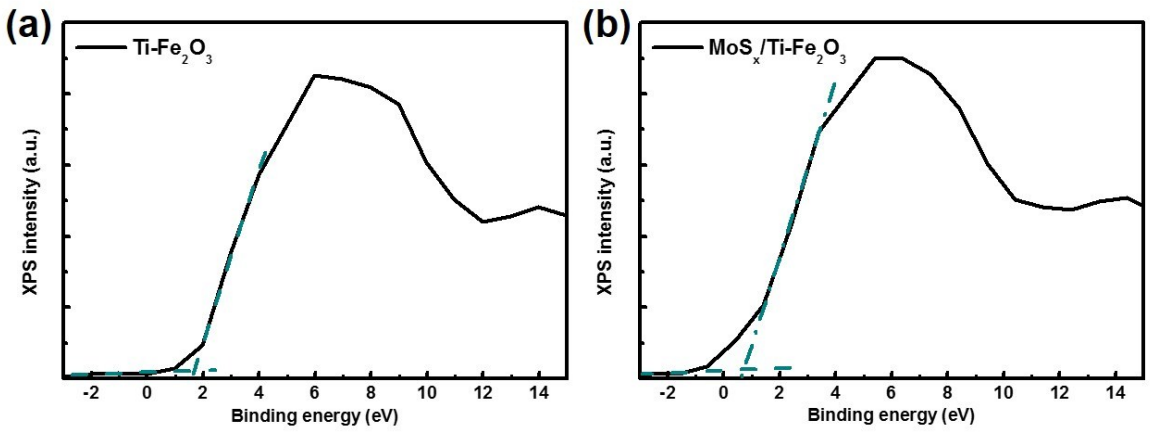

Figure S7. The valence band maximum (VBM) of (a) Ti-Fe_2O_3 (1.65eV) and (b) MoS_x/Ti-Fe_2O_3 (0.78 eV).

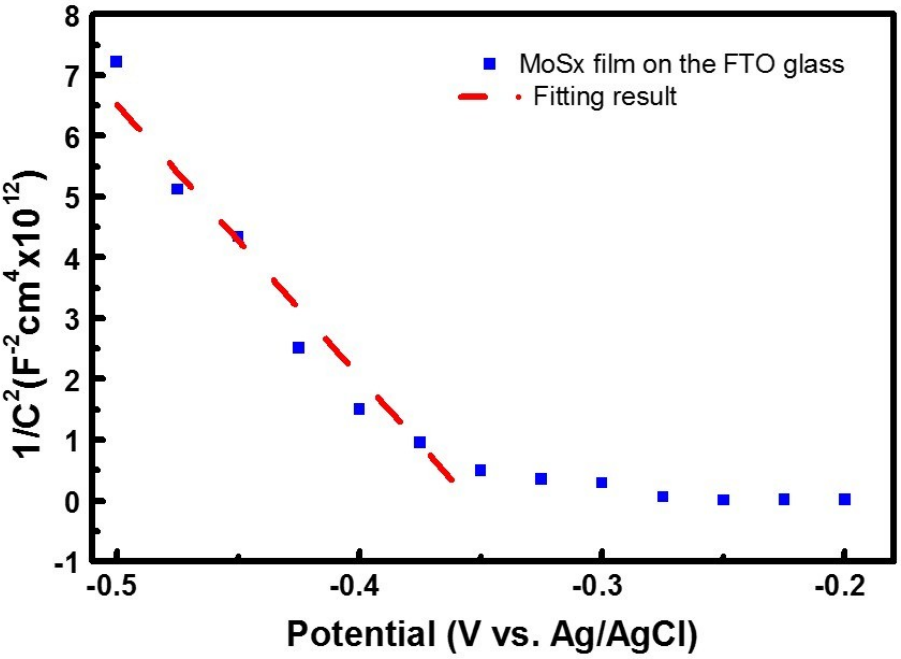

Figure S8. Mott-Schottky plots of MoSx on the FTO glass in 0.5M $NaSO_4$ electrolyte.

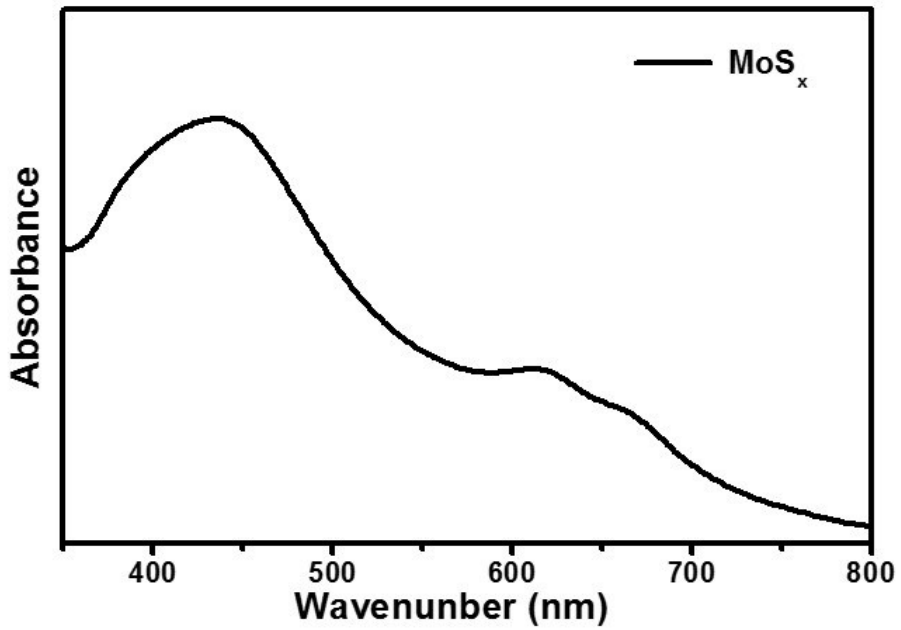

Figure S9. The UV-Vis spectrum of MoS_x on FTO glass.

The absorption at 450 nm is assigned to a direct transition peak from the deep valence band to the conduction band of MoS_2. The peaks at 610 and 670 nm are attributed to the direct excitonic transitions at the K point of the Brillouin zone.[1-3]

1. Gopalakrishnan, D.; Damien, D.; Shaijumon, M. M. *ACS Nano* **2014,** 8, (5), 5297-5303.
2. Frey, G. L.; Elani, S.; Homyonfer, M.; Feldman, Y.; Tenne, R. *Physical Review B* **1998,** 57, (11), 6666-6671.
3. Posudievsky, O. Y.; Khazieieva, O. A.; Cherepanov, V. V.; Dovbeshko, G. I.; Shkavro, A. G.; Koshechko, V. G.; Pokhodenko, V. D. *J. Mater. Chem. C* **2013,** 1, (39), 6411-6415.

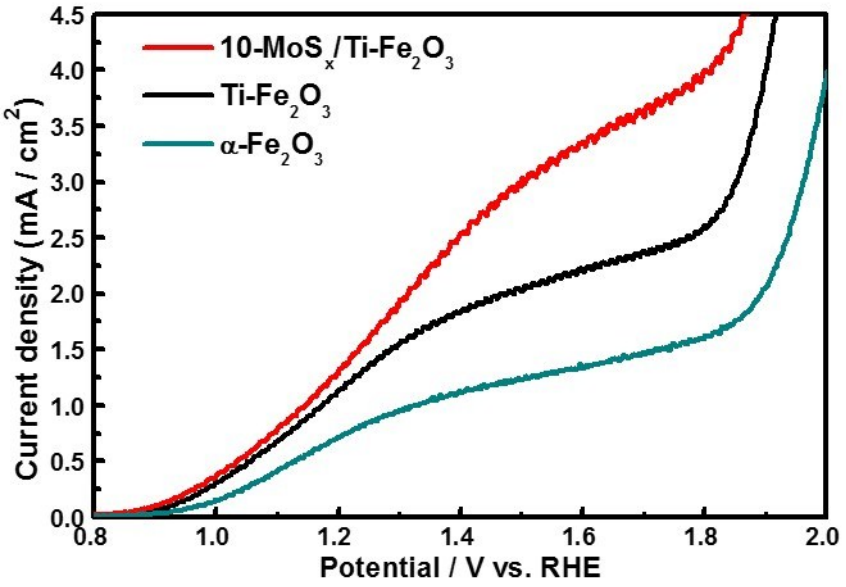

Figure S10. I-V curve of α-Fe2O3, Ti-Fe_2O_3 and 10-MoS_x/Ti-Fe_2O_3.

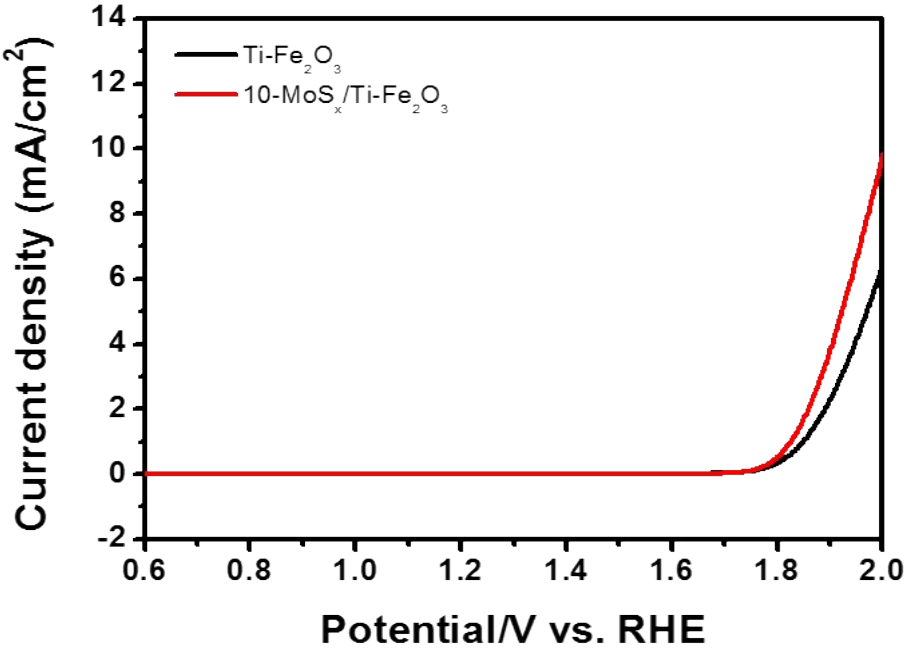

Figure S11. Dark current density of Ti-Fe_2O_3 and 10-MoSx/ Ti-Fe_2O_3

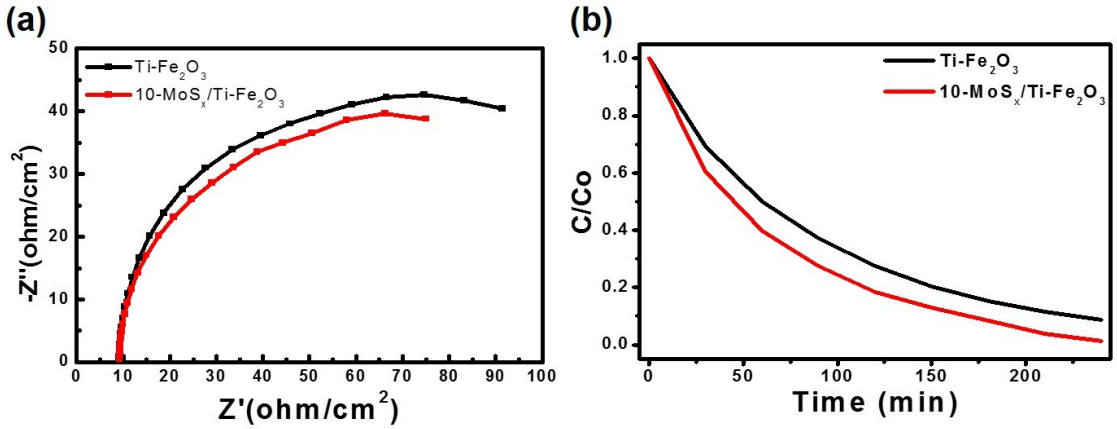

Figure S11. (a) The EIS data of $Ti\text{-}Fe_2O_3$ and $10\text{-}MoS_x/Ti\text{-}Fe_2O_3$ at 1.23 V_{RHE}. (b) The photodegradation of methylene blue by $Ti\text{-}Fe_2O_3$ and $10\text{-}MoS_x/Ti\text{-}Fe_2O_3$ without applying voltage under AM 1.5.

Table S1.Electrochemical parameters of photoanodes from equivalent circuit model.

($R\cdot\Omega\ cm^2$)	R_s	R_1	R_2
(C / F)		C_1	C_2
$Ti\text{-}Fe_2O_3$	14.2	110	380
	·	$7.89e^{-5}$	$9.03e^{-5}$
$10\text{-}MoS_x/Ti\text{-}Fe_2O_3$	14.36	95.6	125
	·	$9.86e^{-5}$	$6.10e^{-4}$
$100\text{-}MoS_x/Ti\text{-}Fe_2O_3$	14.56	100.5	175
	·	$7.99e^{-5}$	$4.36e^{-4}$
$1000\text{-}MoS_x/Ti\text{-}Fe_2O_3$	15.05	280.08	784.6
	·	$5.64e^{-7}$	$1.82e^{-6}$

1. Naguman, P. N.; Karimova, L. M.; Tokaeva, Z. M.; Shinbaev, U. B. *Russ. J. Non-ferrous Metals* **2009,** 50, (4), 330-334.