Electronic Supplementary Material (ESI) for Energy & Environmental Science.

MoS_2/TiO_2 Heterostructures as Nonmetal Plasmonic Photocatalysts for Highly Efficient Hydrogen Evolution

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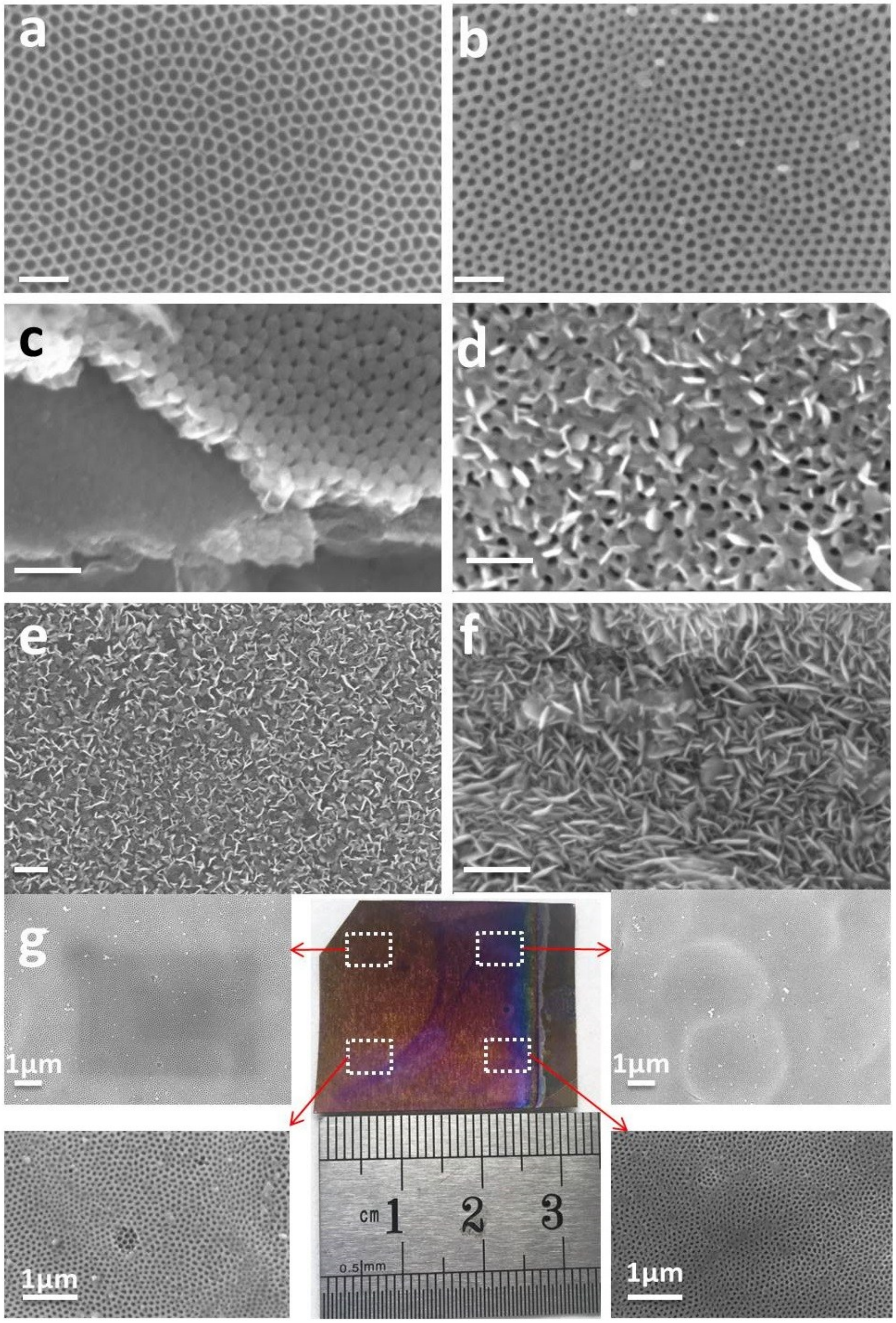

Fig. S1 (a) SEM image of as-anodized TiO_2 nanocavity arrays; (b) after e-Beam deposition of 30 nm Mo; (c) cross-sectional view of $MoS_{2(30)}@TiO_2$; (d) 10 nm Mo sulfurized for 360 min on TiO_2 nanocavity; (e) 10 nm Mo sulfurized for 10 min on Ti foil; (f) Mo foil sulfurized for 10 min (Scale bars: 200 nm); (g) photograph and morphologies of $MoS_{2(10)}@TiO_2$ at different sample locations.

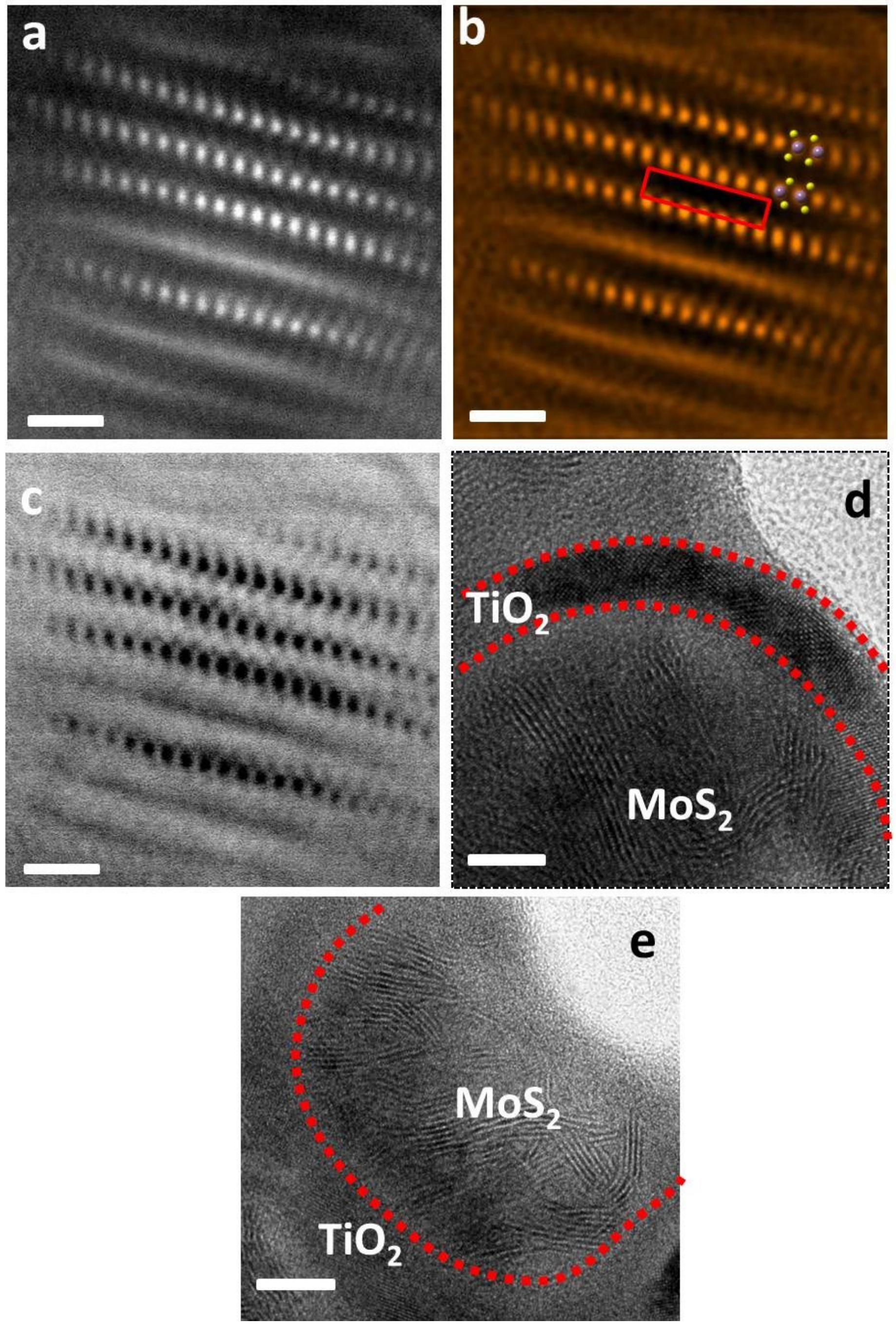

Fig. S2. (a) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and (c) corresponding bright field (BF) image of MoS_2. (b) Filtered and faked HAADF image corresponding to (a). Scale bar is 1 nm. S-vacancies are presented as dark dots along S-Mo-S bond edge (red square). (d, e) Typical TEM image of MoS_2 nanoflakes inside TiO_2.

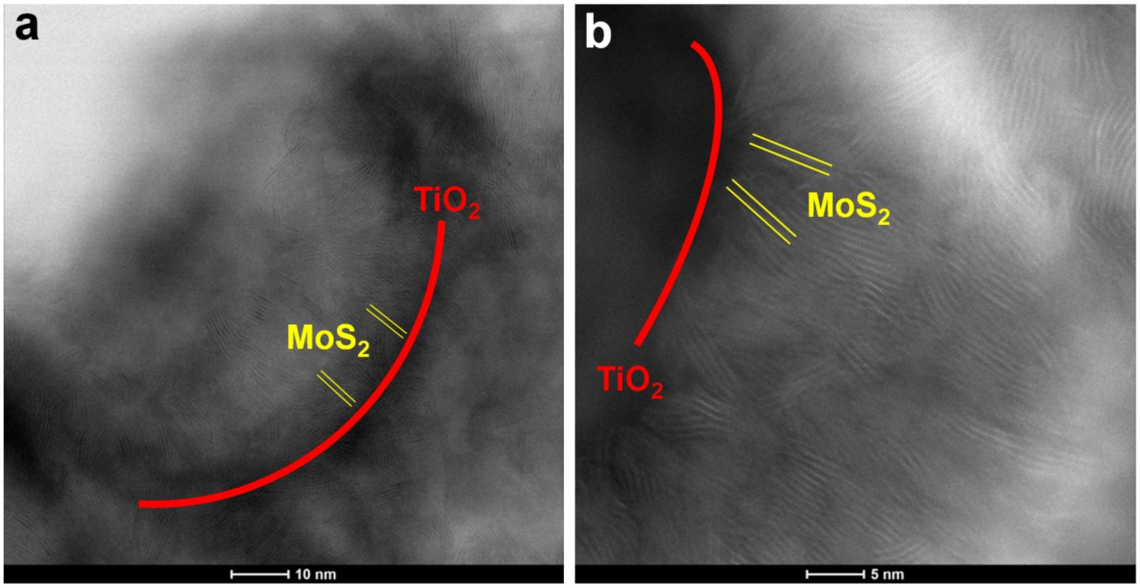

Fig. S3. (a,b) TEM images perpendicular growth of MoS_2 nanoflakes on the TiO_2 surface.

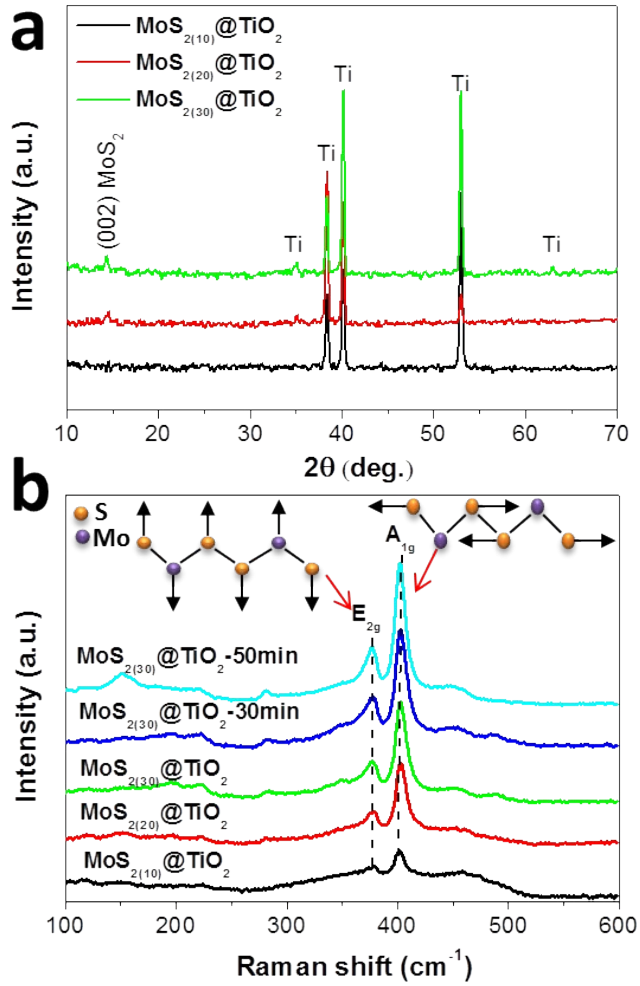

Fig. S4. XRD patterns (a) and Raman spectra (b) for series $MoS_2@TiO_2$ samples. Microscope Raman polarization laser wavelength 532 nm. Peak intensities ratio of E_{2g} and A_{1g} is 0.86, 0.764, 0.759 respectively, as a function of Mo thickness from 10-30 nm.

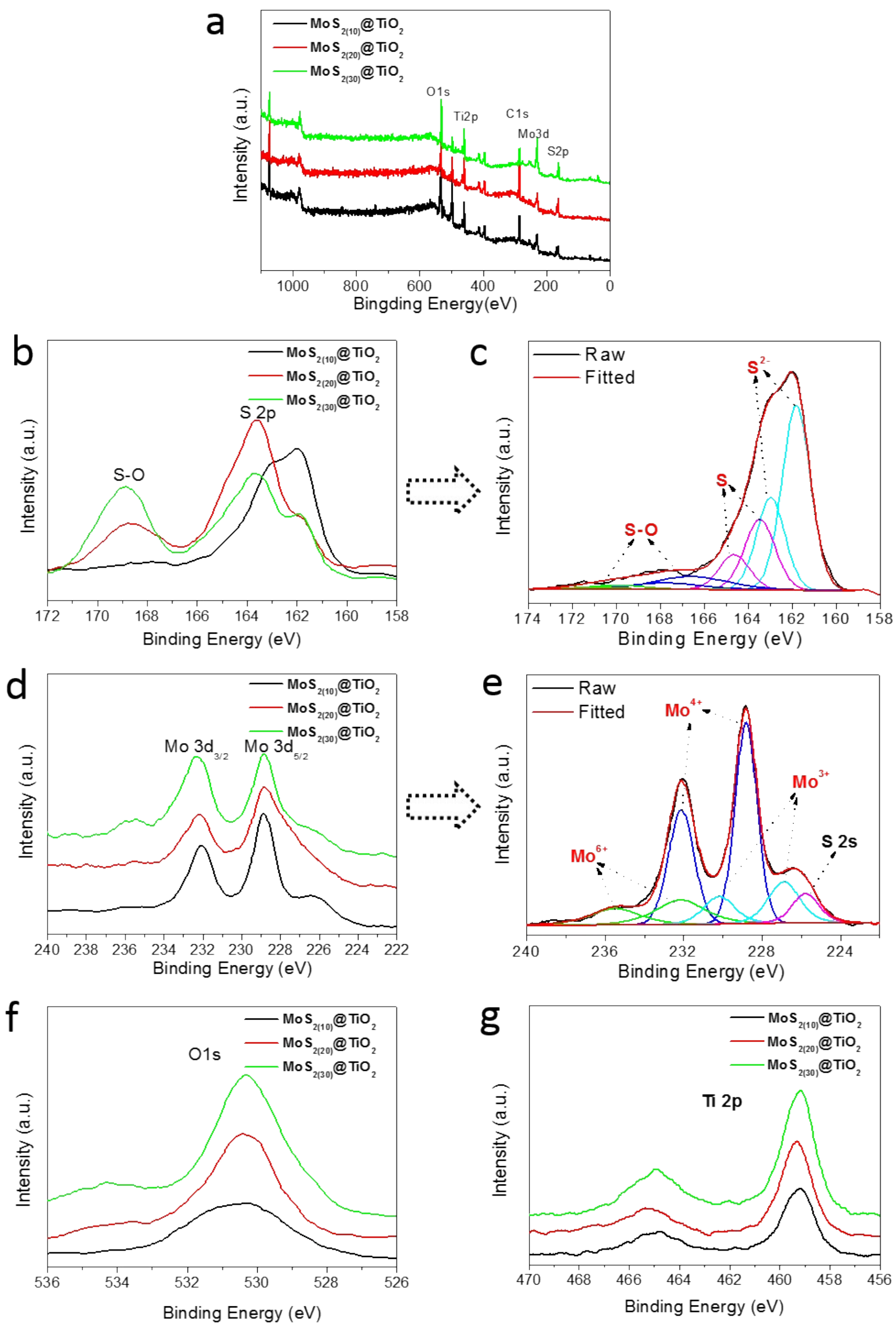

Fig. S5. Survey scan of $MoS_2@TiO_2$ heterostructure. The XPS spectra reveal the peaks of Ti, O, Mo, and S elements in the hybrid. Binding energies for Ti $2p_{3/2}$ (~458.7 eV), Ti $2p_{1/2}$ (~465.2 eV) and O 1s (~530.5 eV) are in agreement with the values of our previous report for pure TiO_2 [2].

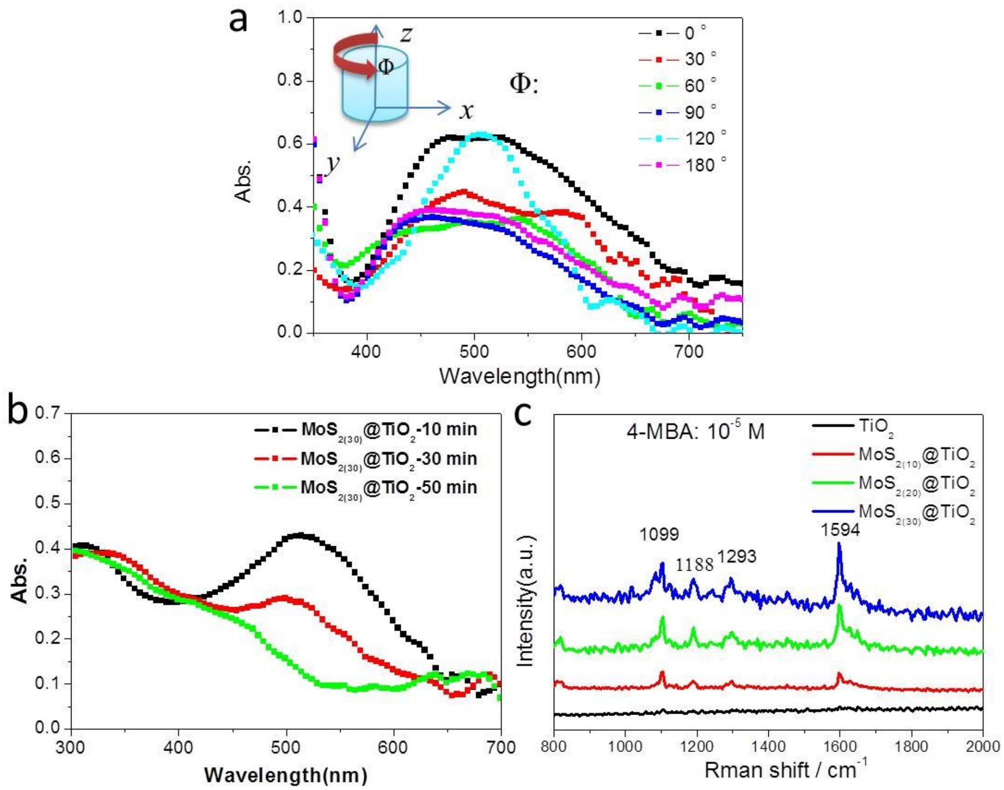

Fig. S6. (a) Excitation angle-resolved plasmonic properties of MoS_2@TiO_2 (Schematic design of the experimental setup is inserted. The substrate can be rotated clockwise around the *z*-axis by an angle Φ). (b) The UV-vis absorption spectra of $MoS_{2(30)}TiO_2$ sulfurized at 400 ^oC for 10, 30, 50 min. This figure shows that the photocatalyst displays weakening absorption in the visible-light region with increasing sulfurization time, which is caused by the complementary of S in MoS_2 crystal and reducing S defects.[3, 4] (c) SERS spectra of 4-MBA recorded from different MoS_2@TiO_2 systems

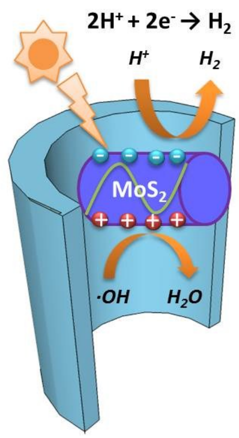

Fig. S7. Schematic diagram of LSPR produced charge separation and reactive equation during H_2 evolution on MoS_2@TiO_2.

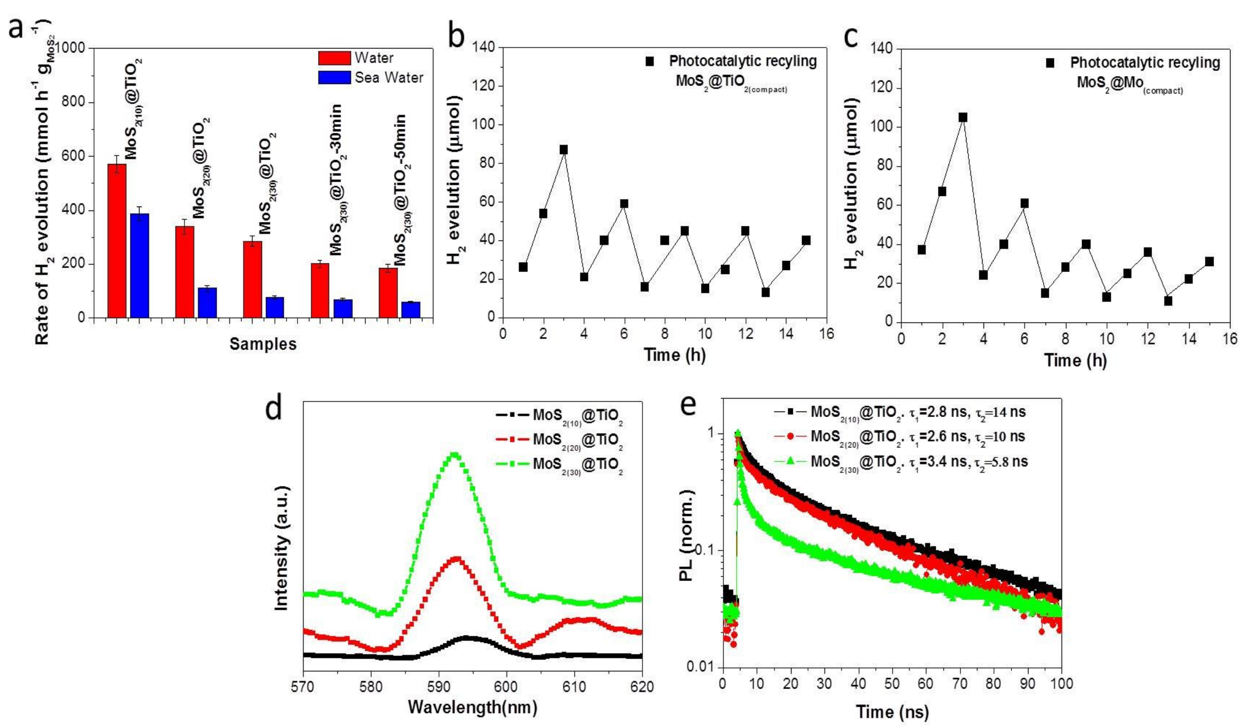

Fig. S8. (a) H_2 evolution rate over MoS_2@TiO_2 films to MoS_2 mass loading (Photocatalytic activity to seawater is inserted following. All testing carried out under simulated solar light). (b, c) Recycling photocatalytic H_2 evolution test of $MoS_{2(30)}$@$TiO_{2(compact)}$ and MoS_2@$Mo_{(compact)}$ over 15 h. (d, e) Photoluminescence (PL) spectra of MoS_2@TiO_2 cocatalysts at steady state and time-resolved transient PL decay, with charge-carriers lifetime inserted accordingly.

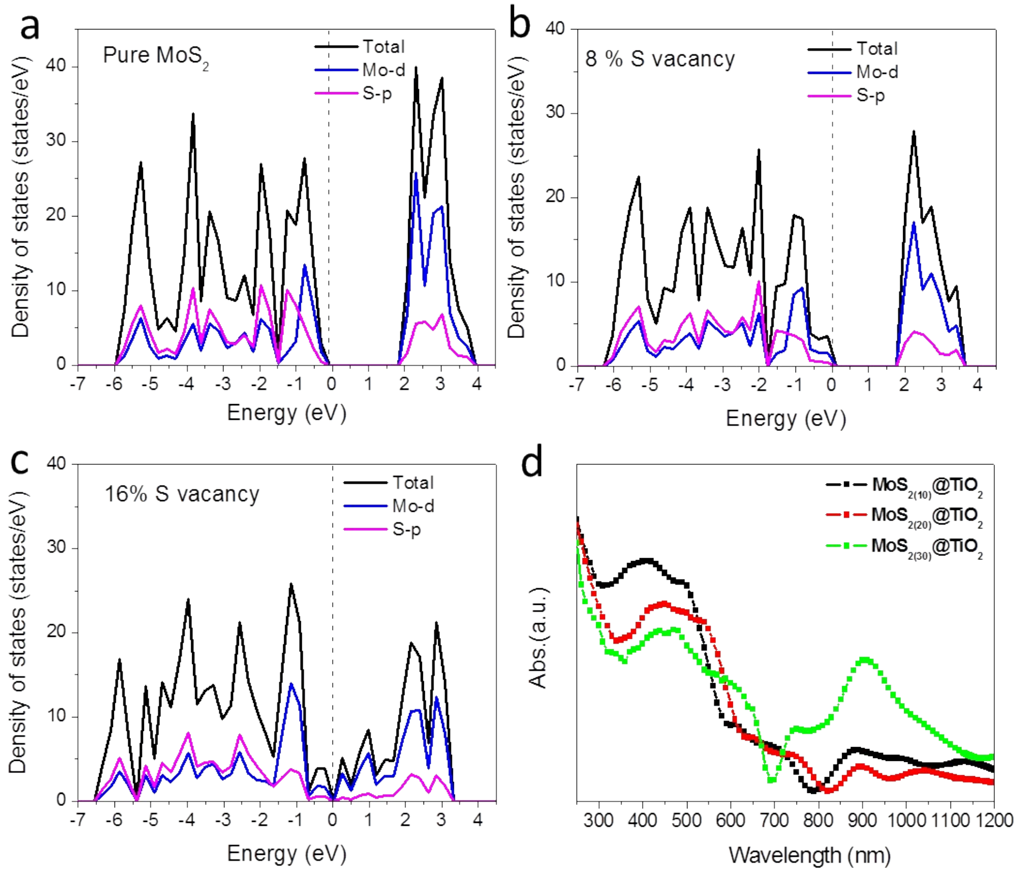

Fig. S9. (a-c) Density of States (DOS) for pristine MoS_2 monolayer and S-depleted MoS_2, DOS projected on Mo 4d orbital and S 3p orbital. (d) FT-IR spectra of MoS_2@TiO_2 heterostructure.

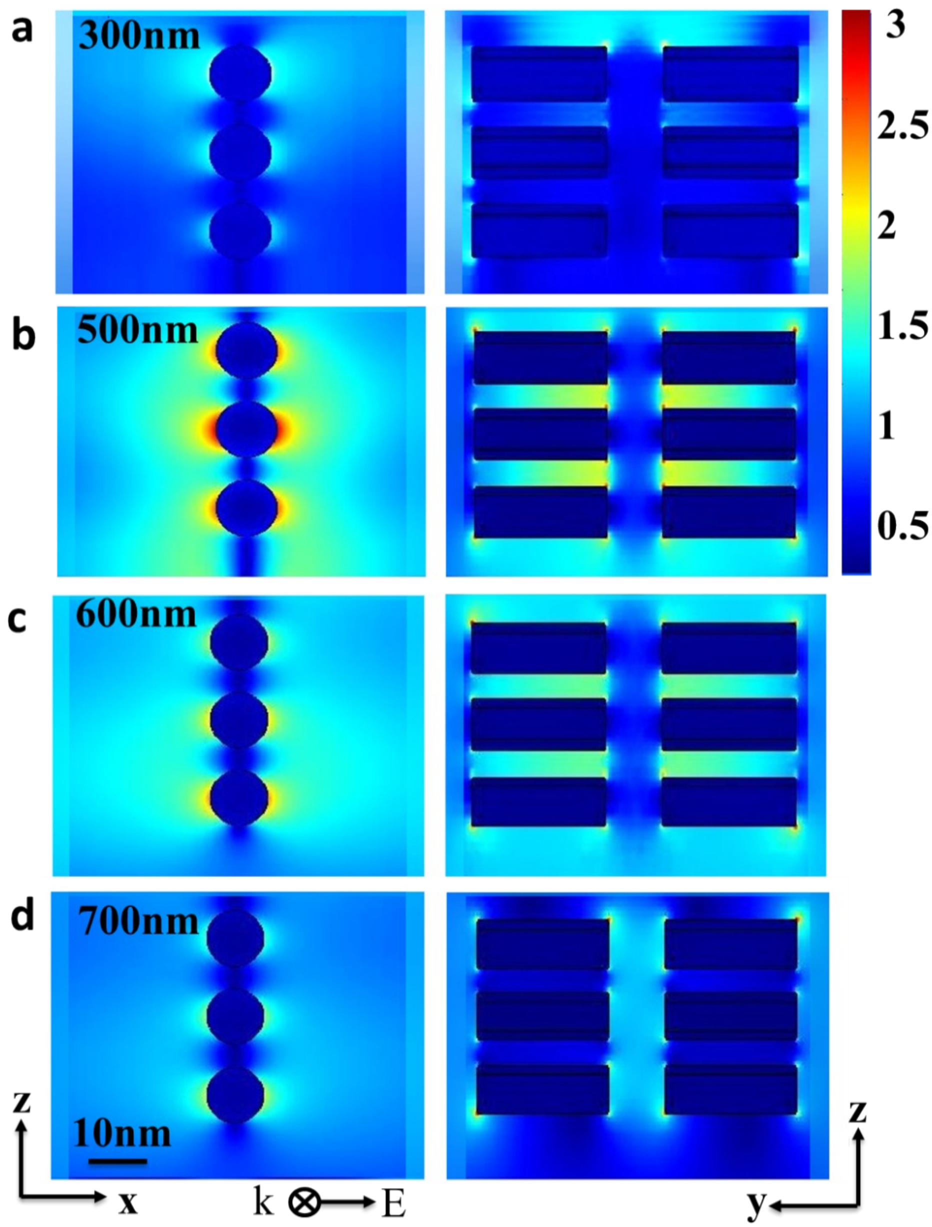

Fig. S10. FEM-simulated electric field distribution of $MoS_2@TiO_2$ heterostructure under (a) 300 nm, (b) 500 nm, (c) 600 nm, (d) 700 nm excitation. Profiles of electrical field intensity along *x-z* plane and *y-z* plane across center of TiO_2 nanotube. The polarization direction is set along the *x*-axis

Table S1. Photocatalytic performance comparison of MoS_2 based catalyst for H_2 evolution in other reports

Method	Materials	H_2 evolution rate ($\mu mol\ h^{-1}$)	Mass activity ($\mu mol\ h^{-1} g^{-1}$)	Ref.
Solvothermal	MoS_2/C_3N_4 nanograss	55.6	11.1	[5]
CVD	MoS_2/TiO_2 nanosheets	42	4200	[6]
Hydrothermal	MoS_2/TiO_2 nanorods	2.7	1500	[7]
CVD	MoS_2/TiO_2 nanotubes	0.44	-	[8]
CVD	MoS_2/TiO_2 nanocavities	89	580000	This work

Reference:

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