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In this study, we report a nonmetal plasmonic $MoS_2@TiO_2$ heterostructure for highly efficient photocatalytic H_2 generation. Large area laminated MoS_2 in conjunction with TiO_2 nanocavity arrays are achieved via carefully controlled anodization, physical vapor deposition, and chemical vapor deposition processes. Broad spectral response ranging from ultraviolet-visible (UV-Vis) to near-infrared (NIR) wavelengths and finite element frequency-domain simulation suggest that this $MoS_2@TiO_2$ heterostructured photocatalyst enhances activity for H^+ reduction. A high H_2 yield rate of 181 µmol h^{-1} cm⁻² (equal to 580 mmol h^{-1} gr⁻¹ based on the loading mass of MoS_2) is achieved using a low catalyst loading mass. The spatially uniform heterostructure, correlated to plasmon-resonance through conformal coating MoS_2 that effectively regulated charge transfer pathways, is proven to be vitally important for the unique solar energy harvesting and photocatalytic H_2 production. As an innovative exploration, our study demonstrates that the photocatalytic activities of nonmetal, earth-abundant materials can be enhanced with plasmonic effects, which may serve as an excellent catalytic agent for solar energy conversion to chemical fuels.

1. Introduction

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Recently, intensive research has focused on solar energy conversion to provide clean chemical fuels (H₂, CH₄, etc.) as a result of an impending global energy crisis as well as hazardous environmental pollution conditions largely induced by fossil fuel consumption.¹⁻³ Solar-to-fuel conversion significantly depends on the semiconductor materials that can harvest photon energy across the wide solar spectrum (from ultraviolet (UV) to near-infrared (NIR) region) and simultaneously generate charge-carriers on the suitable energy levels for H⁺ reduction.^{4,5} Among various materials and technologies, low-cost, nontoxic, and chemical stable TiO₂ has long been studied as a promising photocatalyst for solar-driven water splitting.^{6,7} However, the main disadvantages (e.g., wide band gap and sluggish charge transfer kinetics) of TiO₂ has limited its feasibility within the visible light region, which accounts for approximately 43% of the solar spectrum.⁶ It is possible to overcome these issues by a variety of techniques, including heavily doping (nitrogen), integrating narrow band gap semiconductors, and decorating with noble

metals and co-catalysts (CdS, CdSe, Pt, Au, Ag, etc.), to broaden the passive oxide semiconductor absorption range to include visible or NIR, creating a more efficient photocatalysts.⁸⁻¹⁰ However, the widespread use of scarce noble metals is not ideal due to their high cost and potential to be environmentally toxic. Therefore, the quest for materials that are solar light sensitive and earth-abundant is of utmost importance.

Molybdenum disulfide (MoS₂) belongs to the two-dimensional (2D) layered transition metal dichalcogenides (TMDs) family that has a sandwich-like structure of Mo atoms between two layers of hexagonally packed sulfur atoms. The weak Van der Waals bonding between these 2D layers often gives rise to single- or few-layer nanosheet architectures.^{6,11,12} Recent work shows that MoS₂ can be a promising electrocatalyst for hydrogen evolution reaction (HER), owing to the nanosized MoS₂ edge defects that are preferential to hydrogen adsorption. Therefore, few-layered nanoscale MoS₂ flakes serve as a valuable strategy for improving the efficiency of hydrogen evolution.^{13,14} Chemical exfoliation and solvothermal methods are usually employed for fabrication of nanostructured MoS₂. However, these methods usually promote irregular particle formation or undesirable stacking of multilayer MoS₂ deposit products.^{15,16} Multilayer stacking exposes more catalyst basal planes than edges, rendering much of the material catalytically inert. Additionally, without proper dispersion and immobilization, powdered nanomaterials can suffer from particle aggregation, leading to performance degradation.¹⁷ Until now, an efficient scheme or design principle for the integration of ordered,

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nanostructured MoS_2 with wide band gap semiconducting behavior

Compared with metallic 1T-MoS₂, 2H-MoS₂ exhibits high stability and semiconducting properties at room temperature, allowing them to be used as a co-catalyst coupled with other wide band gap semiconductors for H₂ evolution in a photoelectron reactive medium.^{18,19} However, there is a lack of discussion in present literature that highlights MoS₂ as the main photocatalyst, especially those that attribute to NIR intrinsic absorbance. Theoretical calculations demonstrate that the band gap of MoS₂ can be modulated through control of particle size. In this case, the band gap broadens from 1.2 eV to 1.9 eV when the MoS₂ architecture changes from bulk to monolayer. This characteristic can be ascribed to the quantum confinement of nanomaterials. The energy band structure can also be affected by the metal-chalcogenide stoichiometric ratio.^{16,20} A recent theoretical study showed that nonstoichiometric metal-chalcogenides (e.g., WO_{3-x}, Cu_{2-x}S, and MoO_{3-x}) displayed evidence of an indirect plasmonic absorption, which is distinctly different from previously reported band gap transitions.²¹⁻²³ Therefore, local surface plasmonic resonance (LSPR) can be used to describe the light harvest phenomena, which is mainly deduced from charge collective oscillation on the metalchalcogenide surface propagated by numerous anions (O or S) vacancies within the crystal lattice. It is conceivable that nonmetal MoS₂ with plasmonic absorption may be a solution to fill the visiblelight harvest gap vacated by wide band gap semiconductors, effectively improving the solar-to-energy efficiency of HER photocatalysts.^{22,24} Lastly, MoS₂@TiO₂ hybrid catalysts have been recently reported that aim to enhance photocatalytic efficiency by modulating the TiO₂ energy level with inter-band coupling.⁶

Herein, we demonstrate a combined physical vapor deposition (PVD) and chemical vapor deposition (CVD) strategy to coat fewlayered MoS₂ nanoflakes conformally on the inner surface of anodized TiO₂ nanocavity arrays (referred to as MoS₂@TiO₂) with a highly-ordered 3D hierarchical configuration. Stoichiometric ratio of Mo and S atoms within the MoS₂ lattice and vertically contacting facets of MoS₂ and TiO₂ can be controlled by tuning the S source in the Na_2S_x solution and altering the CVD reaction rate (please refer to experimental details). This highly localized growth enables conformal and uniform MoS₂ nanoflakes to be formed on the surface of TiO₂ nanocavities. Such heterostructures have shown powerful photon harvesting abilities in the UV-Vis-NIR range by tethering the TiO_2 substrate to a plasmonic/intrinsic MoS_2 coating. The facilitated electron transfer pathway and appropriately tuned energetic position of the conduction band results in facile chargecarrier separation and dramatically enhanced H₂ evolution efficiency. UV-Vis spectroscopy analysis, finite element method simulation (FEM), and the monochromatic light irradiated H₂ generation rate conclude that LSPR, mainly excited in the wavelength from 400-600 nm, substantially contributes to photocatalytic activity. Minimal red and NIR light induced H₂

production is observed from the lower photoelectron energetic level of the MoS_2 inter-band excitation 0.1460/C7 by the photoelectron-hole recombination. This nonmetal plasmonic heterostructure is also expected to be applicable to other 2D material systems, which can serve as a new design protocol for highly efficient photocatalysts.

2. Experimental section

2.1 Material preparation

Anodic growth of TiO₂ nanocavities: Titanium foils ($25.4 \times 25.4 \times 0.05$ mm thick, 99.7% purity, MTI Corporation) were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water for 30 min and dried in air. Sample size is rationally chosen but not limit to 1 inch square by this fabrication method. Anodization was carried out in 3 M HF/H₃PO₄ (98%, Alfa Aesar, US). Constant voltage of 10 V was applied to a two-electrode setup for 4 h with Pt foil as a counter electrode. After anodization, the TiO₂ films were rinsed with ethanol, dried in air.

Mo deposition and sulfurization: An e-Beam evaporator (Thermo Scientific) was used to deposit Mo layers into anodized TiO₂ films with a thickness of 10, 20, 30 nm, respectively. The Mo layer thickness was controlled by an automated quartz crystal filmthickness monitor. The as-prepared Mo@TiO2 hybrid was then put in the center of a guartz-tube furnace (MTI Corporation) together with 0.5 M Na₂S solution containing 1 M sulfur (placed in crucible at upstream side, at a temperature of 100 °C, ramping speed of 2 °C min⁻¹). The MoS₂@TiO₂ heterostructure was fabricated at 400 °C for 10 min with heating rate of 5 °C min⁻¹ under vacuum. The obtained MoS₂ mass loading was estimated by depositing Mo on compact Ti foils with the same e-beam rate and time mentioned above, the thickness of obtained Mo was confirmed by SEM and TEM. Loading of Mo was estimated by multiplying volume and density of Mo. The deposited Mo is supposed to be changed to MoS₂ (10.2, 20.4 and 30.6 μ g cm⁻² for 10, 20, and 30 nm Mo deposits, respectively).

2.2 Material characterization

Morphologies of $MoS_2@TiO_2$ films were observed with a fieldemission scanning electron microscope (FE-SEM, ZEISS ultra 55) and a high-resolution transmission electron microscope (FEI Titan 80-300 STEM with probe Cs corrector and ETEM with imaging Cs corrector). The cross-section sample for TEM was cut off by a Tescan LYRA-3 Model GMH focused ion beam microscope and pasted onto Cu ring holder. X-ray diffraction (XRD) was obtained using an X'pert Powder (PANalytical, equipped with a Panalytical X'celerator detector using Cu K α radiation, $\lambda = 1.54056$ Å). The chemical composition was characterized by X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400 ESCA). Raman spectra were measured using a Renishaw InVia Microscope Raman (532 nm laser excitation). Absorption spectra were obtained on a Cary Win

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had eluded researchers.

UV-visible spectrometer from 300 to 700 nm. Incident angle (θ , the angle of excitation light to normal through the center of TiO₂ nanocavity) and excitation polarization angle (ϕ , excitation polarization around the normal through the center of TiO₂ nanocavity) dependent absorption spectra were tested by rotating the sample from 0-180° with an fixed incident angle or rolling over the sample from a vertical direction to a parallel one. A Fourier transform infrared spectroscopy (spectrum 100 FT-IR spectrometer, PerkinElmer) was employed for testing absorbance in infrared region. The photoluminescence spectra were collected by a NanoLog Spec fluorescence spectrometer excited by a helium-cadmium lamp at 400 nm.

XPS fitting: All spectra were analyzed with the CasaXPS software (version 2.3.15). The samples were conductive so the binding energies were not charge referenced. Shirley background subtraction was used for all spectra. Peak models for each photoelectron line were generated using nonlinear least-squares Gaussian/Lorentzian curve-fitting. The S 2*p* line was fitted with multiple sets of doublets and constrained to have the same FWHM within each pair as well as a 2:1 intensity ratio and 1.16 eV separation between the $2p_{3/2}$ and $2p_{1/2}$ peaks. Similarly, the Mo 3*d* line was fitted with multiple sets of doublets as well as a 3:2 intensity ratio and 3.3 eV separation between the $3d_{5/2}$ and $3d_{3/2}$ peaks.

2.3 Photocatalysis characterization

Photocatalytic H₂ evolution: The photocatalytic H₂ production was performed in a sealed 20 ml quartz reactor. $MoS_2@TiO_2$ films with a size 7×7 mm were submerged in 15 ml of mixed solution made of DI water (Sea water) and methanol (8:2 by volume). Subsequently, the reactor was illuminated by a solar light simulator (AM 1.5, 300 W Xe, 100 mW cm⁻²) or monochromatic light (Zahner CIMPS-QEIPCE system with monochromator and light source from 350 to 800 nm.). The gas produced from the upper space above the solution in quartz reactor was periodically analyzed.

2.4 Computational method

Finite Element Method Simulation (FEM). Comsol Multiphysics (version 5.2) was used for FEM Solution. The 3D simulation model was designed as a simplified heterostructure, where three MoS_2 nanorods (diameter: 10 nm; length: 20 nm, parallel to *y*-axis) standing vertically on TiO₂ (diameter: 50 nm; length: 70 nm, parallel to *z*-axis). The incident laser wavelength was set from 300-700, with the polarization direction along the *x*-axis. The electric field distributions of hybrid nanocavity arrays were monitored across the middle of TiO₂ nanotube at *x*-*z* and *y*-*z* planes.

Band structures calculation of MoS₂. First-principles, calculation based on density functional theory (DFT) was used to estimate the electronic property of MoS₂ layer upon S-vacancy deviation (Vienna *ab initio* simulation program, VASP). The ion electron interactions were depicted by projector-augmented wave method. The generalized gradient approximation (GGA) was adopted with Perdew-Burke-Ernzerhof (PBE) exchange-correlation function. 4×4 unit cells were employed as calculation model with S-vacancy of 0%, 8%, and 16% respectively. Band structure was relaxed by a 6×6×1 special k-point mesh grid with 880 eV energy cut off on plane-wave.

3. Results and discussion

3.1 Morphology, microstructure and component analysis

A typical fabrication route of a $MoS_2@TiO_2$ plasmonic heterostructure is schematically illustrated in Fig. 1a. Highlyordered honeycomb-shaped TiO₂ nanocavities are obtained through Ti anodization (Supplementary Fig. S1a, with an average pore size of 50 nm and wall thickness of 10 nm). E-beam evaporation was performed to deposit 10, 20, and 30 nm of Mo onto the anodized TiO₂ nanocavity arrays. An obvious cavity wall thickening (increased from 10 nm to 20 nm) is found after Mo coating (Supplementary Fig. S1b).



CVD sulfurization was carried out at 400 $^{\circ}$ C for 10 min on TiO₂ coated with different Mo thicknesses (abbreviated MoS₂₍₁₀₎@TiO₂, MoS₂₍₂₀₎@TiO₂, MoS₂₍₃₀₎@TiO₂, respectively). It was observed that pore size significantly shrunk after CVD treatment when the deposited Mo thickness increased from 10 to 20 and 30 nm (Fig. 1b-d, Fig. S1c). Transmission electron microscopy (TEM) of MoS₂@TiO₂ nanocavity arrays shows that MoS₂ nanoflakes are grown inside TiO₂ nanocavities with a highly-ordered 3D laminate structure (Fig. 2a-c). These MoS₂ nanoflakes typically consist of less than 10 layers,

Page 4 of 10

Journal Name

which were verified by Raman spectra as shown in Fig. S4b. Part of the MoS_2 nanoflakes stand vertically on the TiO_2 surface or connect with TiO_2 nanocavity walls in a big intersection angle. (Fig. 2d, e and Fig. S2d, e).

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Fig. 2 TEM images of (a, d) $MoS_{2(10)}@TiO_2$, (b, e) $MoS_{2(20)}@TiO_2$, and (c) $MoS_{2(30)}@TiO_2$. (f) HRTEM image of $MoS_{2(10)}@TiO_2$, showing few-layer MoS_2 nanoflakes erect on TiO_2 cavity walls. Inset (e) shows Fast Fourier transform (FFT) pattern taken from red square in (e), corresponding to the (002) facets of 2H-MoS_2. (g) Filtered and colored atomic-resolution STEM image of the MoS_2 nanoflakes. The dark and light dots correspond to Mo and S atoms, respectively, where S atom depletion area is observed with weaker contrast (indicated by blue arrows and dash circles). Atomic model with S-vacancies along b-axis of 2H-MoS_2 is inserted beside (g). (a-d: scale bar is 20 nm; e, f: scale bar is 5 nm; g: scale bar is 1 nm).

High resolution TEM (HR-TEM) identifies lattice fringes of 0.62 nm and 0.35 nm (Fig. 2f), corresponding to the (002) hexagonal facets of MoS₂ and the (101) facets of anatase TiO₂, respectively. It is also revealed that the MoS₂ nanoflakes are bound seamlessly to the TiO₂ nanocavity wall surfaces, indicating a perpendicular growth of MoS₂ nanoflakes on the TiO₂ surface (refer to Fig. S3 for more TEM images showing the perpendicular growth of MoS₂). Spherical aberration corrected high angle annular-dark-field (HAADF) scanning transmission electron microscopy (STEM) and bright-field (BF) STEM were performed to clarify the atomic structure of MoS₂. As shown in Fig. 2g, the image contrast of BF-STEM exhibits a relationship with respect to atomic number (Z), therefore the sandwich structure of MoS₂ is clearly observed. In addition, the Svacancies can be identified, as marked by blue dashed circles and blue arrows.²⁵ Interestingly, it seems the S-vacancy exhibits local 'staging' structures, as seen for most S atoms throughout the structural layers. Where the blue arrows are absent, only a small number of S-vacancies are observed, indicated by the red arrows marked in Fig. 2g. HAADF-STEM image and corresponding filtered image is shown in Supplementary Fig. S2a, b. Conversely, S-

vacancies are displayed as darker spots at the edge of S Mac S layer (red square). Fig. 3a and b show the cross-sectional STEM Theorem of $MoS_2@TiO_2$ heterojunctions, demonstrating that a fully filled MoS_2 laminated network inside the TiO_2 nanocavities was successfully fabricated. Energy dispersive X-ray spectrometry (EDS) mapping analysis shows the distribution of each element at interface of junction (Fig. 3c-f). The separation assignment of Ti to Mo and S further proves the isolated vertical connection of MoS_2 and TiO_2 at the heterojunction.

In a normal S steam based CVD process, Mo conversion takes place almost spontaneously upon S arriving at the metal surface, making it difficult to control the MoS₂ morphology.¹⁹ One method to allow more morphological control is to slow S evaporation using a liquid precursor containing S_x^{2-} ions (see more details in experimental section) and combined with a low temperature ramping rate (2 $^{\circ}C$ min⁻¹). The S source derived from the Na₂S_x solution first arrives at the hollow TiO₂ nanocavities and then will transmit gradually along the cavity walls.⁷ As it is understood, growth direction of MoS₂ nanoflakes is synchronous with S diffusion, from the middle of TiO_2 cavity to the edges.²³ Eventually, a vertically laminated MoS₂@TiO₂ heterostructure was formed inside the TiO₂ cavities. A photograph of the MoS₂₍₁₀₎@TiO₂ heterostructure provided in Figure S1g shows uniform morphologies at different sample locations, indicating a highly uniform MoS₂@TiO₂ throughout the entire sample. Control experiments were carried out by using a normal solid S source, flat TiO₂ film or Mo foil in duplicate reactions. Larger MoS₂ flakes with disordered architecture were obtained for all control experiments (Supplementary Fig. S1d-f), further verifying the significant impact made by the addition of TiO₂ nanocavity arrays and using liquid S source toward the inhibited MoS₂ overgrowth that promotes the formation of a MoS₂@TiO₂ heterostructure configuration.



Fig. 3 (a, b) Cross-sectional STEM images of $MoS_2@TiO_2$ heterostructure. (cf) EDS elemental mapping taken from (b). The distribution of Ti is separated from Mo and S (a: scale bar 200 nm, b: scale bar 50 nm).

XRD patterns of as-prepared $MoS_2@TiO_2$ films are shown in Supplementary Fig. S4a. The main diffraction peaks are indexed to the Ti substrate (PDF file No. 44-1294) because of the thin thickness Published on 28 September 2017. Downloaded by University of Newcastle on 28/09/2017 14:57:41

Journal Name

of the TiO₂ film and low MoS₂ content. Noticeably, a weak peak at 14.5°, corresponding to the c-plane (002) of 2H-MoS₂ (S-Mo-S graphene-like layer, PDF file No. 86-2308), can be observed and intensifies with Mo thickening. Diffraction patterns of Ti substrates are a little different by the orientation diversity of commercial Ti foil, depending on the manufacturing process. Raman spectroscopy is more distinct for demonstrating the MoS₂ layered structure (Supplementary Fig. S4b). Peaks around 378 and 402 cm⁻¹, corresponding to in-plane E_{2g} and out-of-plane A_{1g} vibration modes of 2H-MoS₂ are dominant in the spectra. Red-shift of E_{2g} and blueshift of A_{1g} occurs with increasing Mo thickness from 10 to 30 nm as well as prolonging sulfurization time from 10 to 50 min for the MoS₂₍₃₀₎@TiO₂ film. A frequency difference monotonically increased from 21.25 cm⁻¹ to 24.24 cm⁻¹, which is in excellent agreement with the literature report indicating a thickness of less than 10 stacking layers of MoS_2 per flake.¹⁵ The greater intensity ratio of A_{1g} to E_{2g} is due to the large amount of surface edge exposure and strong interlayer restoring force interactions acting on misalignments or defects in the MoS_2 layers.²⁶ It is very clear that there is no Mo oxide can be found from both XRD and Raman, indicating a complete conversion from Mo to MoS₂ after CVD treatment. Experimental tests also indicate the effect of Mo oxide on the optical and photocatalytic properties can be ignored, which will be further discussed in the following sections.

Surface defects, chemical states and the stoichiometric ratio of Mo and S in the $MoS_2@TiO_2$ heterostructure were investigated by X-ray photoelectron spectroscopy (XPS) analysis. 2H-MoS₂ and TiO₂ were confirmed by XPS results (Supplementary Fig. S5). The highresolution S 2p spectrum demonstrates that there are three overlapping chemical states of S (Supplementary Fig. S5b, c). The doublet centered at 161.7 eV is assigned to S 2p in a Mo-S configuration, the upshifted peaks at 163.4, 166.6 and 169.9 eV are due to the existence of S, Mo-O-S band or oxidized S on the surface of MoS₂.²⁷ More oxidized S was found with an increase the amount of MoS₂. Binding energies for Mo $3d_{3/2}$, Mo $3d_{5/2}$ are fitted to a pair of doublets at 227.9/231.2 eV and 228.9/232.2 eV, respectively, which confirms the $\mathrm{Mo}^{^{3+}}$ and $\mathrm{Mo}^{^{4+}}$ accordingly (Supplementary Fig. S5d, e).²⁸ The existence of Mo^{3+} ions implies the formation of S defects in MoS_2 and account for about 20-30% of the total Mo element semi-quantitatively estimated from the XPS spectral area in the MoS₂₍₁₀₎@TiO₂ sample (S-vacancy is in a range of 5-8% percentage of S atoms deficiency). Mo⁶⁺ ions can be slightly detected because of surface oxidation during in-air storage. Combining the aforementioned investigations, it can be concluded that the S-vacancy and nonstoichiometric features of MoS₂ nanoflakes are where free electrons and plasmonic resonance processes originate. The XPS spectral states of Ti and O are in agreement with crystalline TiO₂ (Supplementary Fig. S5f, g).²⁹

3.2 Spectral response and photocatalytic performance

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The solar light harvesting of MoS₂@TiO₂ heterostructure was investigated through UV-Vis absorption spectra, as shown in Fig. 4a (incident angle: 0°). The intrinsic absorption edge located at about 360 nm belongs to the TiO₂ substrate, suggesting a band gap of 3.2 eV. Furthermore, very broad peaks ranging from 400 to 600 nm can be detected on the MoS₂@TiO₂ heterostructures. This visible light response is distinctly far from band gap excitation of both MoS₂ and TiO₂ portions, consistent with heterostructured films. Consequently, a metal-like LSPR is assigned to this absorbance, which arises from collective oscillations of excess charges (electrons) on the edge of MoS₂. Abundant S-vacancies and highly ordered vertically laminated structures may dominate the free charge interactions.²⁷ It has been well recognized that the catalytic activities of both semiconducting 2H-MoS₂ and metallic 1T-MoS₂ generally arise from edge sites and S-vacancies.²⁶ Both edges and S-vacancies are considered responsible for crystal asymmetry of analyte, where electronic structure is changed slightly. Electrons in a higher Fermi level are easy to transfer to local collected vacancies on surface of MoS₂. When the orbital density vibration of these electrons resonant with incident light, photo-excited local dipoles and charge separation happens, forming a confined local field around MoS₂ surface. Thereby S-vacancies and surface "hot" electrons are applied to plasmonic antennas, which arises a modulation of the Fermi level and drastically change the initial electronic properties of MoS₂.

Combining the plasmonic effect with intrinsic absorption of MoS₂@TiO₂, a full-solar-spectrum harvesting is nearly achieved in this co-catalyst heterostructure. Additionally, the plasmonic resonance is demonstrated to be tunable upon Mo mass loading changes from 10 to 30 nm, with absorption peaks at 420, 480 and 510 nm, accordingly. This process may be similar to the classic size dependent plasmonic effect.²⁹ The maximal light harvesting crosssection is obtained in the sample with 30 nm of Mo loading. Control experiments carried out on pure metal based film (30 nm Mo on TiO_2) and oxidized sample (MoO₃ on TiO_2) give little visible light coverage, but the UV portion from TiO₂ substrate (Fig. 4a). Incident angle and excitation polarization angle dependent absorption spectra were also tested on $MoS_{2(30)}$ @TiO₂ (Fig. 4b and Fig. S6a). The resonance wavelengths is independent of the polarization angle (Fig. S6a). All the absorption peaks of MoS₂₍₃₀₎@TiO₂ locate in a range of 450-500 nm at an incident angle of 15°. The absorbance fluctuation (cross-section of curves) may come from the nonuniformity of MoS₂ flakes inside TiO₂ (as revealed by TEM). Absorption spectra measured at different incident angles were present in Fig. 4b (from bottom to top: 0, 30, 60, 90° , respectively). The absorption peak position increases from 490 nm to 600 nm with the increase of θ to 90°. The absorption peak position can further shift backward when the incident angle decreases to 0°. This dynamic shifting indicates that the resonance has 90° difference in the incident angle dependence, suggesting that the orientations of

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Page 6 of 10

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5

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 MoS_2 flakes affect the resonance modes and charge distribution profiles in the hybrid catalyst. The excitation efficiencies of the samples are also dependent on incident angles. A maximum photoefficiency (absorption cross-section) is achieved at an incident angle of 30°, consistent with the previous findings that the resonance intensity can be optimized at certain angles.³⁰ The relationship of nonstoichiometric features to light harvesting was verified by extending the sulfurization time from 10 min to 50 min on $MoS_{2(30)}@TiO_2$ film (Supplementary Fig. S6b). A strong absorbance degeneration can be observed with longer reaction times and complementary to the S source within the heterostructure, implying that S-vacancy is the main plasmonic charge donor.



Fig. 4 (a) Optical absorption of $Mo@TiO_2$, $MoO_3@TiO_2$ and $MoS_2@TiO_2$ heterostructures. (b) Incident angle-resolved plasmonic absorption of $MoS_{2(30)}@TiO_2$. (c, d) H₂ evolution rate over pristine TiO_2 , $MoS_2@TiO_2$ films and comparison of H₂ evolution rate to MoS_2 geometric area (Photocatalytic activity to seawater is inserted following. All testing was carried out under simulated solar light). (e) Modulated H₂ yield rate as a function of the wavelength by monochromatic light irradiation. and (f) Recycling photocatalytic H₂ evolution test of $MoS_{2(10)}@TiO_2$ over 21 h.

Surface-enhanced Raman scattering (SERS) was used to further determine the enhanced electromagnetic field at the vicinity of MoS₂@TiO₂. Mercaptobenzoic acid (4-MBA) was used as the probe molecule with a laser excitation at 630 nm. The dominant peaks (Fig. S6c) at 1099 and 1594 cm⁻¹ are attributed to the vibration mode of v8a aromatic ring and breathing mode of v12a ring, respectively. The weak peaks at 1293 and 1188 cm⁻¹ are the stretching mode of $v_{(coo-)}$ and deformation mode of C–H, respectively. The stronger SERS signal on MoS₂@TiO₂ substrate (comparing with bare TiO₂

6 | J. Name., 2012, 00, 1-3

nanocavity arrays using 10^{-5} mol L⁻¹ 4-MBA) demonstrates the plasmonic polarization presented on MoS₂@FiO₂ Sufface.CTEE02464A

Photocatalytic activity of series MoS₂@TiO₂ co-catalysts for H₂ evolution was estimated under simulated solar light illumination with methanol as a hole scavenger in DI water (Fig. 4c, d). The photocatalytic reaction kinetics and formula for H₂ producing is shown in Fig. S7. Pure TiO₂, sulfurized TiO₂ and MoO₃@TiO₂ hybrid are photocatalytically inert toward hydrogen evolution, with a reaction rate of lower than 10 µmol h⁻¹. Noticeably, the photocatalytic activity is sharply enhanced with MoS₂ loading and achieves maximal values on the MoS₂₍₃₀₎@TiO₂, reaching 84 µmol h 1 (\approx 8 times that of pure TiO₂). The photocatalytic activities of the samples increase non-linearly with increasing of MoS₂ loading (from 10 to 30 nm Mo deposition) because of the relative lower solar energy input via increasing catalysts amount.^{31, 32} Additionally, a deterioration is found with longer sulfurization time from 10 to 50 min (MoS₂₍₃₀₎@TiO₂), deducing a weakened plasmonic effect by the stoichiometric assignment, according to spectroscopy analysis (Supplementary Fig. S6b). Photocatalytic activities of the samples normalized by geometric area is shown in Fig. 4d. An optimal photocatalytic activity of 181 µmol h⁻¹ cm⁻² is observed on the heterostructure coated with 30 nm Mo. Fig. S8a shows the rate of H₂ production normalized by mass loading of MoS₂ (massmeasurement of MoS₂ catalyst is given in the experiment section). Samples with 10.2 μ g MoS₂ has an activity of 580 mmol h⁻¹ g⁻¹, which is superior to the state-of-the-art photocatalytic systems (Table S1). That may be ascribed to the highly-ordered architecture of MoS₂ nanoflakes on TiO₂ nanocavities with a lower mass loading, which reduces the electron-hole recombination. Furthermore, LSPR induced electron energetic level is more negative in the MoS₂₍₁₀₎@TiO₂ because of the blue-shifted light harvesting and more negative lowest unoccupied molecular orbital level that favours effective charge utilization rates in H⁺ reduction.²⁸ Stability and recyclability of the MoS₂₍₁₀₎@TiO₂ co-catalyst were estimated by repeating intermittent H₂ evolution under simulated solar light (Fig. 4f). 90% of incipient production can be kept for the hybrid films even after 21 h. Control experiments were carried out on the samples using MoS₂ deposited on compact TiO₂ and Mo foils (MoS₂₍₃₀₎@TiO_{2(compact)} and MoS₂@Mo_(compact)) to further confirm the crucial role of TiO₂ nanocavity arrays in the improved photocatalytic stability and recyclability. We found that MoS₂ flakes fell off from these compact substrates during H₂ evolutions testing, leading to a considerably deteriorated H₂ evolution. As shown in Fig. S8b, c, approximately 30% of H_2 yield (less than 15 µmol h⁻¹) was kept for the MoS₂@TiO_{2(compact)} after 5 circles testing. A even less H₂ yield (about 20%, equal to 10 µmol h⁻¹) was observed on the MoS₂@Mo_(compact) after 15 h testing. These control experiments indicate that TiO₂ nanocavity arrays not only contribute to UV-light absorption but also serve as host to immobilize MoS₂ co-catalyst.

Photoluminescence (PL) spectrum is used to detect the charge carrier trapping, migration and transfer mechanism during photocatalytic reactions (Supplementary Fig. S8d, e). The steady-state PL spectra located at 595 nm (Supplementary Fig. S8d), characterizes remarkable quenching along with the Mo thickening from 10 nm to 30 nm, suggesting either a shorter lifetime or faster trapping of photo-electrons with increasing MoS₂ content. Transient-state PL decay curves of MoS₂@TiO₂ heterostructures are compared in Supplementary Fig. S8c. A bi-exponential function was used here for fitting the PL decay curves mathematically:³³

$$y = A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2) + y_0$$
 (1)

where A₁, A₂ and y₀ are amplitude coefficient and basal constant. τ_1 and τ_2 are fluorescent lifetime corresponding to non-radiative recombination and inter-band recombination, respectively. The calculated carrier lifetime is inserted in Supplementary Fig. S8e accordingly. The average fluorescent lifetime of MoS₂₍₁₀₎@TiO₂ (τ_1 : 2.8 ns and τ_2 : 14 ns) is longer than the other ones after integrating by the equation:³³

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$
(2)

This indicates that appropriate MoS_2 loading and periodically patterned morphology provide the $MoS_{2(10)}$ @TiO₂ film with less trapping centers and prolonged retention of hot electrons, as well as enhanced H₂ production.

3.3 Computational study

The photo-electron arising mechanism, transfer pathway and consuming profile were computationally studied to assist in explaining the excellent photocatalytic activity of MoS₂@TiO₂ heterostructures (Fig. 5a). Firstly, the UV portion of solar light is mainly absorbed by the TiO₂ substrate, where photo-excited electrons transfer to the MoS₂ basal plane and diffuse to edge active sites. Here, the designed $MoS_2@TiO_2$ short nanocavity arrays and seamless junctional connection dramatically reduce the charge barriers at active sites. The perpendicular MoS₂-TiO₂ configuration benefits the electron transfer pathways at the basal plane where a lower resistance and suppressed quenching capture are expected. On the other hand, a broad LSPR band (ranging from 400 to 600 nm) renders the MoS₂@TiO₂ heterostructures for visible light-driven H⁺ reduction. This plasmon-enhanced activity is presumably a result of the aforementioned S-vacancies (confirmed by STEM) and provides predominant aspects for H₂ evolution. Finally, photoelectrons excited on the MoS₂ conduction band from NIR-light, can also contribute to H₂ evolution. Although, considerable carrier recombination is unneglectable in this narrow band gap semiconductor. MoS₂ edge defects (S-vacancies) play a dominant

role in plasmonic resonance and hot electron excitation, upon solar light irradiation, but will also capture $free^{1}$ drifters and 2dds unwanted quenching. Moreover, MoS₂ and TiO₂ intrinsic recombination is another way for hot electron consumption in catalytic processes (dash line between band gap), which may weaken photocatalytic performance.

To have an insightful understanding of the inter-band excitation of MoS_2 nanoflakes and eliminate the possibility of MoS_2 intrinsic activity in visible-light, electronic band structure was calculated by density functional theory (DFT, Fig. 5b and Fig. S9a-c, details about the calculation method is given in Supporting Information). Sdepletion was introduced in the computation models with an atom content of 0%, 8%, 16% respectively, mainly at the edge position (Fig. 5c). A fundamental band gap around 2.07 eV is found here for a perfect MoS_2 crystal, with the highest occupied valence band and the lowest empty conduction band located at 1.63 eV and -0.4 eV, accordingly (Fig. 5b). The band structure is modulated by introduction of a S-vacancy, which induces the narrowing of the band gap to 1.73 (8%) and 1.12 eV (16%). Moreover, defect states appear near to the Fermi level for the model with 16% S-depletion,



Fig. 5 (a) Schematic diagram of energy band structure, plasmonic resonance and electron transfer pathway in the $MoS_2@TiO_2$ heterojunction. (b) Band structure of monolayer 2H-MoS₂ with 0%, 8% and 16% S-vacancies, with valence band maximum and conduction band minimum both at the K point. (c) The model used for band gap computation by DFT (4×4 unit cell). (d) FEM simulation of the near-field electric field distribution inside $MoS_2@TiO_2$ heterostructures excited by 400 nm laser and (e) 3D-simplified model used for FEM simulation.

which improves the metallic feature and charge mobility of S-depleted MoS_2 layers.²⁰ The overall electronic density of states (DOS) for MoS_2 before and after S-depletion are shown in Supplementary Fig. S9a-c. Defect states near to the Fermi level

ARTICLE

originate mainly from the d orbitals of Mo and p orbital of S atoms (Fig. S9c), creating pseudo-ballistic electron transport channels within MoS₂. This result is further supported by other literature and fully compatible with our optical spectra in the IR region (Supplementary Fig. S9d), where the MoS₂ band gap absorption peaks are located around 882 nm (1.40 eV).³⁴ A further conclusion can be deduced from the discussion aforementioned that solar light caused activity of MoS₂@TiO₂ films mainly functionalized by the plasmonic effect surrounding MoS₂ surface.

To further confirm this assumption, wavelength-dependent photocatalysis and finite element method (FEM) simulations were performed on MoS₂@TiO₂ heterostructures under monochromatic light illumination (350-700 nm, with a 50 nm interval). A spectrum dependent H₂ evolution rate is revealed over the UV-Vis-NIR region, with a consistent variation in absorption spectra for the MoS₂@TiO₂ (Fig. 4a, e). The largest H_2 yield rate is about 59, 73, 86 μ mol h⁻¹ mW⁻¹ cm⁻² for Mo loading of 10, 20 and 30 nm, respectively, located at 450, 500, 550 nm accordingly. The relative consistency of photoabsorption and H₂ production over solar light indicates that the photocatalytic activity enhancement is primarily driven by the plasmonic effect from blue-green wavelengths. Upon excitation by monochromatic light irradiation, H₂ yield is found higher than equivalent solar light (AM 1.5 100 mW cm⁻²) excitation, especially in the 400-600 nm region. This suggests an additional benefit for use of variant colored light for plasmonic material based H₂ generation. A diagrammatic simulation (FEM) of electric field distribution at MoS₂ nanoflake vicinities is shown in Fig. 5d and Supplementary Fig. S10. A 3D model was designed using a single TiO₂ nanocavity (50 nm in diameter and 70 nm in length) and three vertically loaded MoS₂ nanorods (10 nm in diameter and 20 nm in length) on both sides (Fig. 5e). It was found that light irradiation coupled with LSPR yields strong electric field enhancements at the tip of MoS₂. The field intensity increases with wavelength from 300 to 400 nm and reduces significantly after 500 nm, correlating the LSPR absorption spectra of MoS₂₍₁₀₎@TiO₂ film (Fig. 4a). The maximum electric field enhancement is produced at 400 nm illumination (Fig. 5d). Field intensity between each antinode covers a distance longer than 5 nm, achieving zero-gap field distribution between MoS₂ interspace (< 10 nm). Consequently, a 3D electric field distribution is built throughout the networked MoS₂ laminate heterostructure and responds strongly to photocatalytic H₂ production.

Prospectively, H₂ generation from seawater will be highly desirable. However, few studies have focus on the practical photocatalysis on natural seawater because of the barrier blocking of dissolved salt for photocatalytic activity and durability of catalysts.³⁵ Here we investigated the effect of salt (mainly NaCl) on photocatalytic activity of MoS₂@TiO₂ films with natural seawater (pH: 8.4) splitting under simulated solar light. Obviously, the activity from seawater decreased markedly compared to that of pure water

(Fig. 4c, d). Because the isoelectric point of MOS_2 is $IOWER_A Han_7_h My$ the plasmonic "hot" electrons on the DSUrface.³⁹EFEEFOStatic adherence of hydroxyl group, metal ions and oxidation of sulfides take place severely in the seawater with a weak alkaline environment. Fortunately, 60% of incipient production is kept for samples, where the highly-ordered architecture may be helpful. This control experiment permits our $MOS_2@TiO_2$ heterostructure as a promising material for H₂ production from seawater.

Conclusions

In summary, novel $MoS_2@TiO_2$ laminate heterostructures were synthesized by a facile process that combines anodization, PVD, and CVD. Such structures displayed intense LSPR throughout regulating the S stoichiometry of MoS_2 surfaces. The $MoS_2@TiO_2$ co-catalysts showed nearly full-solar-spectrum absorption and superb photocatalytic activity for H_2 evolution. Samples with 30 nm Mo coating enabled a H_2 yield rate as high as 181 µmol h⁻¹ cm⁻², based on the synergistic plasmonic effect with homogeneity promoting charge-carrier separation and higher conductivity of "hot" electrons in this highly ordered architecture. FEM simulation model and DFT calculations were performed to understand this nonmetal plasmonic system and simultaneously derived light harvest, charge separation and transfer dynamics. Such materials, structures, and design schemes can have significant impact in using plasmonic materials for cost effective solar energy conversion.

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Periodically patterned MoS_2/TiO_2 heterostructures was rationally designed as nonmetal plasmonic photocatalysts for highly efficient hydrogen evolution



10 | J. Name., 2012, **00**, 1-3