

Supporting Information

Efficient charge transfer on tunable morphology of TiO₂/MoS₂ photocatalyst for enhanced hydrogen production

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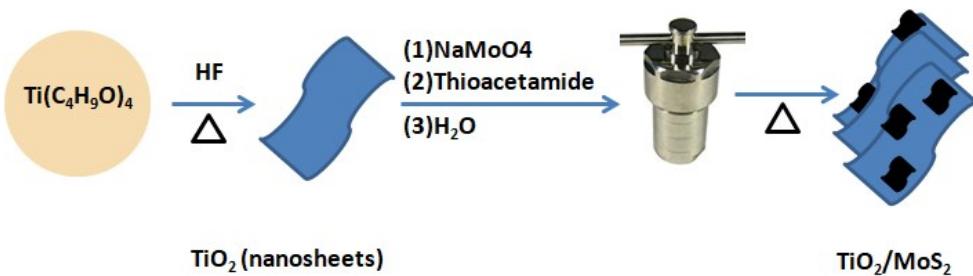
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CHARACTERIZATION

The crystallographic phase of the prepared samples were determined by X-ray diffraction (XRD). The crystallite size was calculated by using the Scherrer formula ($d = 0.9\lambda/B \cos \theta$, where d , λ , B and θ are the crystallite size, Cu K α wavelength, full width at half maximum (FWHM) intensity in radians and Bragg's diffraction angle, respectively. The light harvesting capability of the samples were assessed by using UV-vis diffuse reflectance spectroscopy (DRS) Perkin Elmer Lambda 750 accompanied by an integrating sphere accessory and utilizing BaSO₄ as a diffuse reflectance standard in the wavelength spanning from 300 to 2000 nm. The valance states and surface chemical composition of sample was studied by XPS analysis on a KRATOS AXIS 165 with Mg K α irradiation. About 10⁻⁹ Torr pressure was maintained in the spectrometer. The Field emission scanning electron microscopy (FESEM) images of sample were taken by using JEOL JSM 7610F. The high-resolution transmission electron microscopy (HR-TEM) images of TiO₂@MoS₂ were obtained using FEI Tecnai FE12 transmission electron microscope with a changeable accelerating voltage range of 40- 120V. All TEM samples were prepared by depositing a drop of diluted suspensions in acetone on a carbon coated copper grid and allowed to dry naturally. Photoelectrochemical studies were executed on CHI 6005E electrochemical analyzer (CH Instruments Inc., USA).



Scheme S1. Schematic presentation for preparation of $\text{TiO}_2/\text{MoS}_2$ composite.

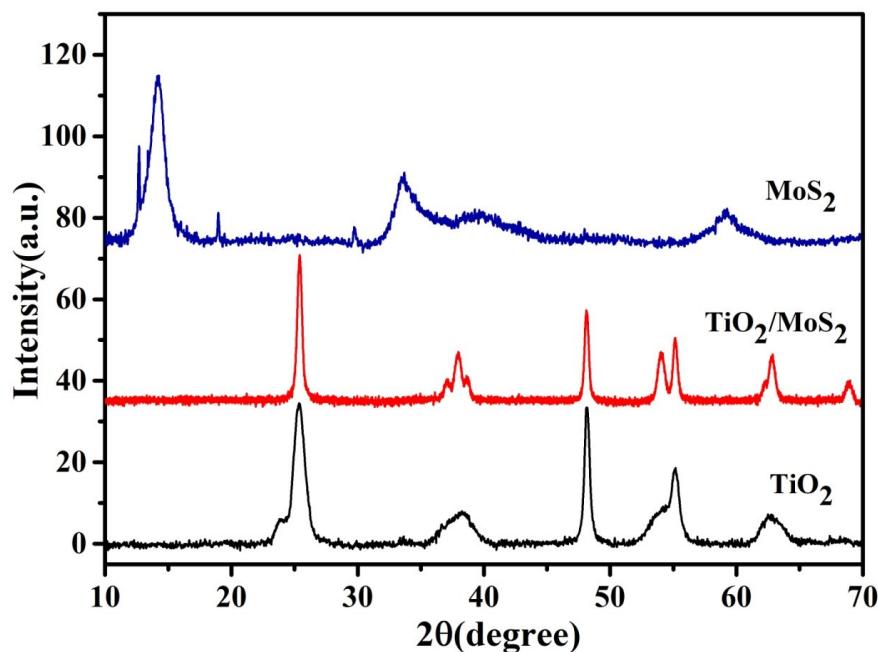


Figure S1. XRD pattern of TiO_2 , MoS_2 And $\text{TiO}_2/\text{MoS}_2$ composite.

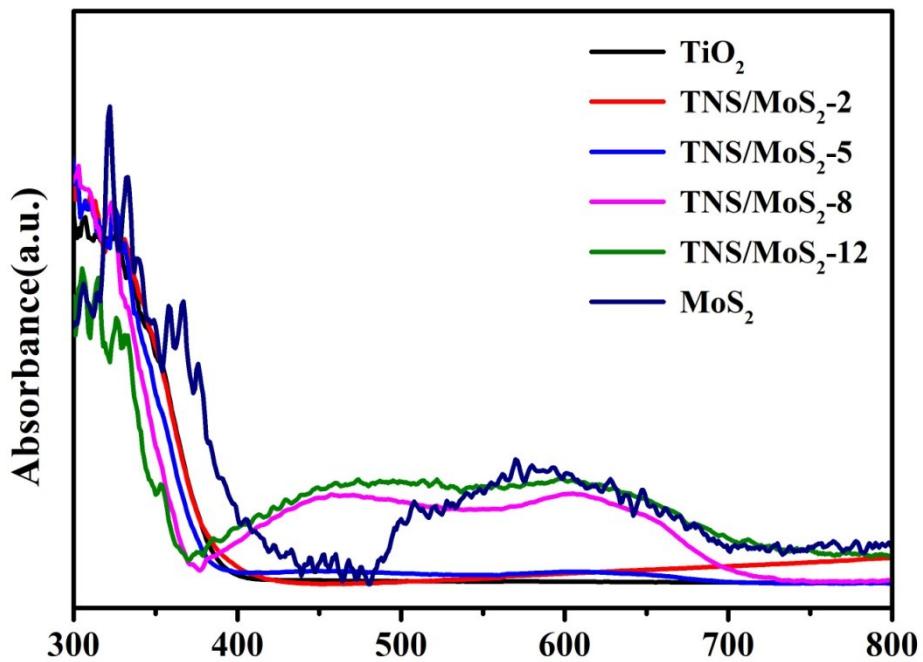


Figure S2. UV-Vis DRS spectra of TNS/MoS₂

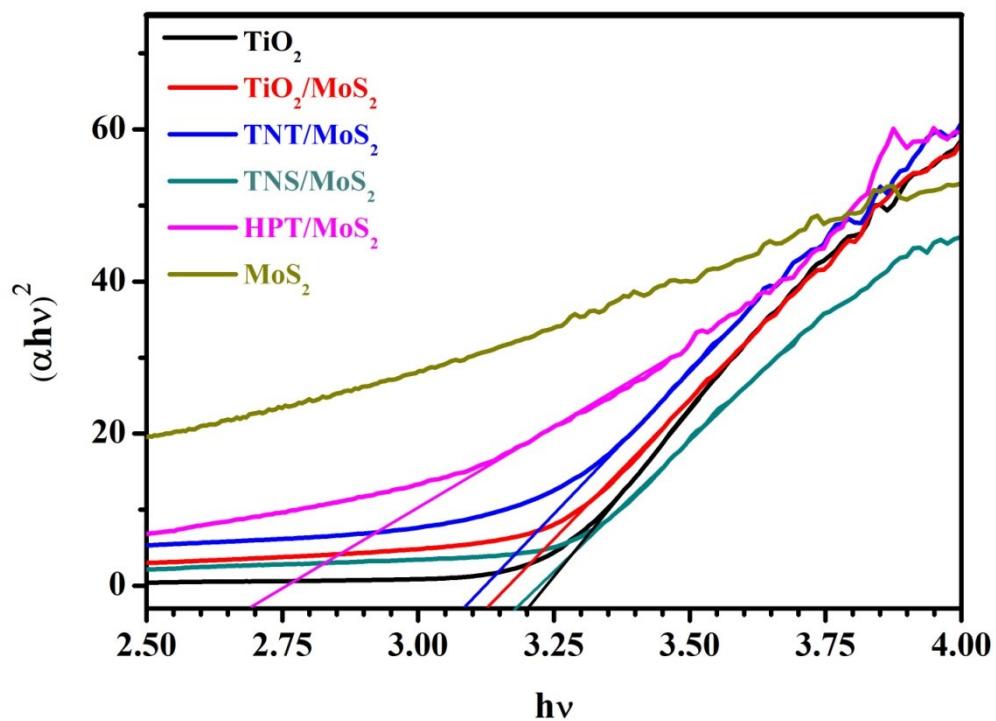


Figure S3. Tauc plot of TiO₂ and TiO₂/MoS₂ composite.

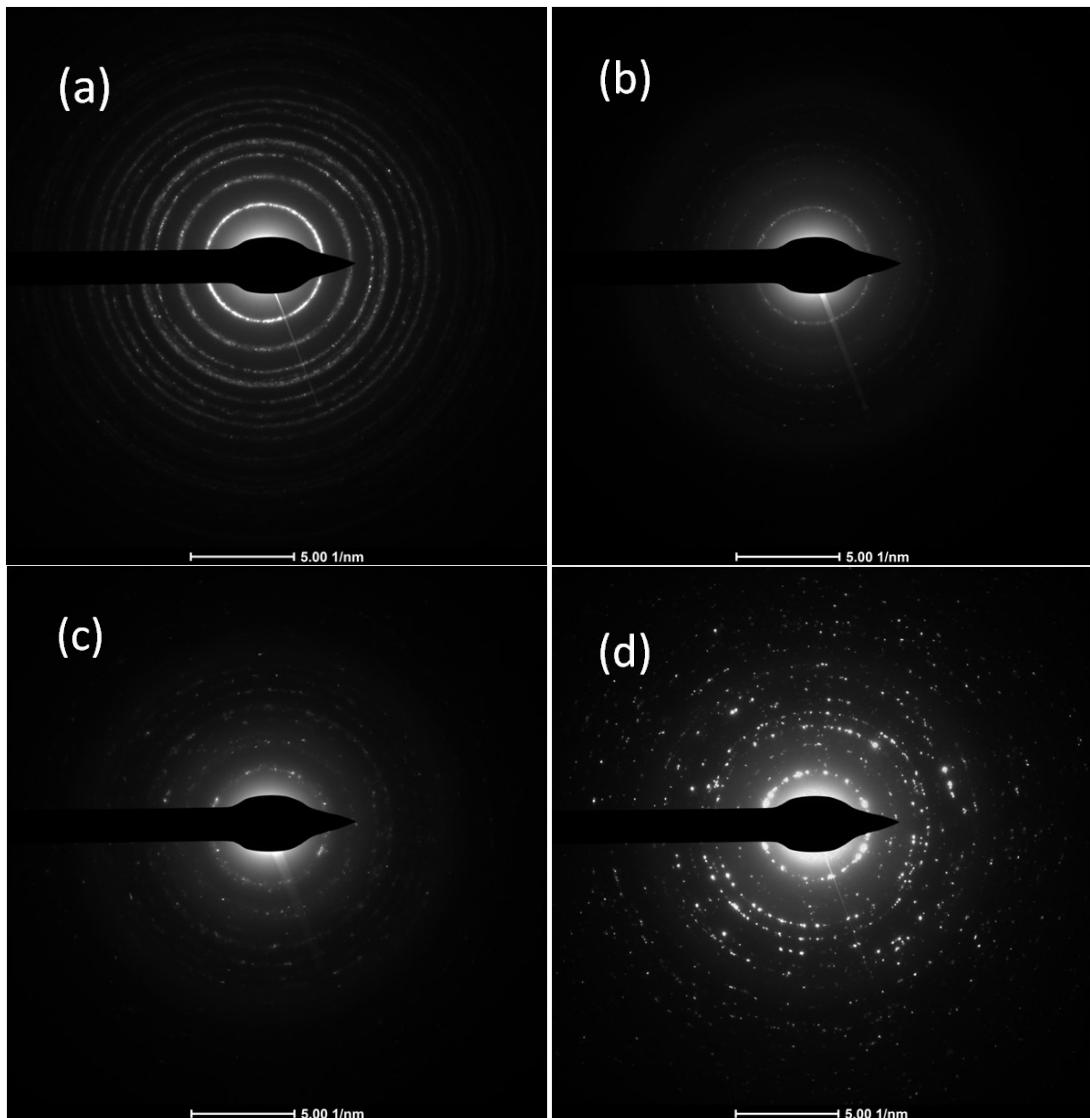
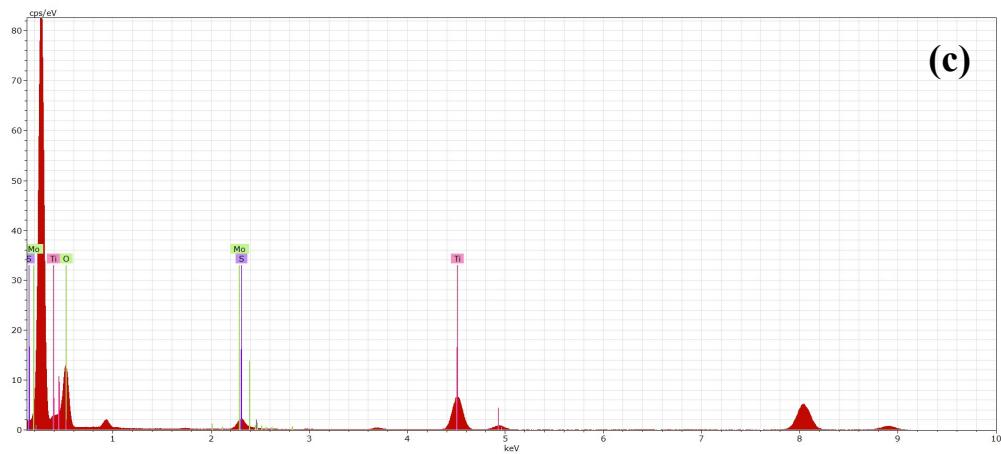
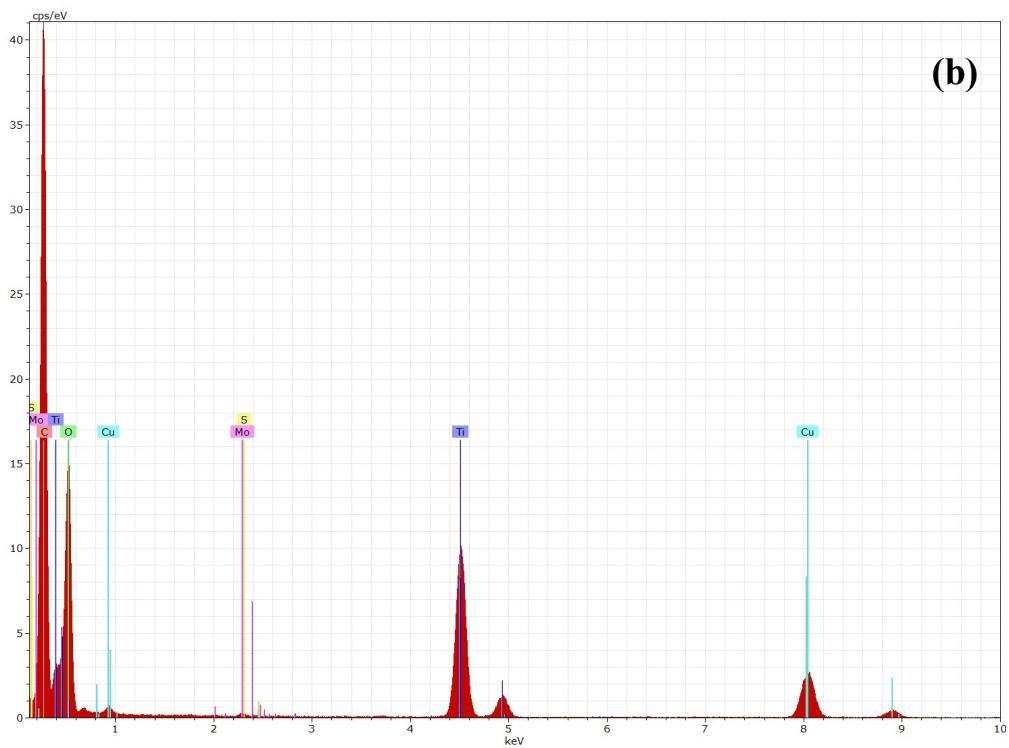
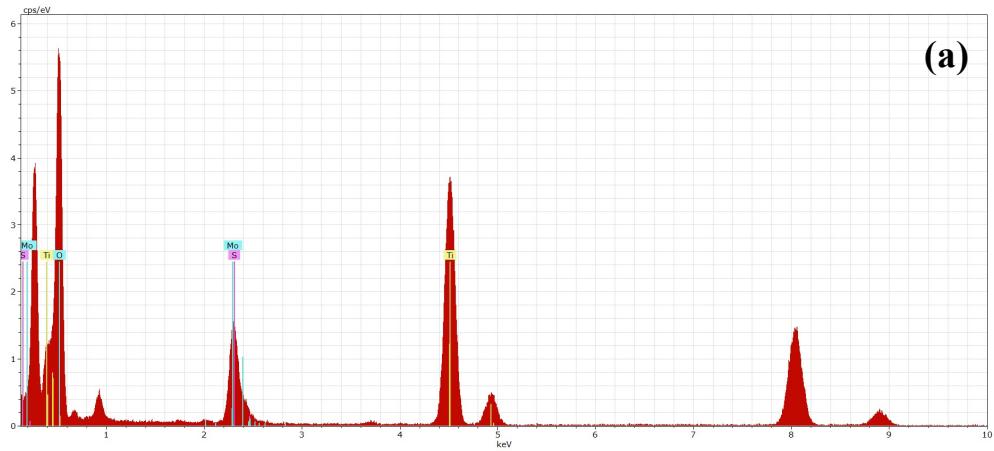


Figure S4. SAED pattern of (a)TiO₂/MoS₂, (b)TNT/MoS₂, (c)HPT/MoS₂ and (d) TNS/MoS₂.



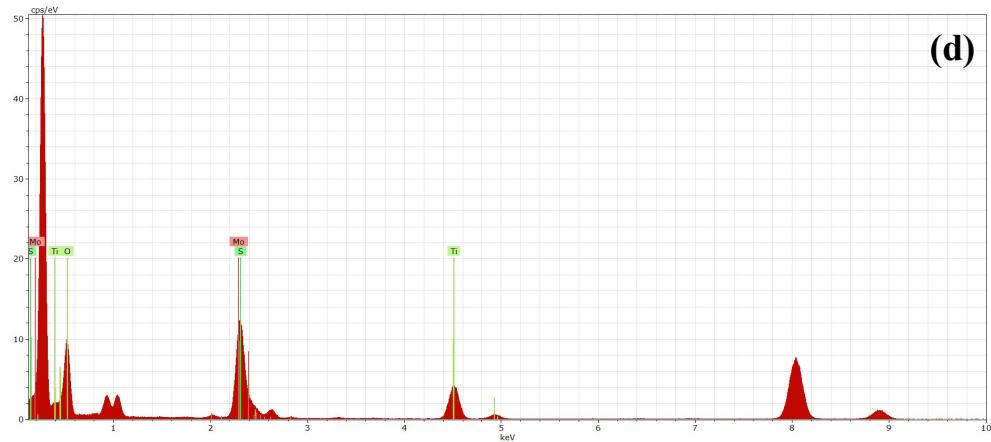


Figure S5. EDAX pattern of (a) TiO₂/MoS₂ (b) TNS/MoS₂ (c) TNT/MoS₂ and (d) HPT/MoS₂.

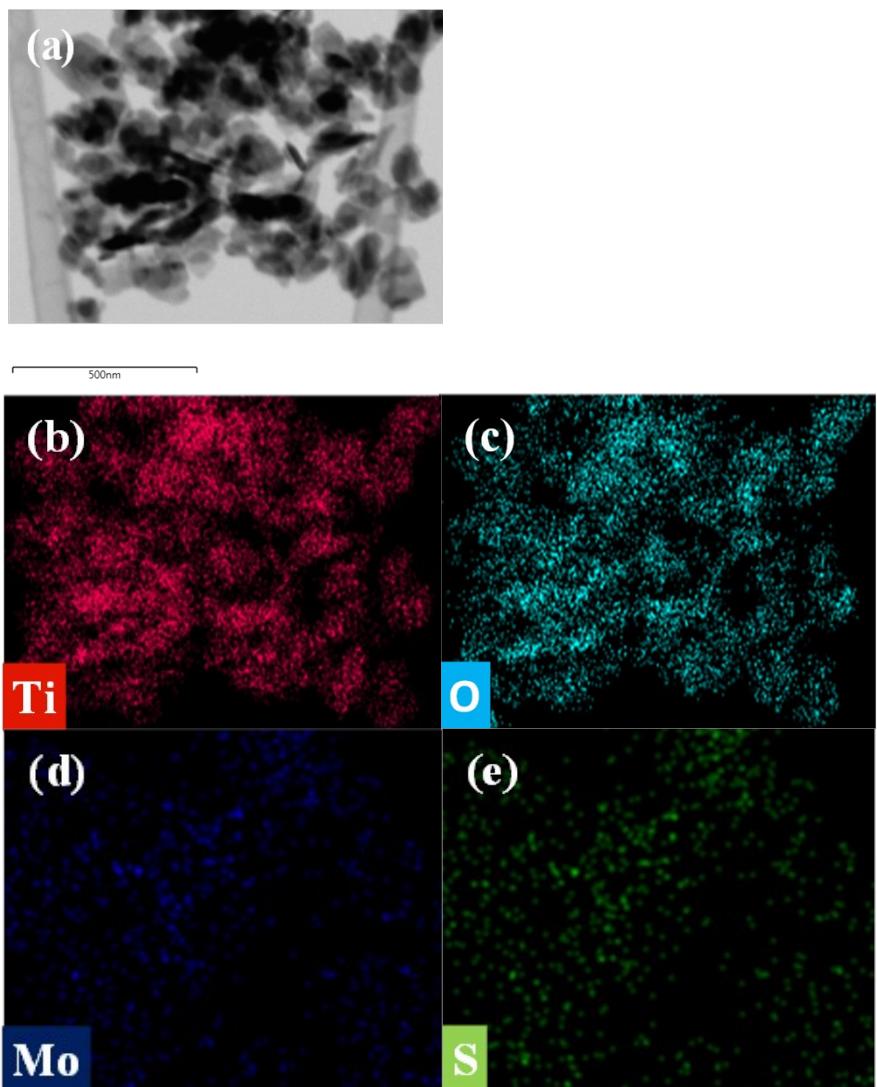


Figure S6. Elemental mapping of TNS/MoS₂

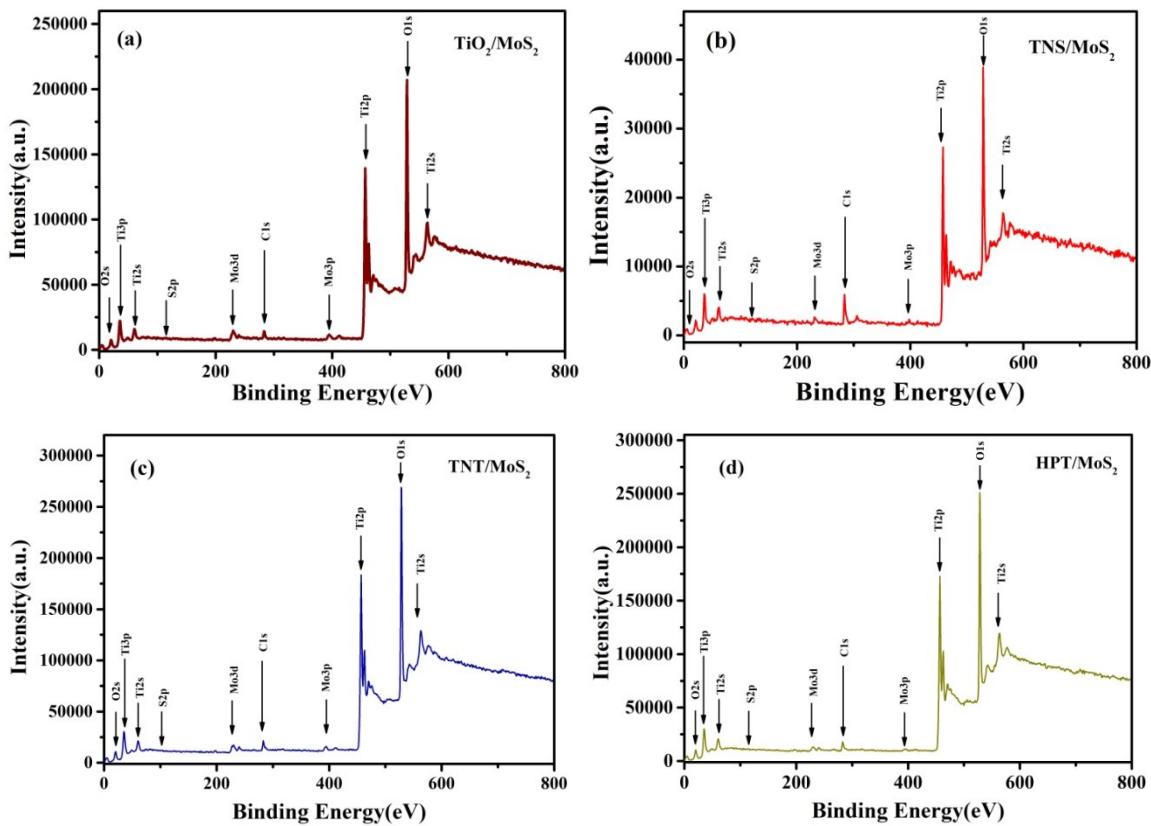


Figure S7. Survey XPS spectrum of (a)TiO₂ /MoS₂ (b)TNS/MoS₂ (c) TNT/MoS₂ and (d) HPT/MoS₂.

Table S1. Standard deviation of XPS analysis of actual data and fitted data (mentioned in %)

| Catalyst | Ti | O | Mo | S |
|------------------------------------|------------|------------|-----------|-----------|
| TiO ₂ /MoS ₂ | 1.42±0.23 | 0.88±0.085 | 4.23±0.12 | 5.13±0.13 |
| TNT/MoS ₂ | 1.63±0.41 | 0.86±0.075 | 5.03±0.17 | 4.9±0.11 |
| TNS/MoS ₂ | 1.57±0.25 | 0.79±0.065 | 4.61±0.12 | 5.09±0.14 |
| HPT/MoS ₂ | 1.61± 0.52 | 0.85±0.054 | 4.83±0.15 | 4.76±0.12 |

Table S2. Comparative table of photocatalytic hydrogen production.

| S.No | Methods | Materials | Light Source | SED | Vessel | H ₂ evolution rate (μmol g ⁻¹ h ⁻¹) | Ref. |
|------|--------------|--|------------------------|---|---------------|---|----------|
| 1 | Hydrothermal | CuInS ₂ /MoS ₂ /TiO ₂ | 300W Xenon arc lamp | Na ₂ S & Na ₂ SO ₃ (0.1M) | Pyrex flask | 141 | 1 |
| 2 | Ball mill | MoS ₂ /TiO ₂ (P25) | 300W Xenon arc lamp | Methanol | Not mentioned | 150.7 | 2 |
| 3 | Hydrothermal | MoS ₂ /TiO ₂ nanofibre | 300W Xenon arc lamp | Na ₂ S & Na ₂ SO ₃ (0.25M) | Quartz flask | 490 | 3 |
| 4 | CVD | MoS ₂ /TiO ₂ nanotube | Not mentioned | Not mentioned | Not mentioned | 440 | 4 |
| 5 | Hydrothermal | MoS ₂ /B-TiO ₂ | 300W UV xenon arc lamp | Methanol | Pyrex flask | 500 | 5 |
| 6 | Hydrothermal | MoS ₂ /TiO ₂ nanofibre | 300W Xenon arc lamp | Na ₂ S (0.35M) Na ₂ SO ₃ (0.25M) | Quartz flask | 1600 | 6 |
| 7 | Hydrothermal | MoS ₂ QD/TiO ₂ | One sun | Methanol | Quartz flask | 3100 | 7 |
| 8 | Hydrothermal | MOF-derived flower like MoS ₂ /TiO ₂ | 300W Xenon arc lamp | TEOA | Not Mentioned | 10046 | 8 |
| 9 | CVD | MoS ₂ /TiO ₂ nanosheet | 300W Xenon arc lamp | Ethanol | Quartz flask | 4300 | 9 |
| 10 | Hydrothermal | MoS ₂ - TiO ₂ /Au Hybrid | 300W Xenon arc lamp | Methanol | Quartz flask | 190 | 10 |
| 11 | Hydrothermal | MoS ₂ /TiO ₂ (commercial anatase) | 300W Xenon arc lamp | Na ₂ S (0.3M) Na ₂ SO ₃ (0.3M) | Pyrex flask | 41.33 | Our work |
| 12 | Hydrothermal | MoS ₂ /TiO ₂ (nanotubes) | 300W Xenon arc lamp | Na ₂ S (0.3M) Na ₂ SO ₃ (0.3M) | Pyrex flask | 29.71 | Our work |
| 13 | Hydrothermal | MoS ₂ /TiO ₂ (nanosheets) | 300W Xenon arc lamp | Na ₂ S (0.3M) Na ₂ SO ₃ (0.3M) | Pyrex flask | 77.41 | Our work |
| 14 | Hydrothermal | MoS ₂ /TiO ₂ (hierarchical) | 300W Xenon arc lamp | Na ₂ S (0.3M) Na ₂ SO ₃ (0.3M) | Pyrex flask | 65.54 | Our work |

Table S3. ICP-AES analysis of different composite.

| S.No | Sample | Mo(mg/l) | Ti(mg/l) |
|------|------------------------------------|----------|----------|
| 1 | TiO ₂ /MoS ₂ | 10.37 | 437.0 |
| 2 | TNT/MoS ₂ | 12.57 | 453.5 |
| 3 | HPT/MoS ₂ | 13.59 | 445.9 |
| 4 | TNS/MoS ₂ | 11.31 | 460.6 |

1. Y-J. Yuan, G. Fang, D. Chen, Y. Huang, Li-X. Yang, D-P. Cao, J. Wang, Yu Z-T and Zou Z-G, *Dalton Trans.*, 2018, **47**, 5652-5659.
2. X. Yang, H. Huang, B. Jin, J. Luo and X. Zhou, *RSC Adv.*, 2016, **6**, 107075-107080.
3. B. Ma, P-Y. Guan, Q-Y. Li, M. Zhang and S-Q. Zang, *Appl. Mater. Interfaces.*, 2016, **8**, 26794–26800.
4. H. He, J. Lin, W. Fu, X. Wang, H. Wang, Q. Zeng, Q. Gu, Y. Li, C. Yan, B-K. Tay, C. Xue, X. Hu, S-T. Pantelides, W. Zhou and Liu Z, *Adv. Energy Mater.*, 2016, **6**, 1600464.
5. Y-Y. Li, J-H. Wang, Z-J. Luo, K. Chen, Z-Q. Cheng, L. Ma, S. Ding, L. Zhou and Q-Q. Wang, *Sci Rep.*, 2017, **7**, 7178.