Metallic MoN Ultrathin Nanosheets Boosting High Performance Photocatalytic H_2 Production

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I. Materials synthesis

All the reagents are of analytical grade and were utilized without further purification. Deionized water was utilized in all the experiments. P25 TiO_2 was purchased from Degussa corporation in Germany. MoN nanosheets were synthesized by a melt-salted method. In detail, MoN nanosheets were synthesized by a modified salt-templated method. First, Mo powder was dissolved in H_2O_2 aqueous to form Mo precursor, which was coated on commercial NaCl to form Mo@NaCl. The Mo@NaCl was heated in flowing NH_3/Ar mixed gas at 650 °C. Finally, the MoN nanosheet was acquired after washing the NaCl by vacuum filtration. TiO_2 nanoparticles dispersed MoN nanosheets (MoN/TiO_2) was prepared by mechanically mixing the P25 TiO_2 with the as-synthesized MoN nanosheet in an agate mortar in ethanol solution. The nominal weight ratios of MoN to TiO_2 were 0.0, 0.5, 1.0, 2.0 and 3.0 wt%, and the resulting samples were labelled as 0.0MT, 0.5MT, 1.0MT, 2.0MT and 3.0MT, respectively.

II. Physicochemical properties characterisations

The XRD patterns were collected on a powder X-ray diffractometer (Miniflex, Rigaku) using Cu Kα radiation. The TEM, HRTEM images and EDX spectra were obtained on JEM-2100F electron microscope (JEOL, Japan). XPS measurement was carried on a VG ESCALAB 210 XPS spectrometer system with Mg Kα source. The synchrotron-based XANES measurements were conducted at the Shanghai Synchrotron Radiation Facility (SSRF) and Australian Synchrotron. The synchrotron-based UPS was obtained with a photon energy of 40 eV at the National Synchrotron Radiation Laboratory (NSRL). The UV-Vis diffuse reflectance spectra were collected on a UV-Vis spectrophotometer (UV2600, Shimadzu, Japan). The steady-state photoluminescence (PL) spectra were obtained on a RF-5301PC spectrofluorophotometer (Shimadzu, Japan) at room temperature. The transient-state PL spectra were collected on a FLS1000 spectrometer (Edinburgh Instruments, UK). A Tristar II 3020 N_2 sorption instrument (Micromeritics, USA) was employed to acquire the Brunauer-Emmett-Teller (BET) specific surface area and the pore volume of the samples.

III. Photocatalytic H_2 production experiment

The photocatalytic H_2 production process were carried out in a 100 ml Pyrex flask sealed with silicone rubber septa at room temperature and atmospheric pressure. The photocatalytic reaction was triggered by a 300 W Xenon lamp as the light source. In a typical photocatalytic experiment, 20 mg photocatalyst was dispersed under continuous stirring in 80 ml 20 v% ethanol aqueous solution. The Ar gas was pumped into the photocatalyst dispersion for 0.5 h to eliminate the air before the light irradiation and make sure that the reactor is under anaerobic conditions. 200 μL gas was sampled intermittently through the septum, and the evolved H_2 was examined by gas chromatograph (Clarus 480, Perkin Elmer, USA, thermal conductivity detector (TCD) with Ar as a carrier gas and 5 Å molecular sieve column).

IV. Electrochemical and photoelectrochemical tests

An electrochemical analyser (CHI650D instruments) was utilized to acquire the Mott-Schottky plots in 0.5 M Na_2SO_4 aqueous solution in a standard three-electrode system, with the as-prepared samples as the working electrode, Ag/AgCl (saturated KCl) as a reference electrode, and a Pt wire as the counter electrode. The EIS measurements were conducted in the same three-electrode system in a range from 1 to 2×10^5 Hz with an AC amplitude of 20 mV. 0.5 M potassium phosphate was employed as the electrolyte. Transient photocurrent (TPC) response measurement was carried out in the identical three-electrode system. A 300 W Xenon light was utilized as the light source. 0.5 M Na_2SO_4 aqueous solution was utilized as the electrolyte. The working electrode were prepared as follows: 10 mg sample, 15 mg polyethylene glycol (PEG; molecular weight: 20000) and 1.0 ml ethanol were ultrasonicated together to make a slurry. Then a doctor blade method was employed to coat the slurry onto a 2 cm × 1.5 cm FTO glass electrode. The obtained electrode was then dried under flowing Ar at 350 °C for 0.5 h.

V. Supplementary Results

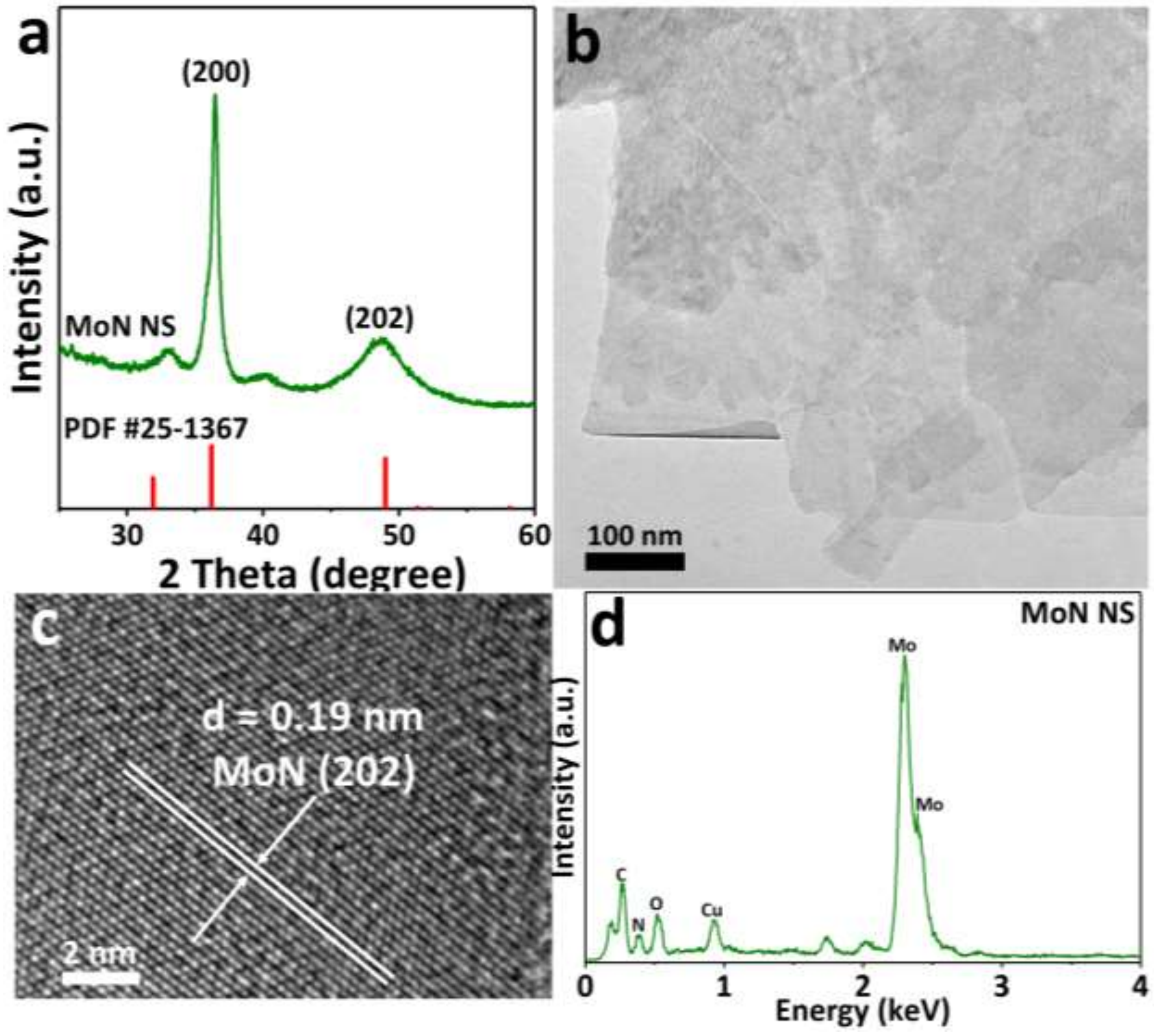

Fig. S1 (a) The XRD pattern of MoN NS. The typical (b) TEM, (c) HRTEM images and (d) EDX pattern of MoN NS.

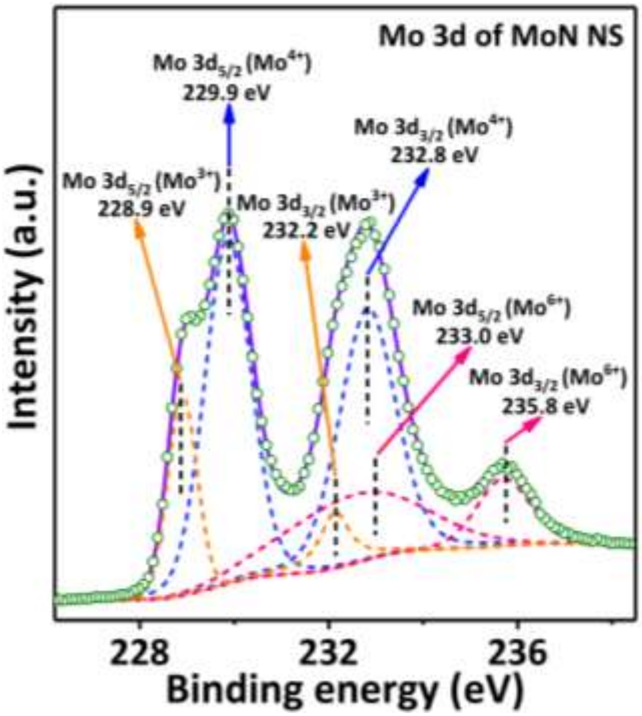

Fig. S2 High-resolution XPS spectrum of Mo 3d for MoN NS.

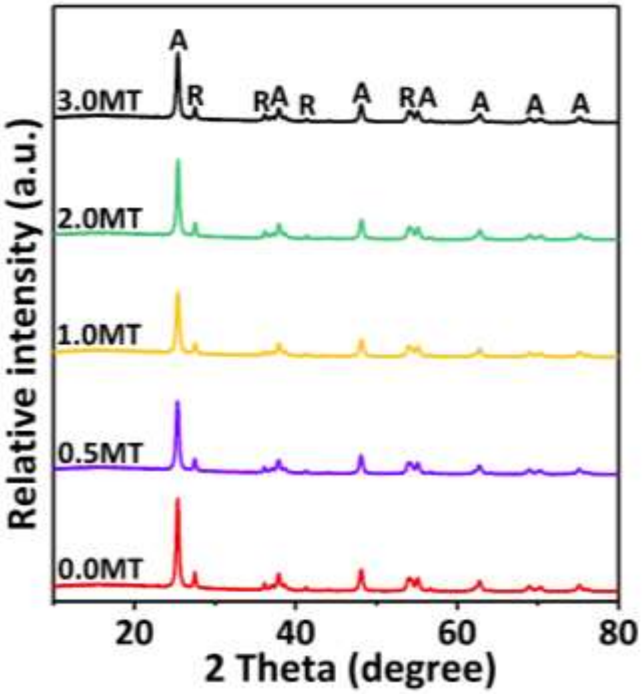

Fig. S3 The XRD patterns of 0.0MT, 0.5MT, 1.0MT, 2.0MT and 3.0MT.

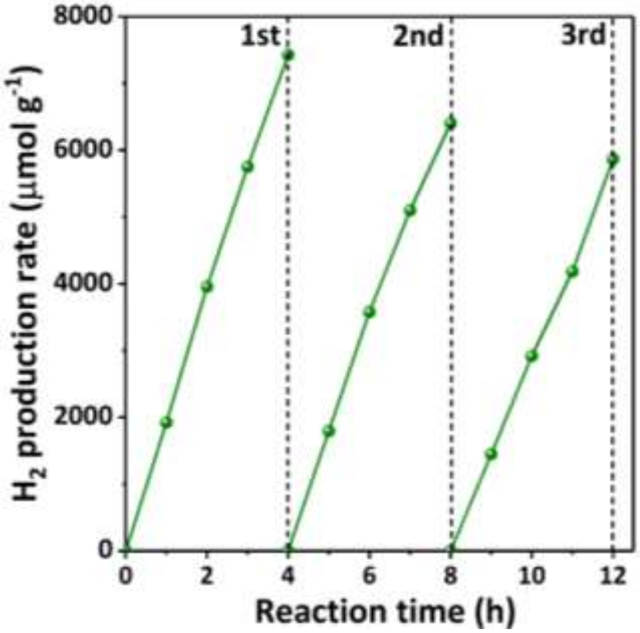

Fig. S4 Time course of photocatalytic H_2 production on 1.0MT (300 W Xe lamp); the reaction system was purged with Argon for 0.5 h to remove H_2 every 4 hours.

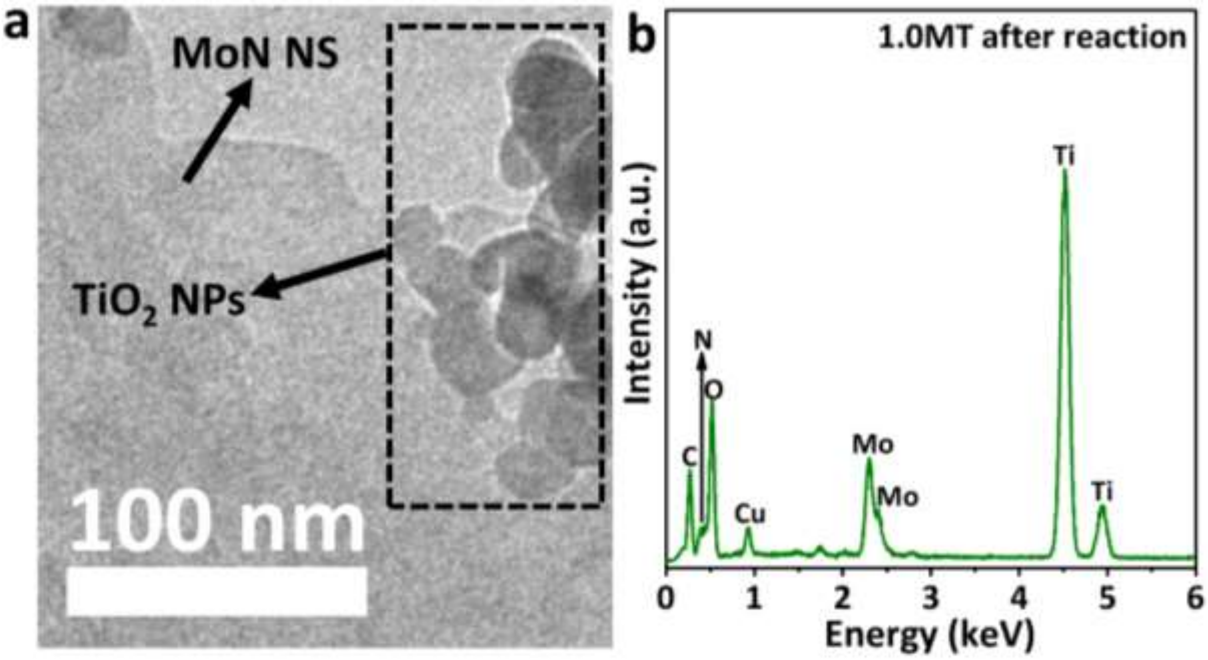

Fig. S5 (a) TEM image and (b) EDX pattern of 1.0MT after a 12-hour reaction.

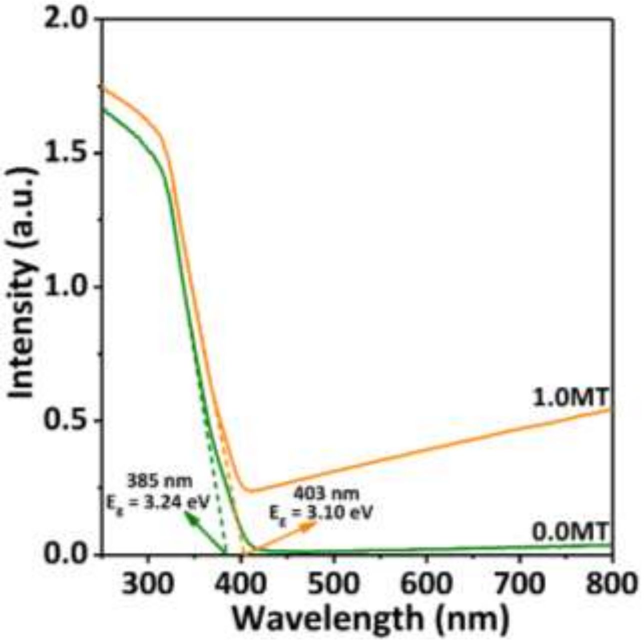

Fig. S6 UV-Vis diffuse reflectance spectra of 0.0MT and 1.0MT.

Table S1. Parameters of equivalent circuit for the impedance data of 0.0MT and 1.0MT.

Samples	*R_t (Ω)*	*R_s (Ω)*
0.0MT	2010	49.9
1.0MT	1410	47.6

Table S2. Physicochemical properties of 0.0MT and 1.0MT.

Samples	*S_{BET} (m^2 g^{-1})*	*PV[a] (cm^3 g^{-1})*	*APS[b] (nm)*	*H_2 production rate (μmol h^{-1} g^{-1})*
0.0MT	45.1	0.13	11.9	51
1.0MT	50.4	0.26	20.3	2034

[a] PV: Pore volume, [b] APS: Average pore size.