Supplementary Information

Integration of plasmonic and amorphous effects in MoO_{3-x} spheres for efficient

photoelectrochemical water oxidation

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EXPERIMENTAL SECTION

Preparation of MoO_{3-x} spsheres.

All the reagents were of analytical grade and were purchased and used as received without further purification. In a typical synthetic procedure, 3 ml of 30 wt.% H_2O_2 aqueous solution was slowly added to a round bottle flask containing of 0.96 g Mo metal powder and 24 mL pure ethanol in an icy water bath with magnetic stirring. After stirring for 15 minutes, a transparent yellow solution was obtained. Then, 0.5 g CTAB was added to the yellow solution. After stirring for 30 min, the precursor solution was sealed in a 45 mL autoclave and solvothermally treated at 160°C for 12 h. After cooling down to the room temperature naturally, the product was collected by centrifugation, washed with ethanol and water for three times and finally dried at vacuum.

Photoelectrochemical measurements.

The photoelectrochemical (PEC) measurements was performed in a threeelectrode cell with an Ag/AgCl (3.0 M NaCl) reference electrode, platinum gauze as a counter electrode, and a MoO_{3-x} /ITO glass plate was used as a working electrode, The MoO_{3-x} /ITO glass plate was tested as a photoanode in the PEC cell, the active area was 0.25 cm². The electrolyte was 0.5 M Na₂SO₄ solution. The photoresponses were measured under chopped irradiation from a 300 W Xe lamp with AM 1.5G illumination. The scan rate for the linear sweep voltammetry was 10 mV s⁻¹. Photocurrent stability tests were carried out under chopped irradiation (light/dark cycles of 400 s) at a fixed electrode potential of 1.1976V versus Reversible Hydrogen Electrode (RHE). Potentials vs Ag/AgCl were converted to the RHE scale by the equation: E_{RHE} (V) = $E_{Ag/AgCl}$ (V) + 0.1976 + 0.059×PH. Throughout the paper, all potential values are referred to this reference electrode. Electrochemical impedance spectroscopy was carried out to understand the charge transfer mechanism between photoelectrode and electrolyte using electrochemical workstation, and all the measurements were performed under the same situation.

XAFS measurement and data analysis. XAFS spectra at the Mo K-edge (20000 eV) was measured at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China. The storage ring was working at the energy of 2.5 GeV with a maximum electron current of 250mA. The hard X-ray was monochromatized with Si(111) double-crystals. XAFS data of as-prepared MoO_{3-X} and bulk MoO₃ samples were collected in the transmission mode in the energy range from -200 below to 1000 eV above the Mo K-edge. The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages¹. The *k*³-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Subsequently, *k*³-weighted $\chi(k)$ data in the *k*-space ranging from 2.1–12.1 Å⁻¹ were Fourier transformed to R-space using a hanning windows (dk = 1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells.

The quantitative curve-fitting was performed using the ARTEMIS module of IFEFFIT software package². Effective scattering amplitudes f(k) and phase shifts $\Phi(k)$ of all the paths for fitting the EXAFS data were calculated by the ab initio code FEFF8.0³. The amplitude reduction factor S₀² was determined to the best-fit value of

1.0 by fitting the data of C-MoO₃. Specifically, to fit the first Mo-O and second Mo-Mo shell in the R-range of 1.0-4.0Å, the coordination number *N* was fixed to be theoretical value of MoO₃ in the orthorhombic phase, while the internal atomic distances *R*, Debye-Waller factor σ^2 were allowed to vary. Meanwhile, the three Mo-O pairs shared common parameter of edge-energy shift ΔE_0 to reduce the number of free parameters, which is the same with the other three Mo-Mo pairs. As for the synthetic A-MoO_{3-x} sample, four distinguished Mo-O paths were included by referring to the standard MoO₃ in the hexagonal phase. The coordination numbers *N*, inter atomic distances *R*, Debye-Waller factor σ^2 and the edge-energy shift ΔE_0 were allowed to run freely. The obtained structural parameters are summarized in Table 1 and the corresponding curve-fitting results are plotted in Figure 4 (c),(d) in the main text and Fig. S1.

Other characterizations

The structure of as-prepared products were characterized by powder XRD (PANalytical X'Pert Pro diffractometer with Cu $K\alpha$ ($\lambda = 1.54178$ Å) radiation and Raman scattering taken by a Horiba microscopic Raman spectrometer (XploRA) with 532 nm laser. Photoemission spectroscopy experiments were performed at the Photoemission Endstation at the BL10B beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The morphologies were obtained by the field-emission scanning electron microscopy (FE-SEM) images taken on a FEI Sirion-200 scanning electron microscope. Transmission electron microscopy (TEM) was performed by using a JEOL-2010 TEM with an acceleration voltage of 200 kV. The UV-vis spectra were recorded using a Shimadzu DUV-3700 spectrophotometer. The photoluminescence spectra of the samples were recorded on a JobinYvon Horiba

Fluorolog-3-Tau Spectrofluorometer. Brunauer-Emmett-Teller (BET) surface area was obtained by analyzing nitrogen adsorption isotherm.



Fig. S1 The fitting curve of k^3 -weighted EXAFS spectra of C-MoO₃ (a-b) and A-MoO_{3-x}(c-d) using the ARTEMIS module of IFEFFIT.



Figure S2. Mo K-edge k^3 -weighted EXAFS oscillations $k^3\chi(k)$ for the A-MoO_{3-x} spheres and C-MoO₃ bulk.

References

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