Supporting Information

Non-stoichiometric MoO_{3-x} Quantum Dots as Light-harvesting Material for Interfacial Water Evaporation

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1. **Experimental:**

Synthesis of MoO_{3-x}. MoO_{3-x} were prepared by a hydrothermal reaction. Firstly, 0.5 g metallic molybdenum powder was dissolved into the 7.5 ml hydrogen peroxide (30 %) to form a homogenous solution. Then, it was sonicated for 4 h to decompose excessive hydrogen peroxide. After that, above solution was diluted into 30 ml by deionized water and 0-3 g chitosan (Mw=2000) was added into the solution. Finally, the solution was transferred to a Teflon-lined autoclave of 100 mL internal volume, followed by hydrothermal reactions in an electric oven at 80 °C. After 8 h reaction, the product was obtained via dialysis and lyophilization process.

Preparation and hydrophobic treatment of MoO_{3-x} QDs membrane. MoO_{3-x} QDs membrane was prepared by filtering 0.02 g MoO_{3-x} QDs through the cellulose acetate filter (CA). Then, the hydrophobic MoO_{3-x} QDs membrane was obtained by fluoroalkylsiane modification. Firstly, the MoO_{3-x} QDs deposited CA filter was placed in a vacuum desiccator, and 300 μL methyltrichlorosilane (MTCS) was added into a small beaker of desiccator. Then, the desiccator was pumped into the vacuum and the samples was placed at room temperature for 24 h.

Characterization. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F30 microscope at an acceleration voltage of 200 kV. The crystal phase composition of the sample was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized CuKα radiation. The Mo3d binding energy of the sample was determined by X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 5600). The optical properties were measured using a spectrophotometer (U-4100. Hitachi). Contact angles were measured on a commercial contact angle system (JC2000D2). The temperature changes and thermal distribution images were obtained by a thermographicmeter (FLIR System i7). A 300 W Xe lamp (HSX-UV300) was used for the water evaporation measurement.

Water evaporation performance measurement. The performance of water evaporation was monitored by the weight loss of the water using an analytical balance (XS 105 DualRange). Firstly, the MoO_{3-x} QDs membrane with a diameter of 2.4 cm was placed on the surface of the water in a 10 mL beaker and was irradiated by the Xe light from the top. The power density of the Xe lamp was adjusted to 5000 W m^{-2}. Then, the surface temperature was monitored as the increment of irradiation time and the mass of water in the beaker were recorded every 5 min.

DFT calculation methods. In our calculation, plane wave ultra-soft pseudopotential (PWPP), the generalized gradient approximation (GGA) and Perdew-Burk-Ernzerhof (PBE) methods were applied to describe core electrons, exchange and correlation effects of valance electrons, respectively. Firstly, we build the 2 x 2 x 2 supercell of MoO_3 crystal model (ICSD #166362, the lattice constant is a = 0.792nm, b = 2.772nm, c= 0.740 nm in orthorhombic symmetry). (Fig. 2b) Then the model was optimized by GGA+PBE method and BFGS algorithm. The *k*-point was set as 1×3×3 and cut-off energy was 340 eV. The convergence tolerances are 1×10^{-6} eV, 0.1 GPa, 0.05 eV/Å, 2×10^{-3}Å for energy, maximum stress, maximum force and maximum displacement, respectively.

Calculation by Localized surface plasmon resonance method

The plamon resonance could be described by applying Mie' theory[S1]. When the size of nanoparticles is much smaller than the wavelength of the light ($\lambda \gg r$), the extinction coefficient α could be given by the complex dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \qquad (1)$$

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \qquad (2)$$

$$\omega_p^2 = \frac{ne^2}{\varepsilon_0 m_e} \qquad (3)$$

$$\alpha \propto 9 \cdot \frac{4}{3}\pi r^3 \frac{\omega}{c} \varepsilon_m \frac{\varepsilon_2(\omega)}{\left(\varepsilon_1(\omega) + 2\varepsilon_m\right)^2 + \varepsilon_2(\omega)^2} \qquad (4)$$

where r = 5nm is the size of nanoparticles, $\omega = \frac{2\pi c}{\lambda}$ is the angular frequency of incident light; $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ are the real and imaginary terms of the dielectric function ε(ω) of MoO_{3-x}; the free electron density $n = 6 \times 10^{21} cm^{-3}$,[S2] the dielectric constant of the localized medium ε_m was set as 2, the electron effective mass m_e=0.38 m_0,[S3] where m_0 is the rest mass of the electron; γ is the full width at half maximum (FWHM) of the LSPR peak. Calculation result in Fig. S2 shows the LSPR peak was at 600nm $\lambda_{max} = 600$ nm.

2. Results

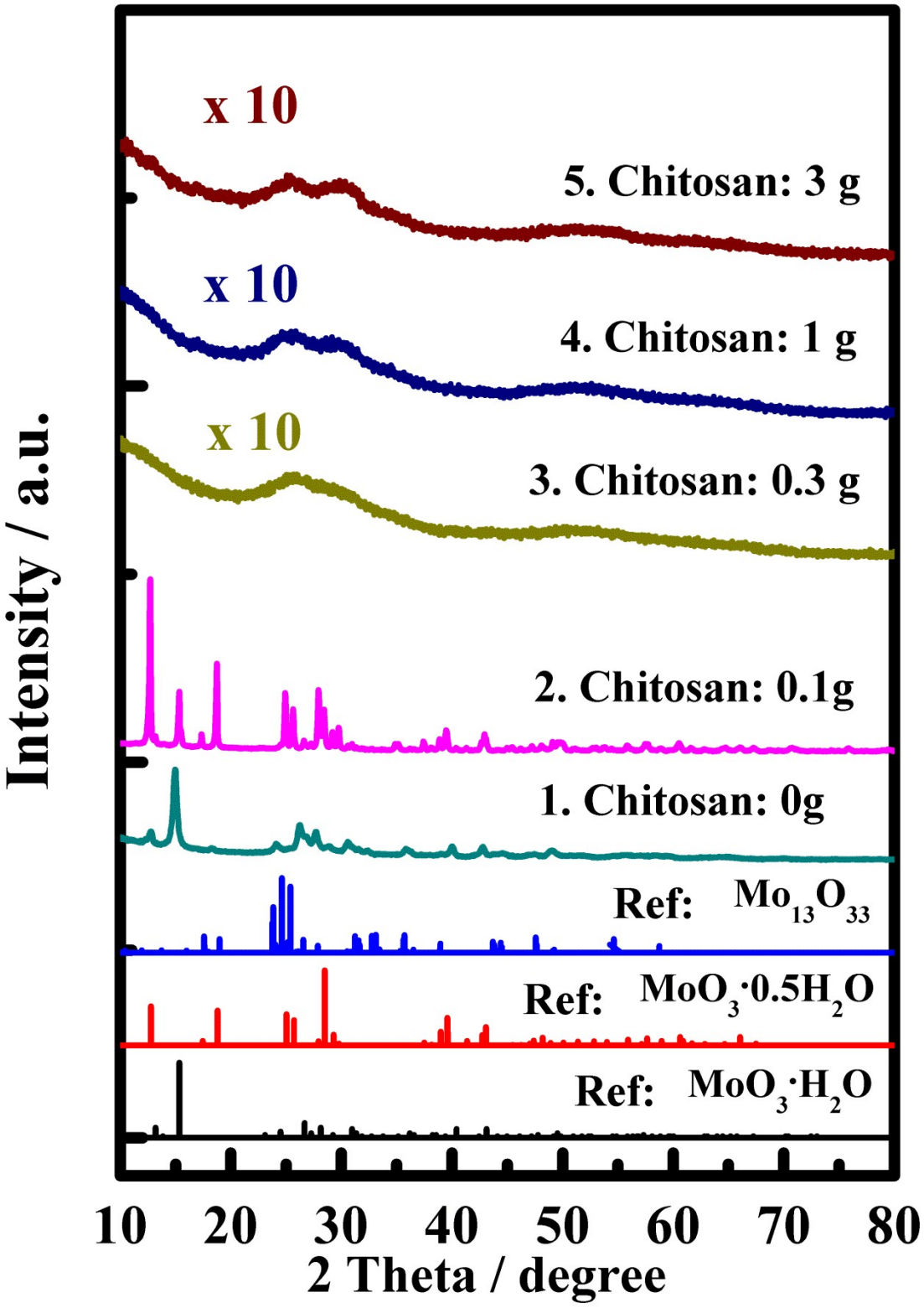

Fig. S1 XRD pattern of samples synthesized with 0, 0.1, 0.3, 1 and 3 g chitosan, respectively.

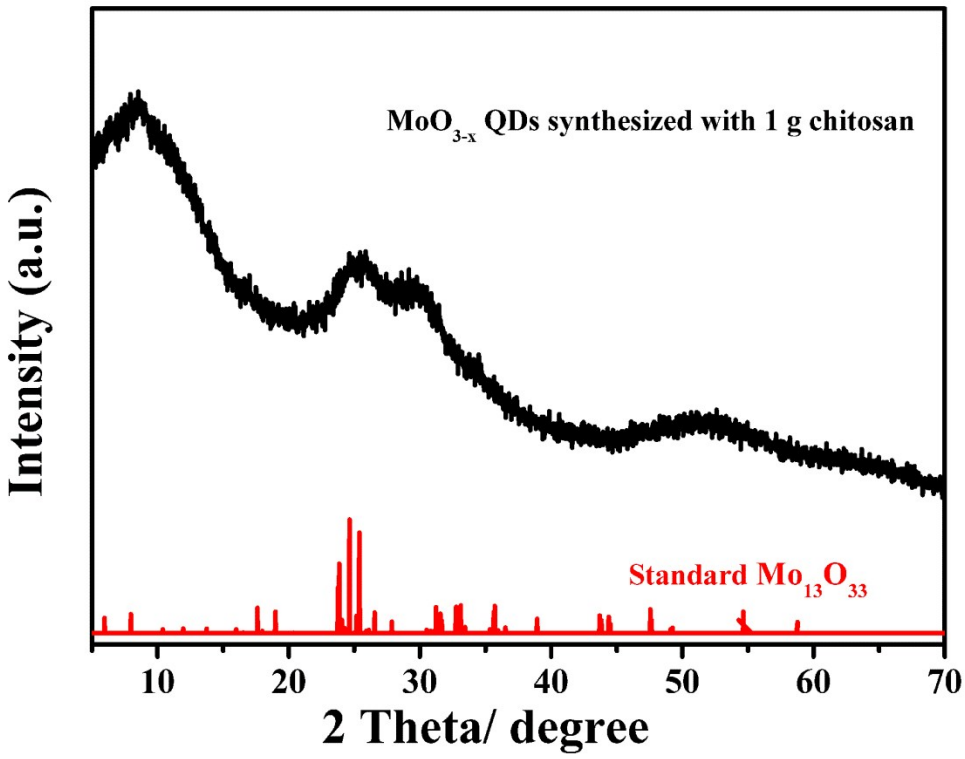

Fig. S2 XRD pattern of sample synthesized with 1 g chitosan.

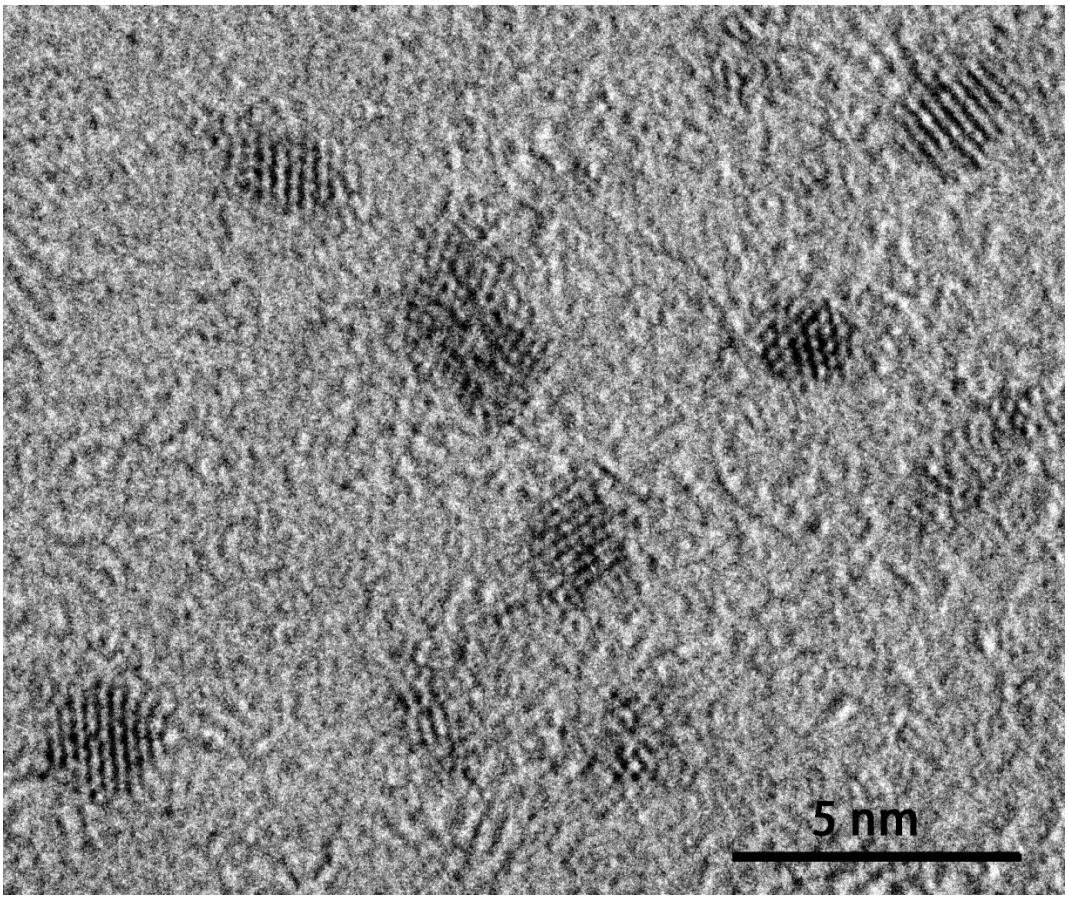

Fig.S3 HR-TEM images of MoO_{3-x} QDs

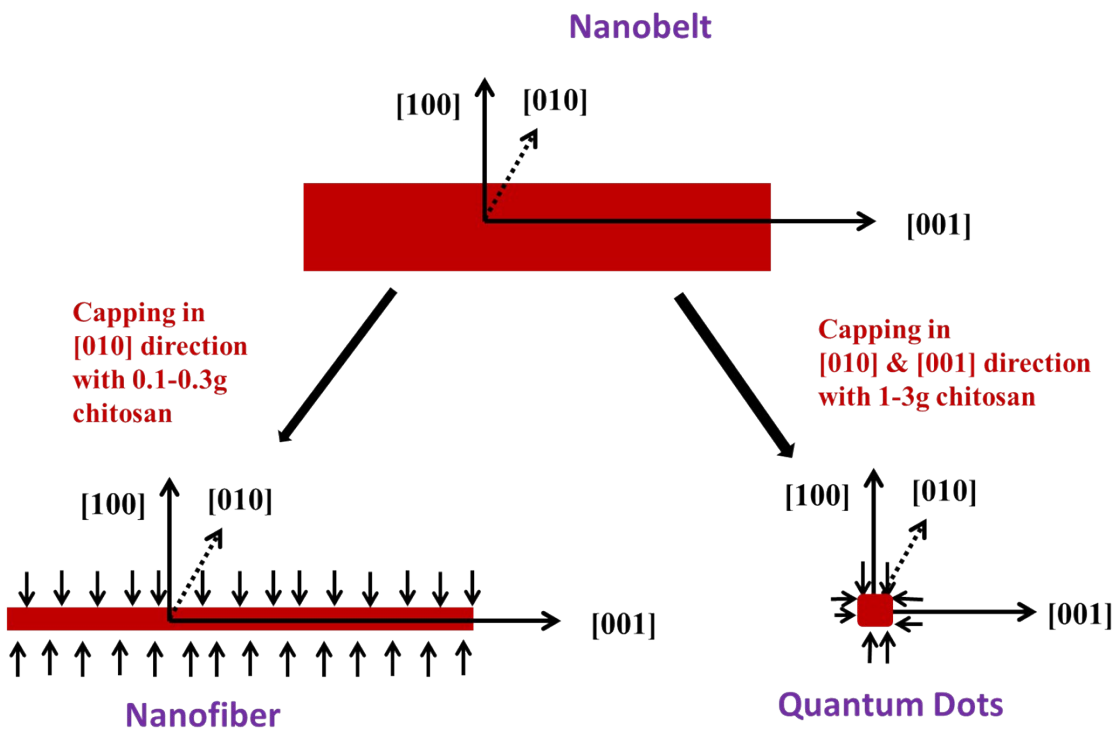

Figure. S4 Schematic illustration of the role of chitosan in determining the particle morphology.

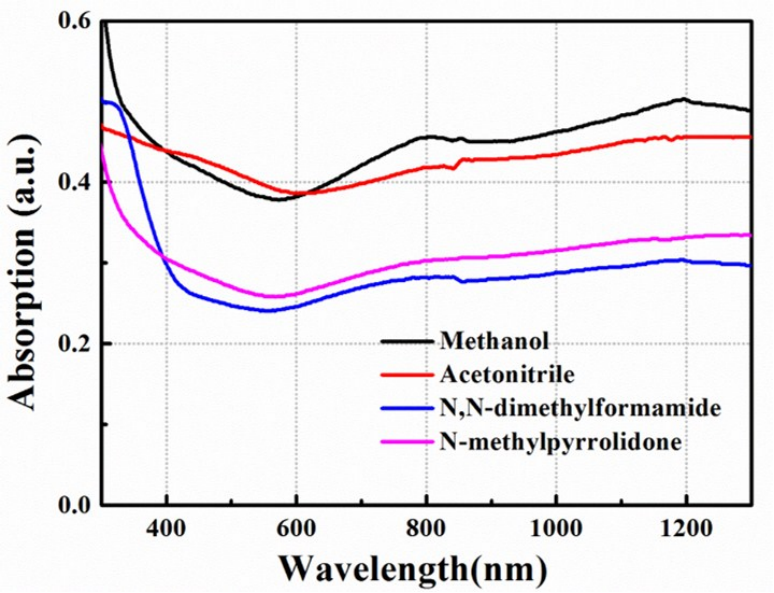

Figure S5 Absorption spectra of MoO_{3-x} dispersed in different solutions.

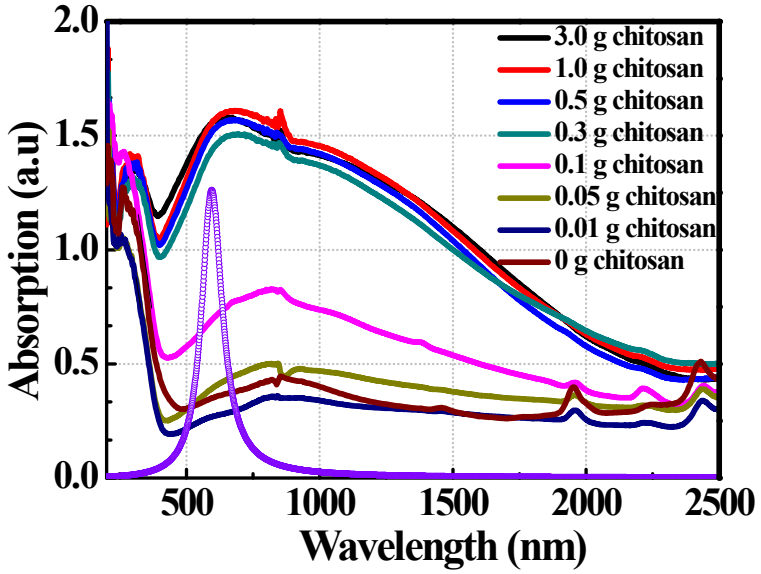

Figure S6 Experimental absorption spectra of samples synthesized with different content of chitosan and simulated result by LSPR method (the dash line).

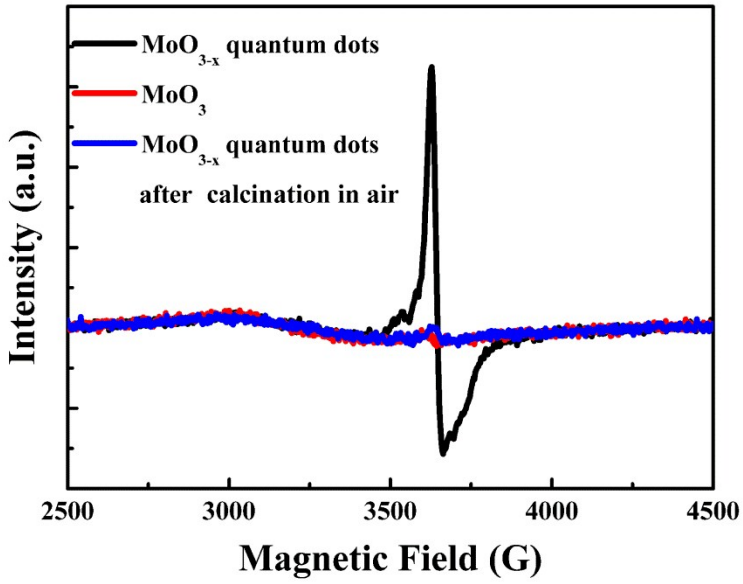

Figure. S7 Electron spin resonance (ESR) analysis of samples.

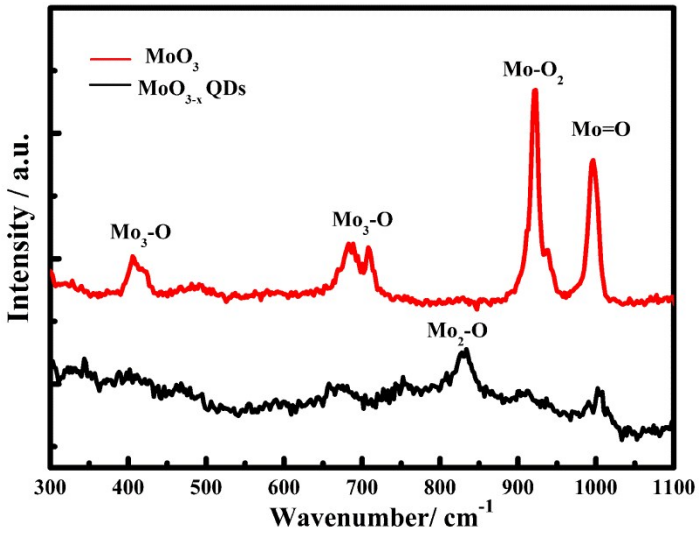

Figure. S8 Raman spectra of samples.

Reference:

S1. Hutter E, Fendler J H. Exploitation of localized surface plasmon resonance. Advanced Materials, 2004, 16(19): 1685-1706.

S2. Alsaif M M Y A, Latham K, Field M R, et al. Tunable Plasmon Resonances in Two-Dimensional Molybdenum Oxide Nanoflakes. Advanced Materials, 2014, 26(23): 3931-3937.

S3. Dandogbessi B S, Akin-Ojo O. First principles prediction of the electronic structure and carrier mobilities of biaxially strained molybdenum trioxide (MoO_3). Journal of Applied Physics, 2016, 120(5): 055105.