

Electronic Supporting Information (ESI)

Top-down Fabrication of Colloidal Plasmonic MoO_{3-x} Nanocrystals via Solution Chemistry Hydrogenation

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Materials

Ethanol, polyvinylpyrrolidone K30 (PVP), glacial acetic acid, and n-hexane were obtained from Sinopharm Chemical Reagent Co. Ltd. Nitromethylpyrrolidone (NMP), molybdic acid (H_2MoO_4 , $\geq 99.95\%$ trace metals basis), and OAm (80 ~ 90%) were bought from Aladdin. OA (90%) and MoO_3 (99.9%) were purchased from Sigma–Aldrich and Maya Reagent, respectively. All reagents were directly used as received without further purification.

Preparations of $\alpha\text{-MoO}_{3-x}$ and h-MoO_{3-x} nanocrystals

In a typical synthesis, 2 mmol MoO_3 or H_2MoO_4 power was added into 6 mL mixture solvent of OAm:OA (OAm:OA = 0:6, 2:4, 2.5:3.5, 3:3, and 6:0) placed in a 100 mL round-bottom flask. The above mixture was first vigorously stirred for 10 min and then rapidly heated to 120 °C for 20 min under vacuum. Then the mixture was quickly heated to 180 °C by sufficient stirring under N_2 atmosphere and kept at this temperature for 1 - 12 h. After N_2 -cooling to ambient temperature, the black product was washed with a mixture of n-hexane and ethanol three times and then dried in vacuum at 60 °C for 2 h.

Ligand Exchange Procedure

The as-prepared samples were added into glacial acetic acid (50 mL) placed in a 100 mL flask. The suspension was constantly stirred for 6 h at 70 °C under N_2 and then centrifuged, and the obtained precipitate was dispersed in n-hexane by ultrasonication and subsequently added into PVP aqueous solution (1.5 g PVP dissolved in 10 mL distilled water) under magnetic stirring for 2 h. The products were centrifuged and washed (three times) with distilled water, and then dried at 50 °C and collected (called

hydrophilic MoO_{3-x}). These water-soluble products were used for the photo-thermal conversion experiments.

Characterizations

The X-ray diffractor (Ultima IV, Cu Ka radiation, scanning rate: 20° min⁻¹) was used to investigate the crystallographic structures of the prepared samples. The Vis-NIR absorption spectra of samples (dispersed in NMP) were measured on a UV-3600 spectrophotometer (Shimadzu). The morphologies of the samples were investigated by transmission electron microscope (JEOL JEM-2010, 200 kV). X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Thermo Scientific Escalab 250 Xi. Raman measurements were carried out using Thermo Fisher (laser wavelength: 532 nm).

Calculation of the photothermal conversion efficiency

The photothermal conversion efficiencies (η) of the α -MoO_{3-x} and h-MoO_{3-x} were calculated by equation (1) as the previous reports.¹

$$\eta = \frac{hS(\Delta T_{max,mix} - \Delta T_{max,H2O})}{I(1 - 10^{-A_{808}})} \quad (1)$$

Where h was heat transfer coefficient and S was the surface area of the container. $\Delta T_{max,mix}$ was the temperature change of the MoO_{3-x} aqueous suspension (100 μ g mL⁻¹) at the maximum steady-state temperature and $\Delta T_{max,H2O}$ was the temperature change of water at the maximum steady-state temperature. I was the laser power (5 W cm⁻²). A_{808} was the absorbance of MoO_{3-x} aqueous solution at 808 nm.

The value of hS could be acquired from equation (2).

$$hS = \frac{\sum_i m_i C_{p,i}}{\tau S} \quad (2)$$

The m and C_p are the mass and heat capacity of solvent (water). In this work, m =

1.8 g, $C_p = 4.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, and $\tau_s = 128.70$ ($\alpha\text{-MoO}_{3-x}$) and 125.96 s (h-MoO_{3-x}) (Fig. S8). The hS values of $\alpha\text{-MoO}_{3-x}$ and h-MoO_{3-x} were determined to be 59.91 and $61.22 \text{ mW }^\circ\text{C}^{-1}$. I was 5000 mW . For $\alpha\text{-MoO}_{3-x}$ and h-MoO_{3-x} , $A_{808} = 1.77$ and 1.48 . The values of $\Delta T_{\text{max,mix}}$ were 43.6 and 43 $^\circ\text{C}$ for $\alpha\text{-MoO}_{3-x}$ and h-MoO_{3-x} . $\Delta T_{\text{max,H}_2\text{O}}$ was 5 $^\circ\text{C}$. Therefore, the photothermal conversion efficiencies (η) were calculated to be 47.1 and 48.1% .

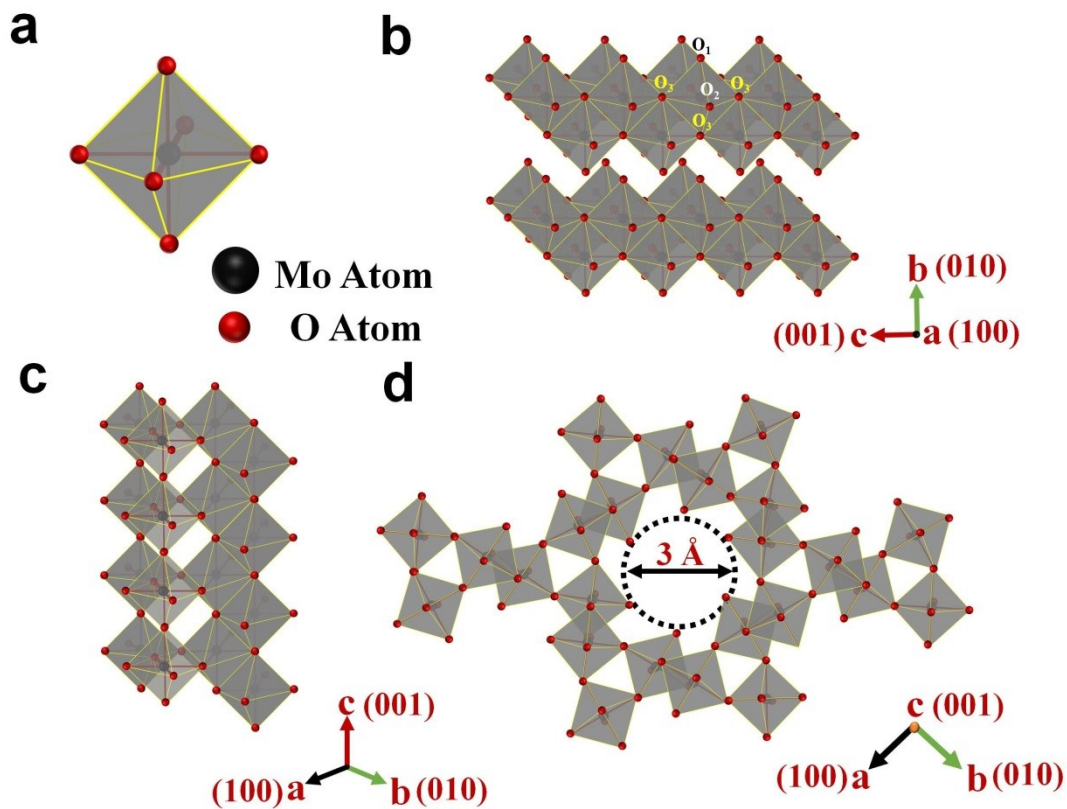


Fig. S1. (a) MoO₆ octahedron building unit, (b) stable α -MoO₃ with layered structure, (c) metastable h-MoO₃, and (d) one-dimensional tunnel structure along the c-axis of h-MoO₃.

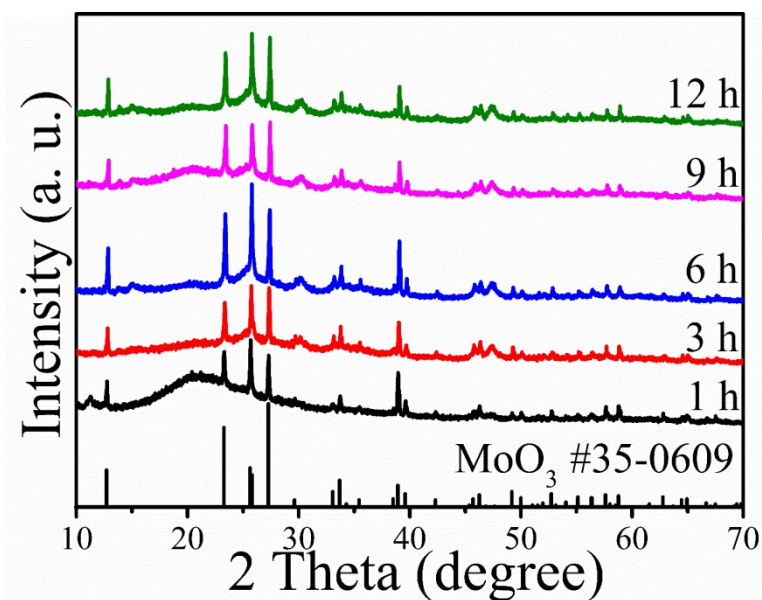


Fig. S2. XRD patterns of α -MoO_{3-x} nanocrystals treated by OAm and OA (OAm:OA = 2.5:3.5). The time labeled on each curve indicated the corresponding reaction time.

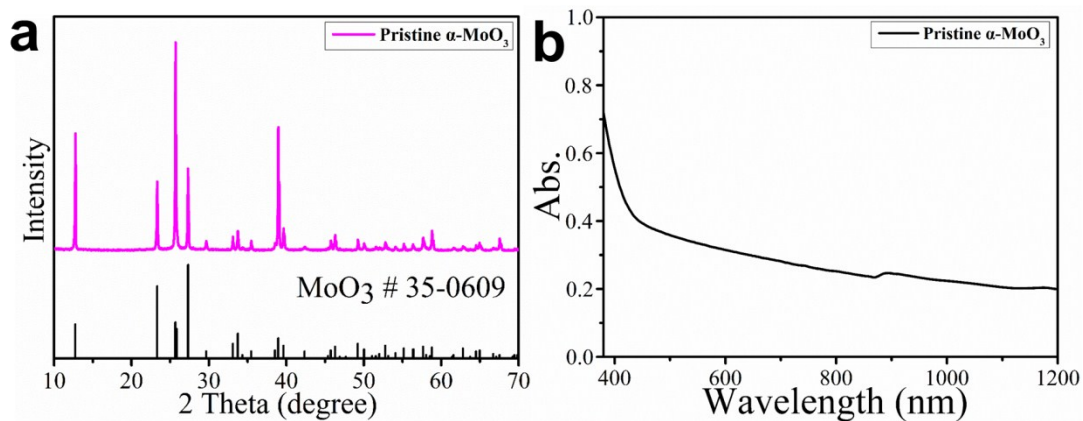


Fig. S3. (a) XRD pattern and (b) optical absorption of pristine α -MoO₃.

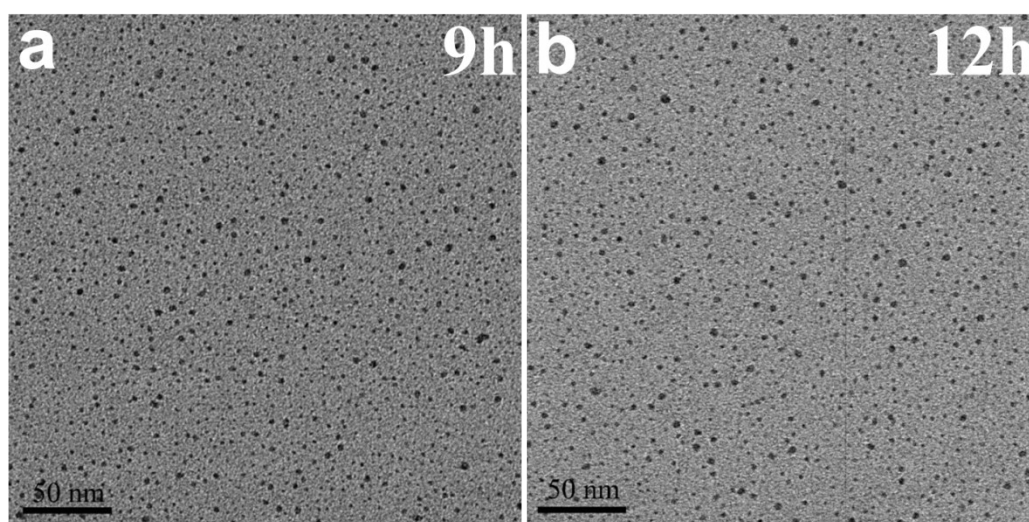


Fig. S4. TEM images of α -MoO₃ treated by using ratio of OAm:OA = 2.5:3.5. The time labeled above the images indicated the corresponding reaction time.

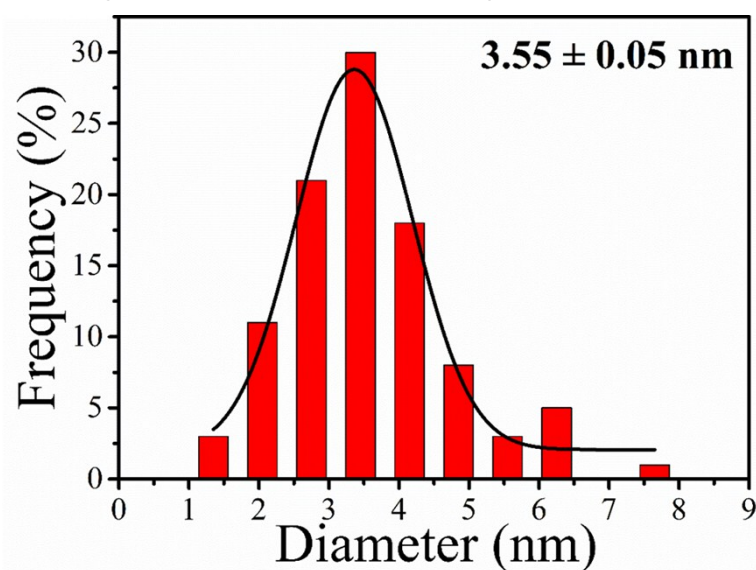


Fig. S5. Size distribution histograms of α -MoO_{3-x} NPs obtained with different OAm:OA ratios of 2.5:3.5. (N = 500)

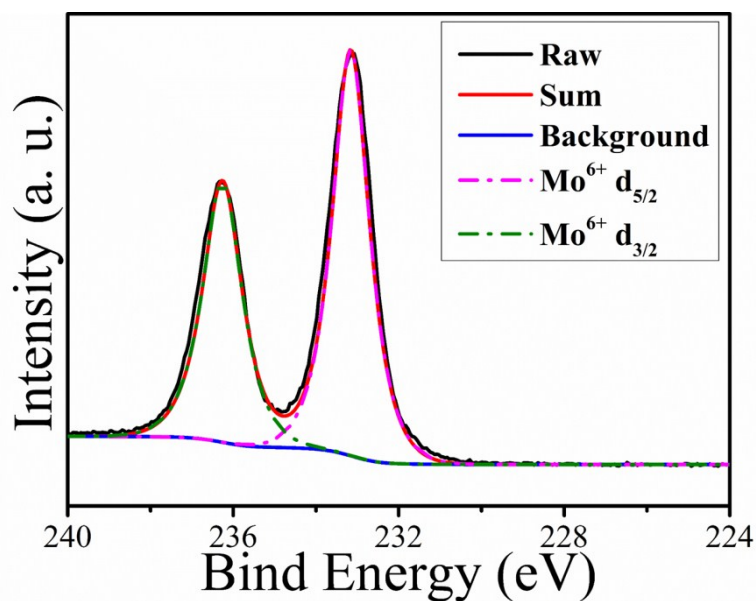


Fig. S6. Mo 3d XPS spectrum of pristine α -MoO₃.

α -MoO₃ treated by different combinations of OAm and OA

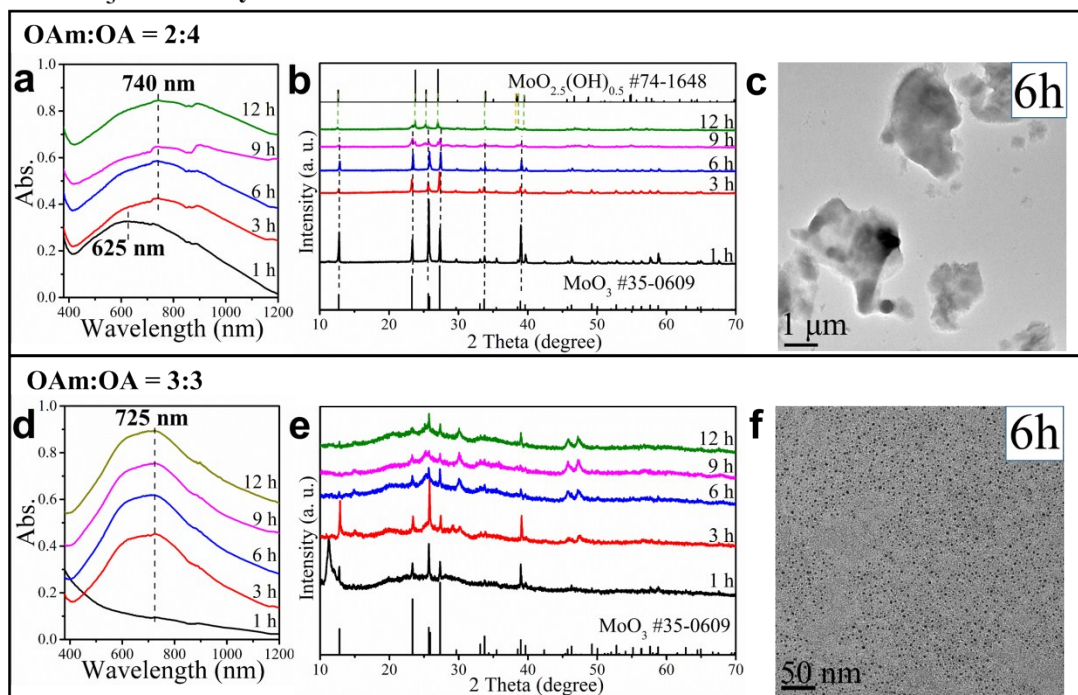


Fig. S7. The TEM images and evolutions of Vis-NIR spectra and XRD patterns of α -MoO₃ nanocrystals treated by different OAm:OA mixtures. The time labeled on each curve indicated the corresponding reaction time.

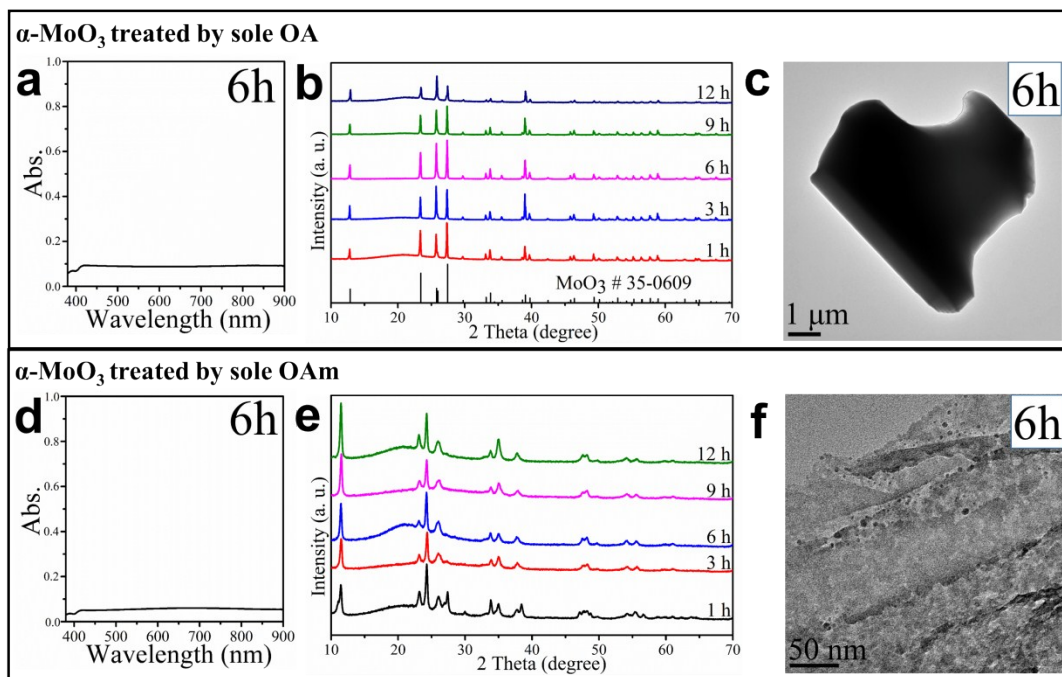


Fig. S8. The Vis-NIR spectra, TEM images, and evolutions of XRD patterns of α - MoO_3 nanocrystals treated by sole OA and sole OAm. The time labeled on each curve indicated the corresponding reaction time.

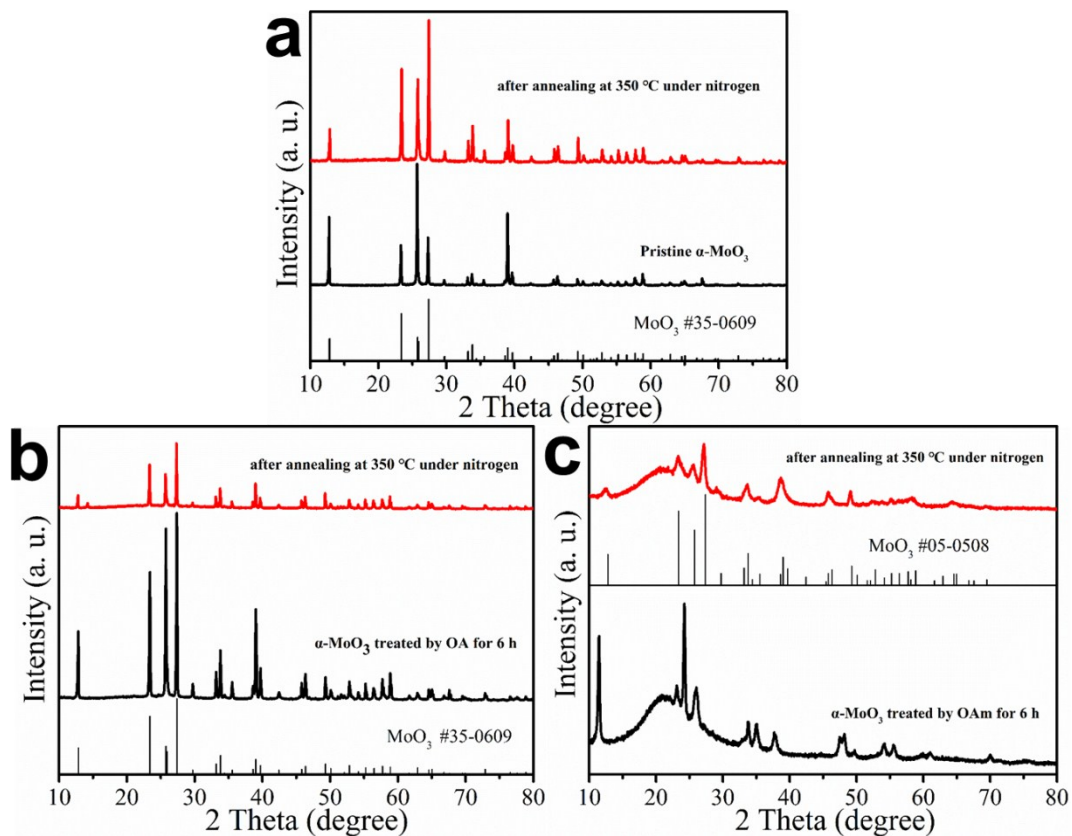


Fig. S9. XRD diffraction patterns of (180 $^\circ\text{C}$ for 6 h) before and after annealing (a) pristine α - MoO_3 , (b) OA treated α - MoO_3 , and (c) OAm treated α - MoO_3 .

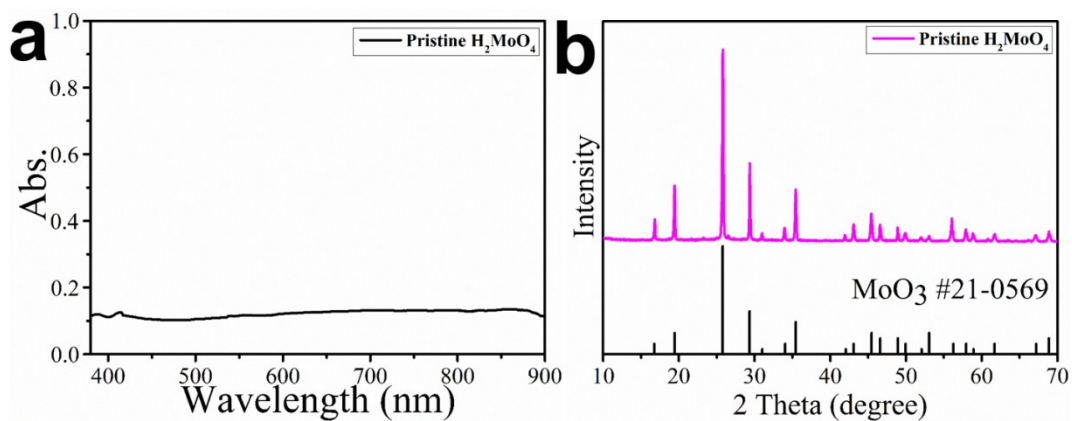


Fig. S10. (a) optical absorption and (b) XRD pattern of pristine h- MoO_3 .

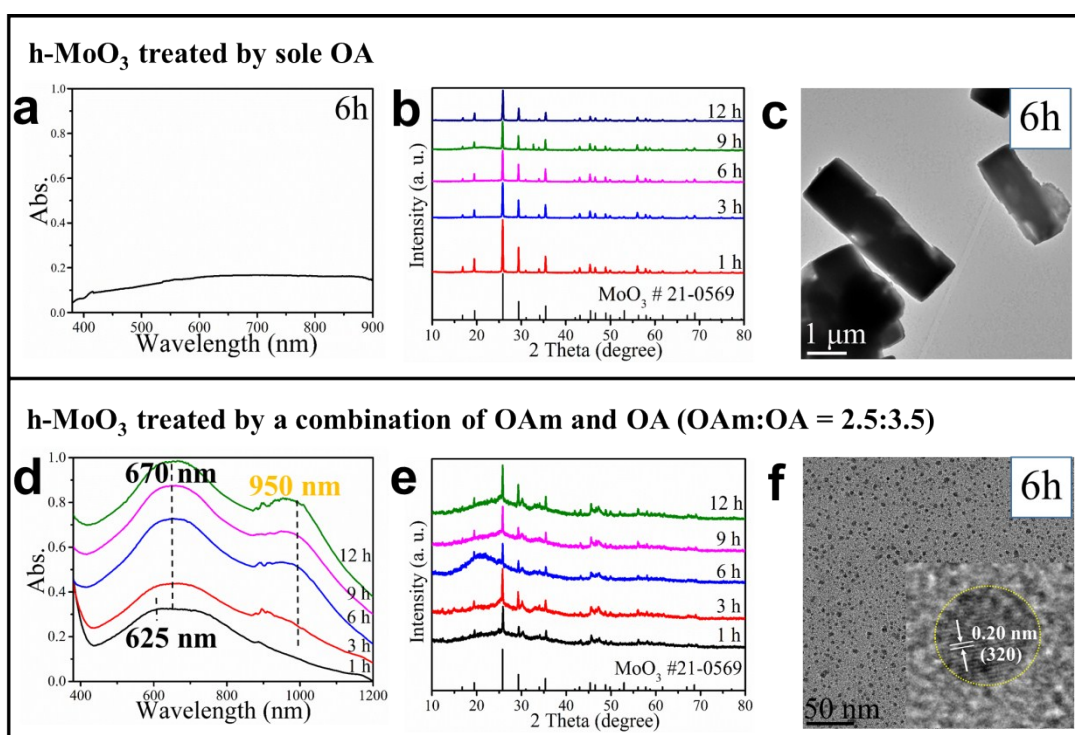


Fig. S11. The evolutions of Vis-NIR spectra, XRD patterns, TEM images and of h- MoO_3 nanocrystals treated by sole OA and a combination of OAm and OA. The time labeled on each curve indicated the corresponding reaction time.

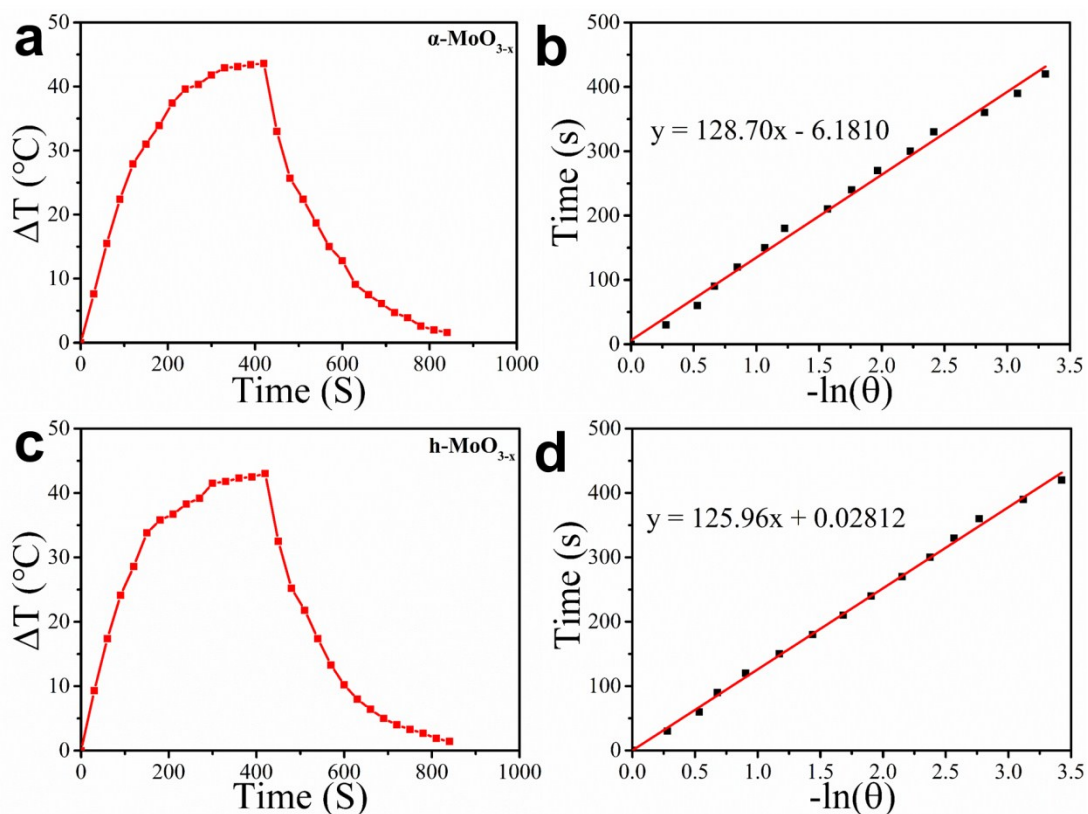


Fig. S12. Photothermal effects of the irradiations of the α -MoO_{3-x} (a) and h-MoO_{3-x} (c) aqueous dispersions with the NIR laser (808 nm, 5 W cm⁻²), in which the irradiation lasted for 7 min, and then the laser was shut off. Time constants for heat transfer from the system were determined to be $\tau_s = 128.70$ s (b) and 125.96 s (d) by applying the linear time data from the cooling period versus $-\ln(\theta)$ of driving force temperature.

References

- (1) Ren, W.; Yan, Y.; Zeng, L.; Shi, Z.; Gong, A.; Schaaf, P.; Wang, D.; Zhao, J.; Zou, B.; Yu, H.; Chen, G.; Brown, E. M. B.; Wu, A. *Adv. Healthcare Mater.* 2015, **4**, 1526-1536.