

## Supporting Information

### Enhanced and tunable photochromism of MoO<sub>3</sub>-butylamine organic-inorganic hybrid composites

Rongguo Wang,<sup>a</sup> Xiaolong Lu,<sup>a</sup> Lifeng Hao,<sup>a\*</sup> Weicheng Jiao,<sup>a</sup> Wenbo Liu,<sup>b</sup> Jian Zhang,<sup>a</sup> Feng Yuan,<sup>a</sup> and Fan Yang<sup>a\*</sup>

<sup>a</sup> Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin, 150080, China. Fax: +86-0451-86402399; Tel: +86-0451-86402399; \*E-mail: [hlf@hit.edu.cn](mailto:hlf@hit.edu.cn), [yangfan01@163.com](mailto:yangfan01@163.com)

<sup>b</sup> School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China.

#### 1. SEM images of commercial MoO<sub>3</sub> powder

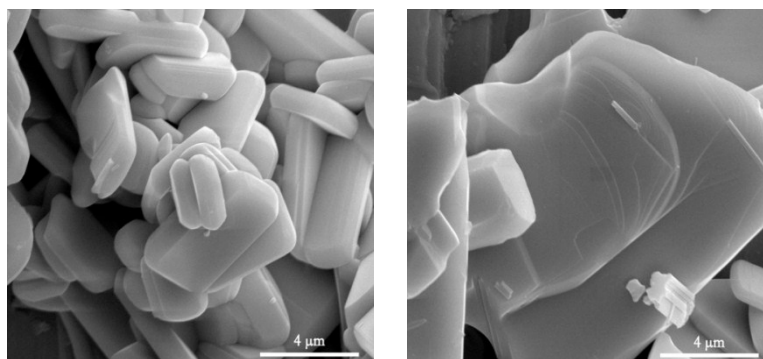


Fig. S1 Scanning electron microscope images of commercial MoO<sub>3</sub> powder showing typical layered structures.

#### 2. XRD pattern of 1:10 products

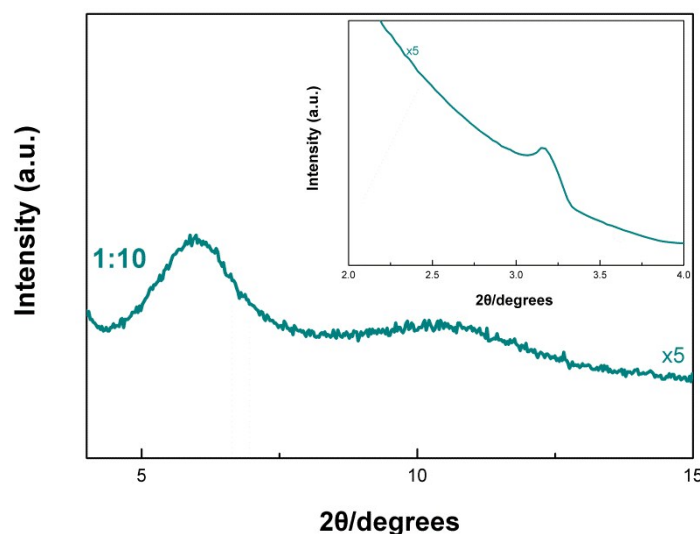


Fig. S2 XRD pattern of the MoO<sub>3</sub>-amine hybrid composites obtained under the molar ratio of 1:10.

#### 3. Photochromism of pure MoO<sub>3</sub>

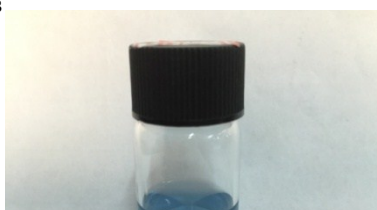


Fig. S3 The blue solution of pure  $\alpha$ -MoO<sub>3</sub> in water/ethanol (50% ethanol) obtained after 4 h irradiation.

For the solution of pure  $\alpha$ -MoO<sub>3</sub>, it showed slow color response and the blue color obtained after irradiation cannot change to others after placing in ambient environment except bleaching by gradual oxidation.

#### 4. Silver mirror reaction

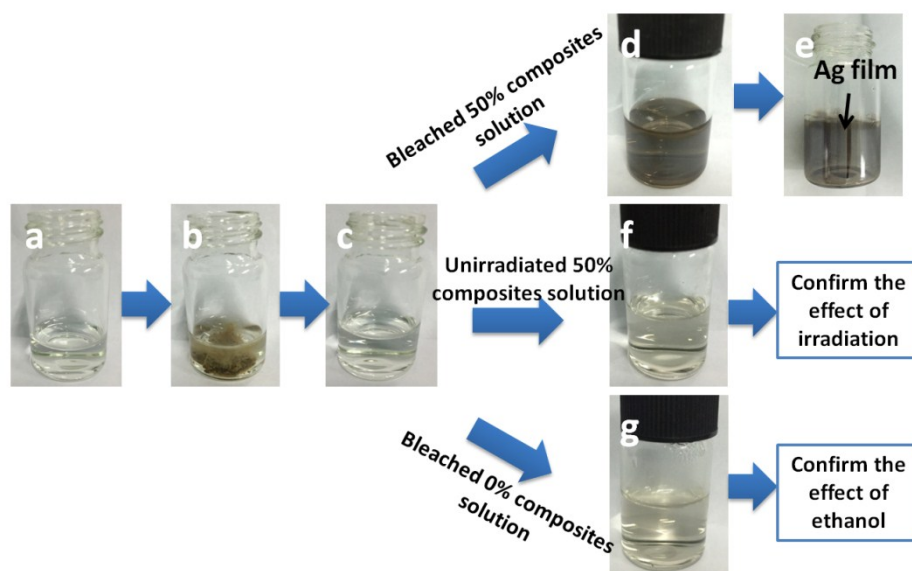
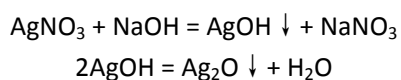


Fig. S4 Photographs showing the process of silver mirror reaction

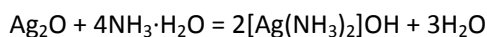
As we speculated that, reaction between the solvent ethanol and photoexcited holes was the reason behind the tunability of photochromism of hybrids' solution. If so, ethanol would be oxidized to acetaldehyde due to the strong oxidative capability of holes. Proving the existence of acetaldehyde should confirm the hole scavenger effect of ethanol. As silver mirror reaction is commonly accepted as a simple and efficient method to examine the existence of aldehydes. Here, it's adopted to confirm the existence of acetaldehyde. The reaction process is described as follows.

2 ml silver nitrate (AgNO<sub>3</sub>) solution (2 wt%) was added into a clean vial (Fig. a). Then two drops of sodium hydroxide (NaOH) solution (10 wt%) was added into the vial (Fig. b). Brown sediment of silver oxide (Ag<sub>2</sub>O) could be obtained through these two reactions:

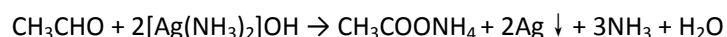


Afterwards, dilute ammonia water (NH<sub>3</sub>·H<sub>2</sub>O) solution (2 wt%) was dropwise added into the vial

with mild shaking till the sediment just redissolved (Fig. c). Silver ammonia solution was obtained through the reaction:



After that, 2 ml of bleached  $\text{MoO}_3$ -amine composites solution (50% ethanol volume content, irradiated for 3 h before bleaching) was injected into the vial. Finally, after shaking, the vial was placed in water bath of  $80^\circ\text{C}$ . Not for a long time, the mixture became dark brown (Fig. d). After 10 min, the vial was taken out and the solution was poured out. Bright silver film mixed with dark components could be seen on the wall of the vial (Fig. e). The dark components were also silver particles with strong scattering effect. The reaction could be described as follows:



This result proved the existence of acetaldehyde.

In the meantime, contrast experiments were also conducted. Adding unirradiated  $\text{MoO}_3$ -amine composites solution (50% ethanol) to the silver ammonia solution, there was no bright silver film formed although the solution slightly turned to yellow color (Fig. f). This result confirmed the effect of UV irradiation. Adding bleached pure water solution of  $\text{MoO}_3$ -amine composites of 3 h irradiation to the silver ammonia solution, there was also no bright silver film (Fig. g) which demonstrated the effect of ethanol.

From above results, we could draw this conclusion that reaction between ethanol and photoexcited holes would contribute to the tunable photochromism of  $\text{MoO}_3$ -amine composites.

## 5. Time –dependent absorption spectra

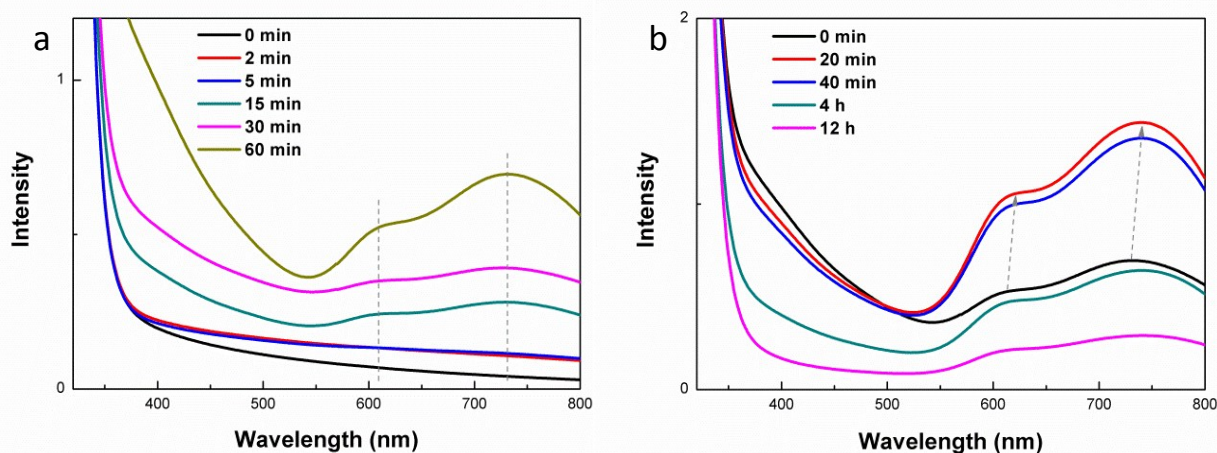
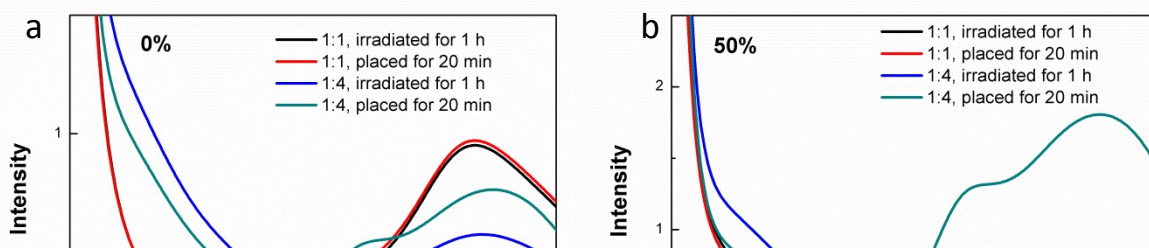


Fig. S5 UV-vis absorption spectra of the solution with 50% ethanol volume obtained after different irradiation time (a) and after removal of 1 h irradiation (b).

Noticeably, the solution showed obvious discoloration after irradiation for 15 min indicating fast response upon photo excitation. In fact, the actual response time was less than 15 min since the solution was taken out for spectra test during different time irradiation.

## 6. Comparison of the photochromism of 1:1 and 1:4 composites' solutions



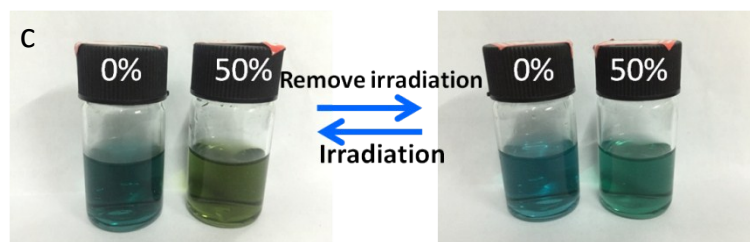


Fig. S6 Comparison of the UV-vis absorption spectra of hybrids' solutions obtained under different molar ratio with the ethanol volume percent of 0% (a) and 50% (b); (c) photographs of 1:1 hybrids' solutions.

Noticeably, UV-vis absorption spectra of the 1:4 solutions here are same to those in Fig. 4 in the main paper. Comparing with the UV-vis absorption spectra of hybrids' solutions obtained under molar ratio of 1:4, the absorption of 1:1 solutions in violet-blue light region are weaker. This is probably due to the small content of amine leading to weak synergy between inorganic and organic moieties. While the absorption of 1:1 solution with 0% ethanol percent in yellow-red light region is slightly stronger than that of 1:4 solution due to a higher content of molybdenum oxide under same concentration. Besides those differences, similarly, there is also a reversible transformation for 1:1 hybrids' solutions after switching irradiation which is especially apparent for the 50% solution. Simultaneously, reversibility is also seen between the colored and the bleached states.

## 7. Color change of heated solutions

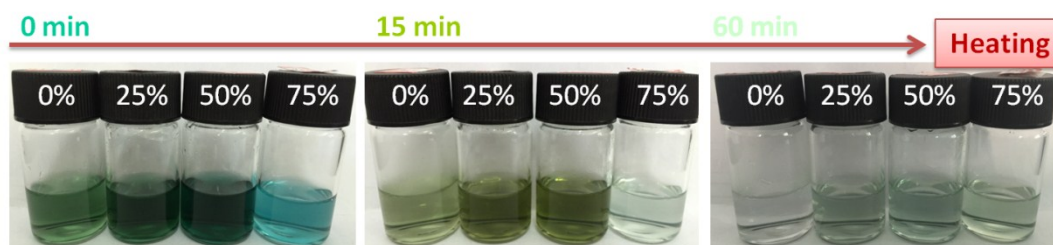


Fig. S7 Photographs of the heated solutions