

Supporting Information

**Mosaic structure effect and superior catalytic
performance of AgBr/Ag₂MoO₄ composite materials**

Jing-Yu Zhang, Yi Lu, Jin-Ku Liu*, Hao Jiang□

Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, School of Chemistry
and Molecular Engineering, East China University of Science and Technology, Shanghai 200237

P.R. China

* Corresponding author; E-mail address: jkliu@ecust.edu.cn

Characterizations

The structures of Ag_2MoO_4 and $\text{AgBr-Ag}_2\text{MoO}_4$ composite materials (CMs) were characterized by X-ray powder diffraction (XRD) ($\text{Cu } K\alpha$ radiation) using a Shimadzu XD-3A diffractometer. The microstructures and morphologies were analyzed by scanning electron microscopy (SEM, Philips S-4800). Philips S-4800 energy dispersive spectroscopy (EDS) was measured to study the surface composition. The optical properties of the products were studied by the Fourier conversion infrared spectroscopy (FT-IR). The UV-Vis spectroscopy (Shimadzu, UV-2450) was measured to explore the absorption properties of products. The surface composition of product was researched by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK II). The special surface area (BET) was determined by isothermal nitrogen adsorption-desorption analysis (Micromeritics ASAP 2400).

S1. Morphologies and composition of $\text{AgX-Ag}_2\text{MoO}_4$ ($\text{X} = \text{Cl, Br, I}$) catalysts

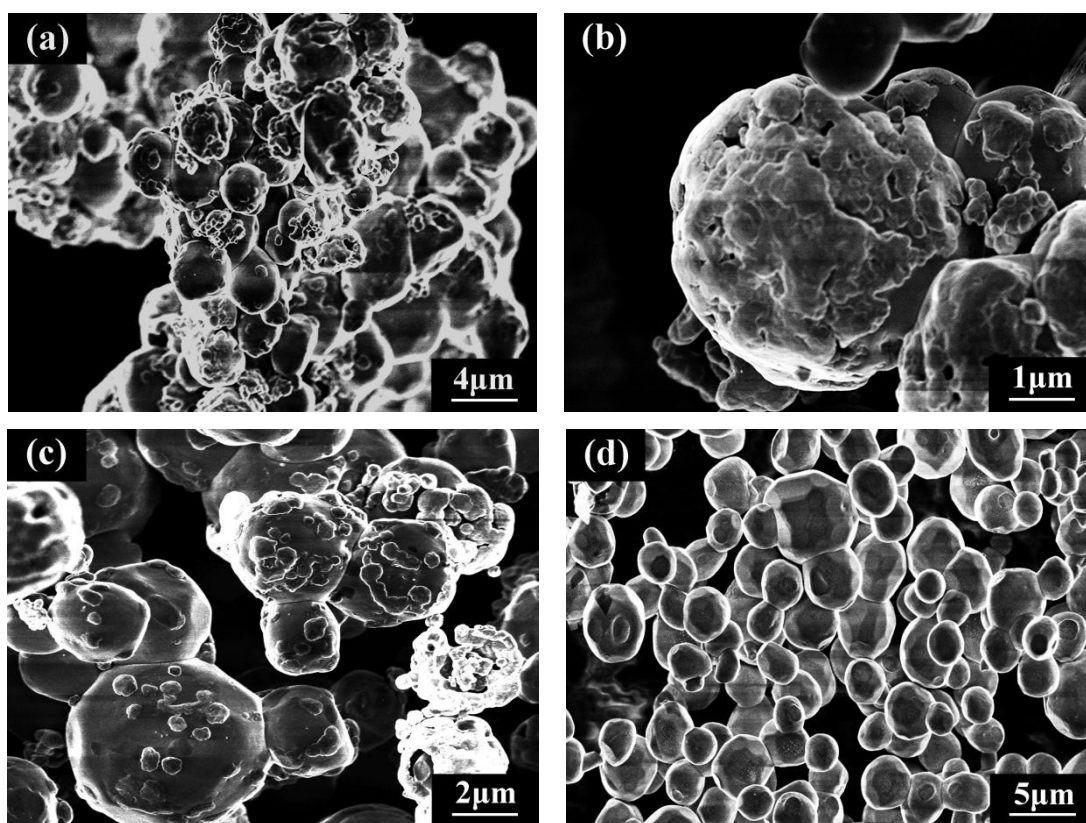


Figure S1. The SEM patterns of (a) AgCl-Ag₂MoO₄; (b) AgBr-Ag₂MoO₄; (c) AgI-Ag₂MoO₄; (d) Ag₂MoO₄ (6h)

S2. The TEM images of the samples melting process

We have tried the TEM test. Unfortunately, the sample could not suffer the thermal radiation from electron beam. When the electron beam focus on the sample, the extreme heat would melt the sample and damage it instantly. Therefore we could not get the clear TEM images which had the details of the sample. The failing TEM images were showed in Figure S2.

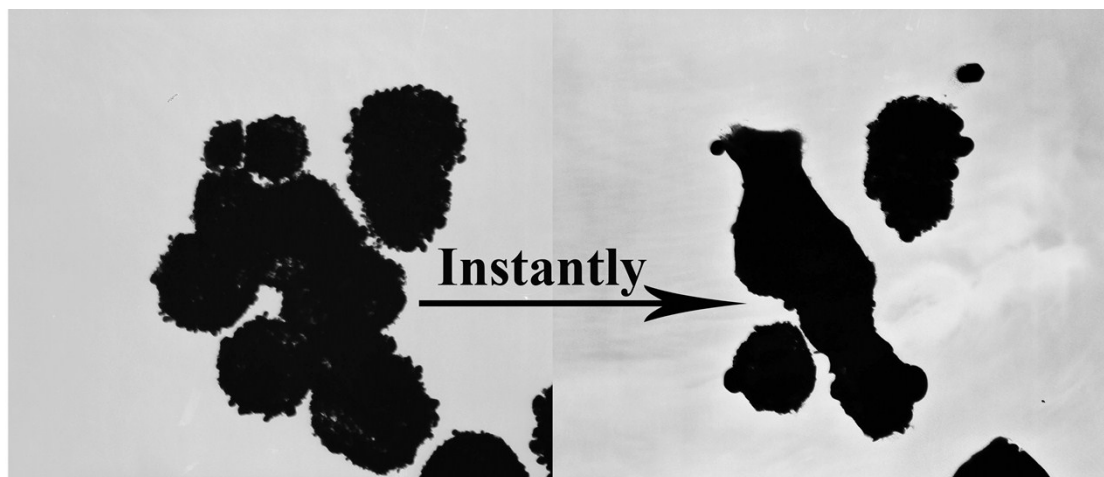


Figure S2. The TEM images of the samples melting process.

S3. Optical properties of AgX-Ag₂MoO₄ (X = Cl, Br, I) catalysts

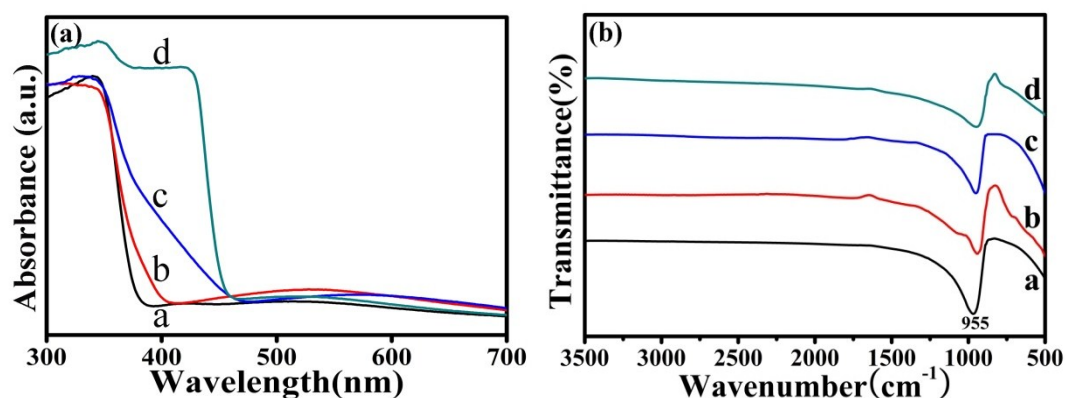


Figure S3. (a) UV-Vis absorption spectra and (b) FT-IR spectra of different catalyst: a

Ag₂MoO₄; b AgCl-Ag₂MoO₄; c AgBr-Ag₂MoO₄; d AgI-Ag₂MoO₄

UV-visible absorption spectra were shown in Figure S3(a), which presented AgX-Ag₂MoO₄ CMs absorption and pure Ag₂MoO₄ absorption spectrum at the same coordinate axis. It indicated that pure Ag₂MoO₄ had no absorption in the visible region, whereas the AgX-Ag₂MoO₄ CMs had a significantly performance in visible-light absorption. When Ag₂MoO₄ was composited with AgCl, the absorption in the visible area enhanced with a certain degree, but not dramatically. When it came to AgBr, it was clear that the absorption in the visible region had been broaden to 450 nm. However, the AgI-Ag₂MoO₄ CMs had a certain performance in the ultraviolet area. The results meant that more efficient absorption overlap with the solar spectrum after compositing AgX with Ag₂MoO₄. The FT-IR spectra of the pure Ag₂MoO₄ and AgX-Ag₂MoO₄ CMs were presented in Figure S3(b). The characteristic peak at 955 cm⁻¹ was assigned to the stretching vibration of O-Mo-O.

S4. Adsorption equilibrium experiment of the catalysts

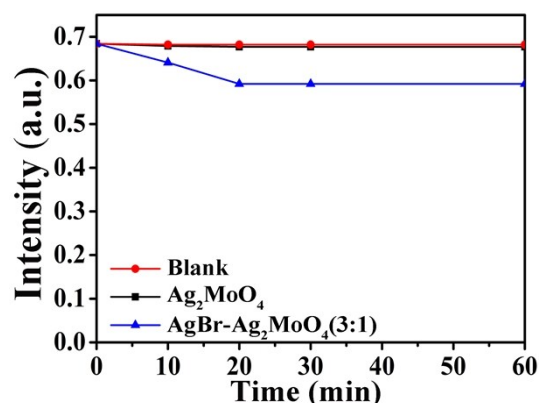


Figure S4. The adsorption capacity of obtained samples in dark environment

S5. Photocatalytic performance of AgX-Ag₂MoO₄ (X = Cl, Br, I) catalysts on degrading Rh. B

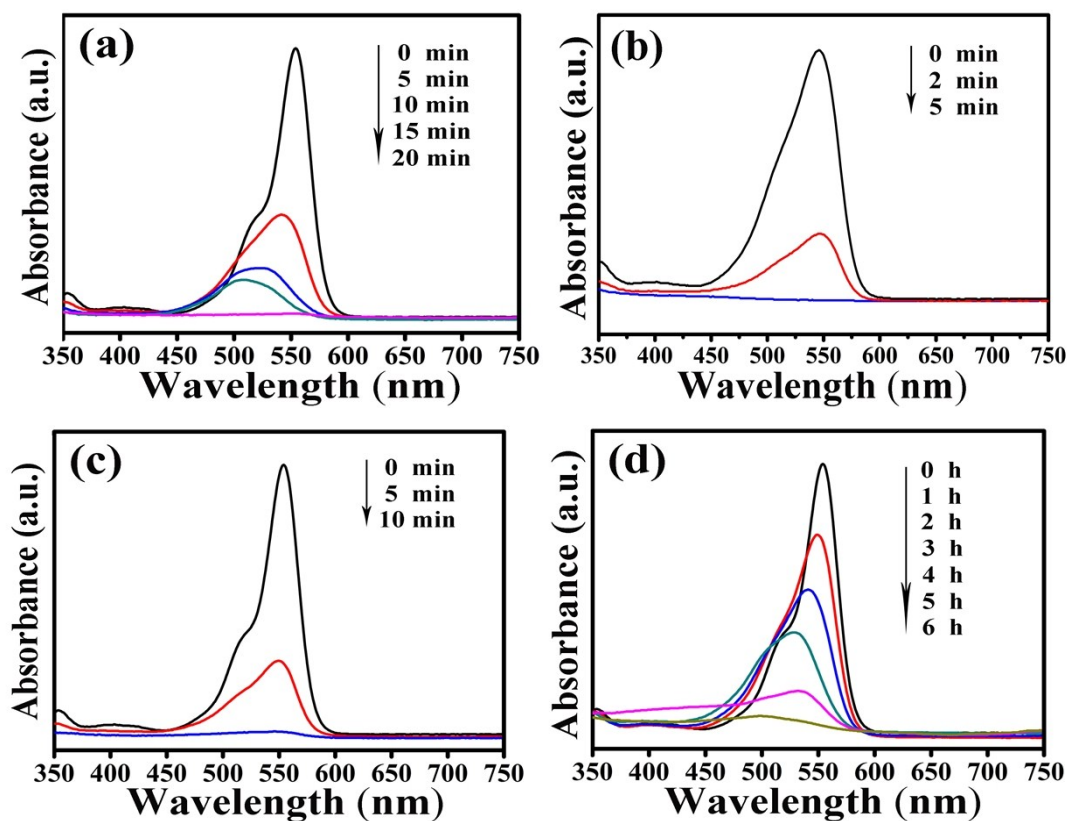


Figure S5. The photocatalytic degradation curves of AgX-Ag₂MoO₄ CMs and pure Ag₂MoO₄ to the Rh.B dyes under the irradiation of 500 W mercury lamp (a) AgCl-Ag₂MoO₄ (1:1); (b) AgBr-Ag₂MoO₄ (1:1); (c) AgI-Ag₂MoO₄ (1:1); (d) Ag₂MoO₄

S6. The cyclic degradation patterns of AgBr-Ag₂MoO₄ to the Rh.B dyes

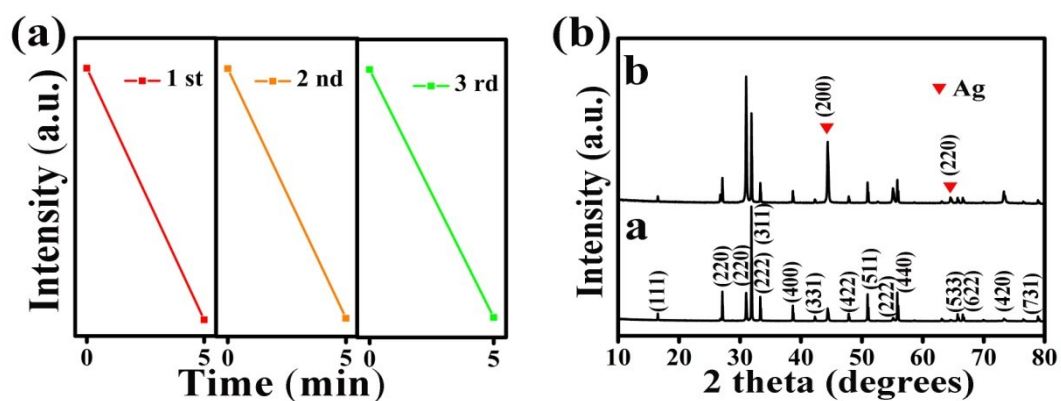


Figure S6. (a) The cyclic degradation patterns of AgBr-Ag₂MoO₄ to the Rh.B dyes under the irradiation of 500 W mercury lamp (b) The XRD patterns of the AgBr-Ag₂MoO₄: a fresh; b recycling process

The good performance ensured the application of AgBr-Ag₂MoO₄ CMs under UV irradiation. The standard of applied photocatalysts included not only the high photocatalytic activity but also the good photostability. Hence, the durability of AgBr-Ag₂MoO₄ CMs was studied and the recycle curves were shown in Figure S6a, where the declining efficiency of AgBr-Ag₂MoO₄ CMs reduced from 100 % (first run) to 92.7% (third run) under UV light within 5 min. The good stability of AgBr-Ag₂MoO₄ CMs under UV light was beneficial to the application in treating wastewater. The possible reason for the decrease of photocatalytic performance was about the losses in the process of operation. After recycling 3 times, the catalyst samples were analyzed by XRD. The diffraction peaks of 44 and 64 degree corresponded to the (200), and (220) crystal face which matched with the Ag cubic crystal system. The result indicated that negligible amounts of Ag element were generated under the strong UV light irradiation. However, these little Ag⁰ have precisely contributed to the photocatalytic reaction. Therefore, the AgBr-Ag₂MoO₄ CMs, as novel catalysts, had good stability and great potential in practical application.

S7. Photocatalytic performance of AgBr-Ag₂MoO₄ (X = Cl, Br, I) catalysts on degrading phenol

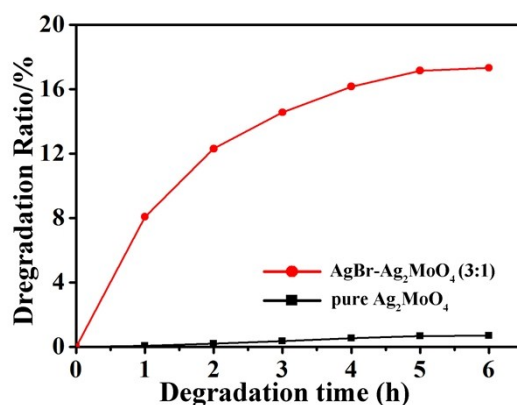


Figure S7. Degradation of phenol by AgBr-Ag₂MoO₄ CMs and the pure Ag₂MoO₄

To further demonstrate the photocatalytic degradation ability of AgBr-Ag₂MoO₄ CMs for colorless organic pollutants like phenol, photoreactions were carried out under UV light. The 0.05 g 3AgBr-Ag₂MoO₄ (the molar ratio was 3:1) CMs and pure Ag₂MoO₄ were added into the phenol solution (100 mg/L) respectively. Figure S7 showed that it was hard for the 3AgBr-Ag₂MoO₄ CMs and the pure Ag₂MoO₄ to degrade the phenol completely within 6 h. However, it is worth pointing out that the photocatalytic activity of 3AgBr-Ag₂MoO₄ CMs was still higher than pure Ag₂MoO₄ under the same condition. It was found that 17.32 % of phenol was decomposed within 6 h by 3AgBr-Ag₂MoO₄ CMs comparing 0.7 % in the case of pure Ag₂MoO₄. The results indicated that the AgBr-Ag₂MoO₄ catalyst could selectively degrade the organics.

S8. Mechanism of degradation of Rh. B under visible light

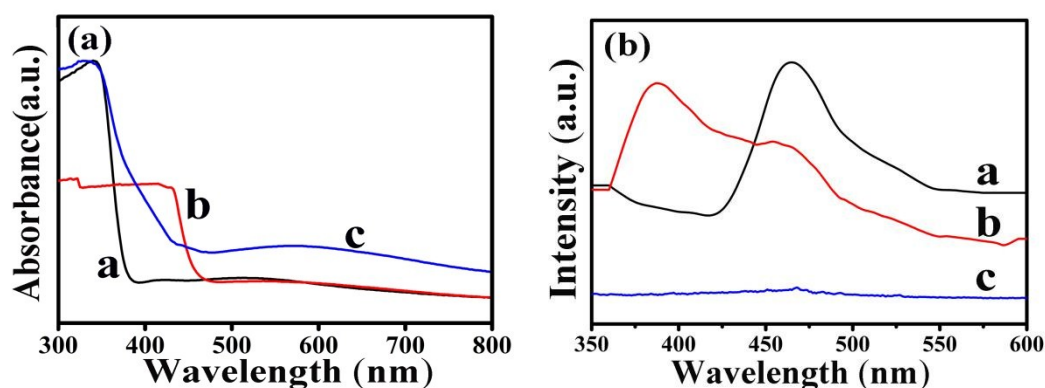


Figure S8. (a) UV-Vis absorption spectra and (b) the fluorescence spectra of a Ag₂MoO₄; b AgBr; c AgBr-Ag₂MoO₄

The properties of AgBr, Ag₂MoO₄, and AgBr-Ag₂MoO₄ CMs were characterized by UV-Vis absorption spectra and fluorescence spectra in order to

explore the reason why AgBr-Ag₂MoO₄ CMs performed outstanding photocatalytic activity. AgBr, Ag₂MoO₄ and AgBr-Ag₂MoO₄ CMs had strong absorption in the ultraviolet region, while the absorption spectra of AgBr and AgBr-Ag₂MoO₄ CMs were wider than Ag₂MoO₄ (Figure S8). Therefore, Ag₂MoO₄ had relatively poor photocatalytic efficiency. The ultraviolet absorption intensity of AgBr was obviously weaker than AgBr-Ag₂MoO₄ CMs. Also, the photoresponse performance of AgBr-Ag₂MoO₄ CMs was the best among these three materials in visible region. There was another distinct absorption peak located at the range of 470-600 nm which due to the surface plasmon resonance (SPR) absorption peak of the metal Ag. The conclusion was that the composite material had better light adsorption ability than monomer material.

Figure S8(b) was photoluminescence spectra of the above materials at an excitation wavelength of 320 nm under the room temperature. Mutual recombination of electrons and holes would release energy in the fluorescence spectra. So the lower fluorescence intensity of electrons and holes illustrated the lower recombination rate. On account of the fact that the photocatalytic properties and the effective separation of electrons and holes had a close relationship, the lower fluorescence intensity of material led to the better photocatalytic performance. The fluorescence intensity of AgBr and Ag₂MoO₄ was stronger than AgBr-Ag₂MoO₄ CMs. The heterostructure complex of AgBr and Ag₂MoO₄ can promote separation of electrons and holes to a great extent, which helped to improve the efficiency of photocatalysis.