

# **Polyoxometalate-based Framework as Chemical Nanoreactors: In Situ Synthesis of Active Silver Nanoparticles in Confined Spaces**

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# S1 Materials

All the chemicals, whether reagents or solvents, were purchased from suppliers and used as received without further purification. Molybdenum trioxide ( $\text{MoO}_3$ , 99.5%) was purchased from Aladdin. Benzoic acid ( $\text{C}_7\text{H}_6\text{O}_2$ ) was purchased from Energy Chemical. Sodium hydroxide ( $\text{NaOH}$ , AR), Nitric acid ( $\text{HNO}_3$ , AR), Silver nitrate ( $\text{AgNO}_3$ , AR), and N, N dimethylformamide ( $\text{C}_3\text{H}_7\text{NO}$ , AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

# S2 General Experimental Section

## Powder X-ray Diffraction (PXRD)

Powder XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer with ( $\lambda$  ( $\text{CuK}\alpha$ ) = 1.5405 Å) radiation in the  $2\theta$  range of 2-50°.

## Fourier Transform Infrared Spectroscopy (FTIR)

FTIR Spectroscopy (KBr pellets) was obtained from a Nicolet NEXUS 670 spectrometer in the range of 400 and 4000  $\text{cm}^{-1}$ .

## Thermogravimetric Analyses (TGA)

Thermogravimetric Analyses were carried out under an  $\text{N}_2$  atmosphere on a TA Instruments STA499 F5 thermobalance at the rate of 10 °C/min heating from 20 °C to 800 °C.

## Elemental Analyses (EA)

H microanalysis was performed on a Perkin-Elmer 240C elemental analyzer, and ICP-OES analyses were carried out on a PerkinElmer Optima 8300 optical emission spectrometer.

## UV-Vis absorption spectra (UV)

The UV-vis spectra in aqueous solution were recorded on a UV5500PC spectrophotometer from 200 to 1200 nm using 1.000-cm-optical-path quartz cuvettes.

## **UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)**

Solid-state UV-Vis absorption spectra were acquired on a Carry 5000 spectrophotometer, in which the range of wavenumber was set at 200 to 800 nm.

## **Transmission electron microscopy (TEM)**

The transmission electron microscopy (TEM) and HRTEM images were carried out on a JEM-2100F microscope at an acceleration voltage of 200 kV.

## **X-ray photoelectron spectroscopy (XPS)**

An ESCALAB 250Xi (Thermo Fisher Scientific) was used for X-ray photoelectron spectroscopy (XPS) analysis, and monochromatic AlK $\alpha$  (1486.6eV) was used as the excitation source. Spectra were analyzed using Avantage software (version 4.1). The intensities were estimated from the integration of each peak, subtraction of the Smart background, and fitting of the experimental curve to a combination of Lorentzian and Gaussian lines of various proportions. All binding energies were referenced to the C1s line at 284.8eV.

## Single-crystal X-ray diffraction (SCXRD)

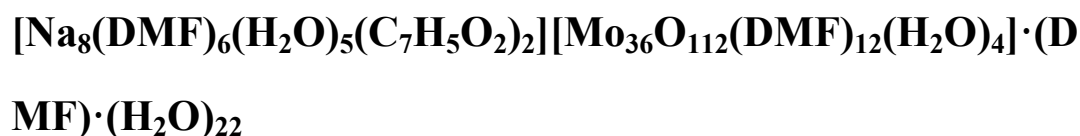
Single-crystal X-ray diffraction data collection of **2** was recorded on Bruker D8 VENTURE diffractometer equipped with a PHOTON 100 CMOS bidimensional detector and MoK $\alpha$  monochromatized radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K. The structure of the target compound was solved by intrinsic phasing methods and refined by full-matrix least squares using the SHELX-TL package<sup>1</sup>. All of the non-hydrogen atoms are dealt with anisotropic thermal parameters. Hydrogen atoms in water are not identified. Further details about the crystal structure determinations may be obtained free of charge via the Internet at <http://www.ccdc.cam.ac.uk/>. CCDC 2175263. Crystallographic data for single-crystal X-ray diffraction studies are summarized in Table S1.

# S3 Synthesis and Experimental Section

## Synthesis of 1

1 was synthesized by the method we reported in the literature.

## Synthesis of 2



The pH value of the aqueous solution of molybdenum trioxide (2.8788 g, 20 mmol) and sodium hydroxide (1.6 g, 40 mmol) dissolved in H<sub>2</sub>O (20 mL) was adjusted to 1.5 by adding nitric acid. Then 2 mL above solution was taken out into a 10 mL glass vial, and 1.5 mL DMF solution of benzoic acid (2 M) was added with vigorous stirring. And the clear solution was allowed to evaporate in an open vial at room temperature. After one day, colorless block crystal was obtained and collected by filtration and air-dried. Yield: 26.5 mg. Elemental analysis: Calc. (found): Mo, 44.69 (47.48); Na, 2.38 (2.5); C, 10.56 (8.24); N, 3.26 (2.98); H, 2.43 (2.35).

## Catalytic reduction of 4-NP

The reduction of 4-nitrophenol (4-NP) by NaBH<sub>4</sub> was chosen as a model reaction to test the catalytic activity of 1. To a mixture of 2.3 mg of NaBH<sub>4</sub> dispersed in 1 mL ice-cold distilled water, 1 mL of 0.12 × 10<sup>-3</sup> mol · L<sup>-1</sup> 4-NP was added. To this solution, a 30 μL catalyst was added. The whole process was monitored by UV- absorption spectra in the range of 250-800 nm.

## S4 Crystal data and structure refinement

**Table S1.** Crystal data and structure refinement for **2**.

|   |  |
|---|--|
| Empirical formula                           | C <sub>68</sub> H <sub>144</sub> Mo <sub>36</sub> N <sub>18</sub> Na <sub>8</sub> O <sub>155</sub> |
| Formula weight                              | 7331.76  |
| Temperature/K                               | 150.0  |
| Crystal system                              | triclinic  |
| Space group                                 | P-1  |
| a/Å   | 17.4290(10)  |
| b/Å   | 19.9091(11)  |
| c/Å   | 29.4525(15)  |
| α/°   | 83.166(2)  |
| β/°   | 86.588(2)  |
| γ/°   | 86.648(2)  |
| Volume/Å <sup>3</sup>                       | 10115.7(10)  |
| Z   | 2  |
| ρ <sub>calc</sub> /cm <sup>3</sup>          | 2.407  |
| μ/mm <sup>-1</sup>                          | 2.277  |
| F(000)                                      | 7036.0   |
| Crystal size/mm <sup>3</sup>                | 0.1 × 0.1 × 0.1  |
| Radiation                                   | MoKα (λ = 0.71073)   |
| 2θ range for data collection/°              | 4.322 to 58.784  |
| Index ranges                                | -24 ≤ h ≤ 23, -27 ≤ k ≤ 27, -37 ≤ l ≤ 40   |
| Reflections collected                       | 250338   |
| Independent reflections                     | 55210 [R <sub>int</sub> = 0.0630, R <sub>sigma</sub> = 0.0595]                                     |
| Data/restraints/parameters                  | 55210/71/2654  |
| Goodness-of-fit on F <sup>2</sup>           | 1.080  |
| Final R indexes [I ≥ 2σ (I)]                | R <sub>1</sub> = 0.0603, wR <sub>2</sub> = 0.1622  |
| Final R indexes [all data]                  | R <sub>1</sub> = 0.0834, wR <sub>2</sub> = 0.1808  |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 3.61/-2.32   |

## S5 Crystal structure of 2

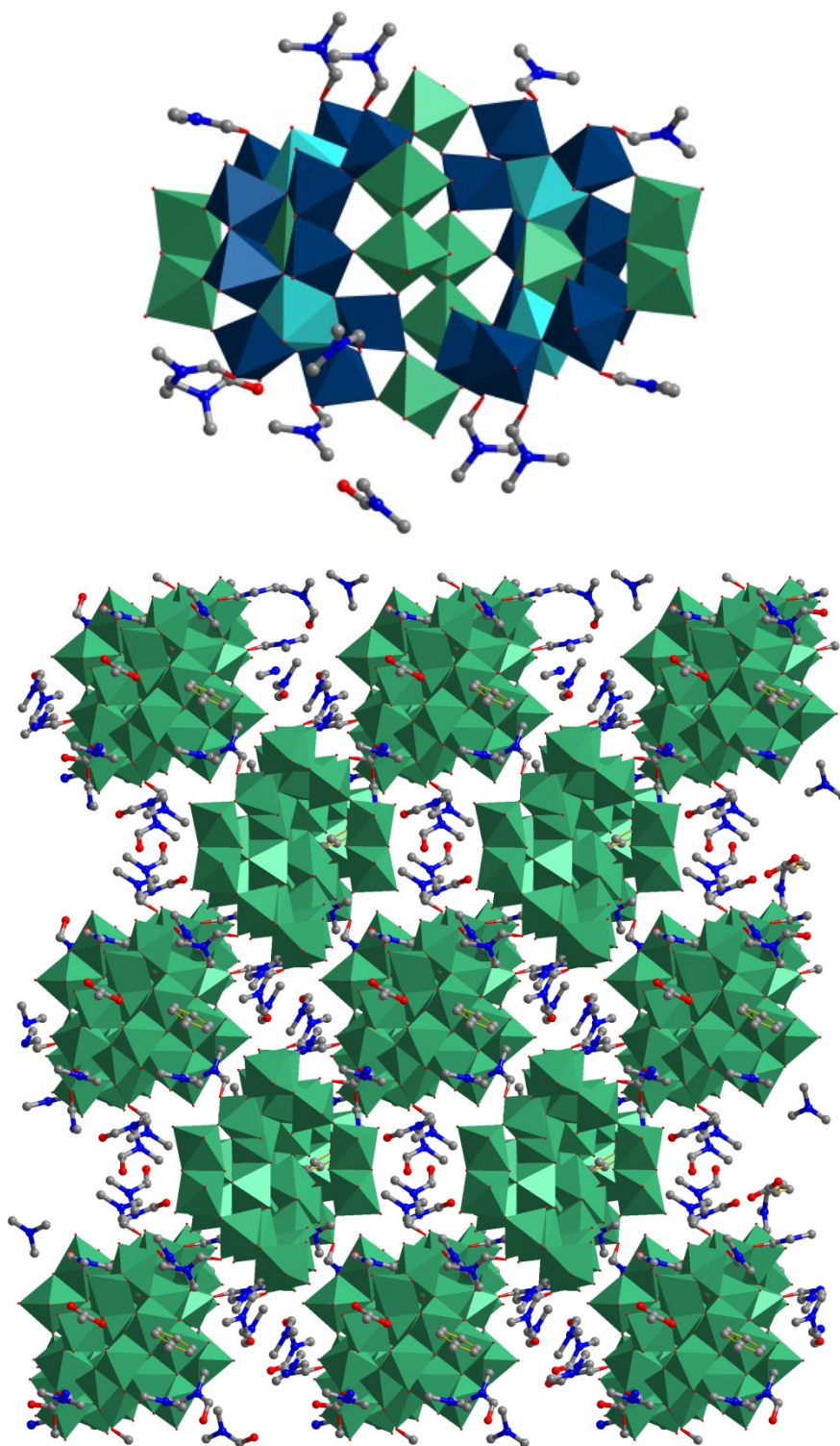


Fig. S1 Crystal structure of 2.



# S6 Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of 1-2 and their discolored samples are shown in Fig. S2-S4. One more signal that could feasibly be assigned is around  $3500\text{ cm}^{-1}$ , which is the characteristic of the O-H bonds of water molecules. Furthermore, there is an obvious peak around  $1680\text{ cm}^{-1}$ , which is assigned to the stretching of the O=C-N bonds of DMF. Features at  $1380$  and  $2900\text{ cm}^{-1}$ , are characteristic absorptions of the  $-\text{CH}_3$ . The characteristic absorption band in the range of  $900\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  belongs to the Mo-O bond of POM.

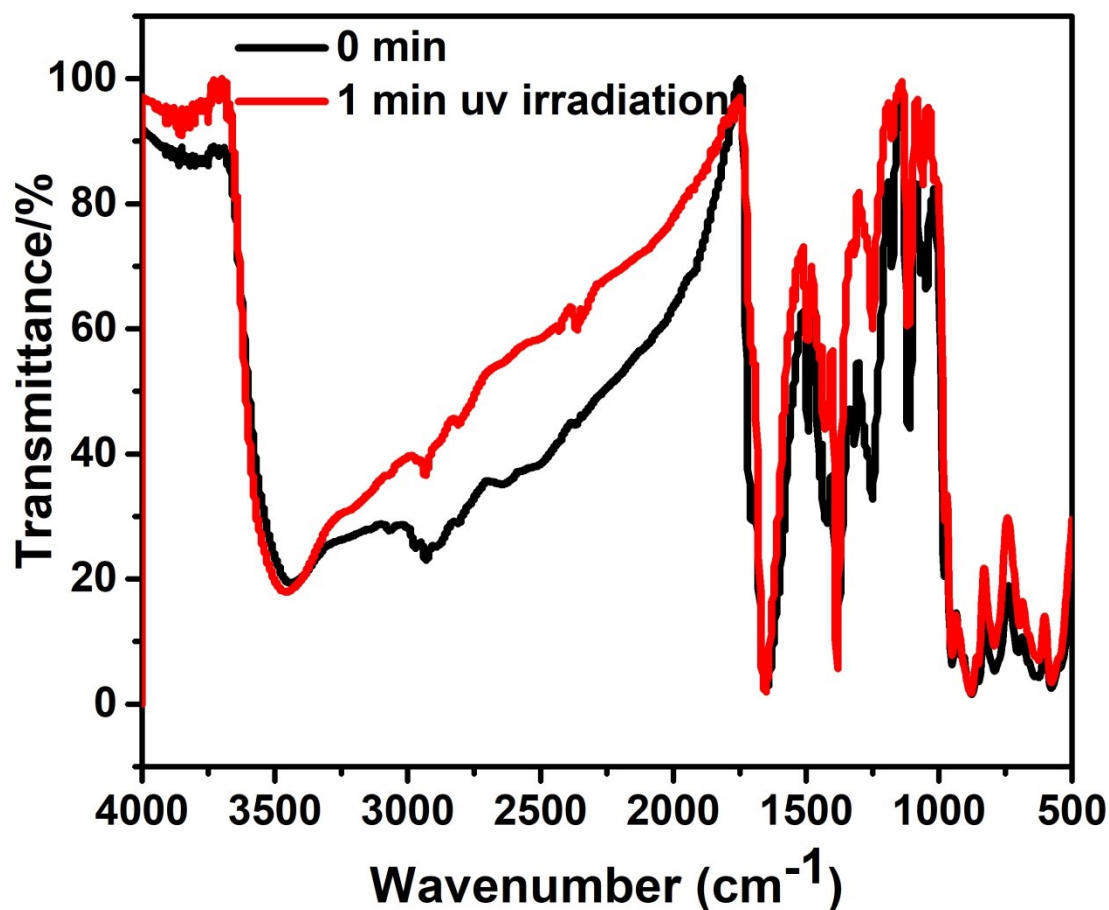


Fig. S2 FT-IR spectra of 1 (black) and 1 exposed to 365 nm UV light (red).

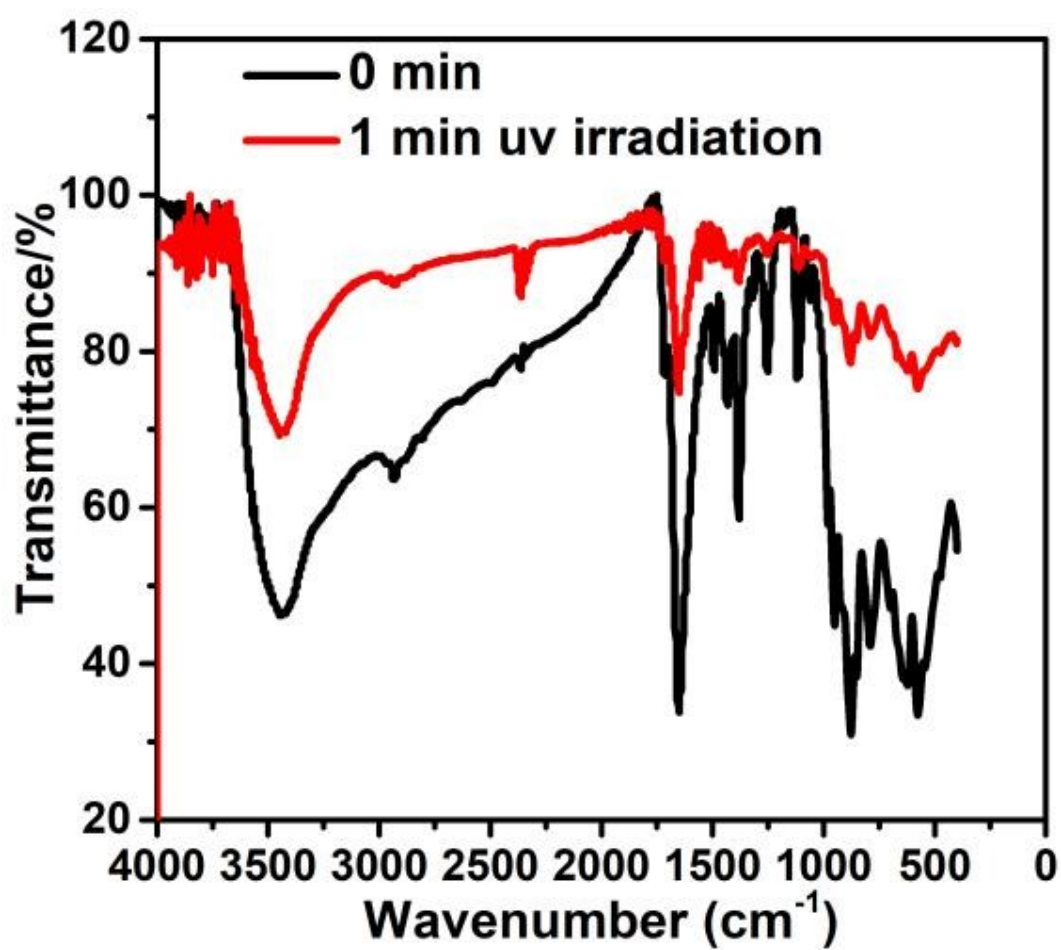
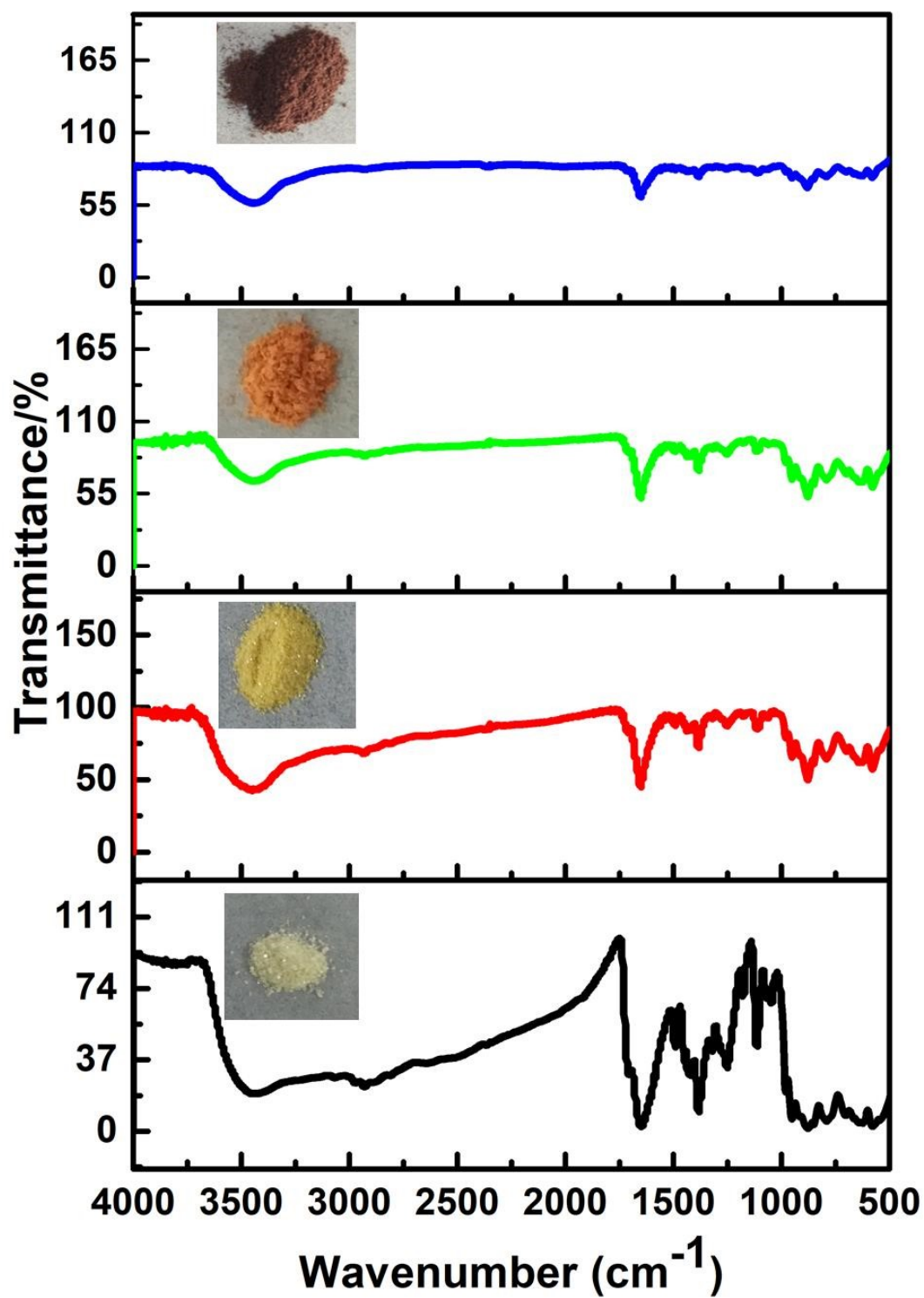


Fig. S3 FT-IR spectra of **2** (black) and **2** exposed to 365 nm UV light (red).



**Fig. S4** FT-IR spectra of **1** (black) and **1** placed at room temperature for different time (red, green, blue).

## S7 UV-Vis diffuse reflectance spectra

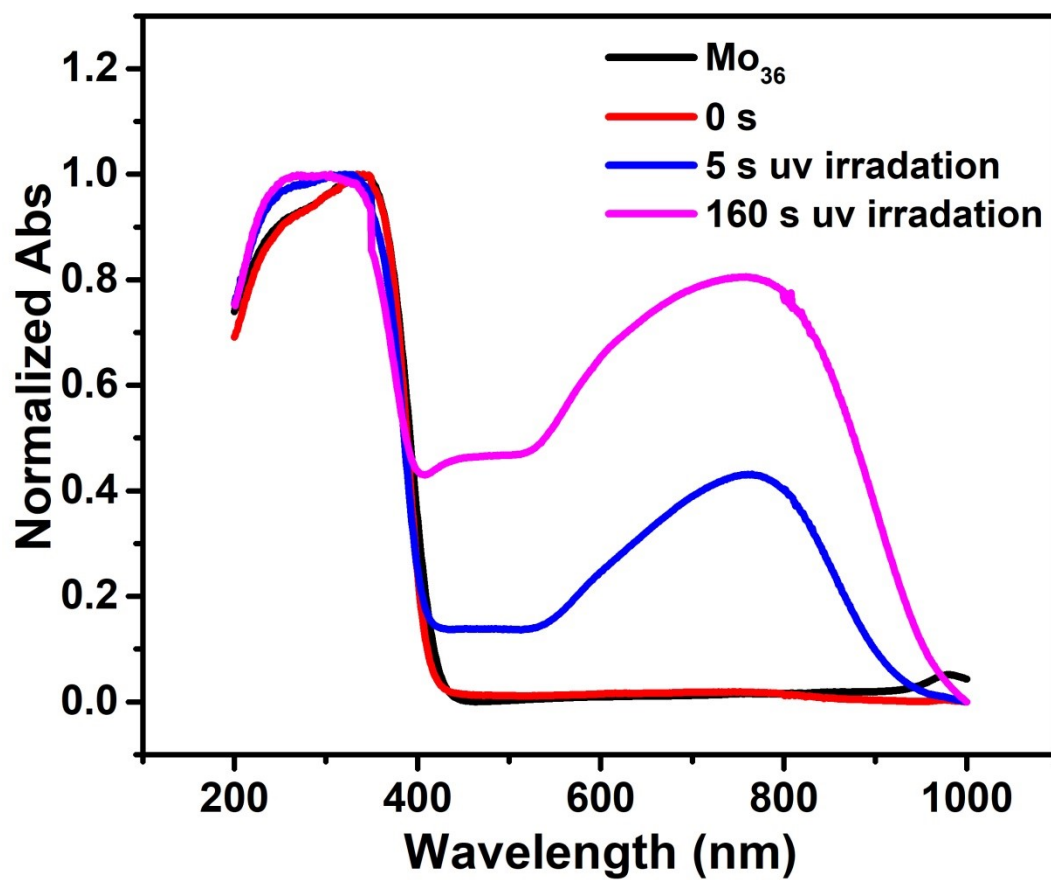


Fig. S5 The solid UV-vis diffuse reflectance spectra of {Mo<sub>36</sub>} (black), 2 (red), 2 under 365 nm UV irradiation for 5 s (blue) and 160 s (pink).

## S8 Thermogravimetric analyses (TGA)

Fig. S6 shows that the thermal decomposition process of **2** can be divided into three steps. The first step corresponds to the remove of lattice water molecules, the second step refers to coordinated water, and the third step means the decomposition of the structure of polyanion framework. The first weight loss of 6.16% in the 25-127 °C is based on the release of 22 lattice water molecules and one free N,N-Dimethylformamide (DMF) molecules. The weight loss of second step from 127-334 °C is 19.14 % (calcd. 23.48%), corresponding to eight coordinate water molecules, two benzoic acid and 18 DMF molecules.

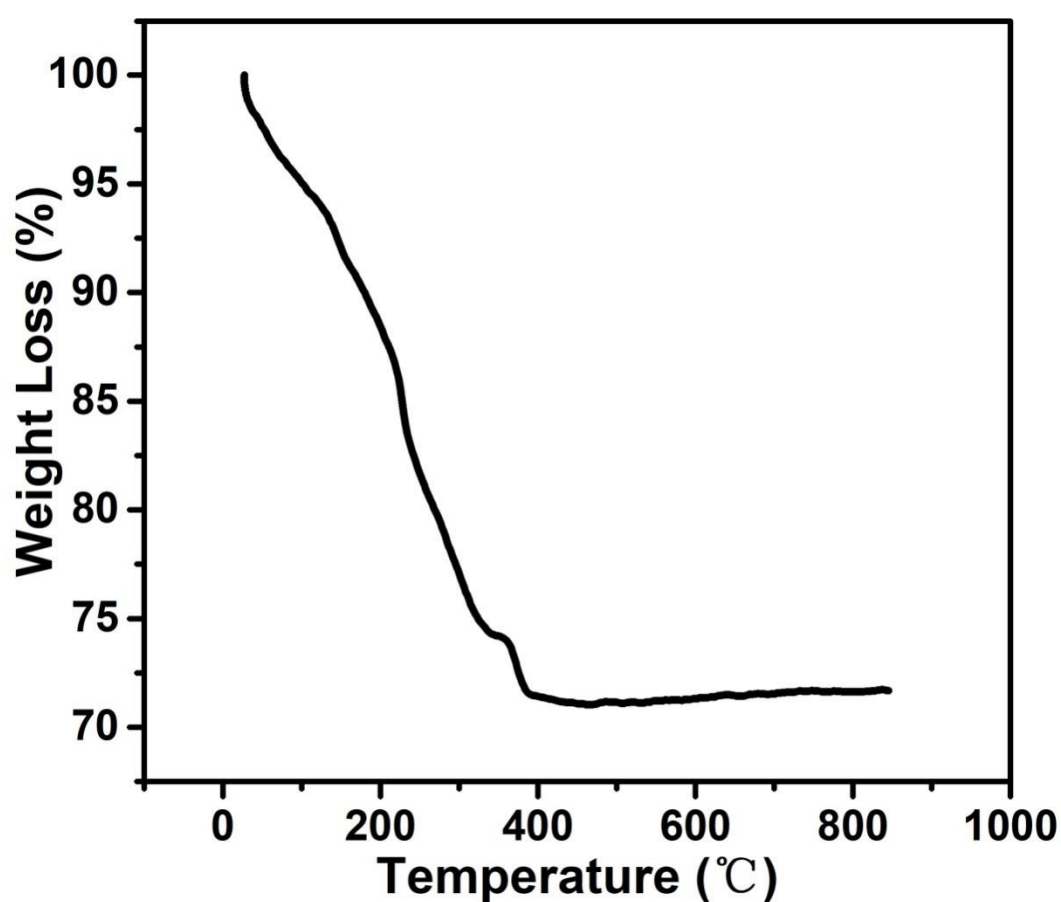
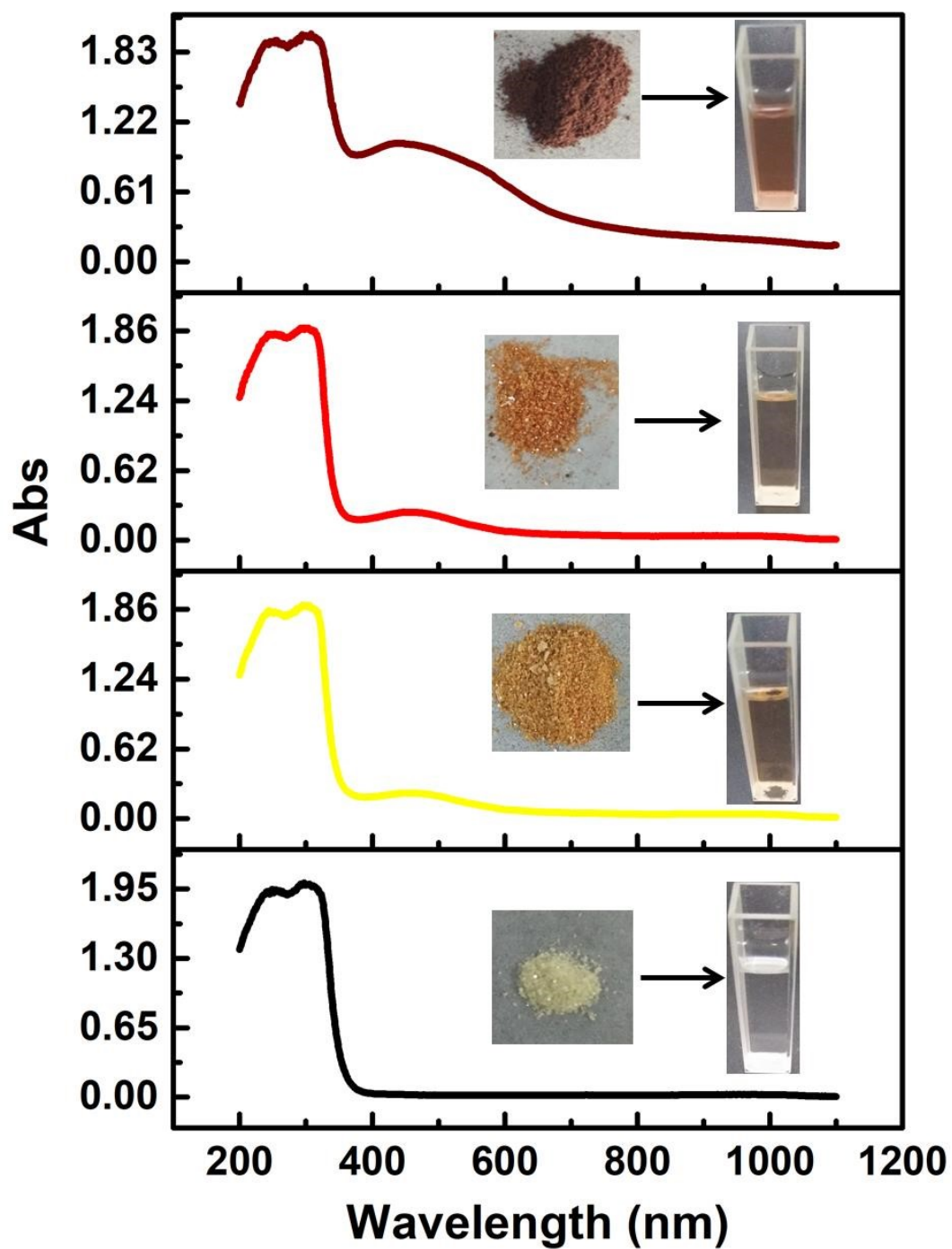


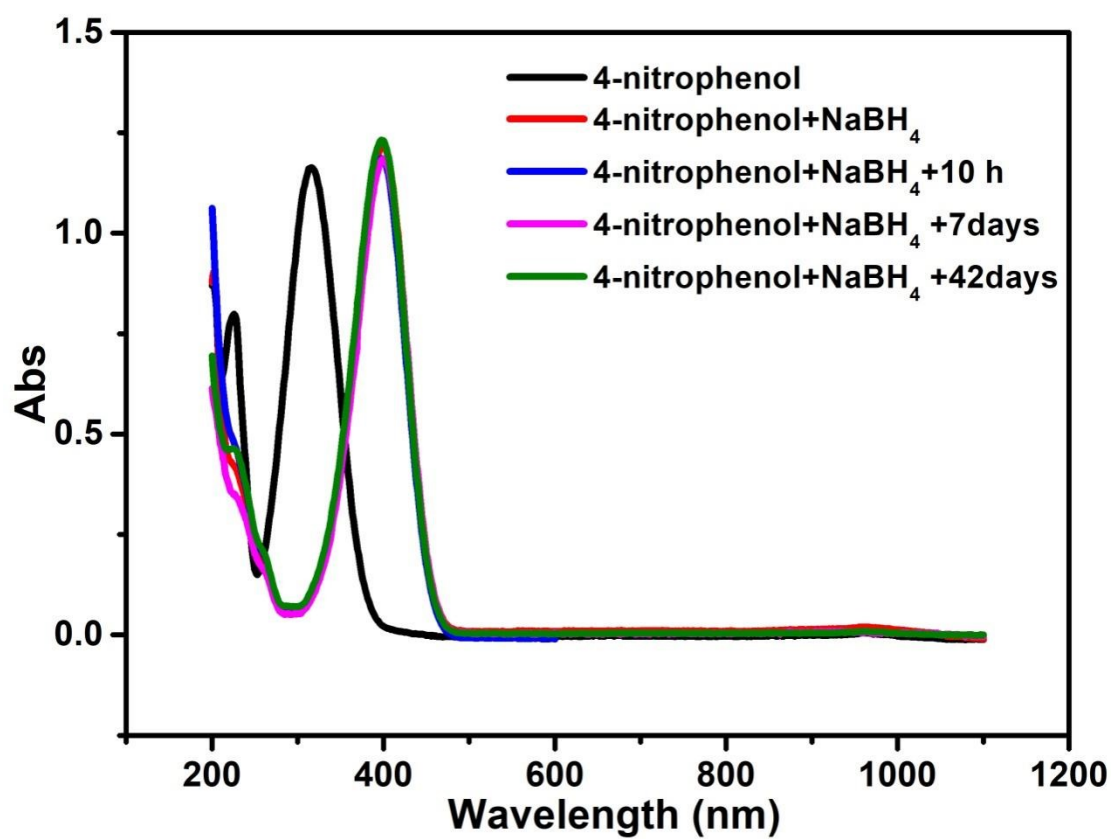
Fig. S6 The TGA curves of **2**.

## S9 UV-Vis absorption spectra



**Fig. S7** The liquid UV-vis spectra of **1** and **1** placed at room temperature for various time. Inset: discolored sample and its aqueous solution.

## S10 Catalytic performance



**Fig. S8** The UV/Vis characteristic peaks of freshly prepared 4-nitrophenol at 317 nm, and 4-nitrophenol and NaBH<sub>4</sub> at 400 nm at different times.

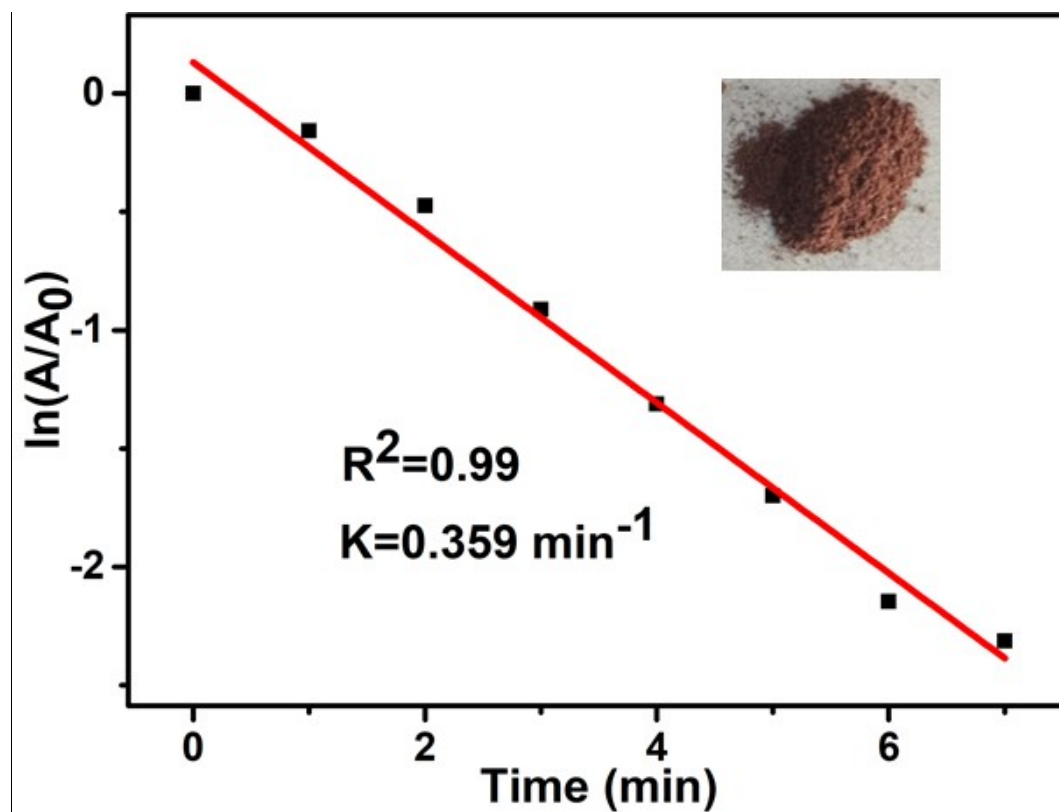


Fig. S9 the plots of the rate constant of the catalytic reduction of 4-NPh over 1 under dark for 12 months.

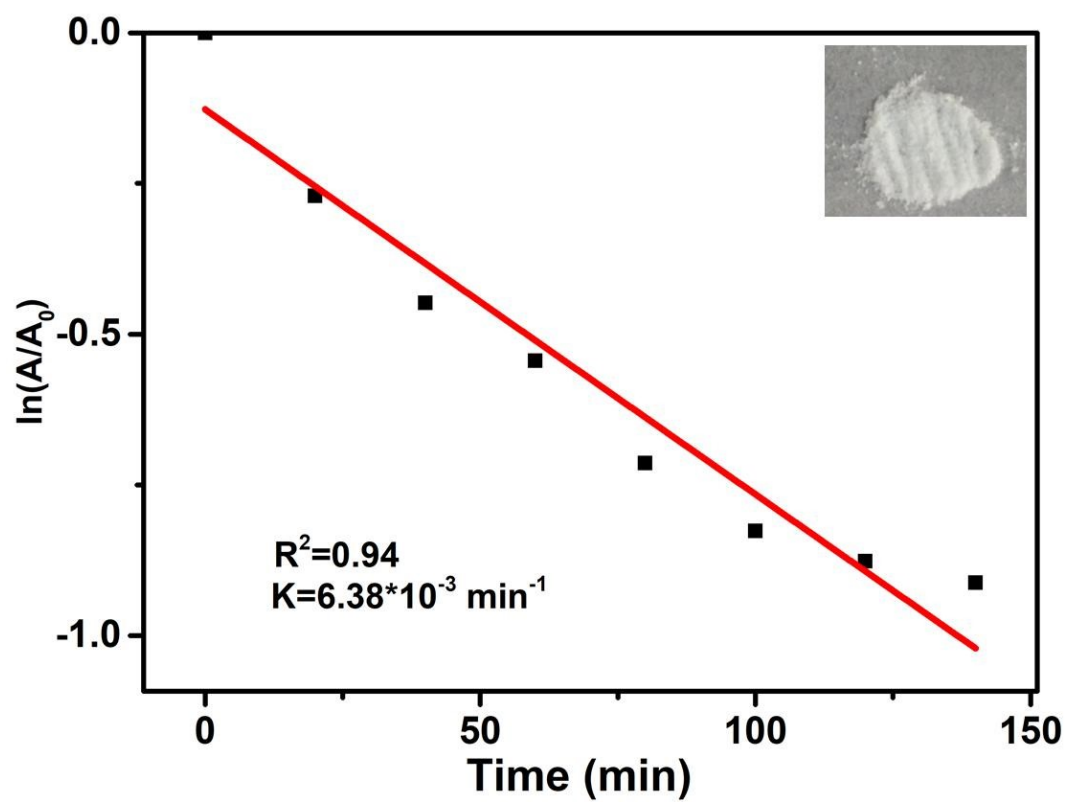


Fig. S10 the plots of the rate constant of the catalytic reduction of 2.



## S11 TEM image

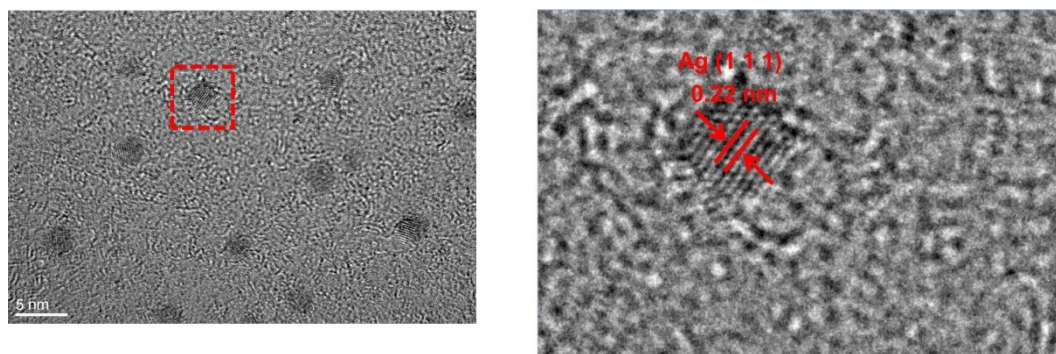


Fig. S11 high-resolution TEM image of **1** under dark for 12 months.

## S12 XPS

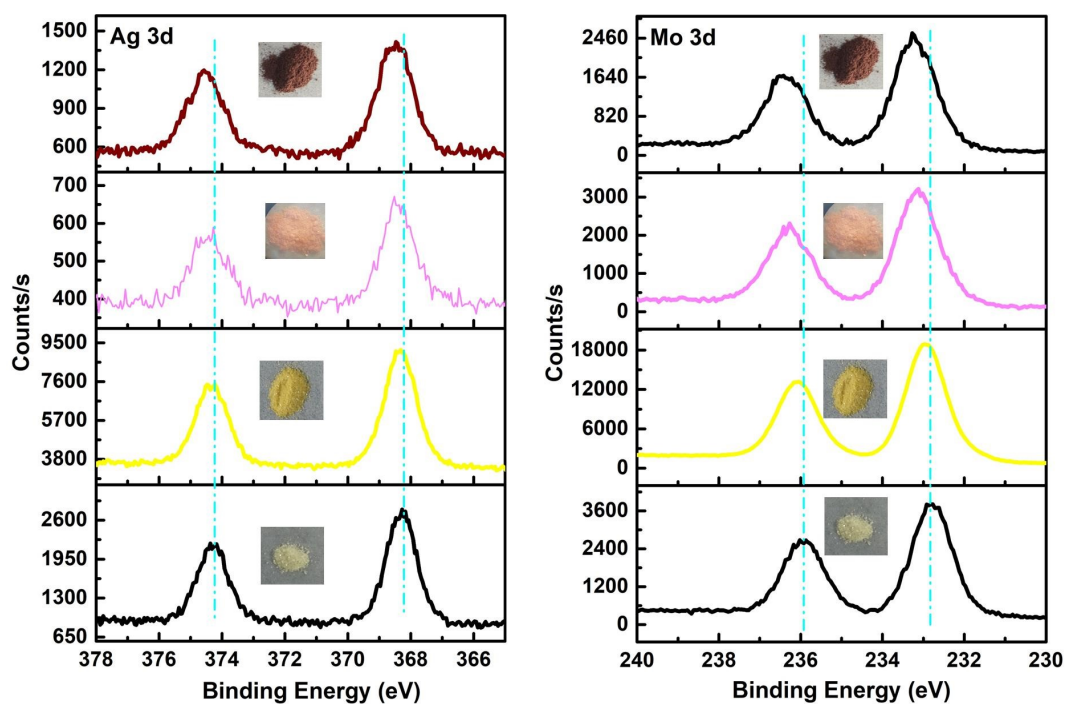


Fig. S12 High-resolution XPS of Ag 3d and Mo 3d.

The Ag high-resolution XPS spectrum of **1** at various state shift to higher energy, indicating the existence of  $\text{Ag}^0$  and the content of Ag NPs is increasing. The Mo high-resolution XPS spectrum of **1** at various state shift to higher energy. This observation supports the hypothesis that the polyoxometalate serves both as a passivation layer of Ag NPs.<sup>2-3</sup>

## S13 Reference

- 1 Sheldrick, G. M. *Acta Cryst. A* **2008**, 64, 112.
- 2 Keita, B.; Zhang, G.; Dolbecq, A.; Mialane, P.; Sécheresse, F.; Miserque, F.; Nadjio, L. *J. Phys. Chem. C* 2007, 111, 8145.
- 3 Klemperer, W. G.; Wall, C. G. *Chem. Rev.* 1998, 98, 297.