

Supporting Information

A distinctive red Ag/AgCl photocatalyst with efficient photocatalytic oxidative and reductive activity

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I. Experimental Details

A. Chemicals

Polyvinylpyrrolidone (PVP, K-30, $M_w = 40000$) were purchased from Sigma-Aldrich and were used without further purification. $AgNO_3$, NaCl, glycerol and were obtained from Beijing Chemical Factory (Beijing, China) and used as received. All aqueous solutions were prepared using deionized water with a resistivity of $18.2\text{ M}\Omega\text{ cm}$, and all glassware used in the following steps were cleaned by freshly prepared 3 : 1 HCl : HNO_3 (*aqua regia*) and rinsed thoroughly by water prior to use.

B. Sample characterization

Scanning electron microscope (SEM) images were performed on FE-SEM (Philips XL30 ESEM-FEG integrated with a EDAX system) at an accelerating voltage of 10.0 kV. We performed gold-spraying on the surfaces of the samples before the SEM characterizations in order to protect the uniform morphologies from decomposition under the high-energy electron beam. X-Ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB MKII X-ray photoelectron spectrometer using monochromated Al $K\alpha$ X-rays. The X-ray diffraction (XRD) measurements were performed on a D8 Focus diffractometer (Bruker) with Cu $K\alpha$ radiation ($\lambda = 0.15405\text{ nm}$). Ultraviolet visible (UV-Vis) absorption and UV-Vis diffuse reflectance spectra (using $BaSO_4$ as the reference) were recorded using a Hitachi U-3900 spectrometer. The bandgaps were calculated by equation of $\alpha h\nu = A(h\nu - E_g)^{n/2}$, in which α , ν , A , and E_g , respectively, signify the absorption coefficient, light frequency, proportionality constant, and bandgap, and n equals 1 or 4, depending on whether the electron transition is direct or indirect, respectively. The HPLC analysis was carried by eluting with methanol (63%) and phosphate buffer solution (37%) and the detector wavelength set at 449

nm. The nitrogen adsorption-desorption measurements were carried out on a Quantachrome Autosorb-1 and the bath temperature was 77.3K.

C. Calculation of lattice parameter

The lattice parameters (α) were calculated based on the XRD results. Specifically, it is calculated in terms of the strongest Bragg peaks, (200), using the formula (1),

$$\alpha = d_{h,k,l} \sqrt{h^2 + k^2 + l^2} \quad (1)$$

in which α is the lattice constant, d is the lattice spacing, and (h, k, l) are the miller indices.

D. The photoreduction of CO₂ into methanol and ethanol

The home-made reactor for photoreduction of CO₂ is illustrated in Fig. S1.

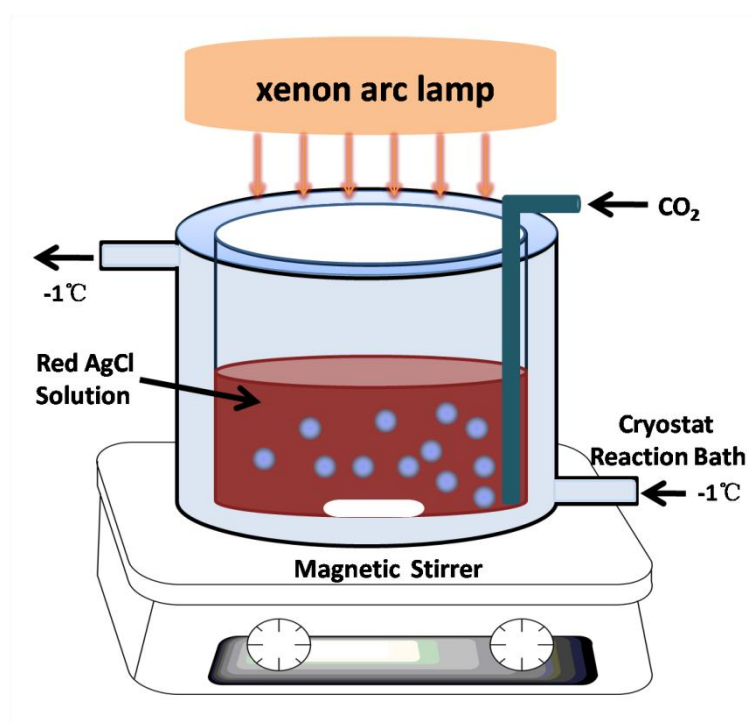


Fig. S1 Schematic diagram of the home-made photocatalytic reduction system.

E. The calculation of apparent quantum efficiency

The CO₂ photoreduction undergoes two kinds of typical reaction processes as follows: CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O and 2CO₂ + 12H⁺ + 12e⁻ → C₂H₅OH + 3H₂O. Thus the apparent quantum efficiency could be calculated as the following equation (1),

(1)

in which $N_{\text{electrons}}$, N_{photons} , N_{methanol} , and N_{ethanol} represent the number of reacted electrons and incident photons, the molecule number of generated methanol and ethanol, respectively. The number of incident photons was measured by the ferrioxalate actinometer method. In a typical procedure, 6 mL of Fe₂(SO₄)₃ solution (0.02 M) were mixed with 6 mL of Na₂C₂O₄ solution (0.12 M) and irradiated for 20 s. Afterwards, 1 mL of the resulted solution, 2 mL of 1,10-phenanthroline solution (0.2 wt %) and 0.5 mL of buffer solution (pH = 4.5, prepared by dissolving 3.36 g of CH₃COONa to 50 mL of H₂SO₄ solution (0.184 M)) were diluted to 100 mL and subsequently kept in the dark under stirring for 30 min. After the reaction, the ferrous ion concentration is subsequently determined via a UV-Vis spectrophotometric determination of its phenanthroline complex at 510 nm. The blank value was measured using the same process without irradiating. The number of incident photons per unit time was calculated as follows,

(2)

in which A and V signify absorbance at 510 nm and corresponding volume of diluted solution (1200 mL), respectively. $N_A=6.02 \times 10^{23}$, $\epsilon=1.11 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $L=1 \text{ cm}$, $\phi=1.21$, $t=20 \text{ s}$. Results show that the number of incident photons (n) was $7.260 \times 10^{16} \text{ photons s}^{-1}$.

II. Supporting Data

A. Characterization of the as-prepared Ag/AgCl NPs

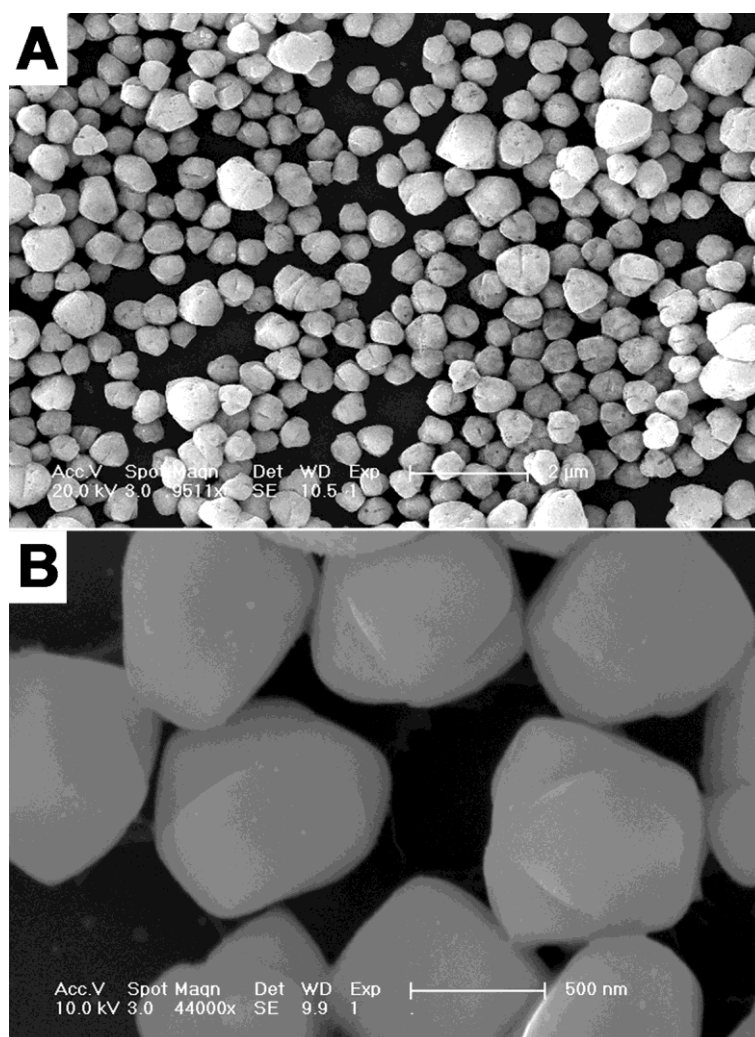


Fig. S2 SEM images of the as-prepared Ag/AgCl NPs. A) low resolution, B) high resolution.

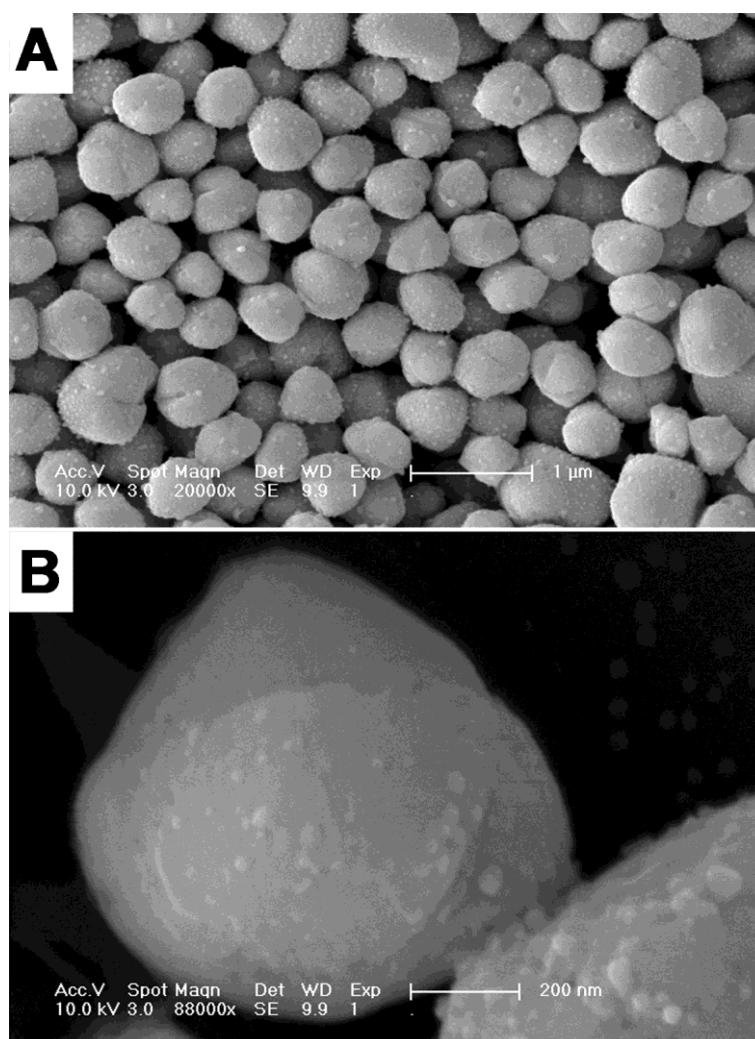


Fig. S3 SEM images of the as-prepared red Ag/AgCl NPs after photocatalytic reaction. A) low resolution, B) high resolution. After the photocatalytic reaction, metallic Ag⁰ species can be clearly detected on the surface of the photocatalysts.

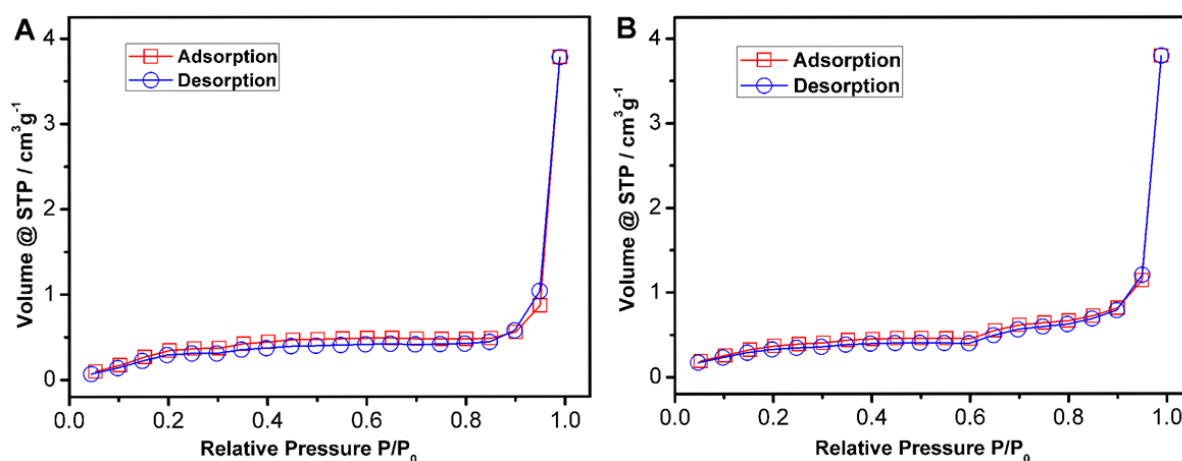


Fig. S4 Nitrogen sorption isotherm of the red AgCl A) and normal AgCl B) samples. The Brunauer–Emmett–Teller (BET) surface areas of red AgCl and normal AgCl were 1.673 and 1.382 m²/g, respectively. And the Langmuir surface areas of the red and normal AgCl are 4.515 and 2.389 m²/g, respectively.

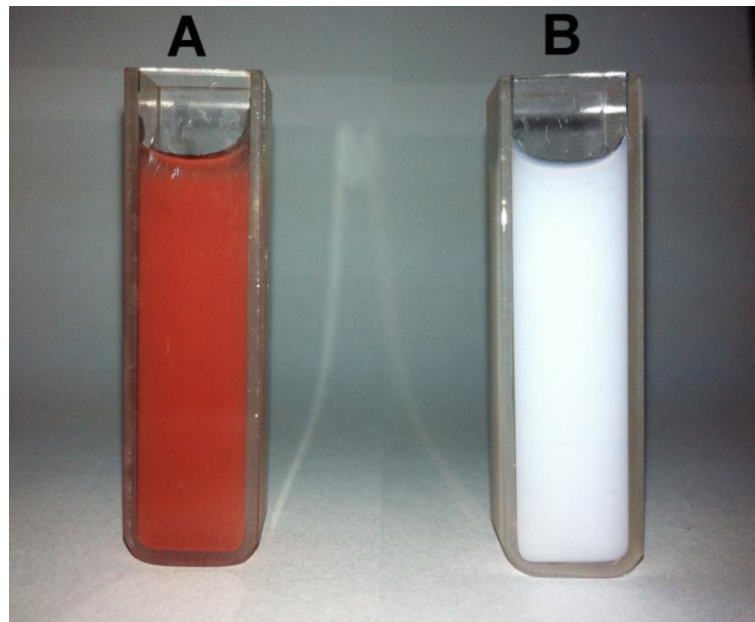


Fig. S5 Digital images of the dispersions of A) the as-prepared red Ag/AgCl samples and B) normal Ag/AgCl materials (1 mg mL⁻¹).

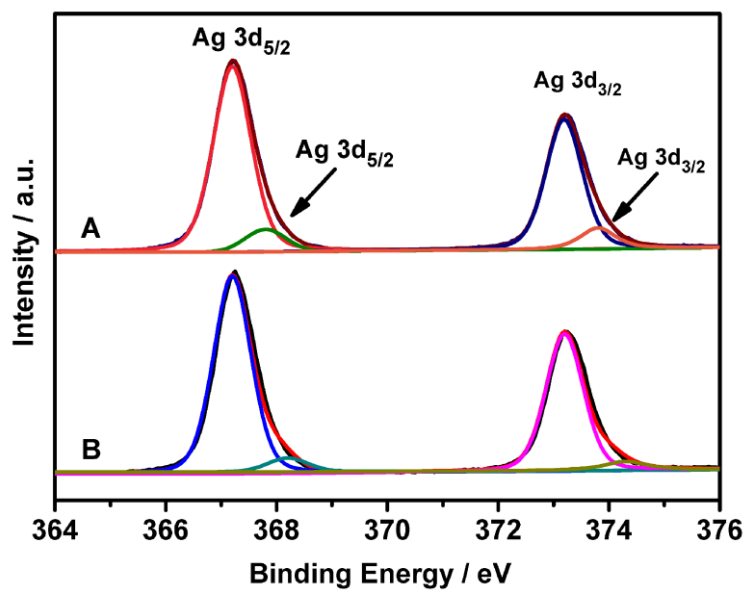


Fig. S6 XPS spectra of Ag 3d of A) the as-prepared red Ag/AgCl sample and B) normal Ag/AgCl materials. The surface mole ratios of Ag⁺ to Ag⁰ species are calculated to be *ca.* 8 : 1 and 13 : 1, respectively.

B. Photocatalytic performance of the red Ag/AgCl photocatalysts

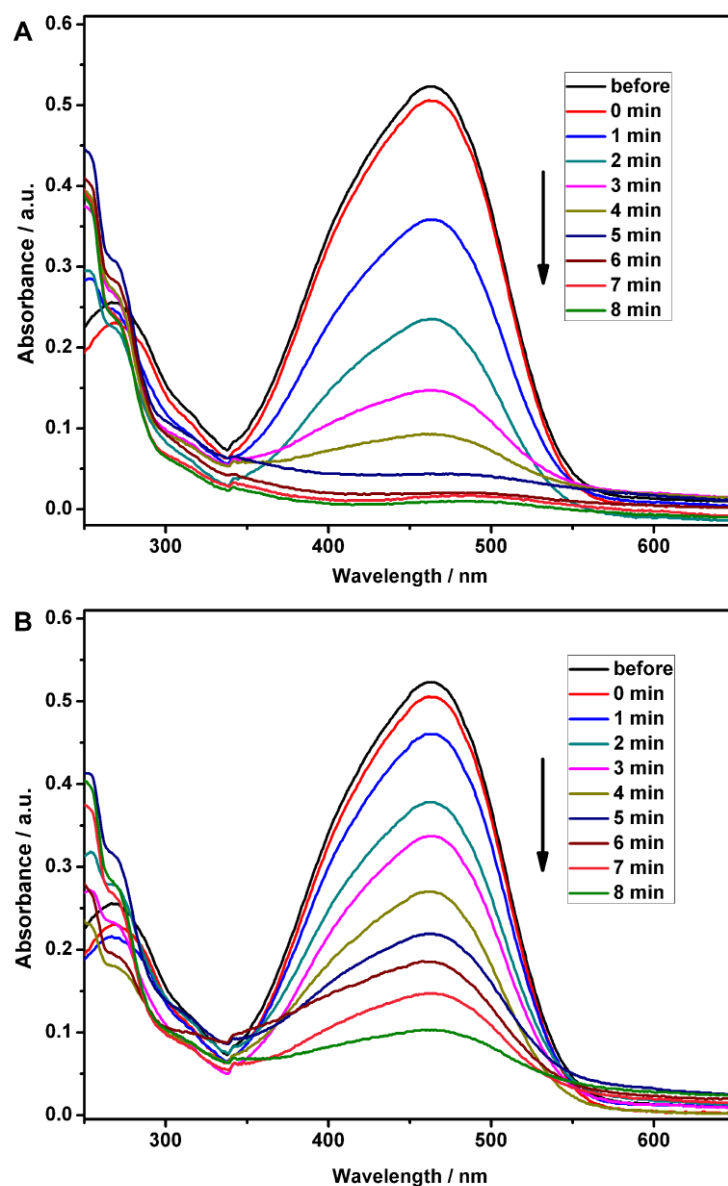


Fig. S7 Typical real-time absorption spectra of the MO dye during the photodegradation process over (A) red Ag/AgCl and (B) normal Ag/AgCl photocatalysts under visible-light irradiation. The black and red curves marked as ‘before’ and ‘0 min’ in each panel are the absorption spectra detected from the original MO solution before and after the dark adsorption experiment, respectively.

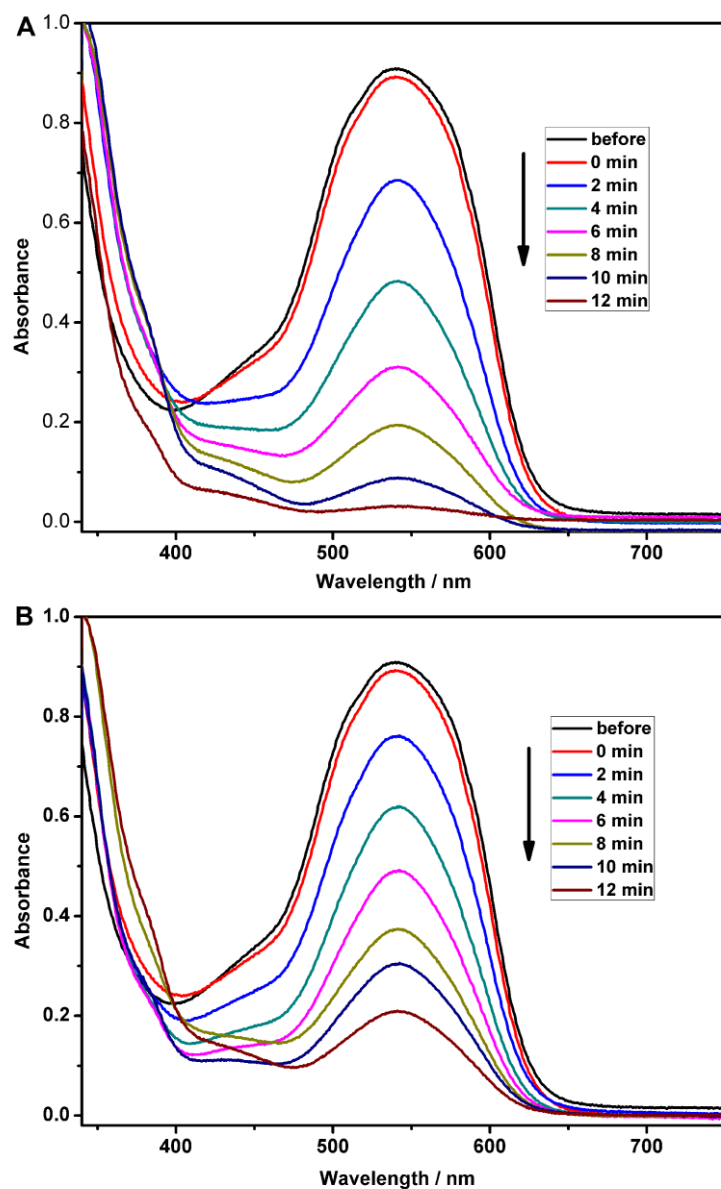


Fig. S8 Typical real-time absorption spectra of the chromium-containing solutions during the photoreduction process over (A) red Ag/AgCl and (B) normal Ag/AgCl photocatalysts under visible-light irradiation. The black and red curves marked as ‘before’ and ‘0 min’ in each panel are the absorption spectra detected from the original solution before and after the dark adsorption experiment, respectively.

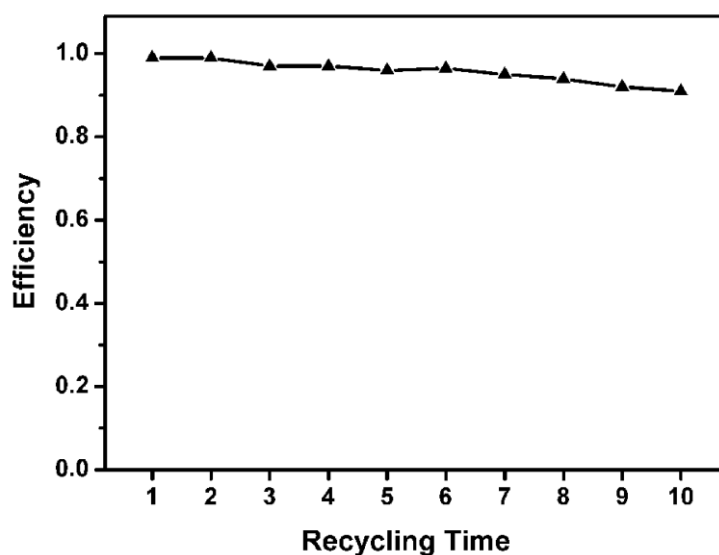


Fig. S9 Recycling experiments of as-prepared red Ag/AgCl samples in the MO degradation reaction.

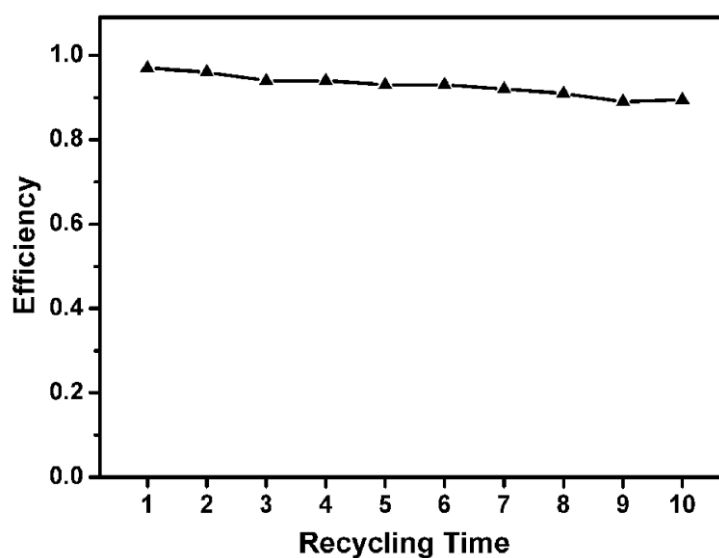


Fig. S10 Recycling experiments of as-prepared red Ag/AgCl samples in the Cr^{VI} reduction reaction.

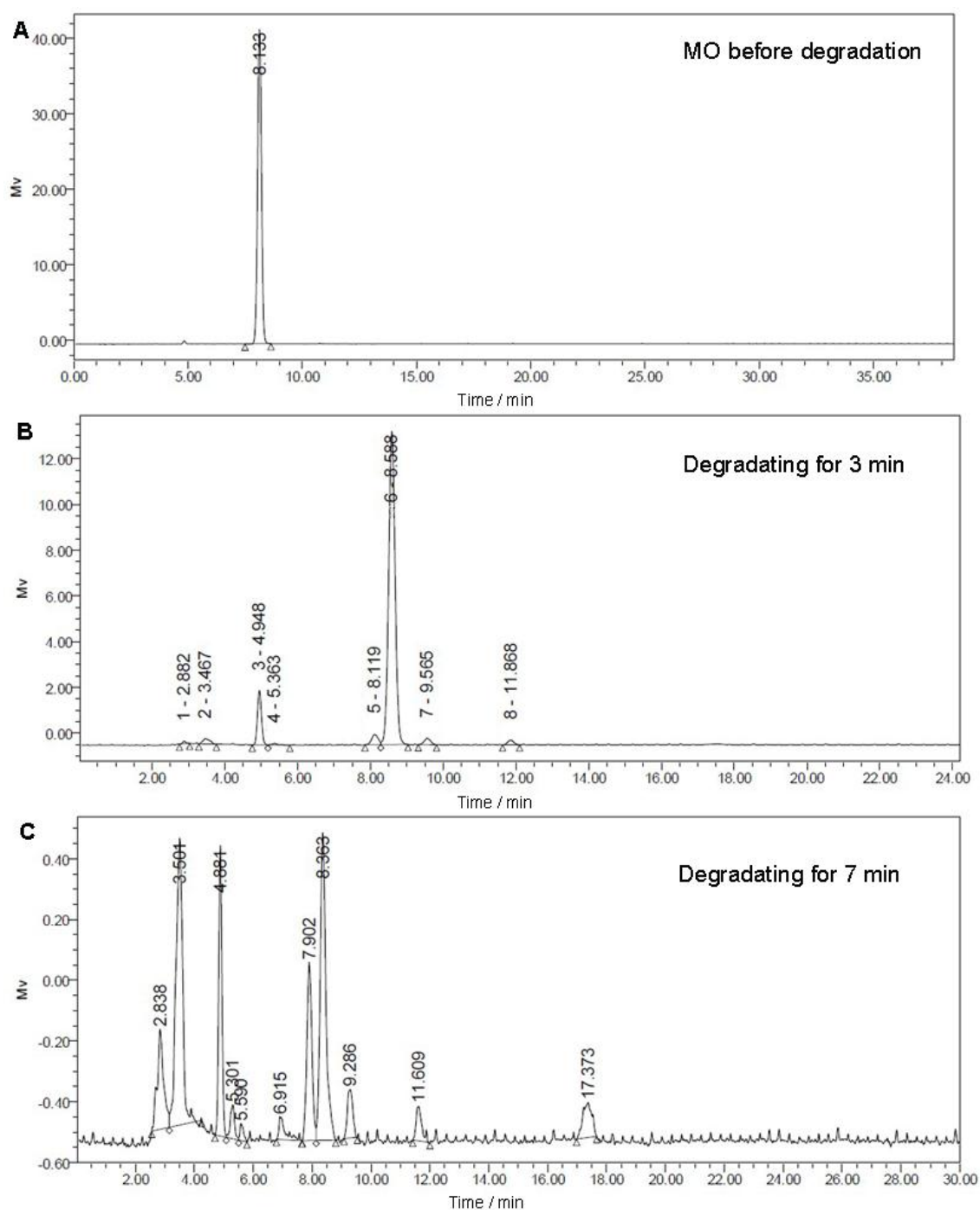


Fig. S11 Chromatograms of MO reaction solutions before irradiation A) and irradiated for 3 min B) and 7 min C). As shown, the retention time of MO is about 8.2 min and the concentration of MO decreases rapidly during the irradiation (2.9 mg/L for irradiated 3min and 0.12 mg/L for irradiated 7min). Furthermore, small molecule products are generated with the degradation of MO.

C. Density of states of the AgCl material.

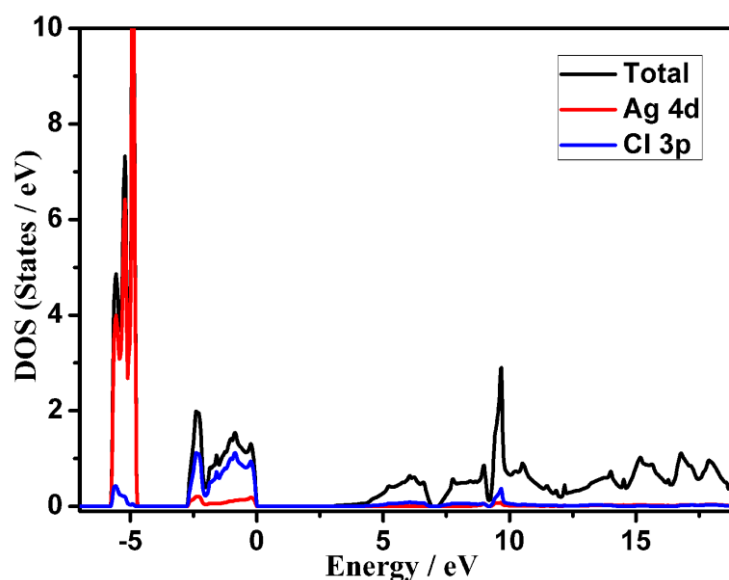


Fig. S12 Total and partial density of states (tDOS and pDOS) of AgCl.

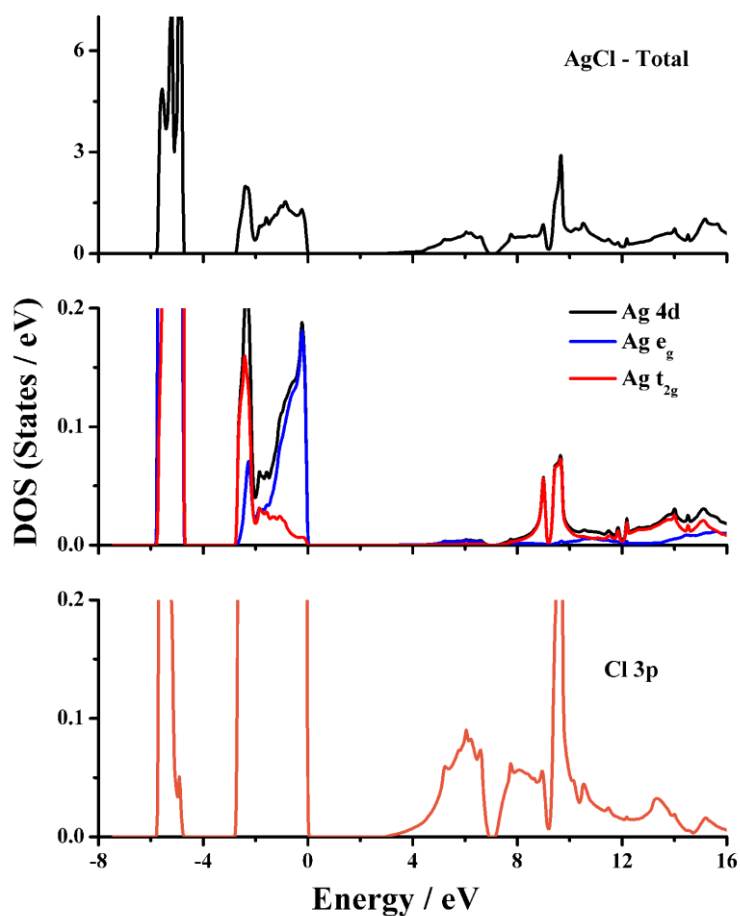


Fig. S13 Total and partial density of states (tDOS and pDOS) of AgCl (magnified image).