

Controllable Synthesis of Coloured Ag⁰/AgCl with Spectral Analysis for Photocatalysis

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Experiment

Chemicals

Sodium chloride (NaCl), Polyvinylpyrrolidone (PVP), Glycerol and Ethylene glycol were both obtained from Beijing Chemical Factory (Beijing, China) and used without further purification. Silver nitrate (AgNO₃) was purchased from Sinopharm Chemical Reagent (Shanghai, China) and used as received. All aqueous solutions were prepared using ultra-pure water (> 18.2 MΩ cm) from a Milli-Q Plus system (Millipore).

Preparation of Ag⁰/AgCl-Blue and Ag⁰/AgCl-Fuchsia

Ag⁰/AgCl-Fuchsia: In the synthesizing apparatus, 2.5 g PVP and 38 mg NaCl were both dissolved in 24 mL glycerol inside a round-bottom flask under 60 °C for 30 min. Then, 2 mL ethylene glycol solution containing 56 mg AgNO₃ was slowly injected into the above reaction system and the temperature remains 60 °C for another 30 min with a milky dispersion. Afterwards, the reaction system was warmed up to 160 °C for 80 min, and a rust red solution

gradually showed up during the heating process. Finally, the Ag⁰/AgCl-Fuchsia nanoparticles were collected through rinsing, centrifugation and freezing drying.

In addition, the Ag⁰/AgCl-Blue nanoparticles were prepared with a similar procedure except that the temperature was raised to 130 °C instead of 160 °C. Normal AgCl material was produced through the blending of 0.01 mol L⁻¹ AgNO₃ and 0.01 mol L⁻¹ NaCl aqueous solutions with stirring under light blocking condition.

Evaluation of photocatalytic activities

During the whole photodegradation experiments, the as-prepared photocatalysts (20 mg) were homogeneously suspended in 20 mL MO solution (10 mg L⁻¹) by sonication. Before the decomposition reaction, the suspensions were stirred for 30 min in dark for preliminary adsorption-desorption equilibrium and then disposed under irradiation to start the photocatalysis. A 300 W Xe lamp equipped with an ultraviolet cutoff filter were used as light source to provide visible light (≥ 420 nm) with output optical density of 28 mW cm⁻². Afterwards, a photodegradation solution with specified volume (800 μ L) was periodically pipetted from the reaction system and centrifuged to remove photocatalyst nanoparticles. MO degradation was monitored based on absorbance changes of its characteristic peak at 463 nm by using a UV-Vis spectrophotometer (ultra-pure water as reference). In this regard, C_t and C_0 have referred to the concentration of MO at real time t and the initial concentration 10 mg L⁻¹, respectively.

In a typical process for photoreduction of CO₂ into liquid fuels, 15 mg photocatalysts were spread into 15 mL 0.1 mol L⁻¹ NaHCO₃ solution under sonication. Before the irradiation, ultrahigh purity CO₂ was bubbled through the above suspension for 10 min in order to remove the air and achieve CO₂ saturation. Through 5 h photocatalytic reaction, the suspensions were

centrifuged and 1 mL solution was drawn to be analyzed using a gas chromatograph (Agilent GC 6890N, FID detector).

To avoid the sensitization of dye, we take phenol as colorless reactant in photocatalytic degradation. In the typical photocatalytic phenol degradation, 20 mg photocatalysts were homogeneously suspended in 20 mL phenol aqueous solution (50 mg L^{-1}) by sonication. Before the degradation process, the mixed solutions have been stirred for 30 min in dark for preliminary adsorption-desorption equilibrium and then disposed under irradiation to start the photocatalysis. A 300 W Xe lamp equipped with an ultraviolet cutoff filter were used as light source to provide visible light ($\geq 420 \text{ nm}$) with output optical density of 28 mW cm^{-2} . Afterwards, a photodegradation solution with specified volume (2 mL) was periodically pipetted from the reaction system and centrifuged to remove photocatalyst nanoparticles. phenol degradation was monitored based on absorbance changes of its characteristic peak at 270 nm by using a UV-Vis spectrophotometer (ultra-pure water as reference). In this regard, C_t and C_0 have referred to the concentration of phenol at real time t and the initial concentration 50 mg L^{-1} , respectively.

Characterization

Field emission scanning electron microscopy (FESEM) images and corresponding element mapping were both performed on FE-SEM (Philips XL30 ESEM-FEG integrated with an EDAX system) at an accelerating voltage of 10.0 kV. In order to increase the conductivity and protect the sample morphology from decomposition under the high-energy electron beam, a gold-spraying layer was first coating on the surface of the samples before the SEM characterizations. X-ray diffraction (XRD) analysis was carried out on a D8 Focus diffractometer (Bruker) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405$) in the range of $20^\circ\sim 80^\circ$ (2θ). X-Ray photoelectron spectroscopy

(XPS) measurements were performed on an ESCALAB MKII X-ray photoelectron spectrometer (VG Co.) with Al K α X-rays radiation as the X-ray source for excitation. Ultraviolet visible (UV-Vis) absorption and UV-Vis diffuse reflectance spectra (using BaSO₄ as the reference) were recorded with a HITACHI UV-Vis U-3900 spectrometer.

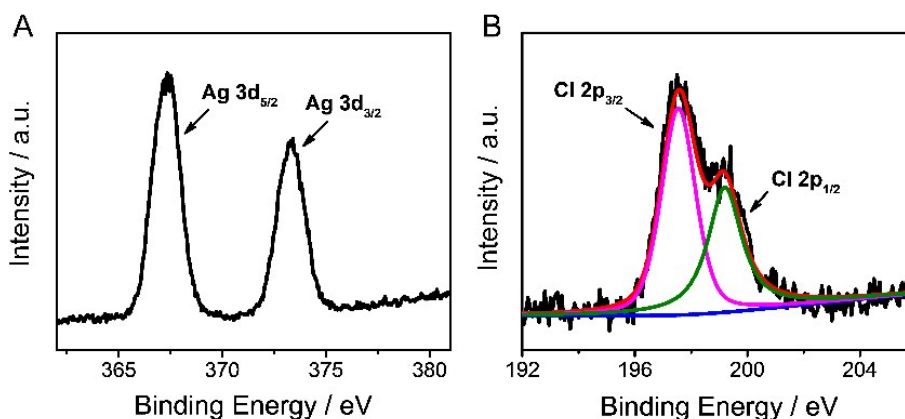


Figure S1. XPS characterizations of Ag (a) and Cl (b) of AgCl-normal.

In Figure S1A, two peaks located at 367.3 eV and 373.4 eV were attributed to Ag 3d_{5/2} and Ag 3d_{3/2} of AgCl-White, which were too sharp to be split. Thus, we considered that there was no metallic Ag⁰ generated, and this is different from coloured Ag⁰/AgCl samples. Figure S1B showed the Cl 2p peaks of AgCl-normal. Two peaks of 197.6 eV and 199.2 eV fitting with Cl 2p_{3/2} and 2p_{1/2} revealed little different from Ag⁰/AgCl-Blue and Ag⁰/AgCl-Fuchsia, as the Cl elements were all coming from AgCl semiconductors.

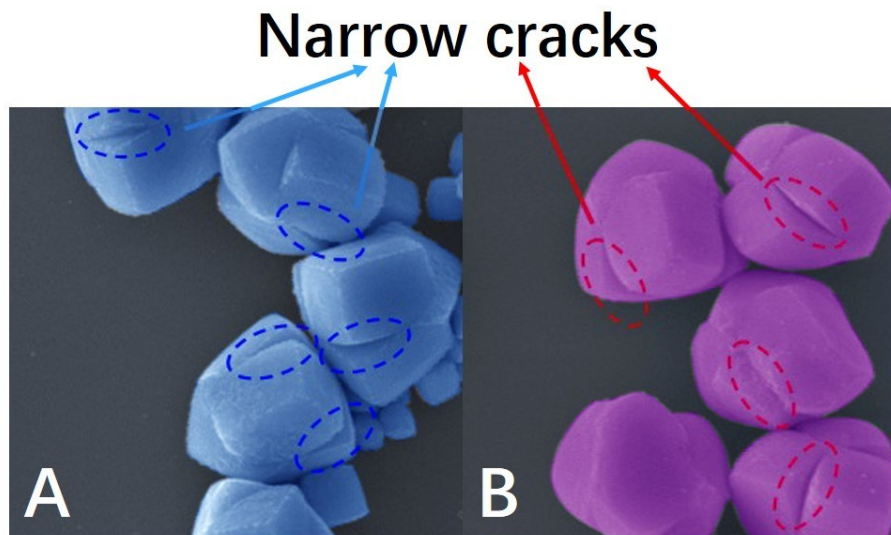


Figure S2. Narrow cracks spread on crystal particles of Ag^0/AgCl -Blue (A) and Ag^0/AgCl -Fuchsia (B).

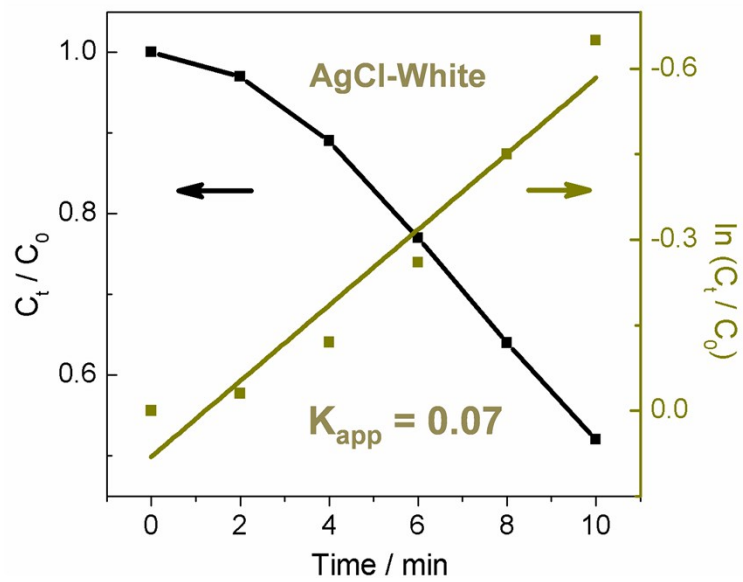


Figure S3. The apparent reaction rate constant (k_{app}) of AgCl-White.

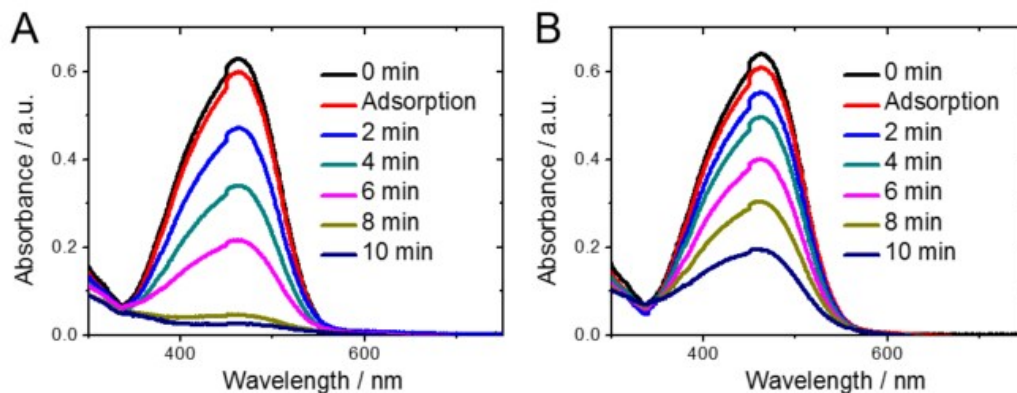


Figure S4. The change of UV-visible spectra for MO with the reaction time of Ag⁰/AgCl-Fuchsia (A) and Ag⁰/AgCl-Blue (B) under visible light.

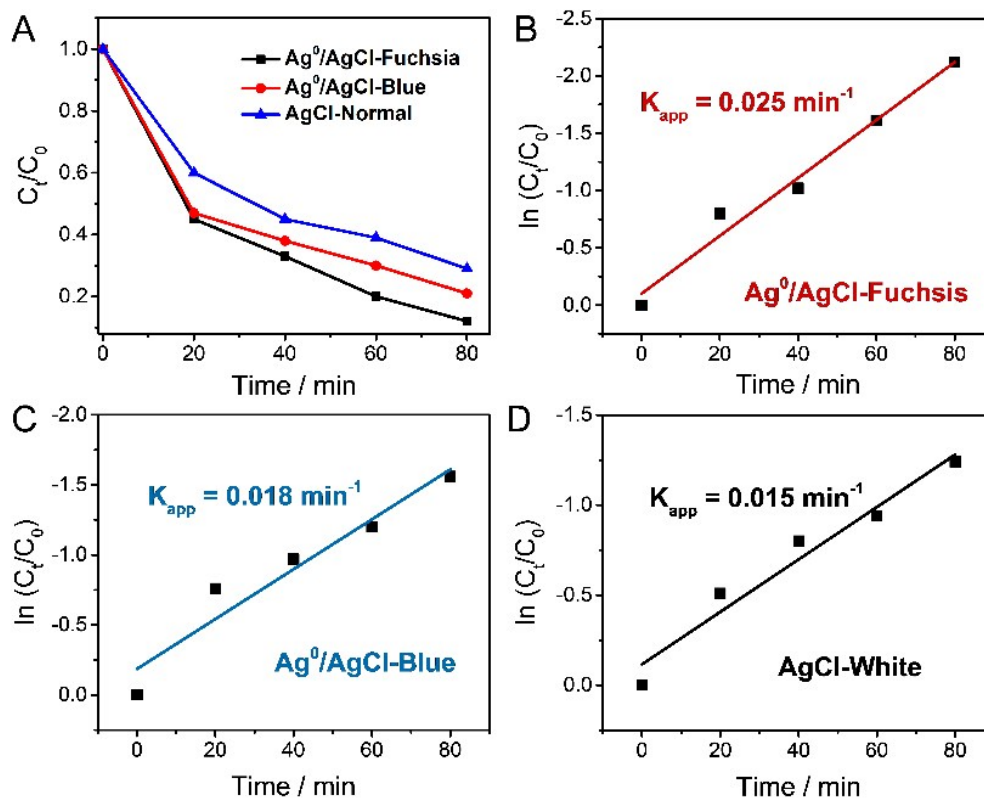


Figure S5. (A) Photocatalytic evaluation of AgCl, Ag⁰/AgCl-Blue and Ag⁰/AgCl-Fuchsia on phenol degradation under visible light ($> 420 \text{ nm}$). And the corresponding apparent reaction rate constant (k_{app}) of Ag⁰/AgCl-Fuchsia (B), Ag⁰/AgCl-Blue (C) and AgCl-White (D) under visible light.

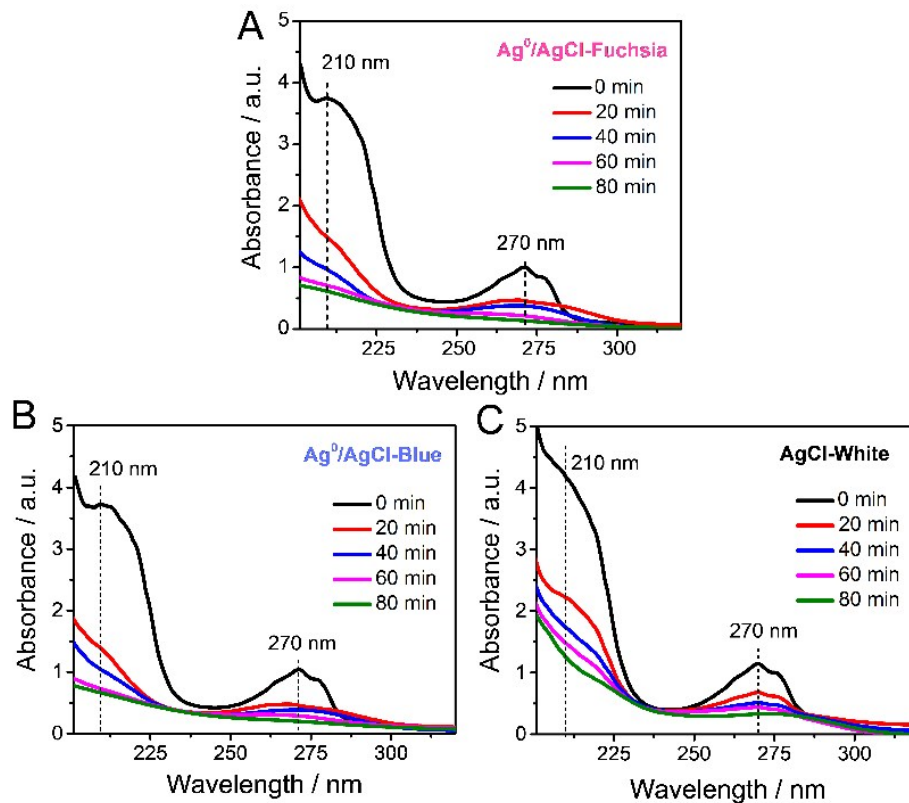


Figure S6. UV spectra of phenol during photocatalytic degradation process by Ag⁰/AgCl-Fuchsia (A), Ag⁰/AgCl-Blue (B) and AgCl-White (C) under visible light.

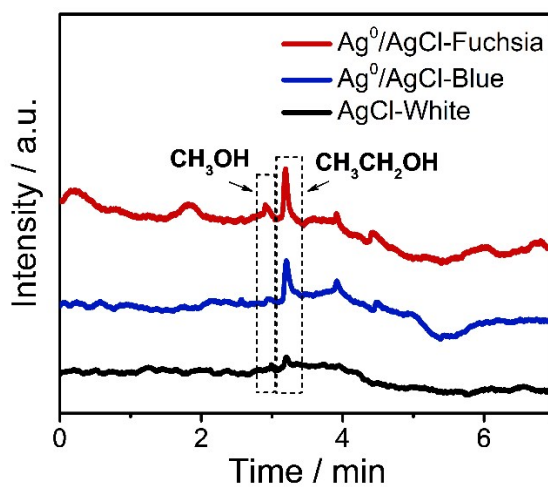


Figure S7. The GC signals of CH₃OH and CH₃CH₂OH generated in CO₂ reduction by Ag⁰/AgCl-Fuchsia, Ag⁰/AgCl-Blue and AgCl-White.

Table S1. The relation between matter's colour and colour absorbed.

No.	Matter's colour	Colour absorbed	Wavelength λ / nm
1	Kelly	Purple	400~450
2	Yellow	Blue	450~480
3	Orange	Greenish blue	480~490
4	Red	Bluish green	490~500
5	Fuchsia	Green	500~560
6	Purple	Kelly	560~580
7	Blue	Yellow	580~600
8	Greenish blue	Orange	600~650
9	Bluish green	Red	650~750

Table S2. The atomic ratio of Ag^0 to Ag^+ and the Ag^0 content in samples of Ag^0/AgCl -Blue and Ag^0/AgCl -Fuchsia.

Sample	Atomic ratio of Ag^0 to Ag^+	Content of Ag^0
Ag^0/AgCl -Blue	1:26	3.7%
Ag^0/AgCl -Fuchsia	1:16	5.9%

Table S3. The mass ratio and atomic ratio of elements in Ag⁰/AgCl-Fuchsia with gold spray on silicon substrate. The elements include Ag, Cl, Au and Si.

Element	Wt%	At%
Ag L	54.69	29.92
Cl K	17.02	28.32
Au M	9.81	2.94
Si K	18.48	38.82
Total	100	100

Table S4. The retention time and integral area of CH₃OH and CH₃CH₂OH from GC.

Sample	CH ₃ OH		CH ₃ CH ₂ OH	
	Retention time (min)	Integral area	Retention time (min)	Integral area
Ag ⁰ /AgCl-Fuchsia	2.9	113	3.2	819
Ag ⁰ /AgCl-Blue	2.9	115	3.2	534
AgCl-White	2.9	92	3.2	339

From Figure S7 and table S4, it can be seen that peaks raised at retention time 2.9 min and 3.2 min from GC curves, indicating the generation of CH₃OH and CH₃CH₂OH, respectively. And the integral area (table S4) for CH₃CH₂OH demonstrated that the photocatalytic CO₂ reduction ability of Ag⁰/AgCl-Fuchsia (819) and Ag⁰/AgCl-Blue (534) were much better than AgCl-White (339).