Supporting Information

Facile Sonochemical Route to Sponge-like Porous AgCl/Malachite for Enhanced Photocatalytic Performance and Stability

Hongbo He *, Simin Zhong, Wanting Xiao, Jianhong Jiang, Yijun Guo, Siyao Tan, Shiya He, Midong Shi, Erjun Zhang *, Bin Deng *

Hunan Provincial Key Laboratory of Xiangnan Rare-Precious Metals Compounds and Applications, College of Chemistry and Environmental Science, Xiangnan University, Chenzhou 423000 P. R. China

*Corresponding Authors:

hehb5@mail2.sysu.edu.cn (H. He); zhz.219@163.com (E. Zhang); ddhbyjs@126.com (B. Deng)

Materials

All the chemicals were analytical grade and applied without further purification. $CuCl_2 \cdot 2H_2O$, Na_2CO_3, $AgNO_3$, Na_2SO_4, methyl orange, p-benzoquinone, ethanol and isopropanol were purchased from Sinopharm.

Synthesis of AgCl

Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 5 mmol) was weighed and dissolved in 15 mL of deionized water under stirring to form Solution A. Separately, silver nitrate ($AgNO_3$, 10 mmol) was weighed and dissolved in 15 mL of deionized water to form Solution B. Under continuous stirring, Solution B was slowly added dropwise to Solution A. This process was conducted in an ice-water bath and assisted by ultrasonic irradiation (LC-UP-400 model, equipped with a Φ6 horn, Shanghai Lichenbangxi Technology Co., Ltd.) in pulse mode (2 s on, 2 s off) at 50% output power for 20 min. The resulting product was collected by centrifugation, washed three times sequentially with deionized water and ethanol, and finally dried in a blast drying oven at 60°C for 12 h to obtain the AgCl nanomaterial.

Synthesis of Malachite

Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 10 mmol) was weighed and dissolved in 15 mL of deionized water under stirring to form Solution A. Separately, sodium carbonate anhydrous (Na_2CO_3, 10 mmol) was weighed and dissolved in 15 mL of deionized water to form Solution B. Under continuous stirring, Solution B was slowly added dropwise to Solution A. This process was conducted in an ice-water bath and assisted by ultrasonic irradiation (LC-UP-400 model, equipped with a Φ6 horn, Shanghai Lichenbangxi Technology Co., Ltd.) in pulse mode (2 s on, 2 s off) at 50% output power for 20 min. The resulting product was collected by centrifugation, washed three times sequentially with deionized water and ethanol, and finally dried in a blast drying oven at 60°C for 12 h to obtain the $Cu_2(OH)_2CO_3$ (Malachite) nanomaterial.

Synthesis and Ratio Control of AgCl/Malachite

To systematically investigate the influence of AgCl loading on the composite's performance, a series of AgCl/Malachite composites with different Ag/Cu atomic molar ratios were synthesized by varying the amount of silver nitrate ($AgNO_3$) while keeping the precursor amount of Malachite constant. The specific procedure is as follows: Firstly, copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 10 mmol) was accurately weighed and dissolved in 15 mL of deionized water under stirring until completely dissolved, denoted as Solution A. Subsequently, sodium carbonate anhydrous (Na_2CO_3, 10 mmol) was weighed and dissolved in 15 mL of deionized water to obtain Solution B. Under continuous stirring, Solution B was added dropwise to Solution A, and the resulting mixture was denoted as Suspension C. Next, different masses of $AgNO_3$ (12, 13, 14 mmol) were weighed separately and dissolved in 3 mL of deionized water to prepare solutions with varying Ag^+ concentrations, denoted as Solution D. Under continuous stirring, Solution D was added dropwise to Suspension C. Immediately, an LC-UP-400 ultrasonic generator (equipped with a Φ6 horn, 50% output power) was employed to assist the reaction for 20 min in pulse mode (2 s on, 2 s off). After the reaction, the mixture was centrifuged to collect the precipitate, which was then washed alternately three times with deionized water and ethanol to remove impurities. Finally, the samples were dried in a blast drying oven at 60°C for 12 h. Based on the theoretical Ag/Cu atomic molar ratio in the feed, the resulting products were labeled as AgCl/Malachite-1.2, AgCl/Malachite-1.3, and AgCl/Malachite-1.4, respectively.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded at a scanning rate of 0.05 $°C \cdot s^{-1}$ using a Bruker D8 advance X-ray diffractometer at 40 kV and 40 mA with a Cu Kα radiation source (λ = 0.15418 nm). The surface morphology and elemental composition of the samples were determined using a Hitachi SU5000 field emission scanning electron microscope (FE-SEM) and an Oxford AZtecLiveOne Xplore 30 energy dispersive spectrometer (EDS), respectively. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was measured on a Micromeritics ASAP2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 200 °C for 4 h before nitrogen adsorption measurement. The light response capability of samples was analyzed by Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) on a UV-vis spectrophotometer (UV-2600, Shimadzu) equipment. Transient photocurrent response (TPR) measurements were performed on a CHI 660E electrochemical workstation in a three-electrode quartz cell. The Ag/AgCl electrode and Pt wire electrode are served as reference electrode and counter electrode, respectively. The working electrodes were coated with ~1 mg of sample film on a 1cm × 1cm ITO. Further, 0.5 $mol \cdot L^{-1}$ Na_2SO_4 aqueous solution was used as the electrolyte and 300 W Xenon lamp served as a light source. The test of the transient photocurrent response with time was conducted through an alternated test of opening and closing a light with no bias voltage. Electrochemical impedance spectroscopy (EIS) in AC polarization was performed under the open circuit potential. A sinusoidal AC perturbation of 10 mV was applied to the electrode over the frequency range of $0.01–10^5$ Hz after a quiet of 10 min.

Radicals capturing experiments

A series of radicals capturing experiments were performed by using isopropanol (IPA, a quencher of $\cdot OH$, 3 mM), p-benzoquinone (BQ, a quencher of $\cdot O_2^-$, 1 mM), and sodium carbonate (Na_2CO_3, a quencher of h^+, 3 mM). The method was similar to the former photocatalytic activity test for MO photodegradation.

Recycling experiments

The stability of AgCl and AgCl/Malachite were examined by recycling experiments in the photodegradation of MO. After each cycle, the photocatalyst was collected by simple filtration, washed by dilute hydrochloric acid (0.5 mol/L) and H_2O for three times, then reused in the next run.

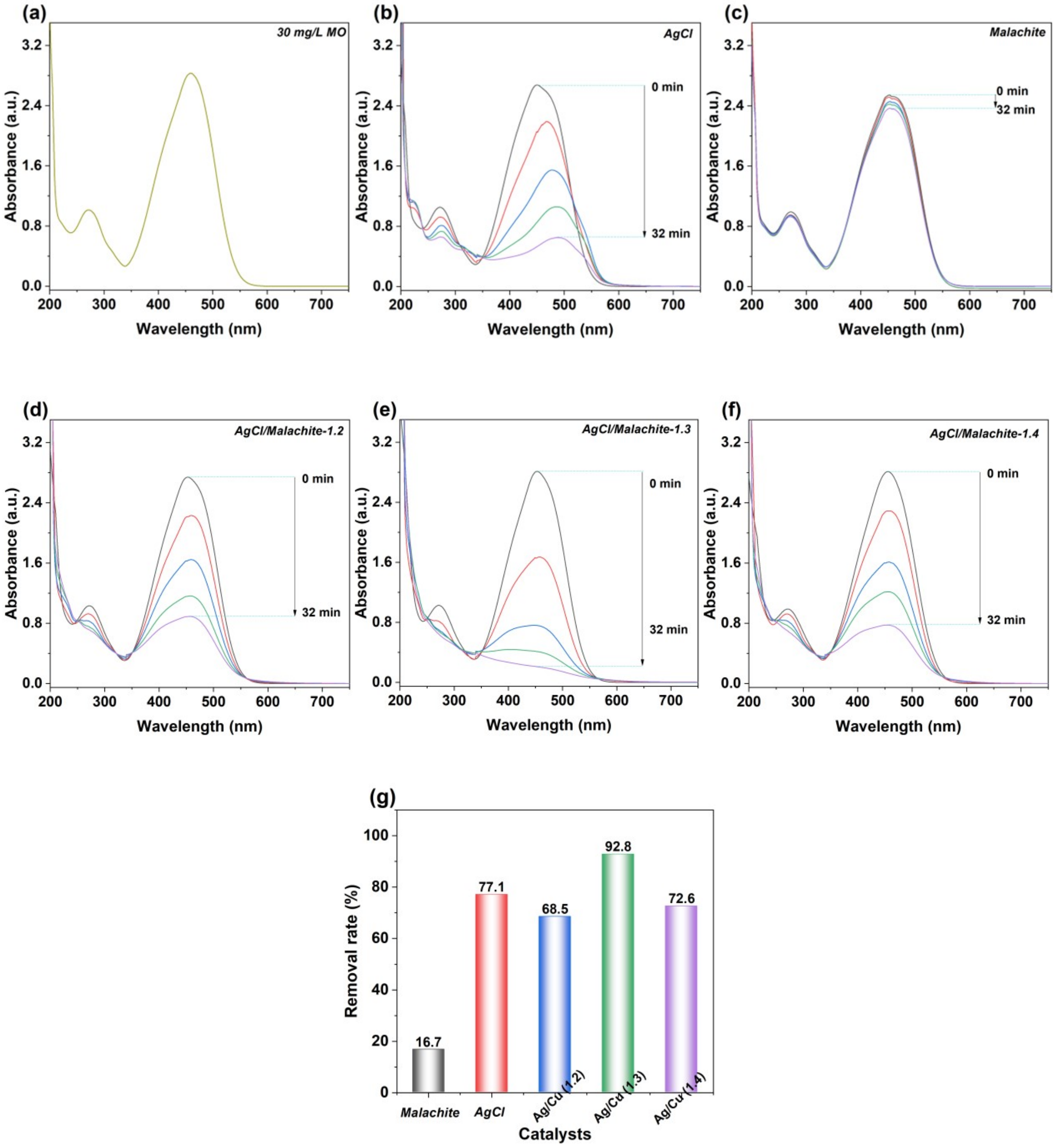

Figure S1. (a) UV-vis absorption spectrum of the initial MO solution (30 mg/L); Time-dependent UV-vis absorption spectra of MO during photocatalytic degradation over (b) AgCl, (c) Malachite, (d) AgCl/Malachite-1.2, (e) AgCl/Malachite-1.3, and (f) AgCl/Malachite-1.4; (g) Comparison of photocatalytic degradation efficiencies of MO over different catalysts after 32 min of light irradiation.