Electronic Supplementary Information

Singlet oxygen formation on bio-inspired synthesis of hollow Ag@AgBr photocatalyst for microbial and chemical decontamination

S. Zhang[a], H. Zhang[b], S. Wang[b]*, L. Liu[b]* and S. Liu[b]

[a.] *Department of Orthopaedics, First Hospital of Jilin University, China*

[b.] *Department of Chemical Engineering, Curtin University, Perth, Western Australia 6845, Australia*

Email: Shaobin.Wang@curtin.edu.au; Lihong.Liu@curtin.edu.au

Experimental Section

Sample Preparation

All chemicals were of at least analytical grade and used as received without further purification. Tryptic Soy Broth (TSB), Yeast Extract (YE) and BBL™ Trypticase™ Peptone in powder form were purchased from BD Company. The 1% w/v YE and 2% w/v peptone solutions were prepared by suspending the powder in 1 L deionized (DI) water followed by autoclave at 121 ºC for 15 min. Silver nitrate, sodium chloride, sodium bromide and 2,2,6,6-tetramethyl-4-piperidinol (TMP, 99%) were purchased from Sigma–Aldrich. Silver nitrate was dissolved in DI water to get an 80 mM stock solution. In a typical procedure of Ag@AgBr hollow nanoparticle preparation, 5 mL $AgNO_3$ solution was added to 2.5 mL mixture of YE and peptone solution followed by addition of 2.5 mL (400 mM) NaBr. The resulting milky white solution was then magnetically stirred under a solar simulator (550 W Xenon lamp, ABET Technologies, Model 11016A Sun 3000) for 5 min. At the same time, a series of silver chlorobromide ($AgCl_xBr_{1-x}$, x = 1, 0.64, 0.36) nanoparticles were synthesized by adjusting the molar ratio of Cl^- to Br^-. All nanoparticles were centrifuged down at 7000 rpm for 30 min and the pellet was washed by water twice. After the washing steps particles were resuspended in 5 mL DI water for further use. For comparison, Ag@AgBr particles prepared in DI water without yeast extract and peptone involvement was named as Ag@AgBr-DI.

Characterization

UV−vis absorption spectra of the samples in DI water were recoded using a JASCO V-670 UV−vis/NIR spectrophotometer. The particle size and polydispersity were characterized by dynamic light scattering (DLS) using a Nano-ZS90 analyzer (Malvern). X-ray diffraction analysis was performed on a Bruker D8 Advance X-ray Diffractometer with Cu Kα (λ = 1.54 Å) radiation. The diffracted intensities were recorded from 20° to 80° at 2θ angles. The morphologies of catalyst structures were investigated by a field-emission scanning electron microscope (Zeiss Neon 40EsB FIBSEM). For transmission electron microscopy (TEM), a drop of solution was placed on carbon-coated copper grids and air dried. Scanning transmission electron microscopy (STEM) was performed using a FEI Titan microscope equipped with a high-angle annular dark field (HAADF) detector operated at 200 kV. The elemental mapping using energy-dispersive X-ray spectroscopy (EDX) was conducted on the same TEM. The electron spin resonance (ESR) signals of 2,2,6,6-tetramethyl-4-piperidinol-

N-oxyl (TMPN) were detected at ambient temperature with a Bruker EMSplus spectrometer under the conditions of modulation amplitude (8G). The irradiation source was a 100 W Hg UV-Vis lamp. The settings for the ESR spectrometer were as follows: center field = 3,515 G; sweep width = 200 G; microwave frequency = 9.48 GHz; modulation frequency = 100 kHz; and power = 1.02 mW. Brunauer–Emmett–Teller (BET, Micromeritics Tristar 3000) was used for determination of the surface area and pore size. Approximately 0.1 g samples were placed in test tubes and degassed at 130 ºC for 16 h. To support the proposed mechanism of singlet oxygen formation, a semi-quantitative determination of peroxides was carried out by using 0.5-25 ppm EM Quant® strips.

Photocatalytic activity of the Ag@AgCl$_x$Br$_{1-x}$ nanoparticles

Methyl orange (MO) was firstly chosen as a probe molecule to test the solar light-driven photocatalytic activities of the particles. The same 500 W Xenon lamp was used as the light source. Typically, 7 mg catalyst was used to degrade 10 mL MO solution (10.0 mg/L). The mixture was kept in dark for 30 min to achieve an equilibrium adsorption before light irradiation. Aliquots of the dispersion were taken out from the reaction system and centrifuged at 7000 rpm for 3 min before measuring absorption spectrum in the range of 300 to 600 nm. Methylene blue and Rhodamine 6G degradation were tested under visible light. The stability of Ag@AgBr has been confirmed by recycling the photocatalyst for MO degradation under solar light for two times. XRD patterns of Ag@AgBr after sunlight irradiation were recorded to check the possibility of phase change.

Antimicrobial test

Gram-negative bacteria, *Escherichia coli* (*E coli*, ATCC 25922) were obtained from the American type culture collection (Rockville, MD). The bacteria were stored in a −80 °C refrigerator. The bacterial cultures were maintained in tryptic soy broth as recommended by ATCC. The inoculum was prepared by suspending the frozen cells in a fresh TSB medium and grown at 37 °C overnight. The suspension of microorganism was diluted to an optical density at 600 nm (OD_{600}) of ~0.1 on a microplate reader. Minimal inhibitory concentrations (MICs) in the dark were determined by microdilution assay. Typically, 100 μL microbial solutions (containing 2–10 $\times 10^7$ cells/mL) were added to 100 μL of sterilized DI water containing Ag@AgBr nanoparticles (ranging from 1.6 to 50 ppm in serial twofold dilutions) in each well of the 96-well microtiter plate. The plates were incubated at 37 °C for 24 h with shaking at 100 rpm. The reported MICs are the minimum concentration necessary to inhibit visible cell growth. Experiments were run in triplicate. To test the light-assisted biocidal effect of Ag@AgBr nanoparticles, all other experimental conditions were kept the same except that the plates were firstly exposed to light source for 30 min and then incubated in the dark till the end of experiment.

Table S1 Z-average diameter and polydispersity index (PDI) of AgCl colloid template and $Ag@AgCl_xBr_{1-x}$ nanoparticles.

	Z-average diameter (nm)	PDI
AgCl	116.9	0.25
Ag@AgBr	118.7	0.081
$Ag@AgCl_{0.36}Br_{0.64}$	105.0	0.086
$Ag@AgCl_{0.64}Br_{0.36}$	77.3	0.084
Ag@AgCl	112.9	0.135

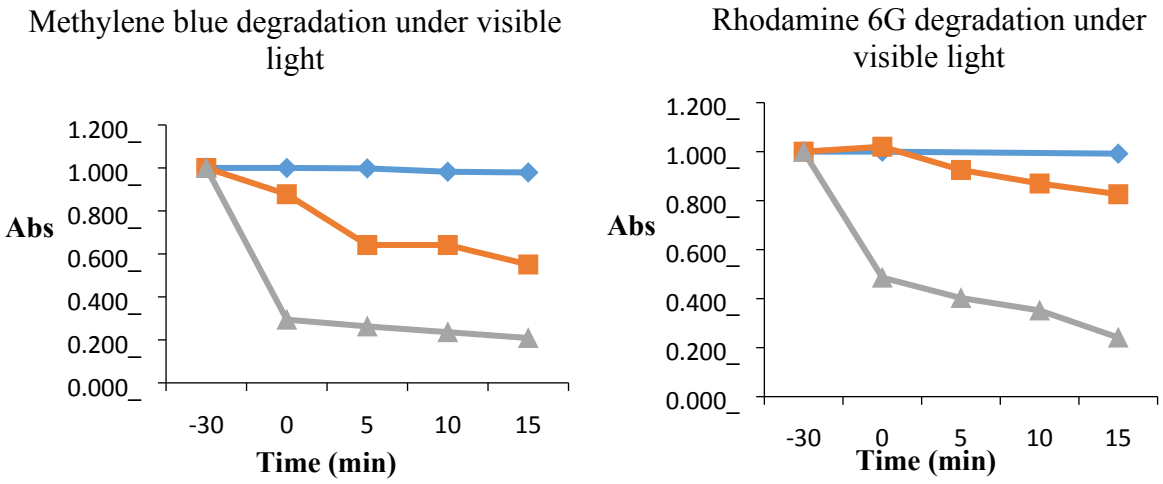

Figure S1 10 ppm Methylene blue and Rhodamine 6G degradation by Ag@AgBr-DI (orange colour line) and Ag@AgBr (gray colour line) under visible light.

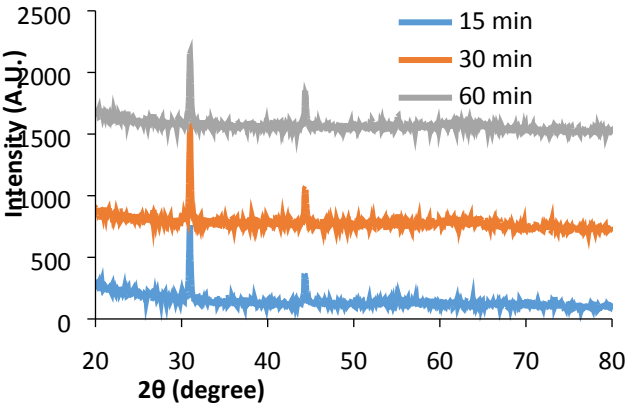

Figure S2 XRD patterns of Ag@AgBr after 15, 30 and 60 min exposure time under sunlight.

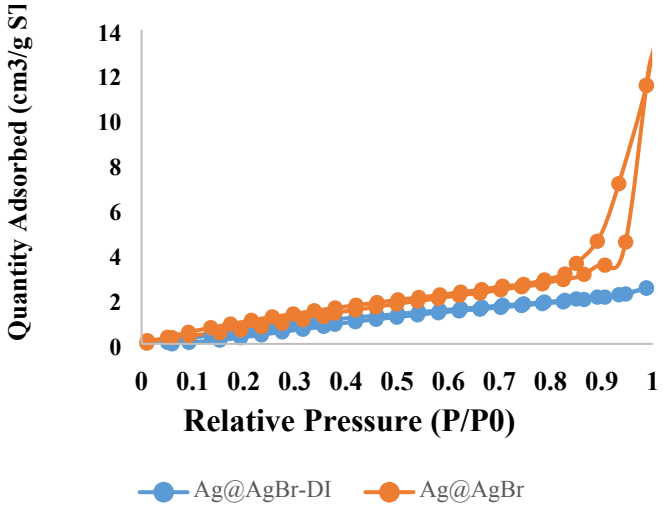

Figure S3 N_2 adsorption-desorption isotherms of Ag@AgBr and Ag@AgBr-DI nanoparticles.

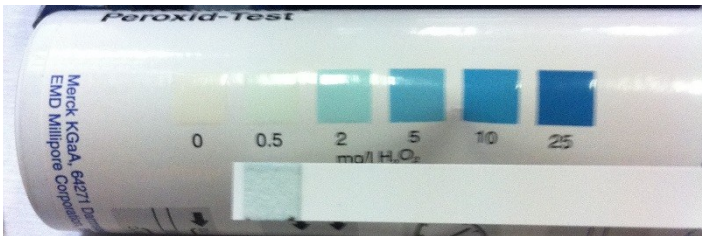

Figure S4 Peroxide-test result of Ag@AgBr (7 mg in 10 mL DI water) under sun simulator. The residual peroxide concentration was about 0.5 ppm.