

Preparation of AgBr on Boron-doped Reduced Graphene Oxide Aerogels for Photocatalytic Removal of Cr (VI) in Water

1. Experiment details

1.1 Synthesis of graphene oxide (GO)

GO is prepared by chemical delamination of graphite powder through applying the modified Hummers' method¹. At the beginning, 1 g of graphite powder was added into 25 mL of concentrated H₂SO₄, and successively, 3 g KMnO₄ was added into this mixture under vigorous stirring in the ice bath. After reaction for 4 h, the mixture was then transferred into water bath and stirred at 35°C for 30 min. In the next step, 46 mL of deionized water was slowly added into the reaction system, and the temperature of the reaction system was then raised to 95°C. After stirring for 30 min, the mixture was transferred into an ice bath environment. Successively, 140 mL of deionized water and 25 mL 30% H₂O₂ solution were added gradually. After stirring for 60 min, the mixture was taken out of the ice bath. The solid product was separated by centrifugation and washed by HNO₃ solution and subsequently by deionized water until sulfate could not be detected by BaCl₂.

1.2 Characterization

X-ray diffraction (XRD) was carried out on a RigakuD/max2550VL/PC system at 35 kV and 200 mA with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), at a scan rate of 3° min^{-1} and a step size of 0.050° in 2θ to characterize the phases in the samples. Dilor LABRAM-1B microspectrometer was applied to record Raman spectra of the samples under 633 nm laser excitation. UV-vis absorption spectroscopy tests were executed on a PerkinElmer 330 spectrophotometer loaded with a 60 mm Hitachi integrating sphere accessory. X-ray photoelectron spectroscopy (XPS) was implemented on a Kratos Axis Ultra^{DLD} spectrometer by using a monochromatic Al K α source.

Field-emission scanning electron microscopy (FESEM) was conducted on a JEOL JSM-6360LV field emission microscope at an accelerating voltage of 30 kV to observe the morphology of pure AgBr nanoparticles, and a Hitachi S-4800 field emission microscope at an accelerating voltage of 10 kV to observe the morphology of AgBr/B-RGO and AgBr/RGO. Transmission electron microscopy (TEM) was executed on a JEOL 2010 microscope at 200 kV. Samples for TEM tests were treated by dispersing the nanocomposites in anhydrous ethanol with the process of ultrasound and then the specimen suspensions were dropped on holey carbon supported copper grids.

The electrochemical impedance analysis was conducted in a conventional three-electrode cell using a Pt plate as the counter electrode while an Ag/AgCl electrode acts as reference electrodes, respectively. The working electrode was prepared on glassy carbon electrodes that were cleaned by ultrasonic treatment in deionized water and then in ethanol for 30 min and dried at 353 K. The sample (10 mg) was dispersed in 1 mL anhydrous ethanol by ultrasonication to get slurry. The slurry was spreading onto the surface of glassy carbon electrodes. The working electrode was dried at room temperature (25°C) for 4 hours. The exposed area of the working electrode was 0.07065 cm^2 . The electrochemical impedance spectroscopy (EIS) measurements were measured on a CHI-660D electrochemical workstation (CH instruments, USA), applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions. The electrolyte contained 0.5 M KCl and 10 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆].

1.3 Photocatalysis tests

The photocatalytic performance of AgBr/B-RGO was investigated by the photoreduction of Cr^{VI} to Cr^{III} under

visible-light irradiation, produced by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd.), with a UV cut filter on it to exclude the light whose wavelength is lower than 420nm. At first, 10 mL solution of HCl (0.6 mol/L) was mixed with 10mL solution of L-tartaric acid (7.575 g L⁻¹, serving as hole scavenger) under stirring. Then, 20 mL solution of K₂Cr₂O₇ (84.87 mg L⁻¹) was added into the mixture under stirring. The concentration of Cr^{VI} is 15 mg L⁻¹. After that, 1.2 mL acetone solution of diphenylcarbazide (DPC, 5 g L⁻¹) was added into the reaction system to acquire violet-like color. The final PH value of the mixed solution is 0.40. Finally, 64.1 mg of AgBr/B-RGO were put in the reaction system, and kept in dark place for 30 minutes. After dark process, the light irradiation begins. A 3 mL solution of the sample was taken out every 7 minutes for analysis on UV-vis spectrophotometer. To prevent the absorbance exceed 10, 2 mL of all taken out samples will be diluted by 2 mL of deionized water and mixed for 10 minutes before measured in UV-Vis spectrophotometer. Through recording the absorbance at 540 nm of the UV-vis spectroscopy, the concentration of Cr^{VI} could be recorded. C/C₀ represents the remaining amount of Cr^{VI} in the solution, while C represents the concentration of Cr^{VI} in the sample and C₀ represents the initial concentration of the Cr^{VI}, 15 mg L⁻¹. For comparison, the same mass of AgBr/RGO and 40.4 mg of AgBr powder are conducted photocatalysis tests under the same condition.

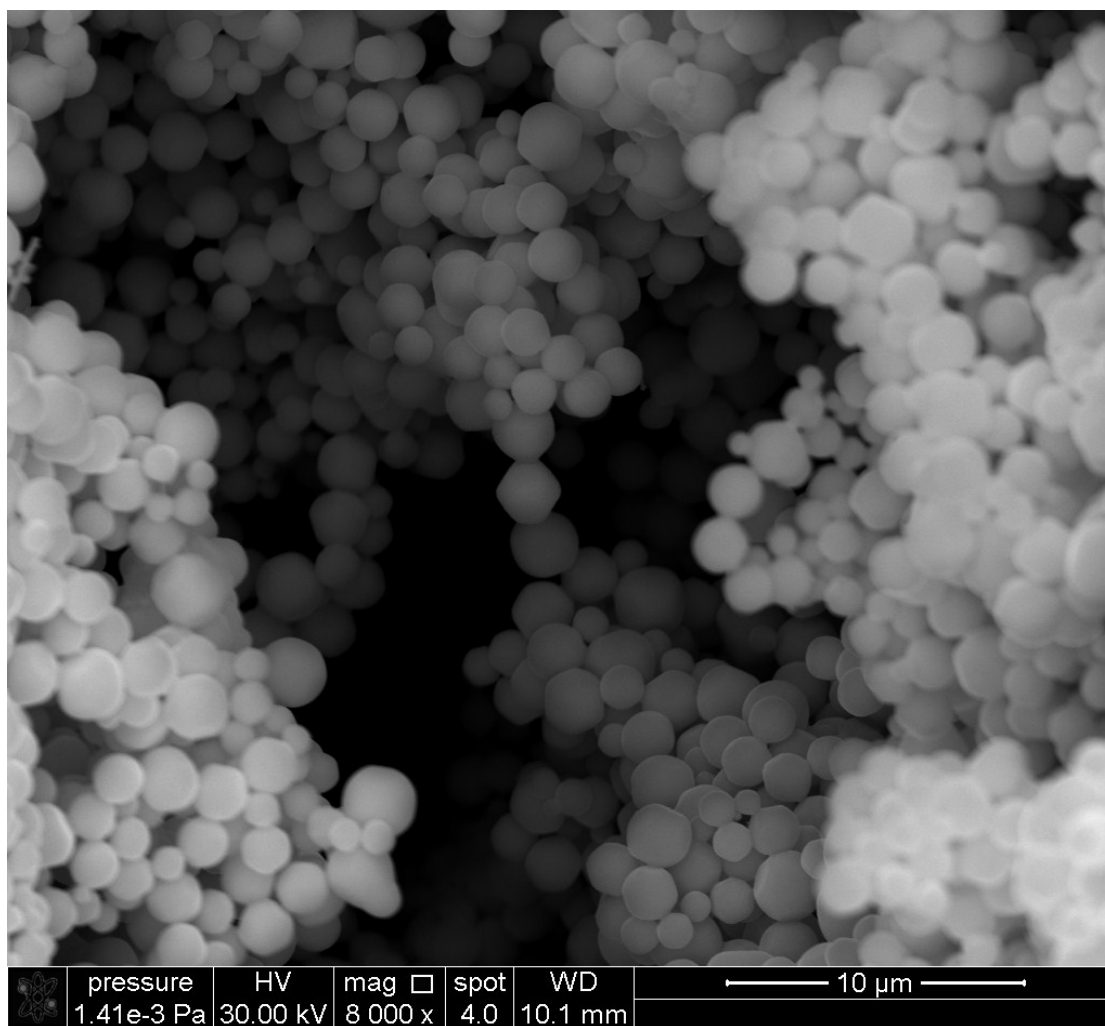


Fig. S1 SEM image of pure AgBr nanoparticles without B-RGO

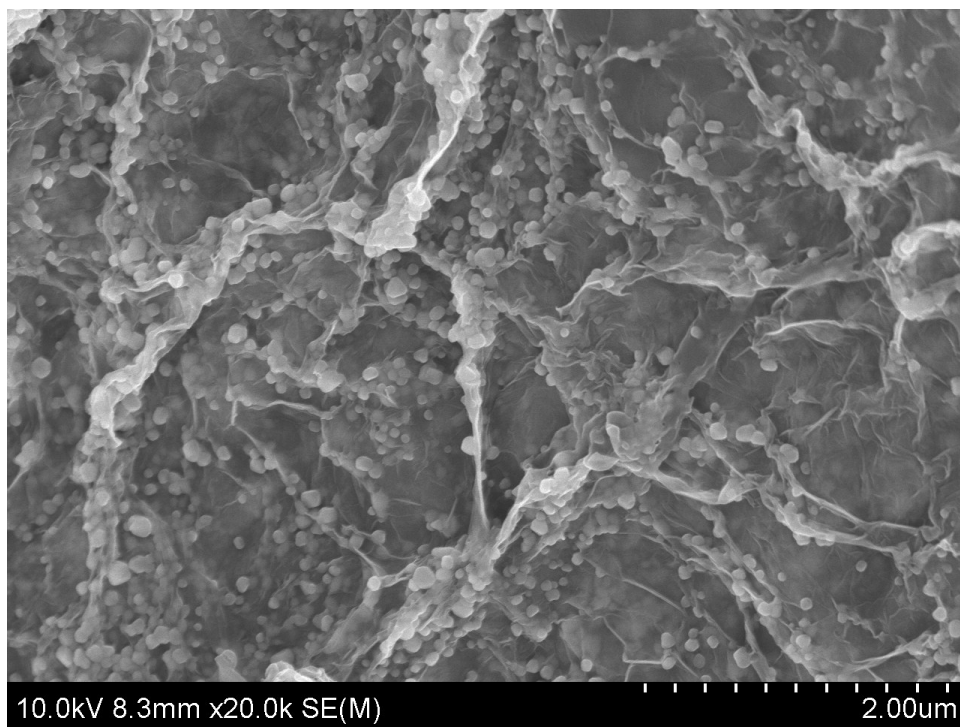


Fig. S2 SEM image of AgBr/RGO

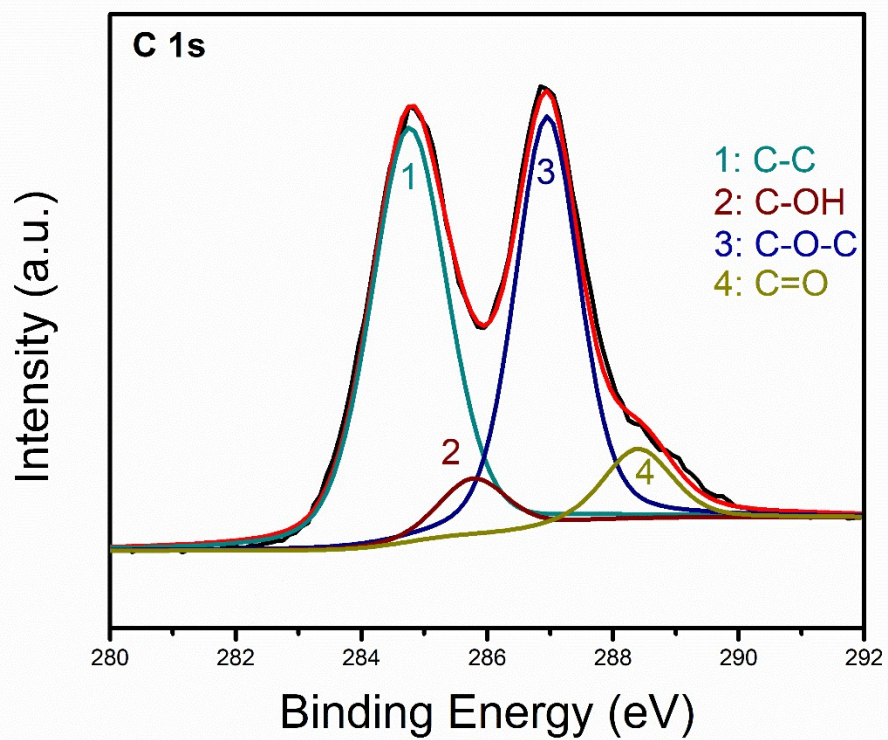


Fig. S3 The XPS spectrum of C 1s of GO

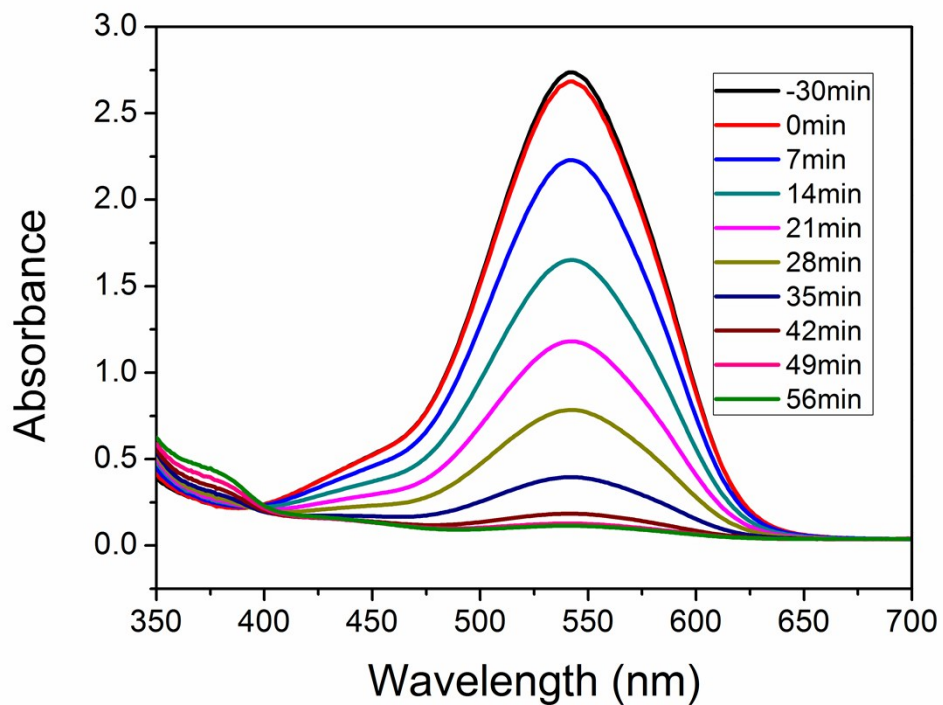


Fig. S4 The real-time absorption spectra of Cr^{VI} during the photocatalytic reduction process by AgBr/B-RGO

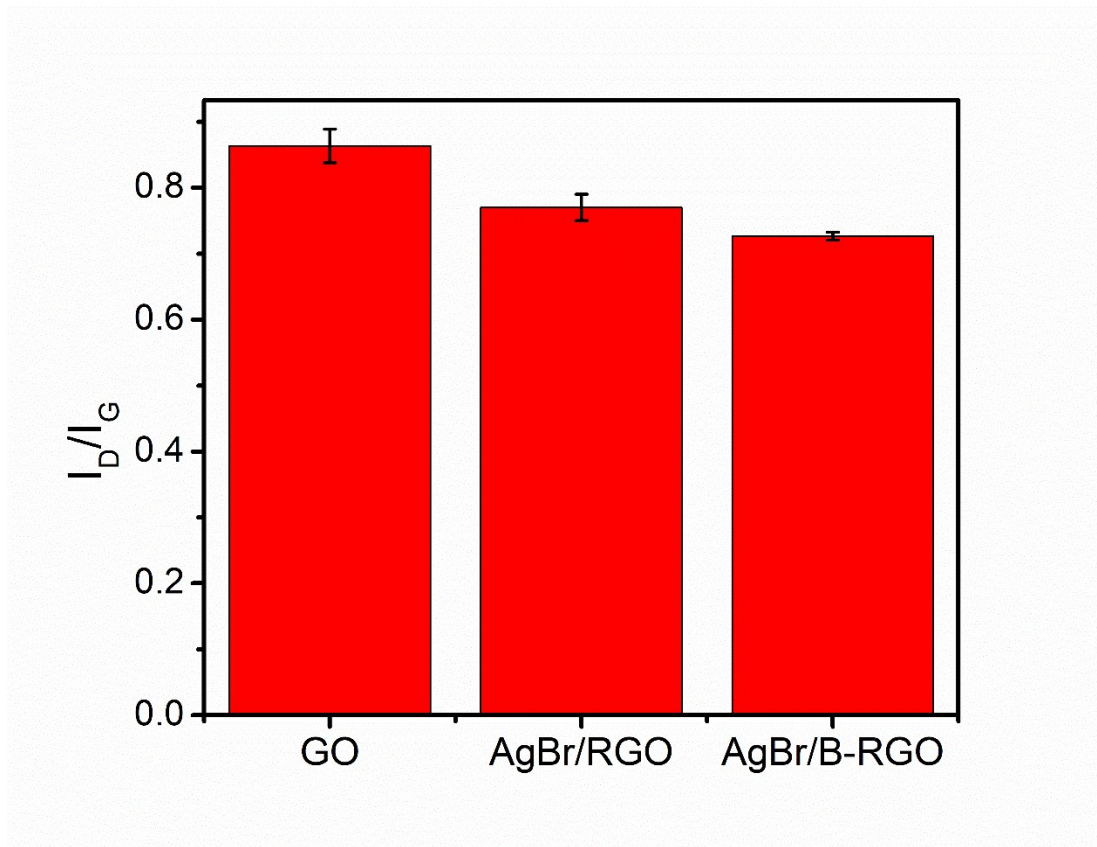


Fig. S5 Error bars of I_D/I_G value of Raman Spectra of GO, AgBr/RGO and AgBr/B-RGO

1. G. Chen, F. Li, Z. Huang, C.-Y. Guo, H. Qiao, X. Qiu, Z. Wang, W. Jiang and G. Yuan, *Catalysis Communications*, 2015, **59**, 140-144.