

Supporting Information

A Bio-inspired Strategy to Interfacial Assembly of Graphene Oxide with *in-situ* Generated Ag/AgCl: Designing Sustainable Hybrid Photocatalysts

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Experimental Section:

Materials: Silver nitrate (AgNO_3), poly(allylamine) hydrochloride (PAH, 15 kDa), poly(allylamine) (17 kDa), potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$), potassium permanganate (KMnO_4), phosphorous pentoxide (P_2O_5), graphite flakes (25 μm), disodium ethylene diamine tetra acetate (EDTA), benzoquinone (BQ), rhodamine B (RhB) and dialysis sacks (12000 Da MWCO) were purchased from Sigma-Aldrich and were used as received. Millipore water (18.2 $\text{M}\Omega$) was used throughout for the solution preparation. Graphene oxide (GO) was synthesized by using modified Hummer's method [(a) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 1958, 80, 1339–1339; (b) T. N. Reddy, J. Manna, R. K. Rana, *ACS Appl. Mater. Interfaces* 2015, 7, 19684–19690)].

Synthesis of Ag/AgCl and GO-Ag/AgCl without using PAH:

Ag/AgCl and GO-Ag/AgCl without PAH were prepared by previously reported method [M. S. Zhu, P. L. Chen and M. H. Liu, *Langmuir*, 2013, 29, 9259–9268]. To 10 mL of 0.01 M AgNO_3 solution, 200 μL of 1M ammonia solution was added followed by the addition of 0.5 mL of GO (1 mg/mL) suspension in a drop wise manner for 5 min under vigorous stirring at room temperature. To the resultant reaction mixture, 500 μL of 0.2 M NaCl was added in a similar manner. After complete addition of NaCl, the stirring was continued for another 20 min. The final solid was obtained after three cycles of centrifugation followed by washing with Millipore water and then dried in air. The bare Ag/AgCl was prepared in the same fashion without the addition of GO.

Synthesis of GO-Ag:

To the 10 mL of GO dispersion, 25 μL of 200 mg/mL poly(allylamine) (17 kDa) solution was added followed by the addition of 500 μL of 0.1 M AgNO_3 solution. The pH of resulting mixture

was adjusted to 5.7 by the addition of HNO_3 (0.1M) and then it was subjected for sonication using a probe sonicator (Vibra cell, VCX750, Sonics & Materials, Inc., USA) with a 40 % intensity for a duration of 20 min. The final solid was obtained after three cycles of centrifugation and washing with Millipore water and then dried in air.

Photocatalytic activity:

The pseudo 1st order rate constant (k) for the photocatalytic degradation of RhB under visible-light irradiation in presence of various catalysts was calculated from the slope (k = -2.303/ slope) obtained from the graph ($\log(C/C_0)$ vs. time(t), Fig. 3b) after the linear fitting.

C_0 = Concentration of RhB at the starting of the reaction after it was mixed with the catalyst and kept in the dark for 30 min to ensure the adsorption–desorption equilibrium.

C = Concentration of RhB at different time intervals during the photocatalytic reaction.

Characterization:

Powder XRD patterns were recorded on a PAN analytical (empyrean, UK) X-Ray Diffractometer using $\text{CuK}\alpha$ ($\lambda=1.5406 \text{ \AA}$) radiation at 45 kV and 30 mA with a standard monochromator, equipped with a Ni filter to avoid Cu $\text{K}\beta$ interference. FE-SEM and EDS analyses were performed on a JEOL-7610F operated at 2, 5, and 15 kV. FT-IR spectra were recorded within $4000\text{--}400 \text{ cm}^{-1}$ on a Bruker ALPHA spectrometer equipped with a DTGS detector. Confocal micro-Raman spectra were recorded on a Horiba Jobin-Yvon LabRam HR spectrometer using 17 mW internal He–Ne laser source having a wavelength of 632.8 nm. XPS analyses were carried out on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg $\text{K}\alpha$ anode. UV-vis absorbance was measured using Varian Cary 5000 spectrometer. For the solid samples, the UV-vis spectra were recorded using Diffuse Reflectance Spectroscopy (DRS) accessory.

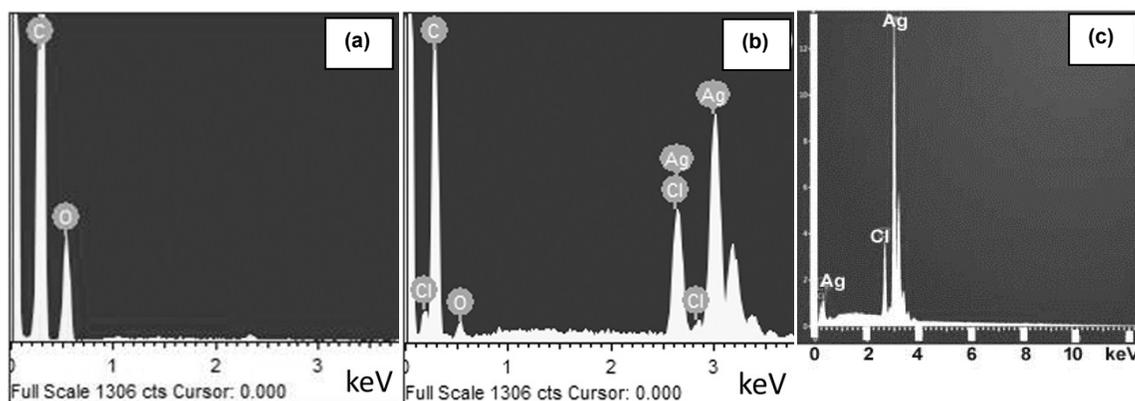


Figure S1. Energy Dispersive Spectra (EDS) obtained for (a) GO and (b) GO-Ag/AgCl; (c) Selected area EDS focused on a particle with brighter contrast on the surface of the Cuboid shaped particle in GO-Ag-AgCl.

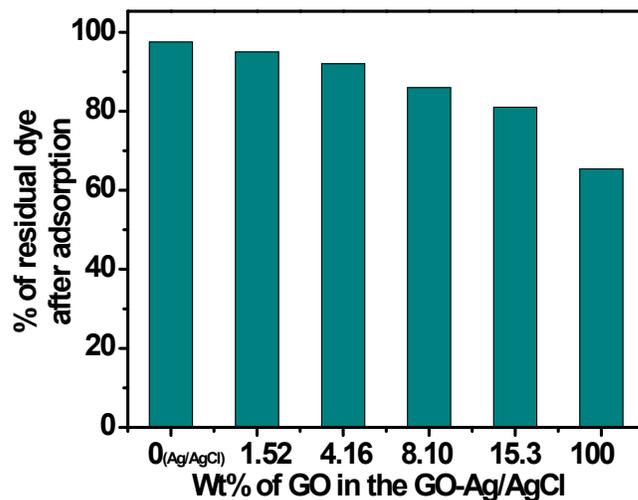


Figure S2. Dye adsorption study on the as-synthesized GO-Ag/AgCl materials with different GO content.

Table S1. Molar atomic ratio of Ag to Cl for various samples determined by EDS analyses.

S. No.	Sample	Ag : Cl
1.	Ag/AgCl (without PAH) ^a	1.1 : 1.0
2.	GO-Ag/AgCl (without PAH) ^a	1.1 : 1.0
3.	Ag/AgCl (with PAH) ^b	1.1 : 1.0
4.	GO-Ag/AgCl (with PAH) ^b	1.1 : 1.0
5.	Ag/AgCl (with PAH) after 5 th Cycle ^b	1.25 : 1.0
6.	GO-Ag/AgCl (with PAH) after 5 th cycle ^b	1.14 : 1.0

^a Samples prepared without using PAH (see experimental section). ^b Samples prepared using PAH.

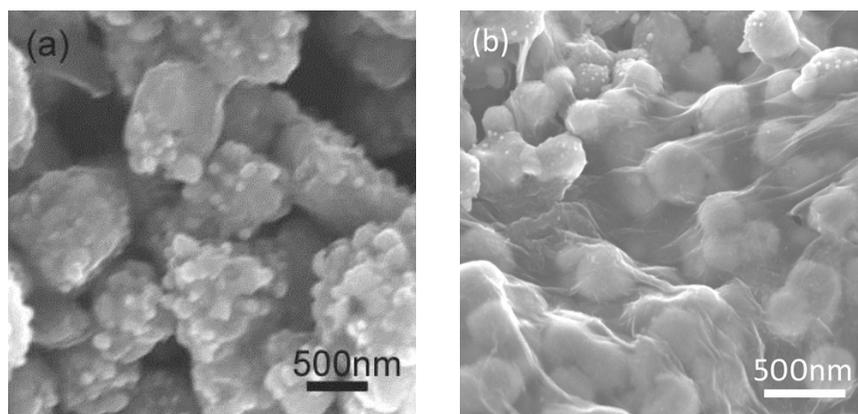


Figure S3. FE-SEM images of (a) Ag/AgCl and (b) GO-Ag/AgCl catalyst after 4th cycle of photocatalytic reaction.

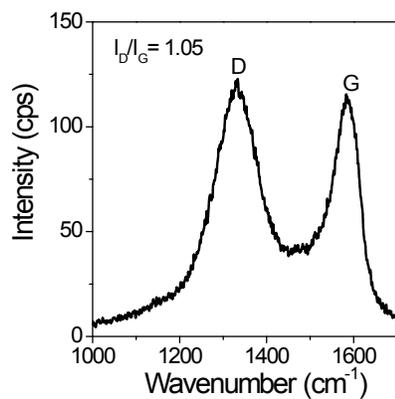


Figure S4. Confocal micro-Raman spectrum of GO-Ag/AgCl after the photocatalytic reaction.