

Electronic Supplementary Information

Pristine Graphdiyne–Hybridized Photocatalysts using Graphene Oxide as Dual–Functional Coupling Reagent

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Synthesis of graphdiyne (GD) and graphene oxide (GO)

Our GD species were synthesized *via* a cross–coupling reaction of hexaethynylbenzene by some of our coauthors. The synthesis was achieved according to the methods reported previously.^{S1} Specifically, 200 mg hexakis[(trimethylsilyl)ethynyl]benzene was dissolved in 50 mL tetrahydrofuran (THF). The solution was kept in an ice bath (ice and ammonium chloride), and was purged with N₂ for 30 minutes. Then, 1 M tetra-*n*-butylammonium fluoride (TBAF) dissolved in THF (2.5 mL) was added into the system, after which the mixture was stirred for 15 minutes at this low temperature. Subsequently, the obtained mixture was diluted with ethyl acetate, washed three times with saturated sodium chloride (NaCl), dried magnesium sulfate (MgSO₄), and filtered. The solvent was then evaporated under vacuum while maintaining the temperature below 30°C. The residue was dissolved in pyridine (50 mL), transferred to a N₂–protected constant addition funnel, and added drop wise into the mixture containing pyridine (50 mL) and the copper foil (2×8 cm²) at 80°C;

this addition process lasted for 8 hours. After addition of the deprotected compound, the reaction mixture was maintained at 120°C for 3 days. Upon completion of the reaction, the pyridine was evaporated under reduced pressure. The copper foil were washed with acetone at first, followed by hot (80 °C) DMF. The combined crude product was washed with hot DMF to remove oligomers. The solid were refluxed at 100°C for 8 hours in 4 mol/L sodium hydroxide, 6 mol/L hydrochloric acid, 4 mol/L sodium hydroxide solution, respectively, to remove silicon and copper. The crude product was collected by centrifuge, washed with hot DMF (80 °C), hot (70 °C) ethanol, then dried to give the black powders. The powders were heated at 100 °C in vacuum for 1h to obtained pure GD powders.

On the other hand, GO nanosheets were synthesized through a chemical exfoliation of graphite powder by using a modified Hummers' method.^{S2, S3} The detailed synthesis was carried out according to the procedures described previously.^{S4} Typically, 1 g of graphite powder was added to 23 ml of cooled (0 °C) concentrated H₂SO₄, after which 3 g of KMnO₄ was added gradually under dramatic stirring. During this process, the temperature of the mixture was maintained below 20 °C using ice bath. The mixture was further stirred at 35 °C for 30 minutes. Subsequently, 46 ml of ultrapure Milli-Q water was slowly added to the system, and the temperature of the system was increased to 98 °C. The mixture was maintained at that temperature for 15 minutes. The reaction was terminated by adding 140 ml ultrapure Milli-Q water, which was followed by 10 ml of 30% H₂O₂ solution. The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution until sulphate could not be detected with BaCl₂. Then the sample was dried in a vacuum oven at 65 °C overnight.

To obtain GO nanosheets dispersed in water, 100 mg of thus-synthesized dried solid product was added to 50 ml ultrapure Milli-Q water, after which the system was treated with an ultrasonic homogenizer (Ningbo Scientz Biotechnology Co., Ltd., Scientz-II D,

frequency: 20 kHz, output power: 400 W) for 1 hour. Subsequently, the suspension was repeatedly treated by high-speed centrifugation (8000 rpm, 5 minutes) for four times to remove impurities.

Supplementary References

S1. G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256–3258.

S2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339–1339.

S3. C. Nethravathi and M. Rajamathi, *Carbon*, 2008, **46**, 1994–1998.

S4. M. Zhu, P. Chen and M. Liu, *ACS Nano*, 2011, **5**, 4529–4536.

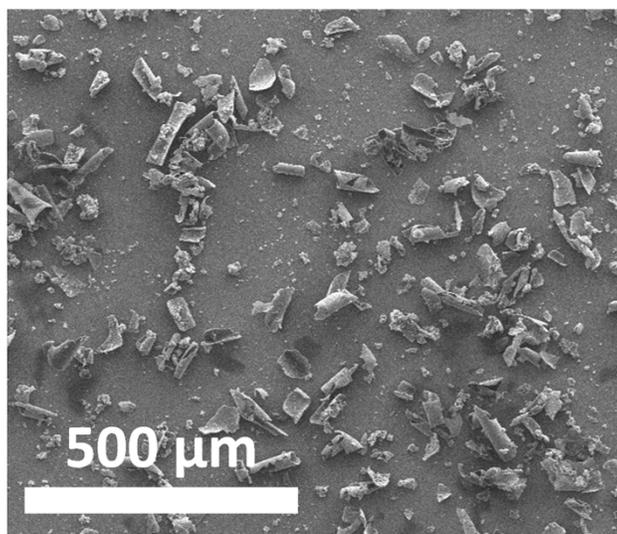


Fig. S1. Typical low-magnification SEM image of our GD sheets.

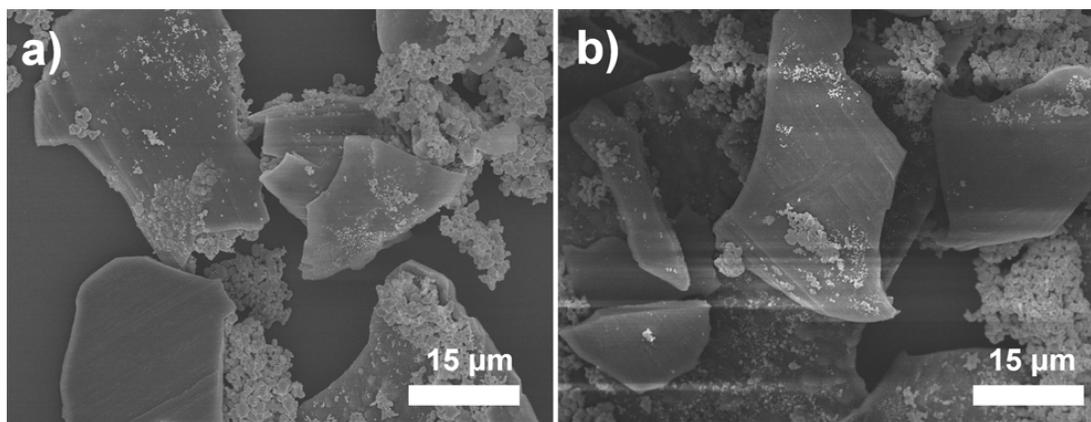


Fig. S2. Typical low-magnification SEM images of the as-formulated Ag/AgBr/GD species.

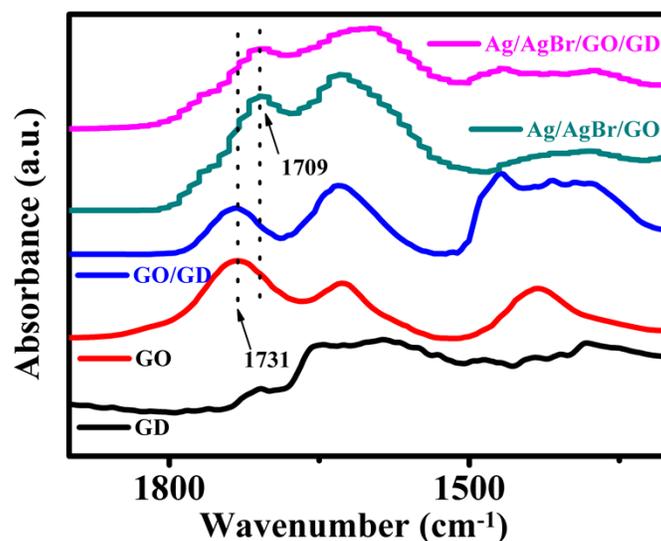


Fig. S3. The FT-IR spectra of our GD, GO, GO/GD, Ag/AgBr/GO, and Ag/AgBr/GO/GD species.

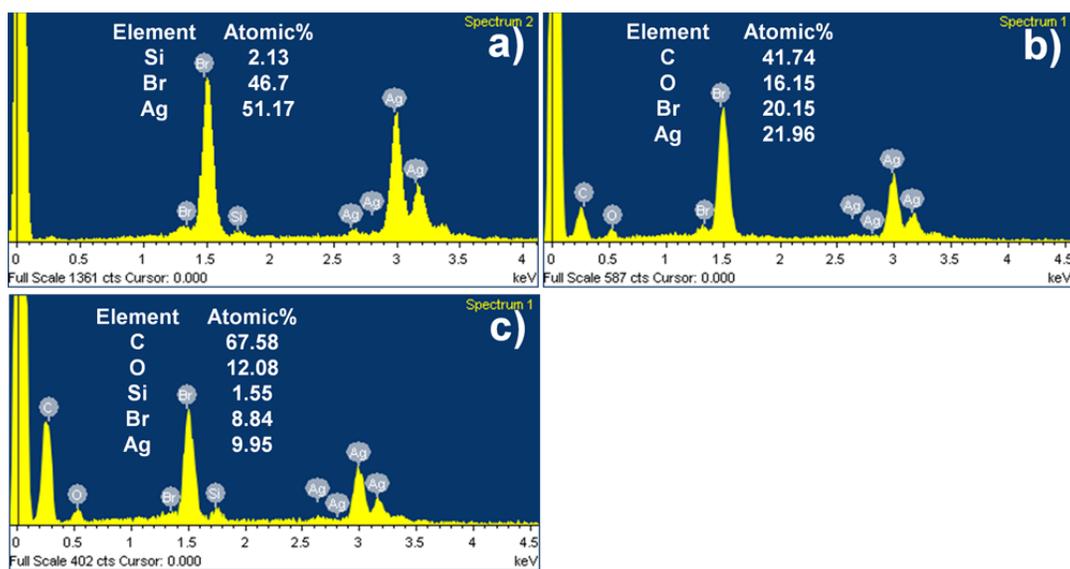


Fig. S4. EDX elemental analysis of our Ag/AgBr (a), Ag/AgBr/GO (b), and Ag/AgBr/GO/GD (c) hybrids. The semiquantitative elemental analysis results for each sample are listed in the corresponding panels. The signals ascribing to Si element could also be detected in some cases, since Si plates were used as the solid support for the measurements.

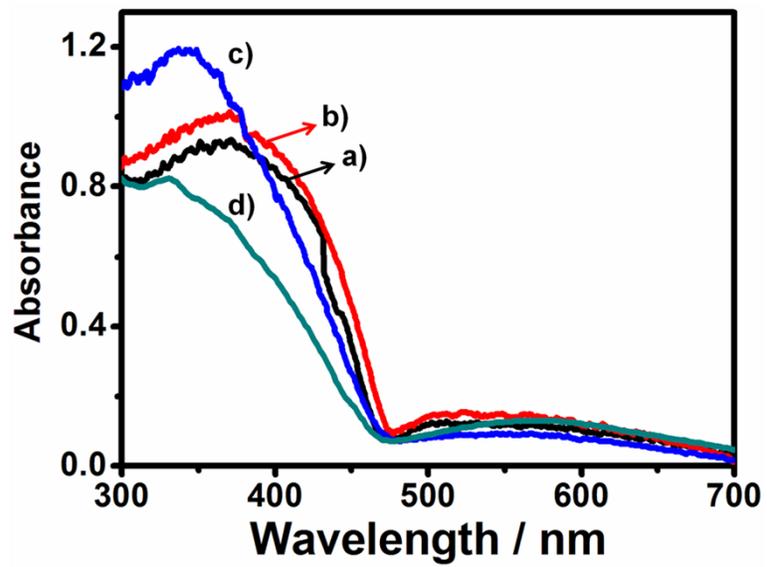


Fig. S5. UV-vis diffuse reflectance spectra of our Ag/AgBr (a), Ag/AgBr/GO (b), Ag/AgBr/GD (c), and Ag/AgBr/GO/GD (d) species.