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Supporting Information

Graphene Oxide-Palladium Modified Ag-AgBr: A Novel Visible-Light-Responsive Photocatalyst for the Suzuki Coupling Reaction**

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Experimental Details

***Materials*:** Graphite powder (320 mesh), silver nitrate ($AgNO_3$), triethanolamine (TEA), dimethyl formamide (DMF), sodium bromide (NaBr), glycerol, polyvinylpyrrolidone (PVP, K-30, MW 40 000), potassium carbonate (K_2CO_3), and ethanol was provided by the Boaixin Co., Ltd. (Baoding, China). Arylboronic acids, aryl halides, and palladium chloride ($PdCl_2$) were purchased from Aladdin Reagent Limited Company and used as received.

***Characterization*:** The size and morphology of the catalyst were observed by scanning electron microscopy (SEM) using a Hitachi S4800 field emission electron microscope operated at 30 kV. The energy dispersive X-ray spectroscopy (EDX) was measured with a Horiba EMAX X-act energy dispersive spectroscopy that was attached to the Hitachi S-4800 system. The XRD patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu Kα radiation (40 kV, 150 mA) in the range $2\theta = 10^o$-80^o. The Pd content was determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 1600 spectroscope using Mg Kα X-ray source for excitation. The diffuse reflectance spectra (DRS) were measured by a UV–vis spectrometer (UV-3600, Shimadzu) in the range of 300–800 nm. $BaSO_4$ was used as the reflectance standard material. The concentrations Pd and Ag were determined by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Thermo Elemental IRIS Intrepid II.

***Synthesis of the photocatalysts*:** Ag-AgBr nanoparticles were fabricated according to the reference method with some modification[S1]. Typically, 39 mg NaBr and 108 mg PVP were added into 15 mL glycerol in a 50 mL flask at 60 °C under stirring. After PVP and NaBr were completely dissolved, 1 mL of glycerol solution of $AgNO_3$ (52 mg mL^{-1}) was injected dropwise to the above solution and stirred for 20 min. Then the mixture was heated to 80 °C and maintained at that temperature for 40 min. Then the flask was placed in 200 °C oil bath and incubated at that temperature for 20 min. The product was rinsed with de-ionized water several times to remove PVP and excess external ions. Without the high-temperature incubation process at 200 °C, the obtained sample was denoted as AgBr.

GO was prepared according to the procedure reported by us[S2]. 0.4 mL of 1 mg mL^{-1} $PdCl_2$ solution was added into 2 mL of 1 mg mL^{-1} GO aqueous dispersion and the mixture was stirred overnight. The as-obtained AgBr nanosheets were dispersed in 8 mL of de-ionized water and then the above GO-Pd solution was added. The mixture was stirred vigorously for 1 h so as to make the GO sheets encase the AgBr evenly. Finally the suspension was dried in a vacuum at 80 °C for 2 h, and the obtained sample was denoted as GO-Pd@Ag-AgBr. Without light irradiated reduction, the sample was denoted as GO-Pd@AgBr. For comparison, Pd@Ag-AgBr was fabricated according to the same procedure for GO-Pd@Ag-AgBr except that 2 mL of the GO aqueous dispersion was replaced by 2 mL of water. GO-Pd sample was obtained by evaporation of GO-Pd aqueous dispersion under vacuum at 80 °C for 2 h.

The concentration of palladium in GO-Pd@Ag-AgBr was 0.5 wt%, which was determined by ICP-AES.

Catalytic Evaluation: In a typical reaction, 2 mL of water, 2 mL of ethanol, 0.5 mmol of aryl halide, 0.60 mmol of aryl boronic acid, 1.5 mmol of potassium carbonate and 25 mg of GO-Pd^{2+}@Ag-AgBr were mixed in a 25 mL round bottom flask and sonicated for 2 minutes to get a homogeneous dispersion. The light irradiation was performed with a HSX-F/UV 300 Xe lamp (Beijing NBET Technology Co., Ltd). The mixture was irradiated with a 300W Xe lamp (focused through a shutter window) equipped with a water filter and an ultraviolet cutoff filter to provide visible light with >400 nm for 1 h under magnetic stir. The distance between the lamp and sample were 25 cm. The temperature of the reactant solution was maintained at 25°C by a water bath during the reaction. Upon the completion of the reaction (monitored by thin layer chromatography), the reaction mixture was diluted with 20 mL H_2O and extracted with ether (3 × 10 mL). The organic phase were combined together and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum. The pure products were obtained by flash chromatography using petroleum ether-ethyl acetate as the eluent.

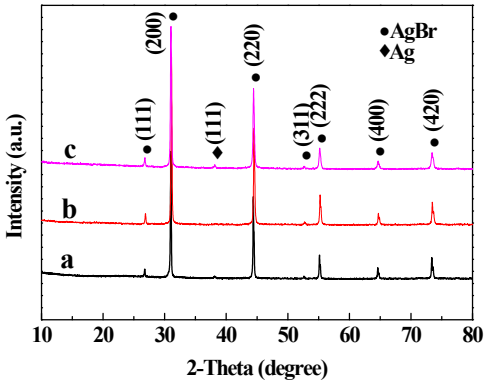


Figure S1. XRD patterns of (a) Ag-AgBr, (b) AgBr, and (c) GO-Pd@Ag-AgBr.

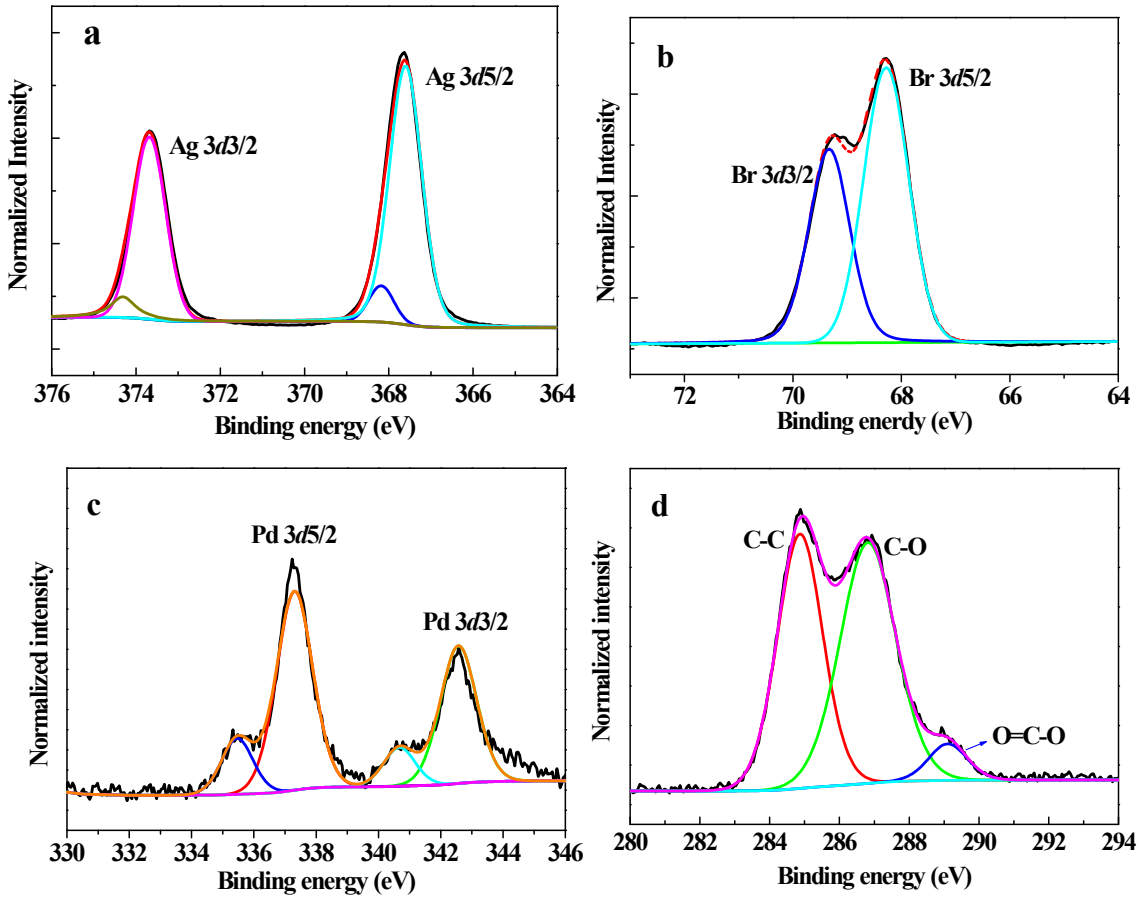
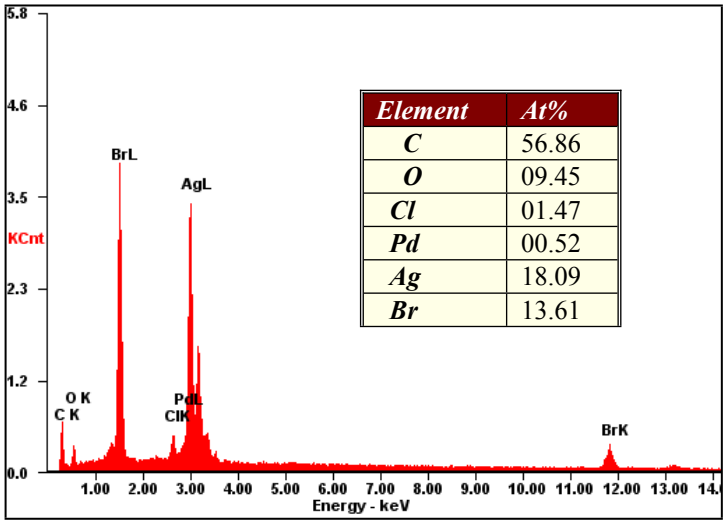


Figure S2. XPS peaks of (a) Ag 3d, (b) Br 3d, (c) Pd 3d and (d) C 1s for GO-Pd@Ag-AgBr.



Element	At%
C	56.86
O	09.45
Cl	01.47
Pd	00.52
Ag	18.09
Br	13.61

Figure S3 EDX elemental analysis of the as-synthesized GO-Pd@Ag-AgBr. The quantitative elemental analysis results are also listed in the inserted panel.

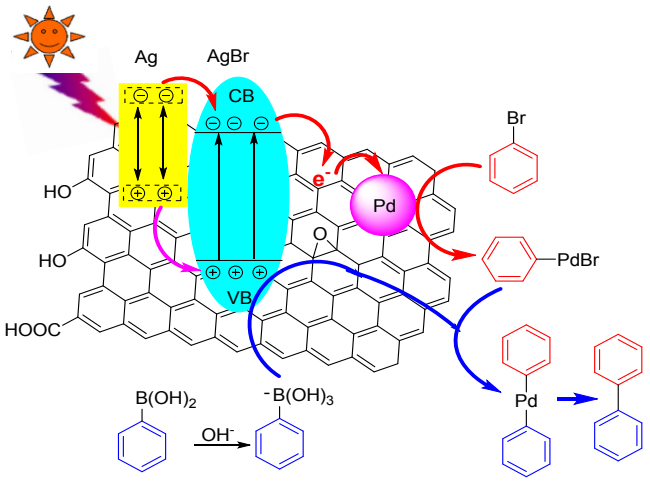


Figure S4. Schematic diagram illuminating the possible photocatalytic mechanism of GO-Pd@Ag-AgBr composite photocatalyst.

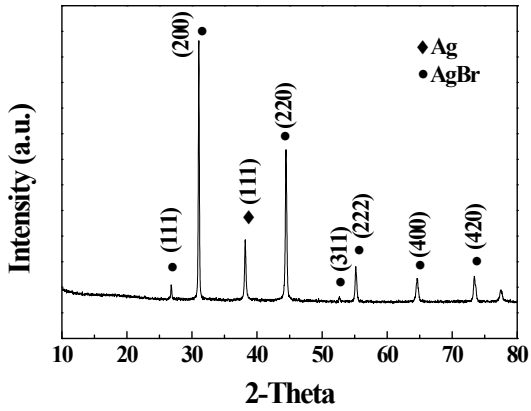


Figure S5. XRD patterns of the used GO-Pd@Ag-AgBr

Table S1. Screening and control experiments for Suzuki coupling of bromobenzene and benzeneboronic acid [a]

Entry	Catalyst	Other changed parameters	hv	Yields (%)
1	GO- Pd @Ag-AgBr	-	+	99
2	GO- Pd @Ag-AgBr	-	-	9
3	GO- Pd @Ag-AgBr	-	UV-light	99[b]
4	Ag-AgBr	-	+	0
5	GO- Pd	-	+	0
6	GO- Pd @Ag	-	+	8
7	Pd @Ag-AgBr	-	+	88
8	GO- Pd @Ag-AgBr	adding 0.5 mL TEA	+	0
9	GO- Pd @Ag-AgBr	adding 0.5 mL TEA, 80 °C, 2h	-	83
10	GO- Pd @Ag-AgBr	without N_2	+	87

[a] Reaction conditions: 2 mL of water, 2 mL of ethanol, 1.5 mmol K_2CO_3, 0.6 mmol benzeneboronic acid, 0.5 mmol bromobenzene, 25 mg of catalyst, N_2 atmosphere, 300 W Xe lamp with UV cutoff filter (providing visible light with >400 nm), 25 °C, 1 h. [b] reaction time 30 min.

Reference

[S1] J. Wang, C. An, J. Liu, G. Xi, W. Jiang, S. Wang, Q.H. Zhang, *J. Mat. Chem. A* **2013**, *1*, 2827-2832.

[S2] C. Wang, C. Feng, Y. Gao, X. Ma, Q. Wu, Z. Wang, *Chem. Eng. J.* **2011**, *173*, 92-97.