



Supporting Information:

New Approach for the Reduction of Graphene Oxide with Triphenylphosphine Dihalide

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Synthesis of GOs

GO (graphene oxide) was synthesized by a modified Hummer's method from natural graphite. After 5 g natural graphite (Sigma Aldrich) and 3.75 g NaNO₃ were added to 98% sulfuric acid (375 ml), the mixture solution was stirred for 20 min in an ice bath. 22.5 g KMnO₄ was gradually added to the mixture solution over 30 min at a temperature less than 25 °C. This solution was then heated to 40 °C with stirring for 3 days. The reaction mixture was cooled to room temperature and poured into deionized ice water (1 L) with 30% H₂O₂ (15 mL). The mixture was heated at 80 °C for 1 hour as the suspension changed color from dark brown to bright yellow. After cooling to room temperature, the mixture was centrifuged (6000 rpm for 30 min) and washed four times with 10% HCl. The mixture was then centrifuged at 8,000 rpm and washed several times with deionized water until the pH was 4. Finally, the resulting solid was dried at 40 °C under vacuum for two days.

Reduction of GOs

To an oven dried 250ml round-bottom flask was added PPh₃ (1.573 g, 6 mmol) and in nitrogen-degassed acetonitrile (8 ml), and then bromine (0.32 ml, 6mmol) was added dropwise to the reaction mixtures for 10 min at 0 °C under a nitrogen atmosphere. After 30 min, 100 mg GO suspended in 100 ml in nitrogen-degassed acetonitrile was added to the reaction mixtures. The reaction flask was fitted with a distillation apparatus containing *sat.* sodium thiosulfate (4 ml) in receiving flask (Figure S1) and heated at 90 °C until the acetonitrile had distilled out. At that time, HBr and Br₂ were trapped by *sat.* sodium thiosulfate into white solid in receiving flask(Figure S2). The resulting reaction mixture in flask was heated at 180 °C for 1 hour under a nitrogen atmosphere (Figure S3). After cooling down to room temperature, the resulting solid was dissolved in chloroform (100 ml) and stirred for

30 min. Subsequently, rGO dispersion was filtered through 0.45 μm PTFE membranes and washed with methanol, ethanol, and dichloromethane. The reduced product was dried overnight in a vacuum oven at 40 $^{\circ}\text{C}$, and rGO nanosheets were collected.

Supplements I

General procedures

Phosphine was dissolved in acetonitrile and degassed with nitrogen for 10 min. Then, halogen was added slowly at 0 $^{\circ}\text{C}$. After 30 min, GO suspended in acetonitrile was added to the reaction mixture and heated at various conditions (temperature and time, Table 1) under nitrogen protection. The resulting mixture was dissolved in chloroform and stirred for 30 min. The rGO dispersion was filtered with 0.45- μm PTFE membranes and filter paper and successively washed with methanol, ethanol, and dichloromethane. Finally, the reduced product was dried overnight in a vacuum oven at 40 $^{\circ}\text{C}$.

<Table 1>

<i>Reagent (mmol)*</i>	<i>Temp (°C)</i>	<i>Time</i>	<i>C</i>	<i>O</i>
PPh_3Br_2 (3)	180	1h	87.1	11.9
PPh_3Br_2 (6)	120	1h	88.4	11.2
"	180	1h	93.8	5.8
"	180	2h	89.7	7.3
"	180	4h	89.9	8.2
"	250	1h	89.4	8.3
PPh_3Br_2 (9)	180	1h	91.1	7.8
"	180	2h	90.5	8.4
"	180	4h	90.7	8.2
PPh_3Br_2 (12)	180	2h	93	5.9
"	180	4h	91.6	5.7
PPh_3 (6), Br_2 (12)	140	1h	85.2	12.6
PPh_3 (6), NBS (6)	180	1h	78.8	14
PPh_3 (6), $\text{Cl}_2(\text{g})$	120	8h	85.1	13.2
"	140	1h	79.4	13.2
"	140	8h	86.6	11.7
PPh_3 (6), CCl_4 (6)	180	1h	77.6	18.6
PPh_3I_2 (6)	60	1h	77.1	22.1
"	80	1h	84	14.8
"	120	2h	82.7	15.6
"	140	1h	86.1	13
"	140	8h	88.8	9.9
"	180	1h	93.1	6.1
"	180	2h	90.1	8.3
"	180	3h	88.6	9.4
"	180	4h	87.9	9.3
PPh_3 (6), I_2 (12)	180	1h	85.4	9.2
PPh_3 (12), I_2 (6)	180	1h	90.1	9.1

* GO (100mg) used for each reaction.

<Table 2>

<i>Reagent (mmol)*</i>	<i>Temp (°C)</i>	<i>Time</i>	<i>C</i>	<i>O</i>
PPh ₃ (6)	140	1h	81.5	18.3
OPPh ₃ (6)	180	1h	88.4	10.3
AsPh ₃ (6)	140	1h	79.2	20
P(cy-hex) ₃ (6)	140	1h	82.4	16.3
P(Et) ₃ (6)	140	1h	77.8	19.8
OP(Oct) ₃ (6)	140	1h	82	17.4
AsPh ₃ (6) Br ₂ (6)	180	1h	81.3	17.6
PBu ₃ (6), Br ₂ (6)	140	1h	84.1	14.6
P(cy-hex) ₃ (6), I ₂ (6)	140	1h	82.5	11.4

Supplement II

Triphenylphosphine was dissolved in solvent (Table 2) and degased with nitrogen for 10 min. Then, bromine (iodine) was added drop-wise for 10 min at 0 °C. After 30 min, GO suspended in acetonitrile was added to the reacted mixture and heated at various conditions (temperature and time, Table 1) under nitrogen protection. The resulting mixture was dissolved in chloroform and stirred for 30 min. The rGO dispersion was filtered with 0.45- μm PTFE membranes and filter paper and successively washed with methanol, ethanol, and dichloromethane. Finally, the reduced product was dried overnight in a vacuum oven at 40 °C.

<Table 3>

<i>Reagent</i>	<i>Solvent</i>	<i>Time</i>	<i>Temp.</i>	<i>C</i>	<i>O</i>
GO, PPh ₃ Br ₂	Chlorobenzene	2h	120°C	88.1	10.5
"	NMP	2h	180°C	79.4	11.7
GO, PPh ₃ I ₂	Chlorobenzene	1h	50°C	77.1	22.1
"	"	1h	60°C	86.3	12.1
"	"	2h	120°C	85.1	12.5

<Table 4> XPS-determined atomic percentage of GO treated with various reductants.

Reductant	C:O atomic ratio	Ref
N ₂ H ₄	6.2	S1
NaBH ₄	5.3	S1
HI	12	S2
Ph ₃ PBr ₂	16	Our Method

[Ref S1] H. Shin *et al.*, *Adv. Func. Mater.*, 2009, **19**, 1987-1992.

[Ref S2] S. Pei *et al.*, *Carbon*, 2010, **48**, 4466-4474.



Fig. S1 The reaction flask was fitted with a distillation apparatus containing sat. sodium thiosulfate (4ml) in receiving flask



Fig. S2 HBr and Br₂ were trapped by sat. sodium thiosulfate in receiving flask



Fig. S3 The resulting solid was heated at 180 °C for 1 hour under a nitrogen atmosphere.

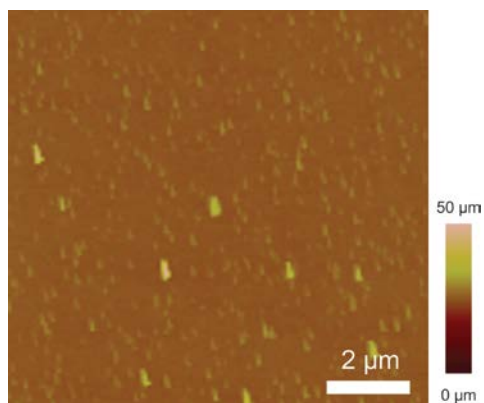


Fig. S4 Atomic force microscope (AFM) topography image of GO on the SiO₂ substrate. Here, scale bars indicate 2 μm.