Supporting Information

Bifunctional Graphene-Based Metal Free Catalysts for Oxidative Coupling of Amines

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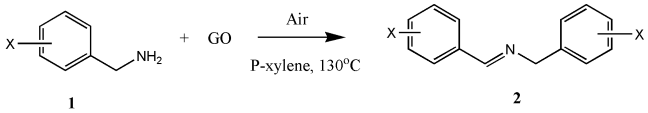
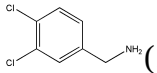
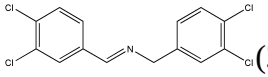
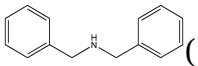
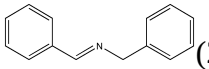
Table S1 Aerobic Oxidation of Various Amines to Corresponding Imines Using GO[a]



1 2

Entry	Substrates (1)	Products (2)	Time (h)	Yield (%)[b]
1	X=H (1a)	X=H (2a)	8	87.39
2	X=p–Cl (1b)	X=p–Cl (2b)	10	96.7
3	X=p–F (1c)	X=p–F (2c)	8	95.06
4	X=p–Me (1d)	X= p–Me (2d)	8	95.48
5	X= p–OMe (1e)	X= p–OMe (2e)	8	98
6	 (1f)	 (2f)	10	75.4
7	 (1g)	 (2g)	8	88.35

[a] reaction conditions: amine (2.5 mmol), GO (26 mg) and p–xylene (5 mL) at 130 °C in air condition. [b] isolated yield.

Table S2 The atomic C/O ratio and atomic percentages of surface functional groups from deconvolutted C 1s XPS spectral fitting. GO-blank: GO obtained after the heating in p-xylene at 130 ^{o}C for 8 hours.

Entry	Sample	C/O	C=C	C–C & C–H	C–O	O–C=O
1	GO	1.93	32%	17.6%	40.7%	9.7%
2	IGO	1.89	24.4%	16.1%	44.9%	14.6%
3	GO–Ar_5	8.13	59.3%	20.1%	10.8%	9.7%
4	GO–Ar_5–P	3.25	44.9%	18.8%	20.7%	15.6%
5	GO–air_5	7.7	47.5%	27.2%	15.2%	10.1%
6	GO–air_5–P	3.35	52.3%	17.4%	17.5%	12.8%
7	GO-b	2.74	51.11%	26.5%	5.09%	17.3%
8	GO-ba	2.86	51.41%	10.5%	22.66%	15.43%
9	mGO	24.71	62.8%	20.41%	5.41%	3.84%
10	GO-blank	5.26	50.5%	18.81%	17.78%	12.91%

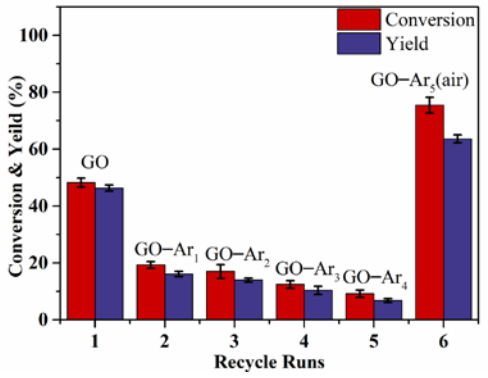


Figure S1 Recyclability of GO in benzylamine oxidation reaction in argon condition (6: the performance of GO–Ar_5 in air).

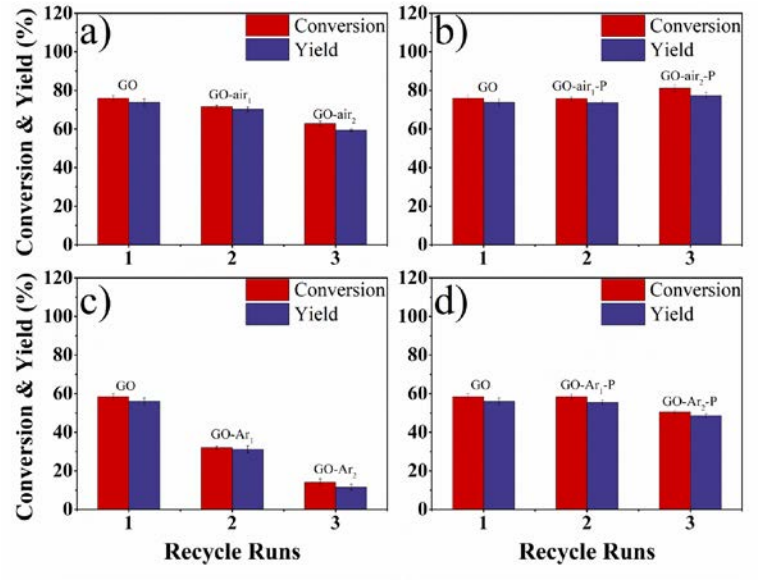


Figure S2. (a) Recycling experiment without continuous treatment of the piranha solution in air. (b) Recycling experiment with continuous treatment of the piranha solution in air. (c) Recycling experiment without continuous treatment of the piranha solution in argon. (d) Recycling experiment with continuous treatment of the piranha solution in argon.

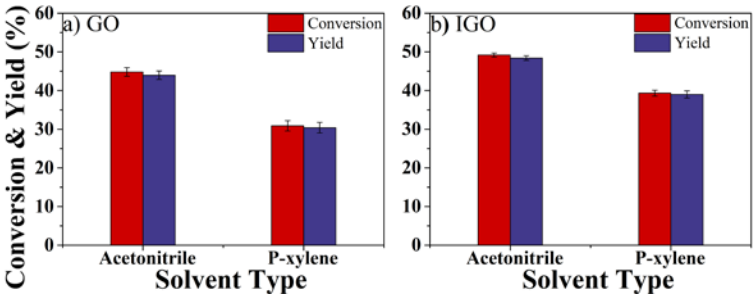


Figure S3 Oxidation of Benzylamine to N–benzylidene Benzylamine catalyzed by GO (a) and IGO (b) in different solvents[a].

[a] reaction condition: benzylamine (2.5 mmol), GO or IGO (26 mg) and solvent (5 mL) at 80 ^{o}C for 8 h in air.

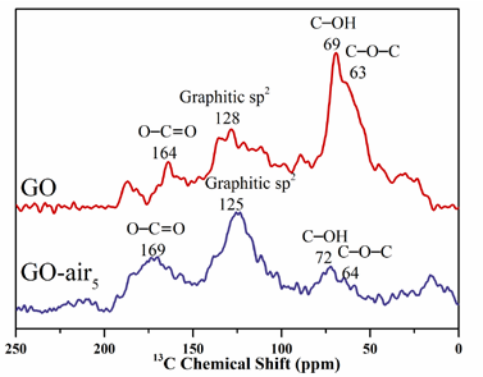


Figure S4 Solid–state ^{13}C NMR spectra of GO and GO–air$_5$.

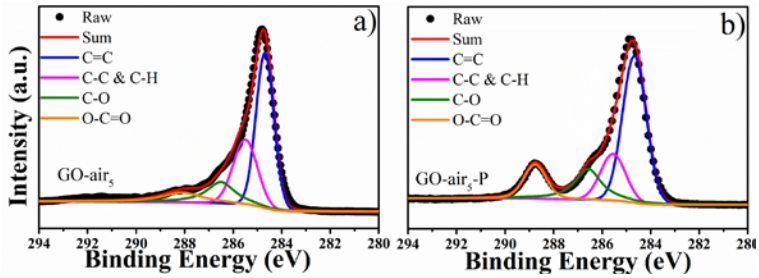


Figure S5 XPS C 1s spectra of GO–air$_5$ (a) and GO–air$_5$–P (b).

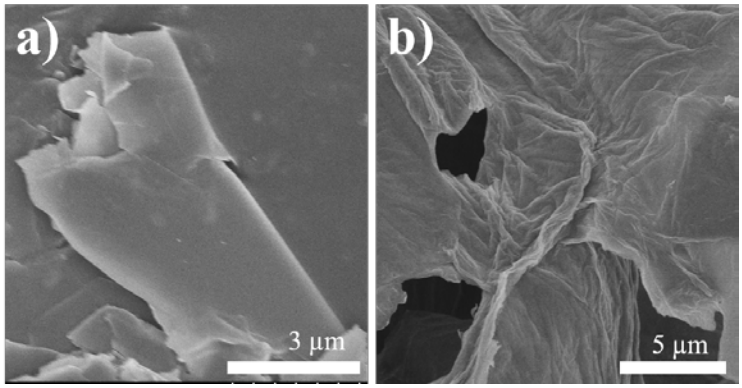


Figure S6 SEM image of GO (a) and IGO (b).

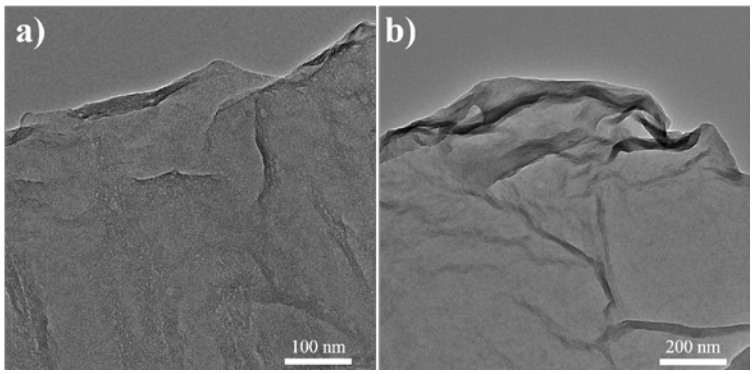


Figure S7 TEM image of GO (a) and IGO (b).

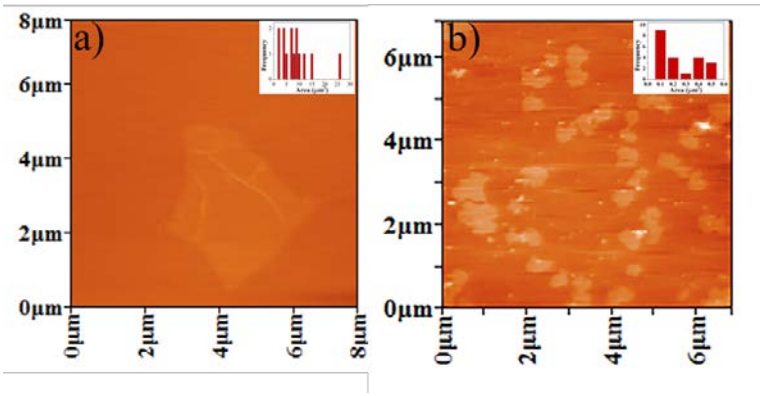


Figure S8. AFM images of GO (a) and IGO (b) (inset is the corresponding size distribution). The average area of GO and IGO is 9.09 and 0.29 μm^2, respectively.

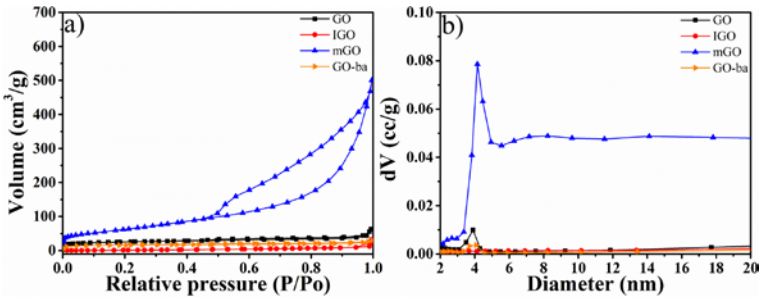


Figure S9. N_2 adsorption/desorption isotherms (a) and pore size distributions (b) of GO, IGO, mGO and GO-ba.

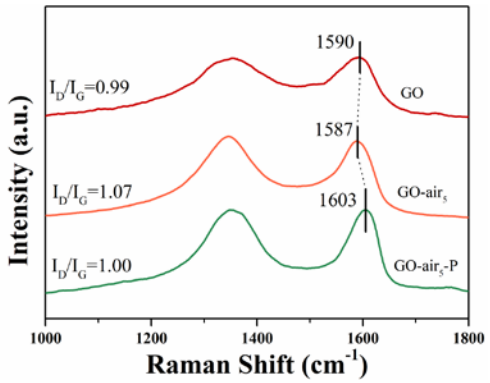


Figure S10 Raman spectra of GO, GO–air$_5$ and GO–air$_5$–P.

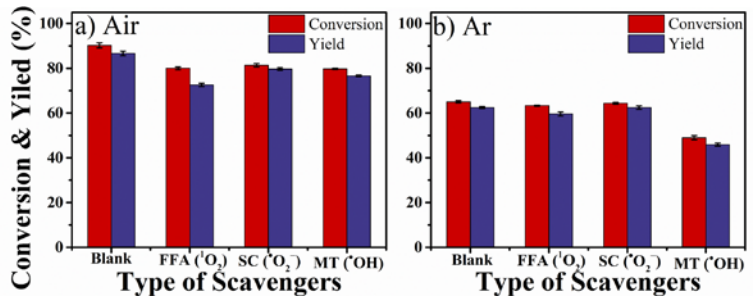


Figure S11 Oxidation of Benzylamine to N–benzylidene Benzylamine adding scavengers in air (a) and argon (b) conditions[a].

[a] reaction conditions: benzylamine (2.5 mmol), GO (26 mg), p–xylene (5 mL) and scavengers [FFA (1.15mmol), SC (50mg) and MT (2.47mmol)] at 130 ^{o}C in air or argon condition.

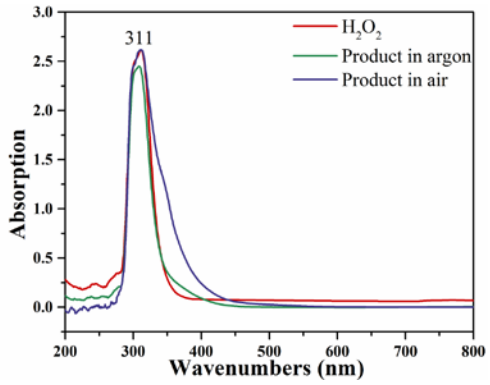


Figure S12 Ultraviolet-visible absorption spectroscopy of the oxidation of benzylamine system in air and argon.

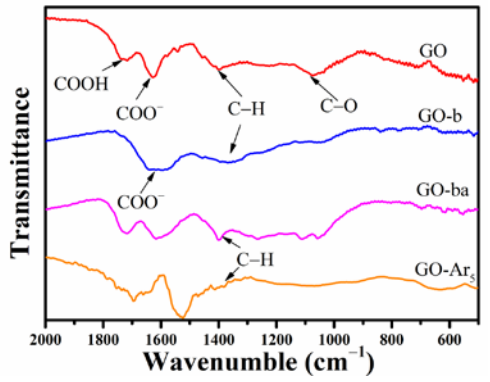


Figure S13. FTIR spectra of GO, GO-b, GO-ba and GO-Ar_5.

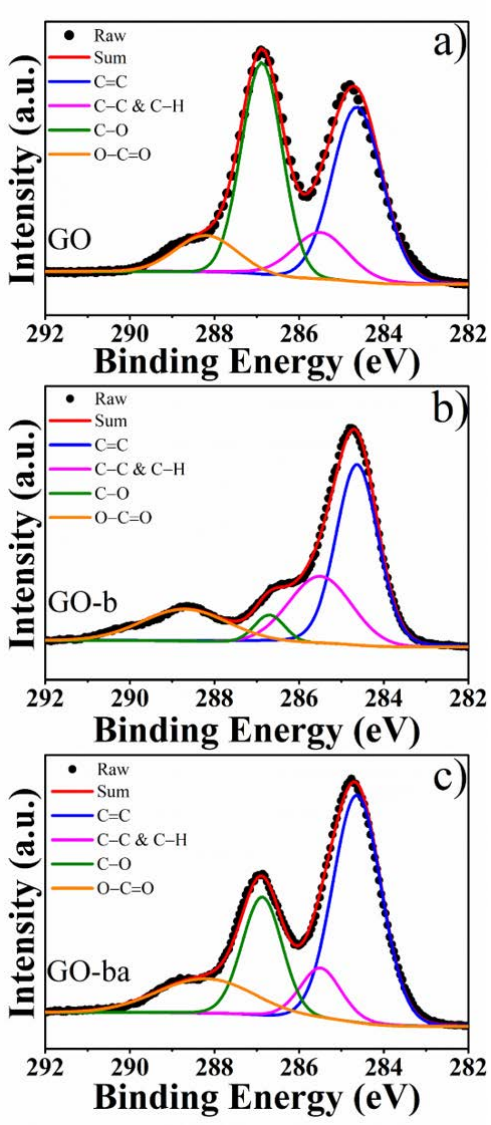


Figure S14. XPS C 1s spectra of GO (a), GO-b (b) and GO-ba (c), respectively.

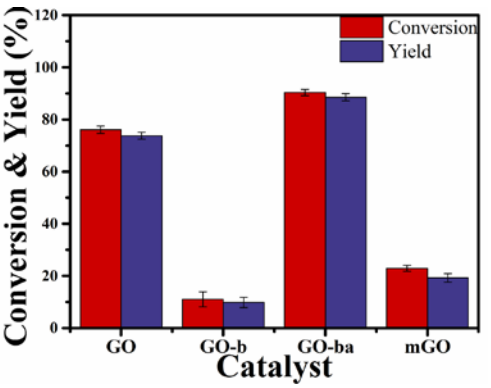


Figure S15. The performance of GO, GO-b, GO-ba and mGO in the benzylamine oxidation in air condition.

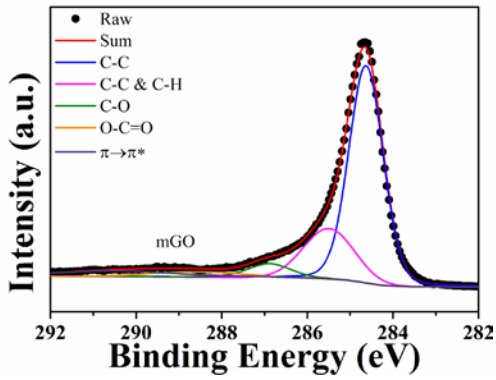


Figure S16. XPS C 1s spectrum of mGO.

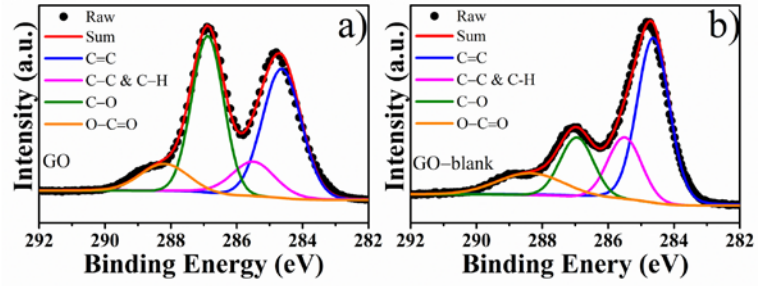


Figure S17. XPS C 1s spectra of GO (a) and GO-blank (b). GO-blank: GO obtained after the heating in p-xylene at 130 ºC for 8 hours.