Supplementary Information for

Kraft lignin derived S and O co-doped porous graphene for metal-free benzylic alcohol oxidation

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1　Catalyst preparation

1.1　Extract alkali metal ions from Kraft lignin

0.2 g Kraft lignin was added into 100 mL water under vigorous stirring at 50 ℃ for 2 h. The sample was collected by washing and centrifugation, dried at 80 ℃ overnight, and pyrolyzed with the same procedure as above.

1.2　Extract organosolv lignin

Organosolv lignin was extracted from hardwood locust based on the previous method.[1] The locust sawdust was provided by a local manufactory (ca. 40 mesh), and dried at 100 ℃ for 1 day prior to its use. 1.0 g locust sawdust, 30 mL ethanol and 30 mL water were loaded into a 0.1L high-pressure autoclave and heated at 180 ℃ for 5 h. Subsequently, a reddish-brown solution was collected by centrifugation, and solvent was separated by a rotary evaporator. Finally, the obtained organosolv lignin was dried at 80 ℃ overnight, and pyrolyzed with the same procedure as Kraft lignin.

1.3　Synthesis of conventional graphene and graphene oxide (GO)

Conventional graphene was fabricated by rapid heating-up of GO under high vacuum, in which GO was synthesized from a modified Hummer's method described in our previous reports.[2-3] The as-prepared GO was sharply heated to 200 ℃ at a ramp rate of 30 ℃/min under a pressure lower than 2.0 Pa. The layered graphene can be formed through the abrupt expansion.

2　Catalytic tests

2.1　Reduction of nitrobenzene with 2-propanol to aniline

0.5 mmol nitrobenzene, 8 mL 2-propanol, 3 mmol KOH and 0.05 g catalyst were

put into an autoclave. The reactor was purged into 0.1 MPa N_2 and heated at 120 ℃ for 24 hours. The procedure for product analysis was the same as benzyl alcohol oxidation.

2.2 Oxidative coupling of benzylamine

0.05 g benzylamine, 0.05 g catalyst, 0.5 mmol KOH and 10 mL ethyl acetate were loaded into an autoclave. The reactor was purged into 0.5 MPa O_2 and heated at 120 ℃ for 10 hours. The same method for product analysis was used as above.
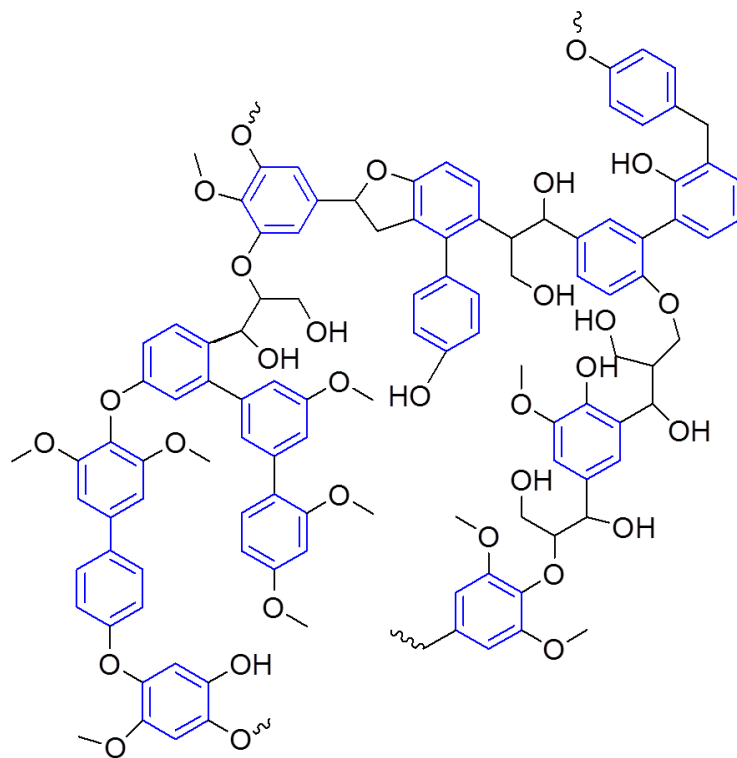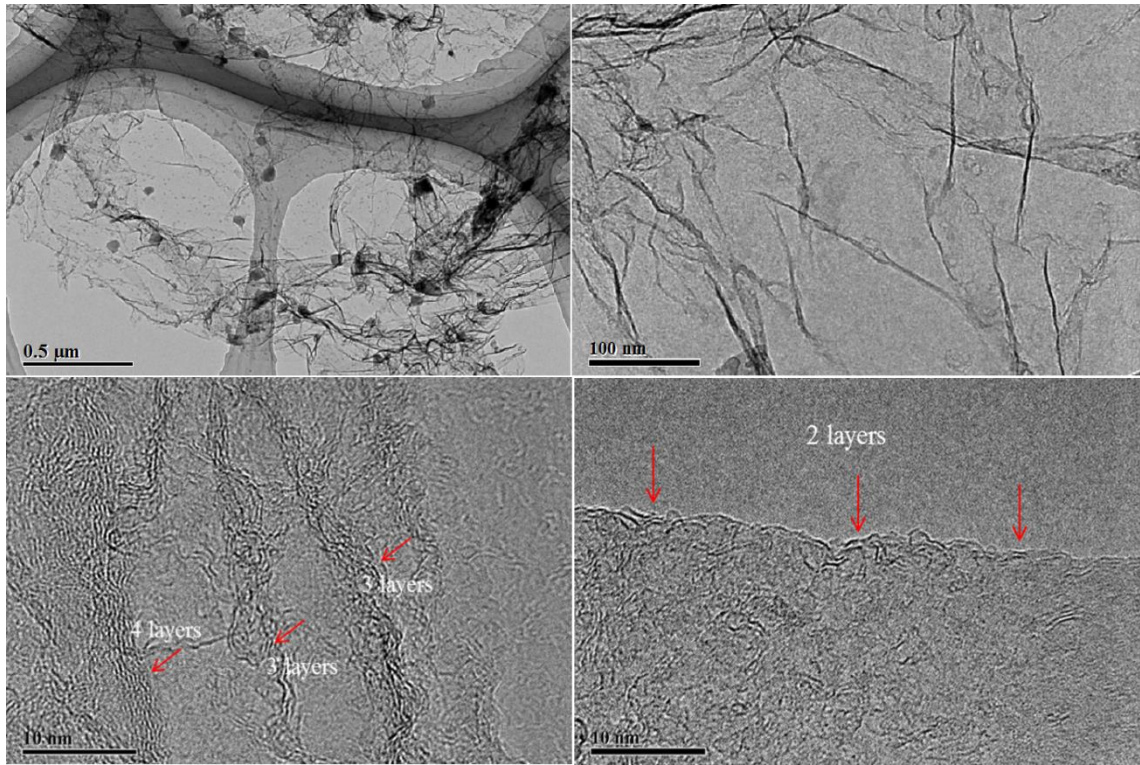
Scheme S1 Chemical structure of lignin.

Fig. S1 TEM and HRTEM images of G900.
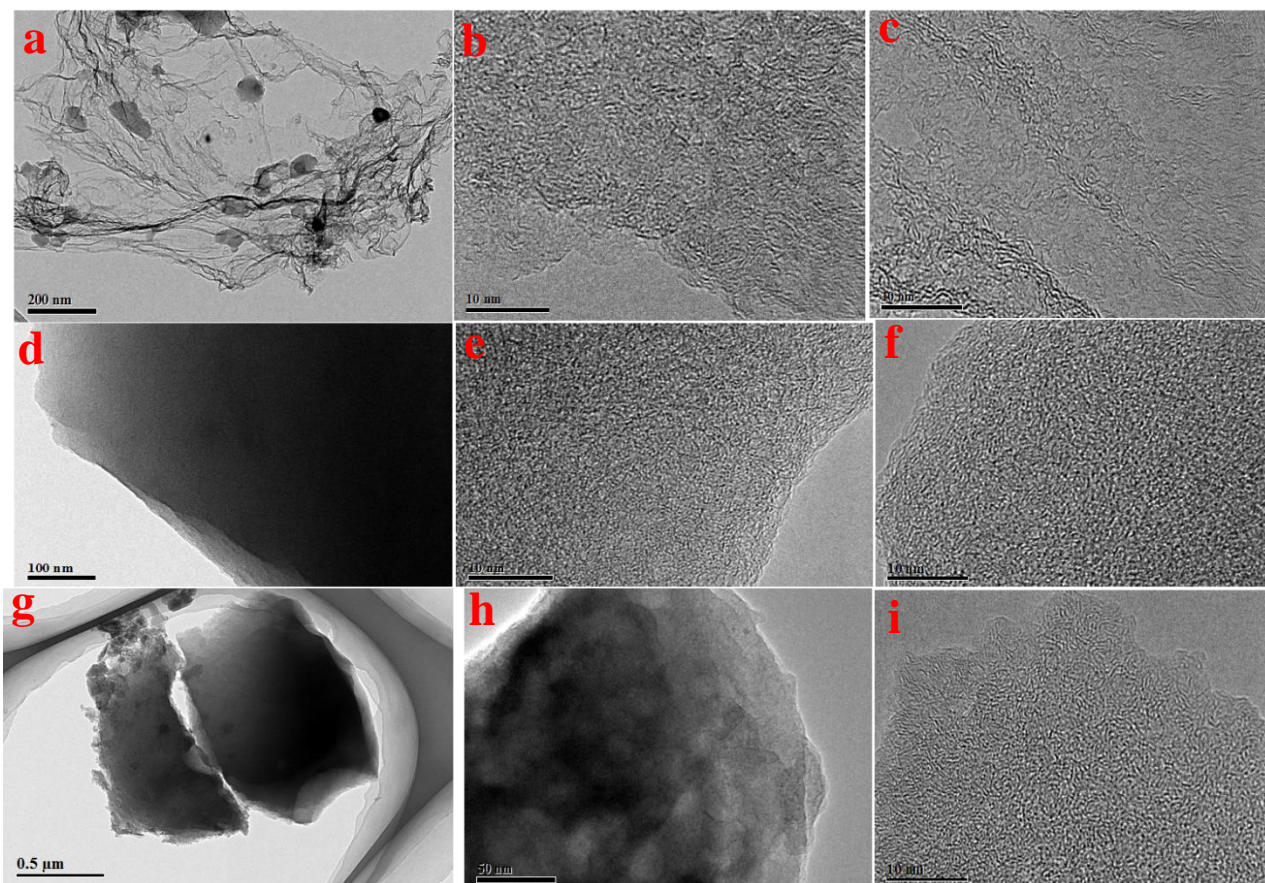
Fig. S2 TEM and HRTEM images (a to c) of G800, (d to f) G700 and (g to i) G600.
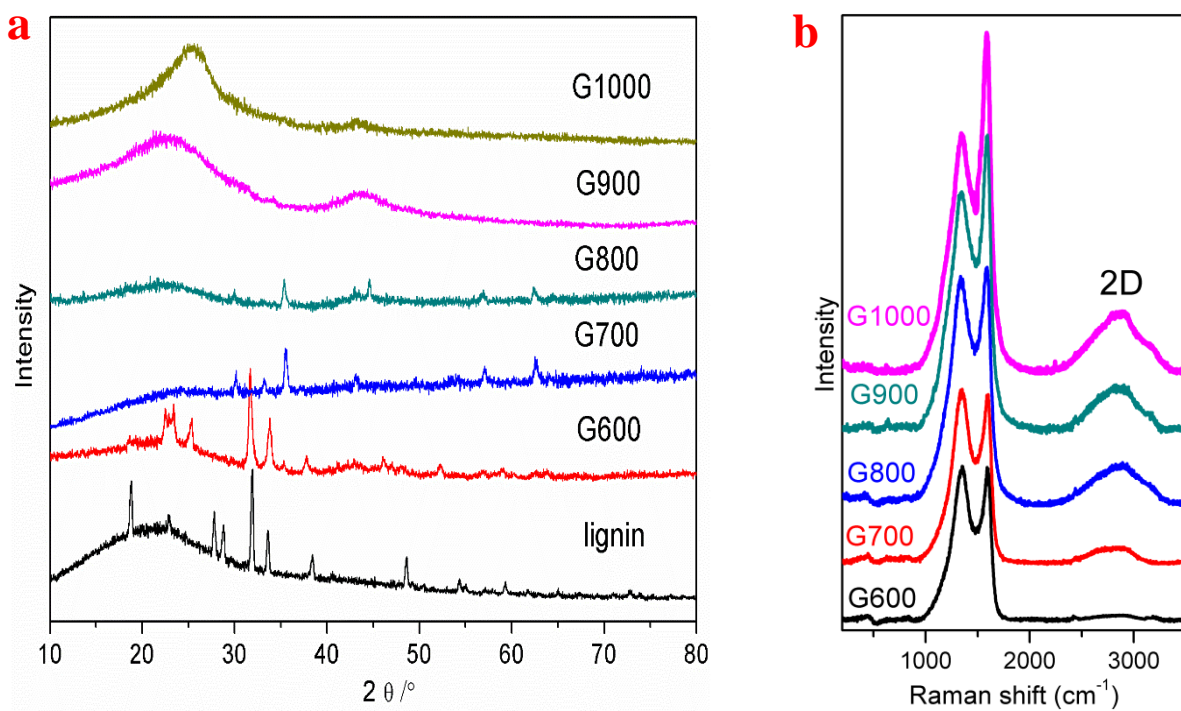
Fig. S3 (a) XRD patterns of lignin and related carbon materials at various annealing temperature. (b) Raman spectra of various carbon materials. The horizontal axis is shortened to clearly observe the 2D peaks.
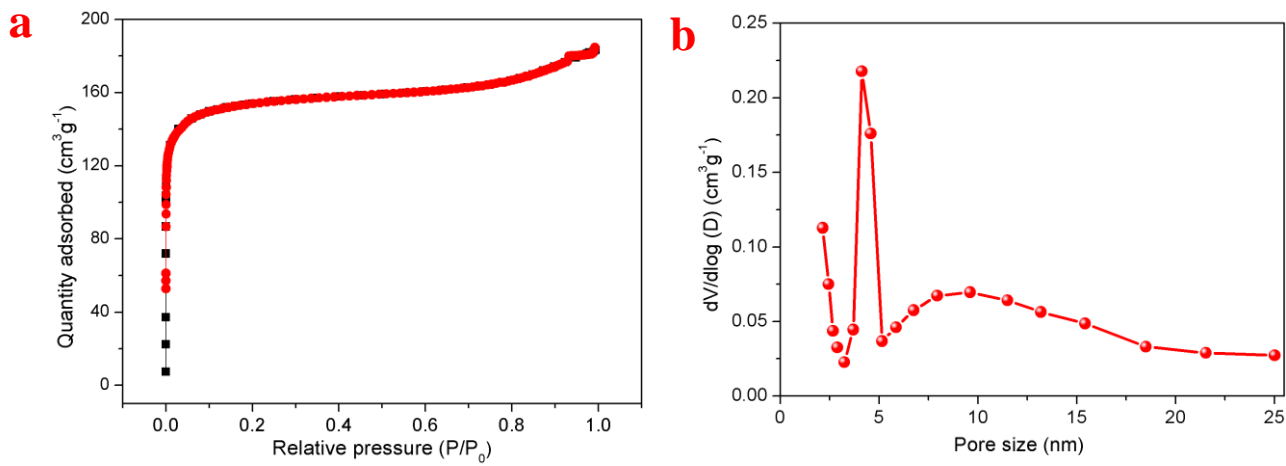
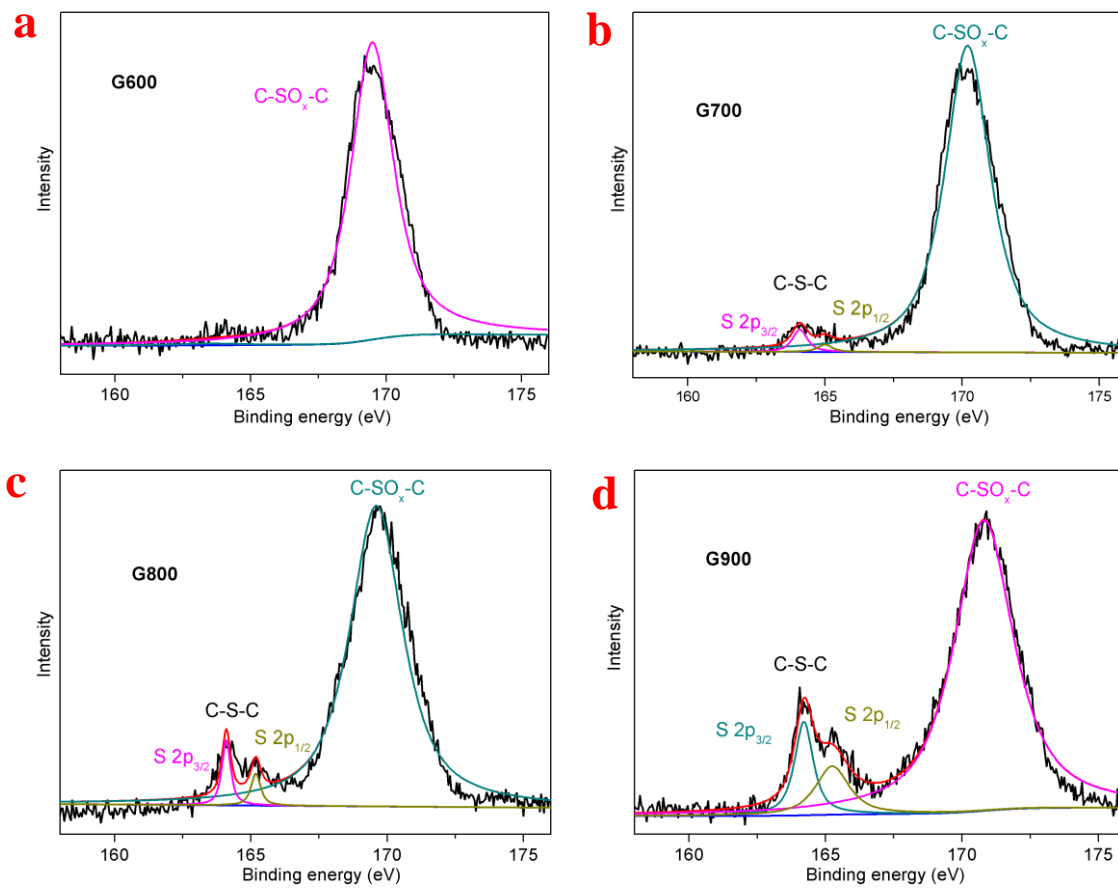**Fig. S4** (a) N$_2$ adsorption-desorption isotherm and (b) pore size distribution of G1000.

Fig. S5 S 2p XPS peaks of (a) G600, (b) G700, (c) G800 and (d) G900.
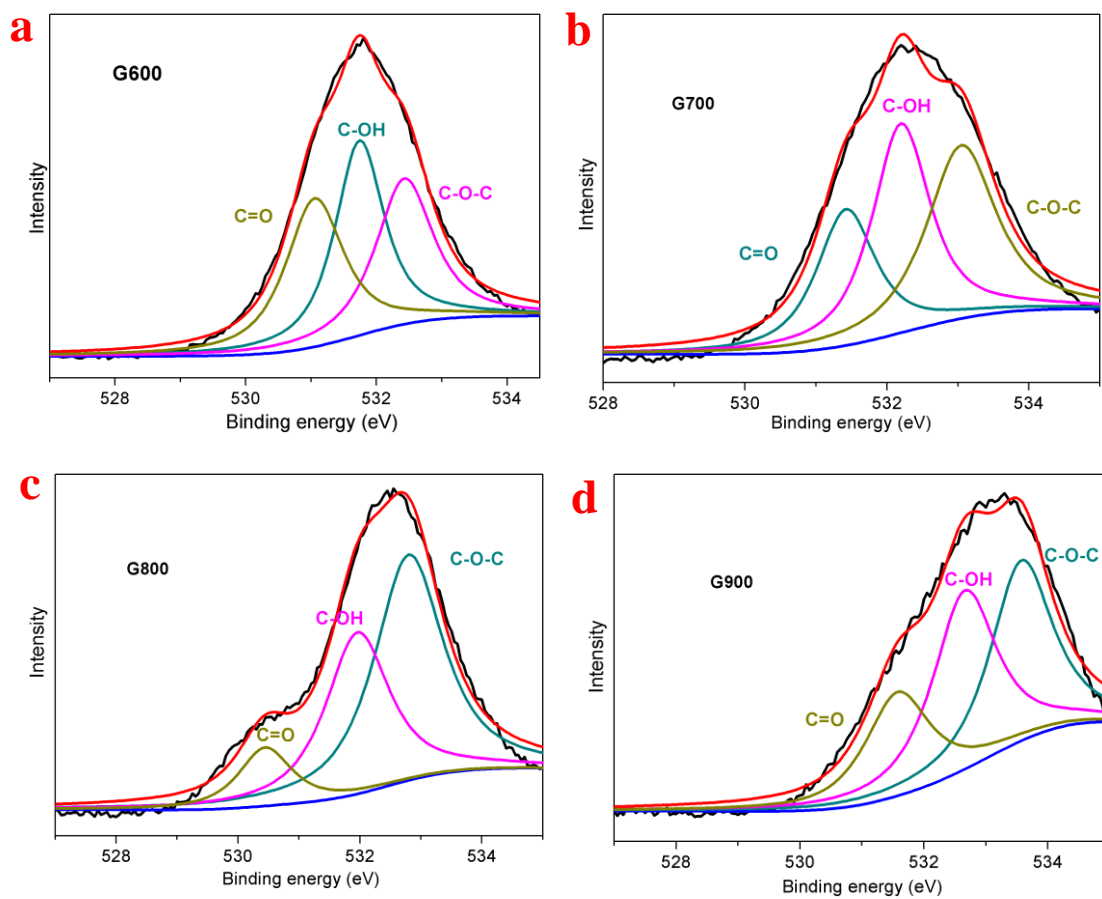
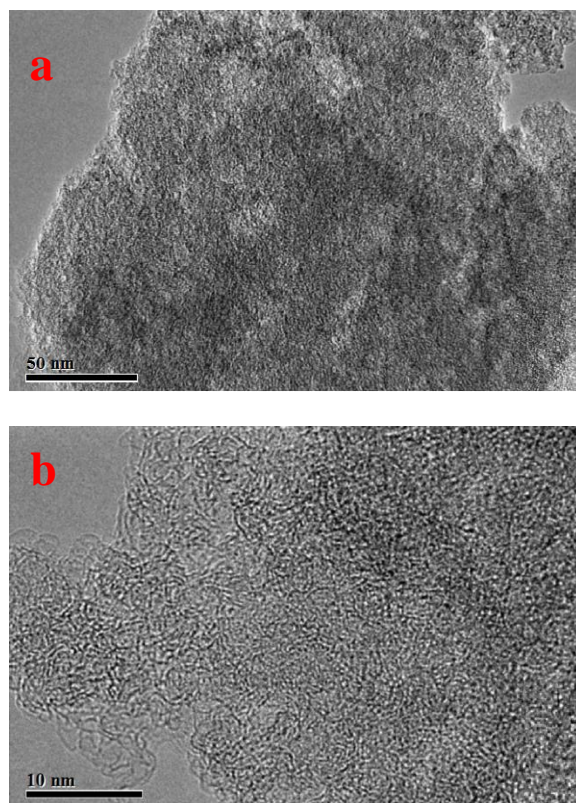**Fig. S6** O 1s XPS peaks of G600 (a), G700 (b), G800 (c) and G900 (d).

Fig. S7 Extended TEM (a) and HRTEM (b) images for lignin pyrolysis at 250 ℃ for 2 h.
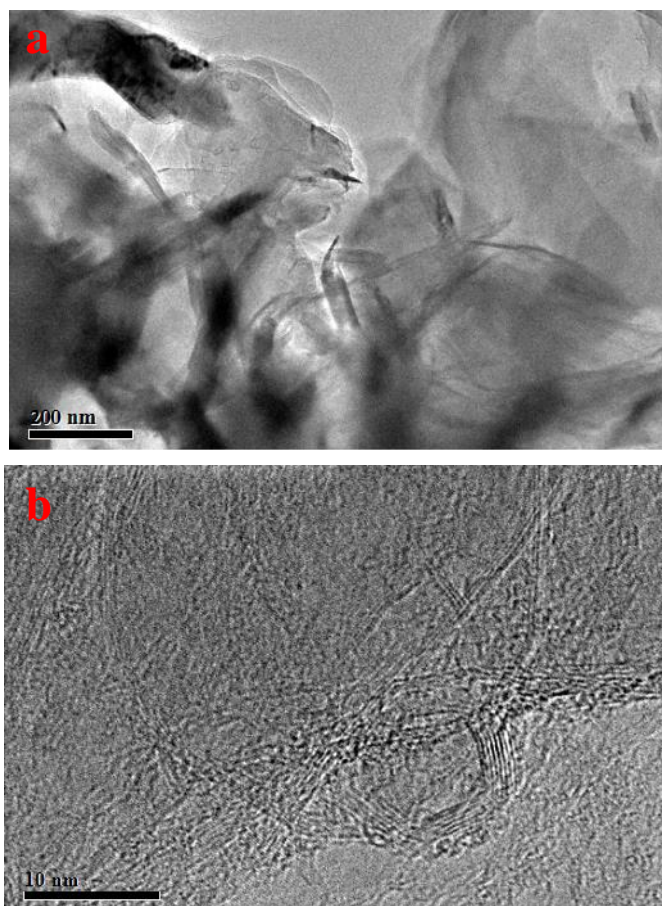
Fig. S8 Extended TEM (a) and HRTEM (b) images for lignin pyrolysis from room temperature to 1000 °C
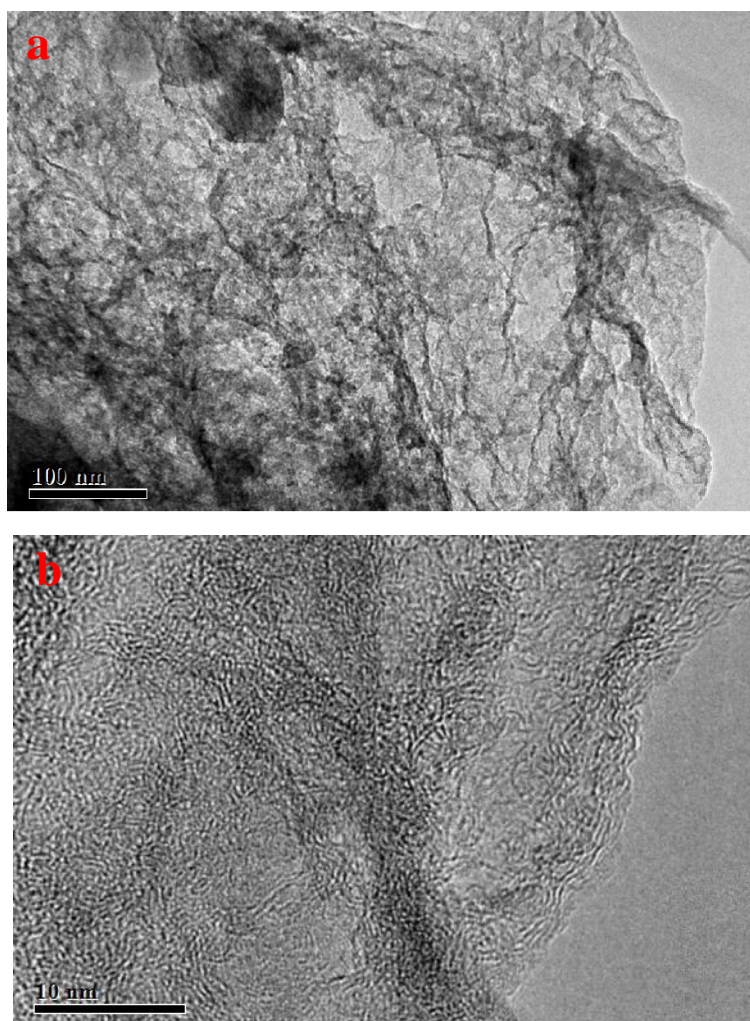
Fig. S9 Extended TEM (a) and HRTEM (b) images for Kraft lignin pyrolysis at 1000 ℃ for 3 h.
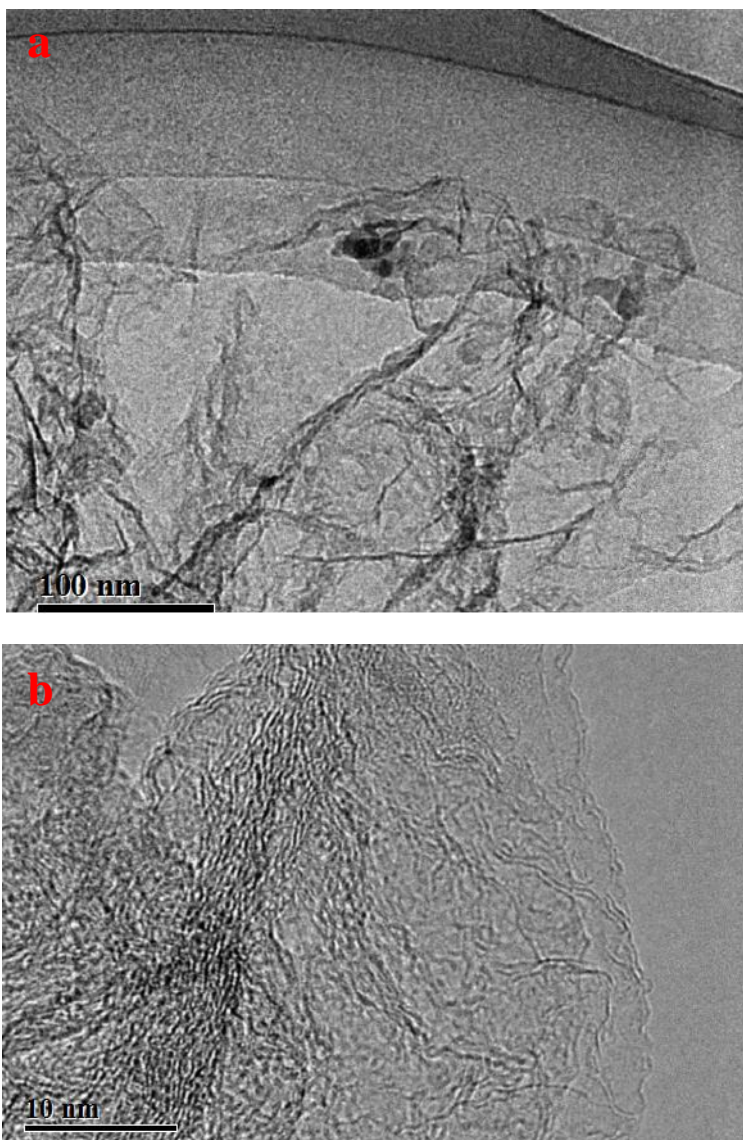
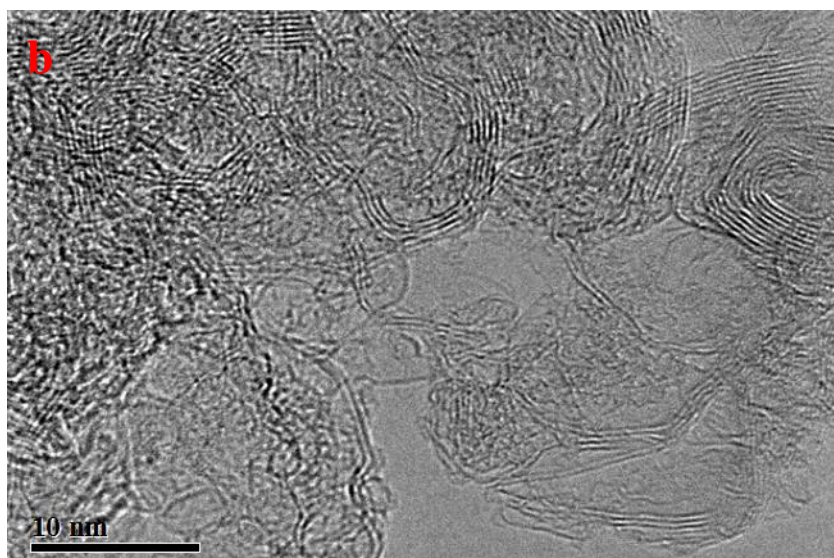**Fig. S10** TEM (a) and HRTEM (b) images for annealing Kraft lignin after its washing.
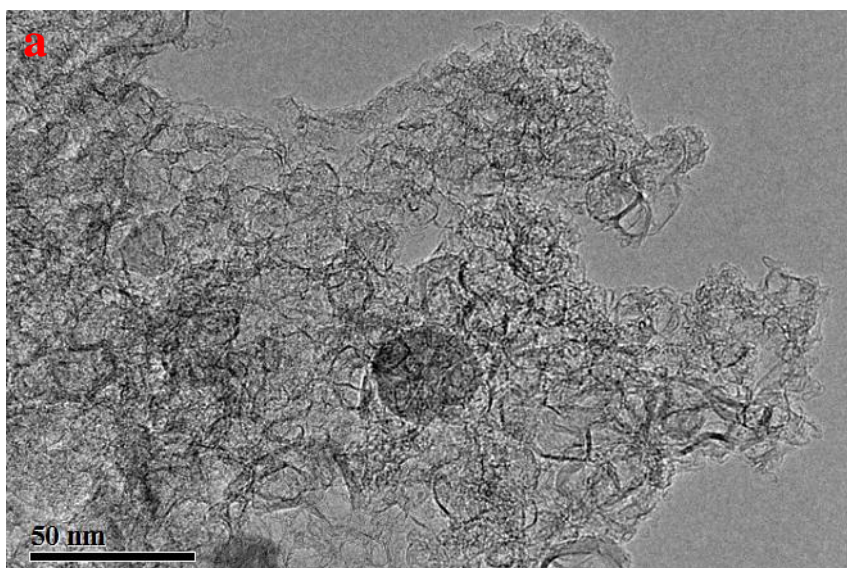
Fig. S11   TEM (a) and HRTEM (b) images for annealing organosolv lignin.
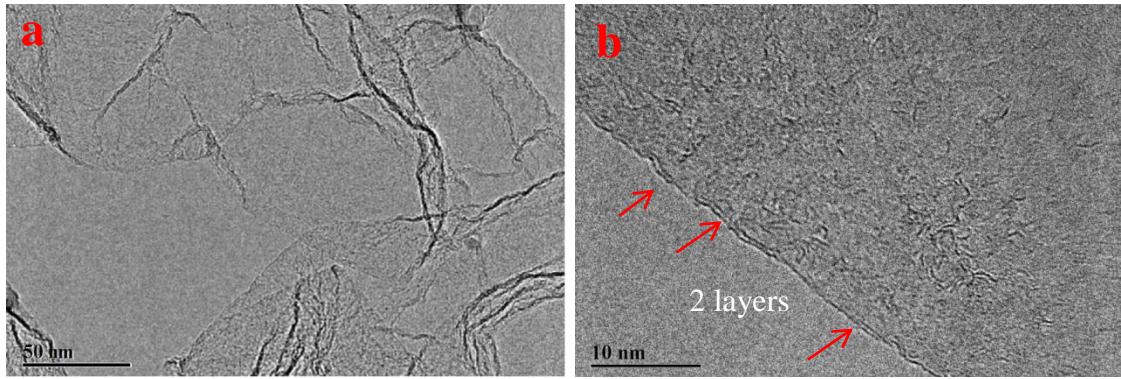
Fig. S12 TEM and HRTEM images of spent G1000.
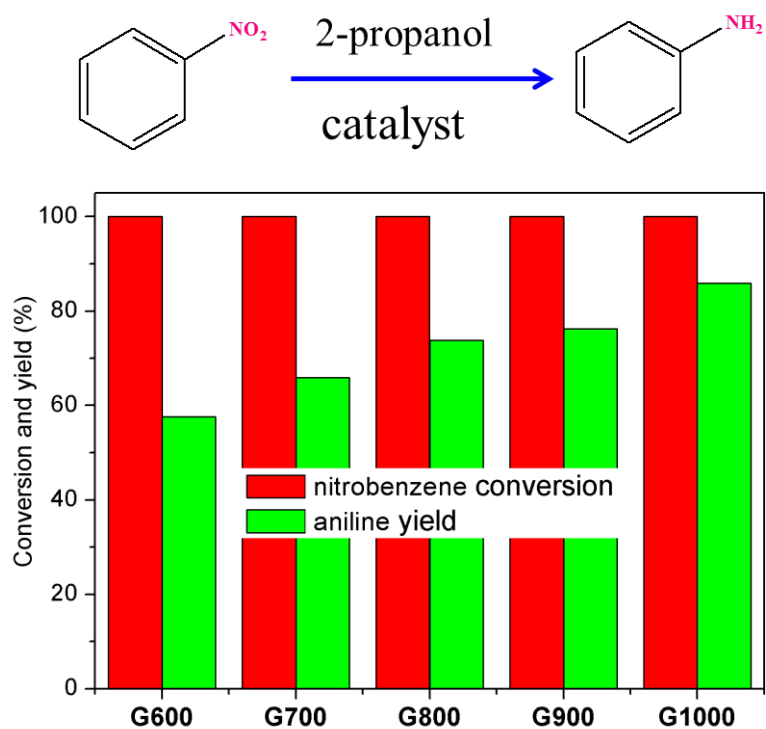
Fig. S13 Catalytic performance for nitrobenzene reduction with 2-propanol to aniline over G1000. Reaction conditions: 0.5 mmol nitrobenzene, 0.05 g catalyst, 3 mmol KOH, 8 mL 2-propanol, 120 ℃, 24 h, 0.1 MPa N_2.
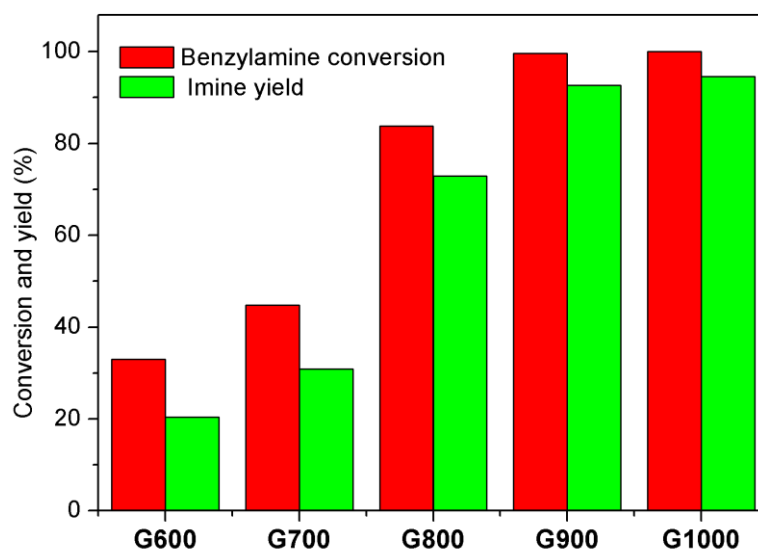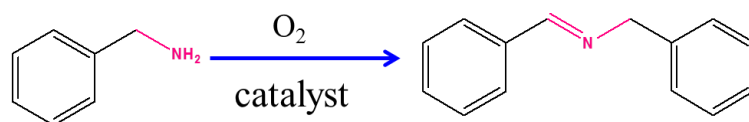
Fig. S14 Catalytic performance for oxidative coupling benzylamine to imine over G1000. Reaction conditions: 0.05 g benzylamine, 0.05 g catalyst, 0.5 mmol KOH, 10 mL ethyl acetate, 120 ℃, 10 h, 0.5 MPa O_2.
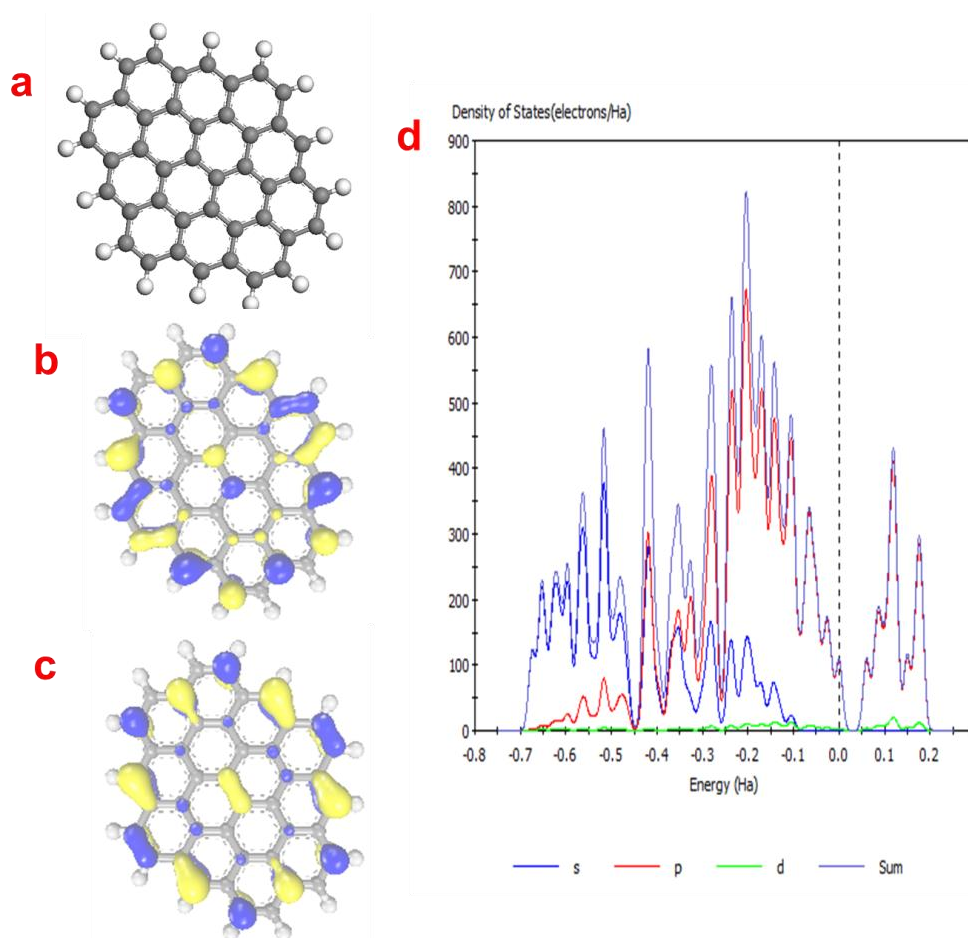
Fig. S15　(a) Optimised graphene model for DFT calculation. (b) HOMO shape; (c) LOMO shape (d) PDOS plots of graphene.
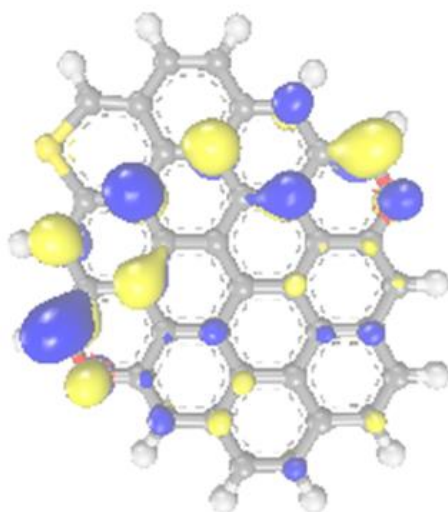
Fig. S16   HOMO shape of S and O co-doped graphene.

Table S1 Textural properties of various carbon materials.

catalyst	surface area ($m^2\ g^{-1}$)	Micropore surface area ($m^2\ g^{-1}$)	Pore size (nm)	Pore volume ($cm^3\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)
G600	273.8	178.3	3.8	0.034	0.085
G700	295.2	209.6	4.1	0.042	0.108
G800	321.1	235.2	4.7	0.062	0.115
G900	441.6	263.7	5.2	0.073	0.120
G1000	524.5	327.8	5.8	0.079	0.133

Table S2 The catalytic performance of G1000 and reported carbon-based catalysts

in benzyl alcohol oxidation to benzaldehyde.

Catalysts	Oxidant	Reaction temperature ($^\circ C$)	O_2 pressure (MPa)	Reaction time (h)	Conversion (%)	Selectivity (%)	Yield (%)	References
nanoshell carbon	O_2 + HNO_3	90	0.1	5	96	92	88.3	4
carbon nanotube	O_2 + HNO_3	90	0.1	5	96.2	88.3	84.9	5
carbon nanotube	O_2	130	1.5	10	24.1	89.5	21.6	6
N-doped graphene	O_2	70	0.1	10	12.8	100	12.8	7
graphene oxide	air	150	0.1	24	97	87.6	85	8
50 wt% P-doped carbon	O_2	100	0.1	24	56.1	95.7	53.7	9
graphene	O_2	120	0.5	5	25.5	95.8	24.4	this work
G1000	O_2	120	0.5	5	99.2	96.7	95.9	this work

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