Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

Aerobic Selective Oxidation of 5-Hydroxymethyl-furfural over Nitrogen-doped Graphene Material with 2,2,6,6-Tetramethylpiperidin-oxyl as Cocatalyst

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1. Chemicals

Graphite powder (Aladdin), H_2SO_4 (98 wt.%,Xilong Chem. Co., Ltd, China), $NaNO_3$ (Kermel Chem. Reagent Co., Ltd. China), $KMnO_4$ (Kermel Chem. Reagent Co., Ltd. China), H_2O_2 (30%, Dong Fang Chem. Co., Ltd. China), 5-Hydroxymethylfrufural (98%, DEMO Medical Tech Co., Ltd. China), 2,5-Diformylfuran (98%, TCI). Acetonitrile (Kermel Chem. Reagent Co., Ltd. China). All the regents were used as received without further purification.

2. Preparation of Graphene Oxide (GO)

GO was prepared by Hummers' method with post treatment by sonication and centrifugation. Typically, graphite powder (8000 meshes, 5 g) and $NaNO_3$ (2.5 g) were mixed with sulfuric acid (115 mL, 98 wt. %) under magnetic stirring for 0.5 h, then the mixture was put into an ice bath before $KMnO_4$ (15 g) was slowly added, during which the temperature was kept below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5 h. After that, 230 mL water was slowly added to the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another addition of 700 mL water. And the reaction was terminated by the addition of H_2O_2 (50 mL, 30 wt. %). The mixture was filtered and washed with HCl (1 L, 1 $mol \cdot L^{-1}$) and a large amount of distilled water in sequence. The resulting graphite oxide was separated from the colloid by spray drying.

The obtained graphite oxide (1.0 g) was placed into an Al_2O_3 boat in the center of a tube furnace, and the tube was connected to a vacuum pump to maintain the pressure in tube at 25 Torr. The temperature of the furnace was raise to 200 ^{o}C in 10 min and remained for 4 hours. After that, the furnace was cooled down naturally to room temperature, and the graphite oxide was exfoliated to graphene oxide and partially reduced.

The procedure of thermal reducing GO materials under different temperatures were described as follow: the GO sample (300 mg) was placed into the tube furnace center. After flowing with He (200 mL·min^{-1}) for 20 min, the temperature of the furnace was raised to the indicated temperature at a heating rate of 10 K·min^{-1}.

Nitrogen-doped graphene samples were prepared by a postnitridation of GO in a flow of NH_3 atmosphere at a temperature in the range of 400-1000 ^{o}C. In a typically procedure, the GO sample (300 mg) was placed into the tube furnace center. After flushing with NH_3 (200 mL·min^{-1}) for 20 min, the temperature of the furnace was raised to the indicated temperature at a heating rate of 10 K·min^{-1} and remained at the indicated temperature for 4 hours. The NH_3 flow rate maintained at 200 mL min $^{-1}$ during this period. After that, the furnace was cooled down naturally to room temperature in flowing NH_3. The obtained N-doped graphene were named NG-T (T stands for the annealing temperature, 400, 600, 800 and 1000 ^{o}C).

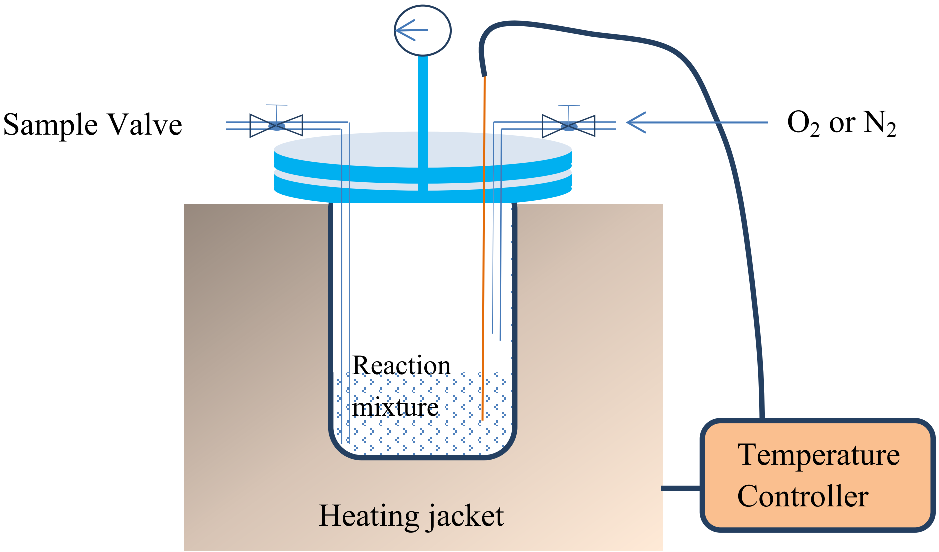
3. GO Characterization

X-ray diffraction (XRD) patterns were conducted on a Rigaku MiniFlex II desktop X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA with a scanning speed (2θ) of 4°/min. N_2 adsorption-desorption isotherms were exhibited at –196 °C on a Micromeritics TriStar 3000 instrument. The samples were first degassed under vacuum at 150 °C for 8 h. Scanning Electron Microscopy (SEM) was measured on a JSM-7001F microscope. TEM (Transmission electron microscope) was conducted on a JEM-2100F microscope. XPS were performed under an ultrahigh vacuum on a Kratos AXIS ULTRA DLD spectrometer with Al K radiation and a multichannel detector. The collected binding energies were calibrated by the C1s peak at 284.6 eV as reference. Raman spectroscopy was performed using a Raman Microprobe (HR-800 Jobin-Yvon) with a 532 nm Nd:YAG excitation source at room temperature. The amount of element was determined by elemental microanalysis (EA) (vario MICRO cube, Elemental).

4. Reactivity Tests

All the reactions were performed in a 100 mL Teflon-lined stainless steel autoclave with vigorous stirring. Typically, 100 mg NG-XXX, 1 mmol HMF, 1mmol TEMPO and 30 mL acetonitrile were added into the reactor. The reaction mixture was stirred and heated at 100 °C. After a fixed reaction time, the reactor system was quickly cooled to room temperature in an ice-water bath. For reusability tests, the spent NG was filtrated, washed in acetonitrile and dried at 80 °C.

The schematic diagram of experimental set-up as following:



5. Analytic Method

The products were separated by a reversed-phased C18 column (200 × 4.6 mm) at 25 °C with a detection wavelength of 280 nm. The mobile phase was acetonitrile and 0.1 wt % acetic acid aqueous solution (30:70 v/v) at 0.5 mL/min. The HMF conversion and DFF yield were expressed in mol%, based on the total HMF amount. The product was identified by NMR.

^{1}H NMR (400 MHz, $CDCl_3$): δ /ppm 7.34 (s, 2H), 9.86 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ /ppm 119.23 (2C), 154.23 (2C), 179.24 (2C).

Fig. S1-S6

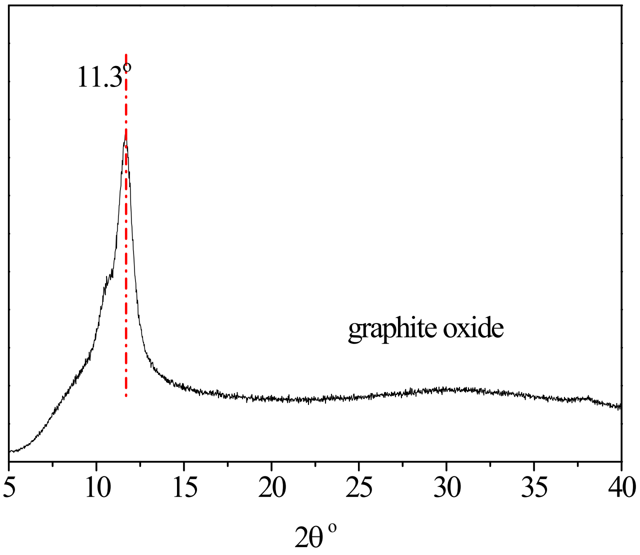
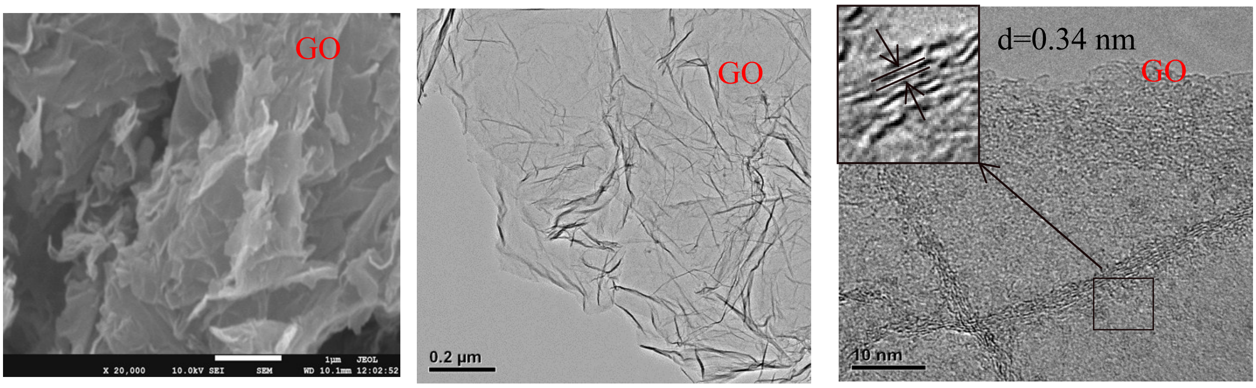
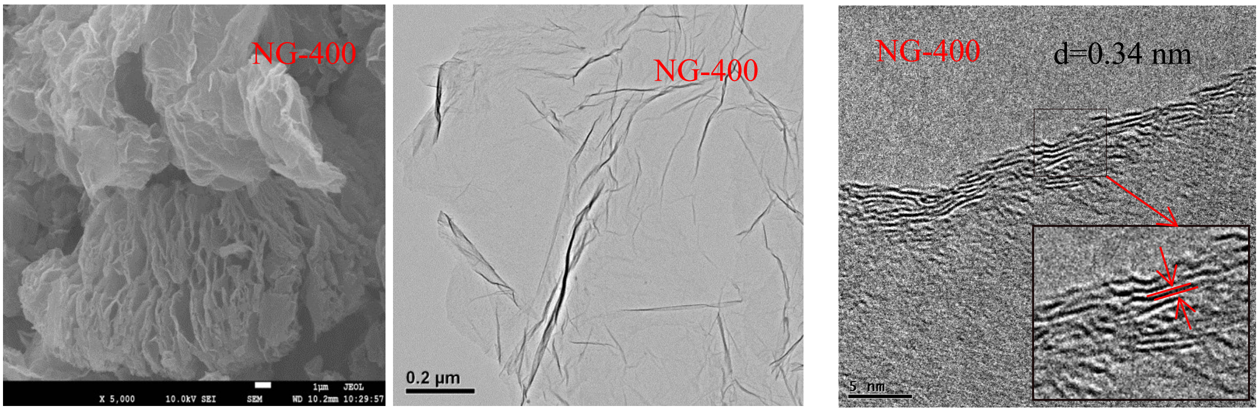


Fig. S1 XRD patterns of graphite oxide.

a.



b.



c.

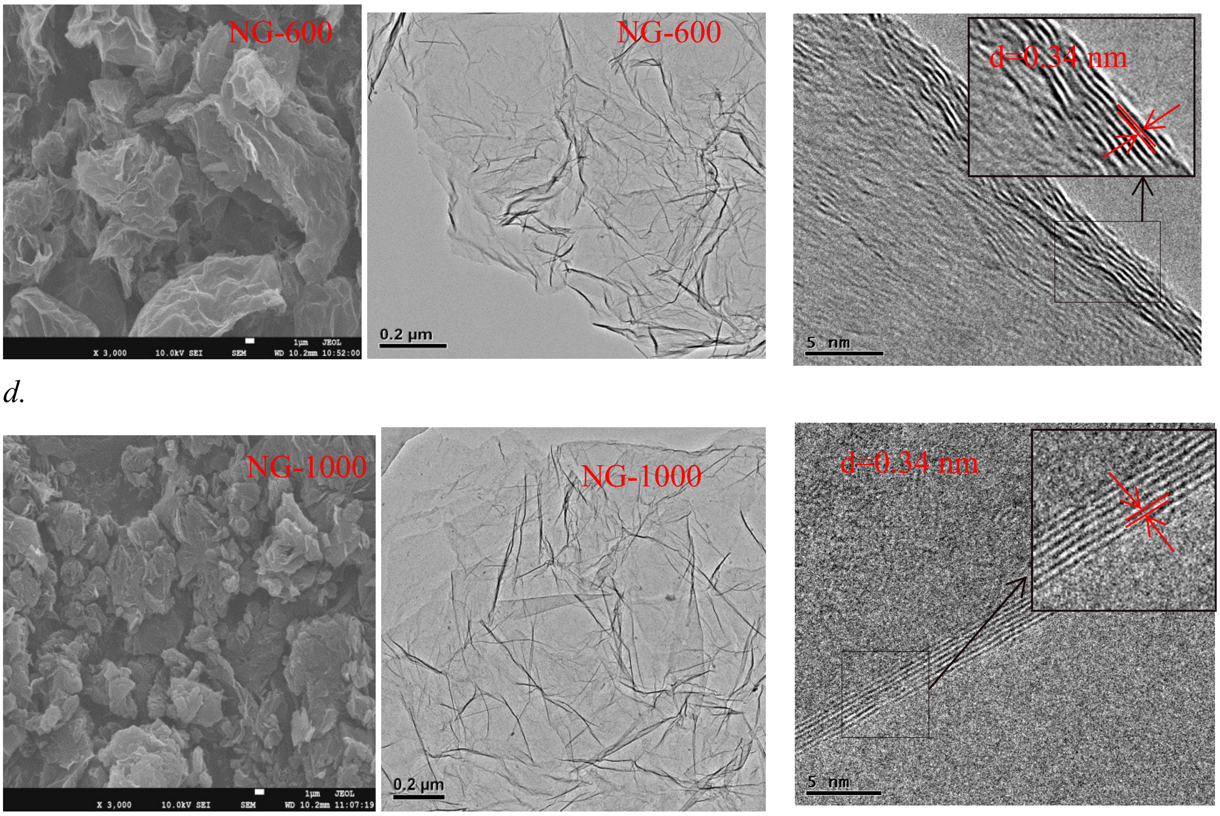


Fig. S2 SEM, TEM, and HRTEM images of GO (a), NG-400 (b), NG-600 (c) and NG-1000 (d).

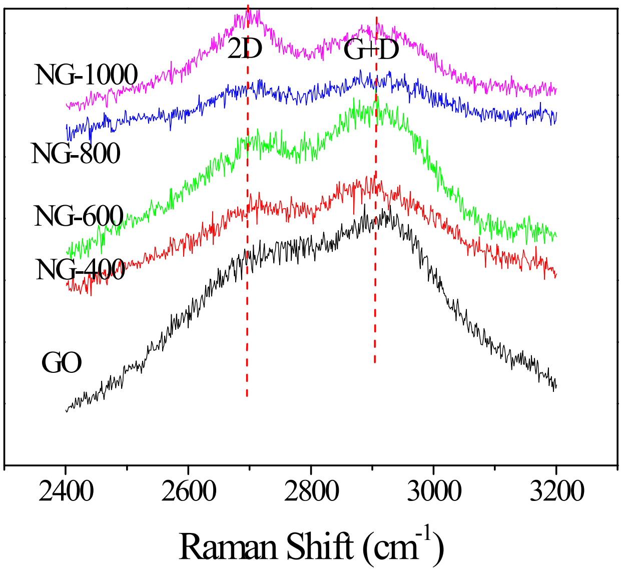


Fig. S3 The 2D band and D+G bands in Visible-Raman spectra of the GO and NG-samples.

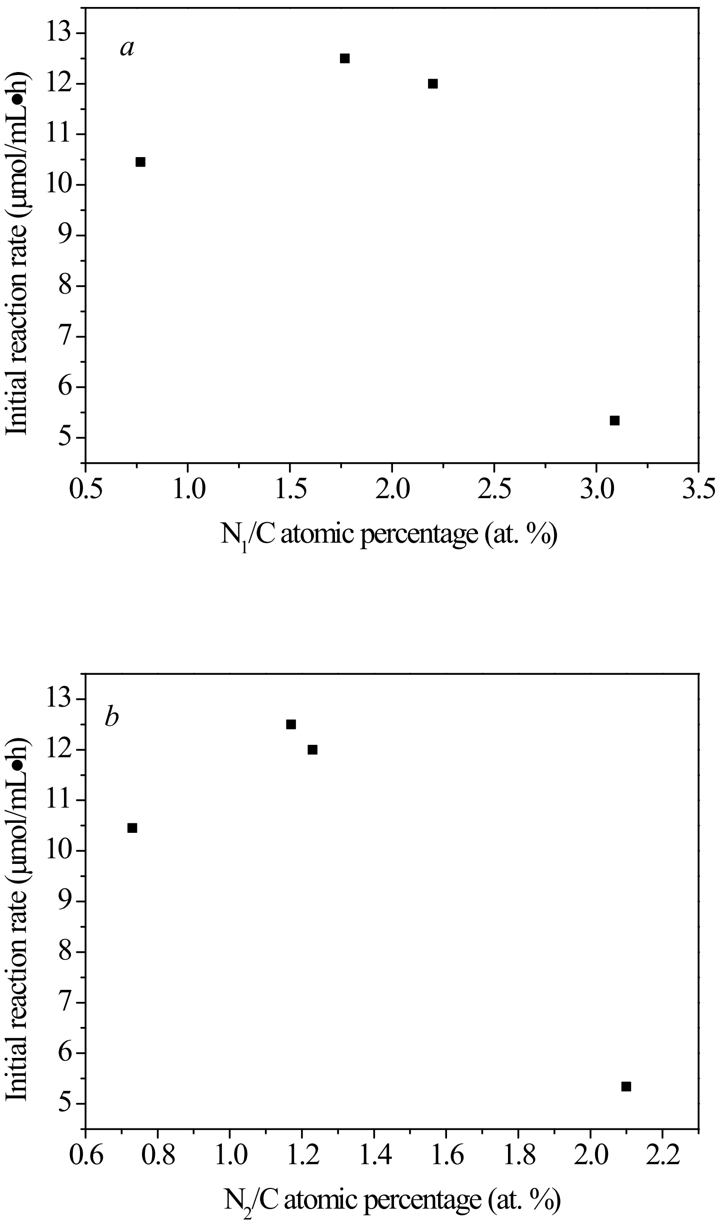


Fig. S4 Relationship between initial reaction rate and N_1 (a), N_2 (b) species in N-doped graphene.

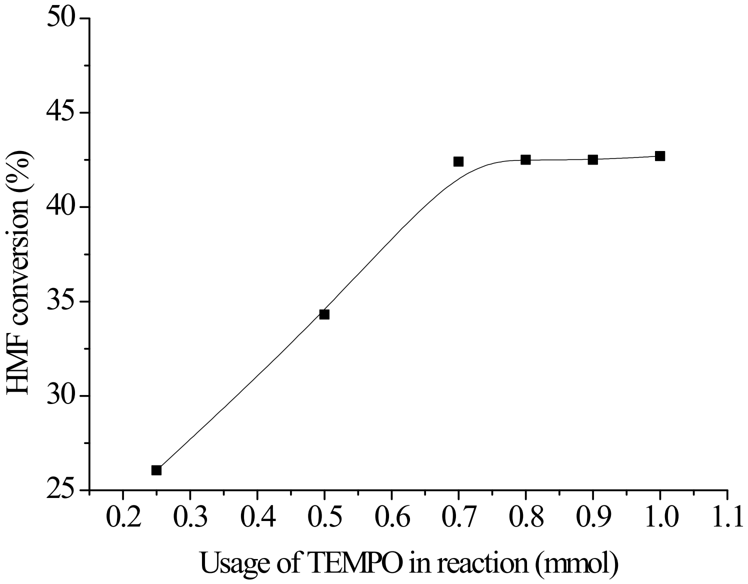


Fig. S5 HMF Conversion after 1 h versus the usage of TEMPO. Reaction conditions: HMF, 1 mmol, 126 mg; acetonitrile, 30 mL; NG-800, 100 mg; reaction time, 1 h; reaction temperature ,100 ^{o}C; 1 atm air pressure in 100 mL stainless autoclave; stirring speed, 800 rpm.

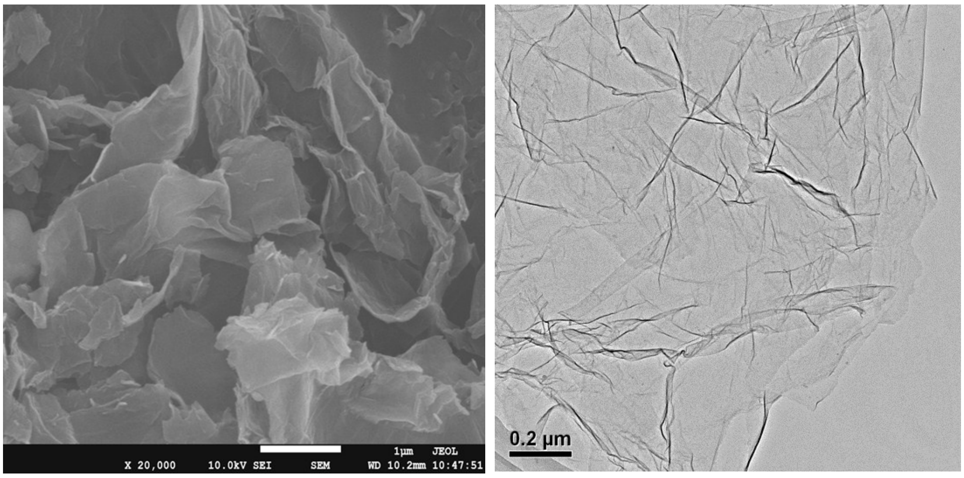


Fig. S6 SEM, TEM images of used NG-800 for 6 times.

Table S1-S3

Table S1 BET analysis of GO and NG-T samples.

Sample	S_{BET}	PV (cm^3 g^{-1})	Average PD (nm)
GO	340.6	1.22	14.3
NG-400	351.8	1.33	15.2
NG-600	331.3	1.24	16.5
NG-800	360.1	1.25	15.8
NG-1000	354.7	1.24	15.6

Table S2. Elements content by EA and intensity ratio of I_D/I_G and I_{2D}/I_{2G} for GO and NG-T by Raman.

Samples	EA	Raman	
	C/O ratio	I_D/I_G	I_{2D}/I_{2G}
GO	4.68	0.92	0.91
NG-400	10.26	0.94	0.93
NG-600	13.31	0.97	0.96
NG-800	22.49	1.03	0.98

GO-He-800	14.35	0.95	0.96
NG-1000	24.28	1.12	1.05

Table S3. Mn content in NG-T determined by ICP method and catalytic activity of nitrogen-doped graphene materials with different Mn content on the aerobic oxidation of HMF[a].

Entry	Samples	Mn (ppm)[b]	N[c]	Graphitic N[c]	HMF conv.%	DFF Selec.%
1	NG-400	319	6.07	0.14	76.6	98.2
2	NG-600	315	4.39	0.95	84.1	99.2
3	NG-800	315	4.16	1.22	89.9	98.1
4	NG-1000	340	2.42	0.92	80.7	97.3
5[d]	NG-1000	37[b]	2.42	0.92	81.1	98.2
6[d]	Mn/NG-1000	3400	2.42	0.92	79.7	98.3
7[d]	Mn/NG-1000	6800	2.42	0.92	78.9	99.2
8[d]	Mn/NG-1000	10200	2.42	0.92	80.1	98.3

[a] Reaction conditions: HMF, 1 mmol, 126 mg; acetonitrile, 30 mL; TEMPO, 1 mmol, 155 mg; reaction time, 3 h; reaction temperature, 100 °C; catalyst, 100 mg; 1 atm air pressure in 100 mL autoclave; stirring speed, 800 rpm.

[b] Determined by ICP.

[c] Determined from XPS results.

[d] The prepared GO was dispersed in 500 mL DI water at a concentration of 0.5 mg mL^{-1}. 5 mL HCl (37%) was added into the solution slowly. The mixture was kept in room temperature for 12 h with stirring. The final GO was filtered and washed by DI and acetone.

Mn/NG-1000 samples were prepared by impregnation method. The NG-1000 was dipped into a certain amount of $KMnO_4$ aqueous solution, stirred for 30 min. Dried in oven and followed by thermal treatment at 1000 ^{o}C in 200 mL min^{-1} NH_3 flow for 2 h.