

# Supporting Information

## Surface Modification of C<sub>3</sub>N<sub>4</sub> through Oxygen Plasma Treatment: A Simple Way toward Excellent Hydrophilicity

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## Experimental Section

### Materials

Melamine (99.5 %), NaOH (99.5 %), H<sub>2</sub>SO<sub>4</sub> (98 wt%), H<sub>2</sub>O<sub>2</sub> (28%), hexaaminobenzene (99.5 %), hexaketocyclohexane(99.5 %), Tifluoromethanesulfonic acid (98%), Methanol (99.8%), Al<sub>2</sub>O<sub>3</sub> (99 %), Fe (98 %) and N-methyl-2-pyrrolidone (99.5 %) were purchased from Aladdin (Shanghai, China) and used as received without further purification. N-doped graphene were purchased from SIBAT (Shanghai, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

### Synthesis of C<sub>3</sub>N<sub>4</sub> nanosheet

The preparation of C<sub>3</sub>N<sub>4</sub> has been reported elsewhere<sup>1</sup>. The bulk C<sub>3</sub>N<sub>4</sub> was prepared by polymerization of melamine molecules under high temperature. In detail, melamine was heated at 600°C for 2 h under air condition with a ramp rate of about 3°C/min for both of the heating and cooling process. Then 3 g of bulk C<sub>3</sub>N<sub>4</sub> powder dispersed in 3000 mL water, and then ultrasound for about 24 h. The initial formed suspension was then centrifuged at about 5000 rpm to remove the residual unexfoliated C<sub>3</sub>N<sub>4</sub> nanoparticles and large-area nanosheets before used for further study.

### Synthesis of N doped carbon nanotube

N doped carbon nanotubes were synthseized the according to the method previously reported<sup>2, 3</sup>, further refluxed in 6M NaOH at 110 °C for 4 h to remove the Al<sub>2</sub>O<sub>3</sub> support, followed by refluxing in 1M H<sub>2</sub>SO<sub>4</sub> for 8 h to remove residual Fe catalysts.

### Synthesis of C<sub>2</sub>N

the preparation of C<sub>2</sub>N was previously reported<sup>4</sup>. hexaaminobenzene (2 g, 7.20 mmol) and hexaketocyclohexane (2.248 g, 7.20 mmol) were charged in a three-necked round bottom flask under argon atmosphere and placed in ice bath. Deoxygenated NMP (80 ml) with a few drops of sulfuric acid or freshly distilled

trifluoromethanesulfonic acid (80 ml) was slowly added. The reaction flask was allowed to warm up to room temperature for 2 h. The ice bath was replaced with oil bath and heated to 175 °C for 8 h. Then, the flask was cooled to room temperature and water was added. The solid product that precipitated was collected by suction filtration using polytetrafluoroethylene (PTFE) (0.5 mm) membrane. The resultant dark solid was further Soxhlet extracted with methanol and water, respectively, and freeze-dried at 120 °C under reduced pressure (0.05mm Hg) for 3 days.

### Synthesis of $C_{2.38}(C-OH)_{0.62}N_4$

$C_{2.38}(C-OH)_{0.62}N_4$  was prepared based on the previous report.<sup>5</sup> 0.2 g of  $C_3N_4$  powder was dispersed in the solution under magnetic stirring at 30 °C. After one day, the solution was evaporated at 80 °C and a dry compound was obtained. After doing this three times, the compound was washed and filtered.

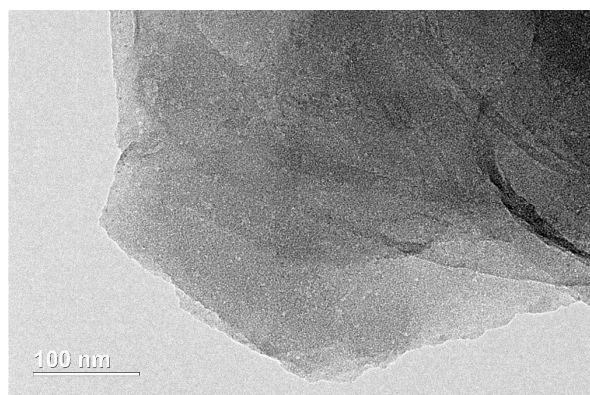


Figure S1: TEM images of pristine  $C_3N_4$ .

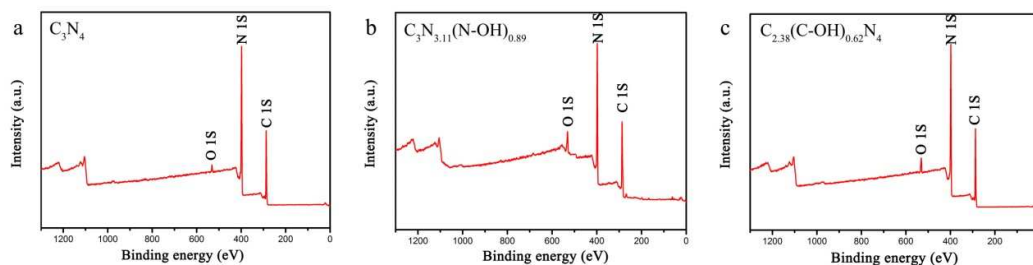


Figure S2: XPS spectrum of synthetic pristine (a)  $C_3N_4$  nanosheet, (b)  $C_3N_{3.18}(N-OH)_{0.82}$  and (c)  $C_{2.38}(C-OH)_{0.3}N_4$ , respectively.

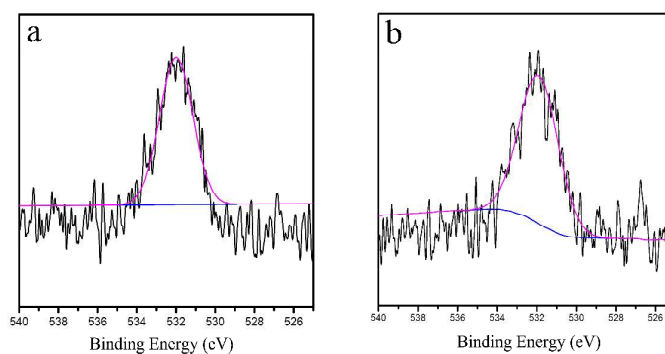


Figure S3: O 1S of (a)  $C_3N_{3.18}(N-OH)_{0.82}$  and (b)  $C_{2.7}(C-OH)_{0.3}N_4$ , respectively.

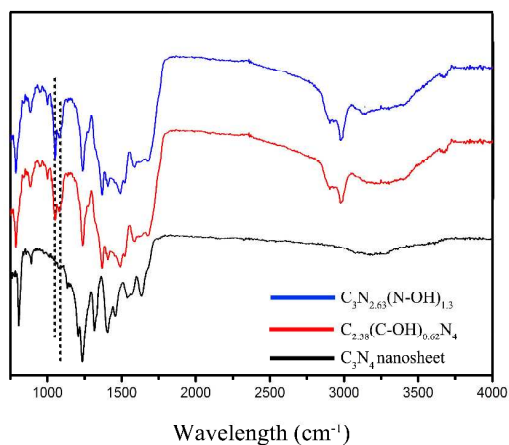


Figure S4: FT-IR spectrum of  $C_3N_4$  nanosheet,  $C_3N_{3.18}(N-OH)_{0.82}$  and  $C_{2.7}(C-OH)_{0.3}N_4$ , respectively.

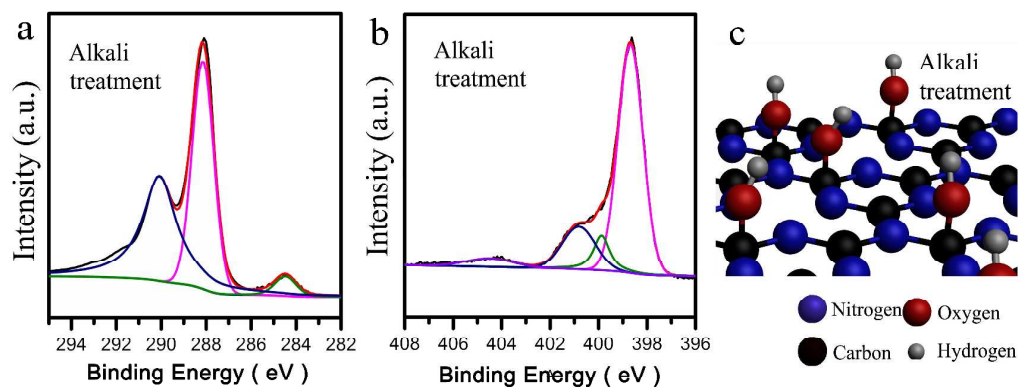


Figure S5: High-resolution C 1s (a) and N 1s (b) spectra of alkali treated  $C_3N_4$ , respectively. Schematic diagram of the structure of (c)  $C_x(C-OH)_yN_4$ .

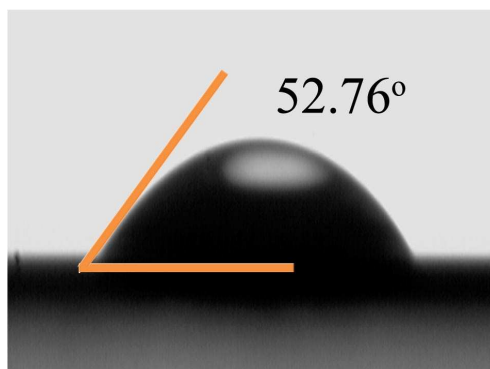


Figure S6: Contact angle of  $C_{2.7}(C-OH)_{0.3}N_4$ .

Table S1: N-OH content ( $\gamma$ N-OH) can be controlled by changing the plasma treating time (t).

Sample	N 1s			Chemical formula
	Position (eV)	Assignment	N/N <sub>total</sub> atomic ratio	
1 (treated 10 min)	399.8	$sp^2$ N	0.982	$C_3N_{3.93}(N-OH)_{0.07}$
	402.3	N-OH	0.018	
2 (treated 30 min)	399.8	$sp^2$ N	0.947	$C_3N_{3.79}(N-OH)_{0.21}$
	402.3	N-OH	0.053	
3 (treated 60 min)	399.8	$sp^2$ N	0.897	$C_3N_{3.59}(N-OH)_{0.41}$
	402.3	N-OH	0.103	
4 (treated 90 min)	399.8	$sp^2$ N	0.845	$C_3N_{3.38}(N-OH)_{0.62}$
	402.3	N-OH	0.155	
5 (treated 120 min)	399.8	$sp^2$ N	0.795	$C_3N_{3.18}(N-OH)_{0.82}$
	402.3	N-OH	0.205	

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