# **Electronic Supplementary Information for**

## Polymeric carbon nitride nanomesh as an efficient and durable metal-free catalyst for oxidative desulfurization

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### **Materials and Reagents**

Trithiocyanuric acid (95%) was purchased from Aladdin Co. Melamine ( $\geq$ 99.0 %), Graphitic carbon were purchased from Sinopharm Chemical Reagent (Shanghai, China). Commercial Fe<sub>2</sub>O<sub>3</sub> was purchased from Fuchen (Tianjin, China). Deionized water was supplied from local sources. All of the materials were used as received without further purification.

### **Preparation of samples**

**Preparation of CNM.** CNM samples were synthesized *via* an air-assisted thermal polymerization method. Typically, a certain amount of trithiocyanuric acid (6.0 g) in an open crucible was heated in static air with a ramp rate of 5 °C/min to certain temperature where it was held for 2 h. The temperatures were set at 500, 525, 550, 575 and 600 °C, respectively. The resulting samples were labeled as CNM-500, CNM-525, CNM-550, CNM-575 and CNM-600, respectively.

Preparation of bulk CN reference. For comparison purpose, the bulk CN was also

synthesized via a modified method reported previous.<sup>1</sup> In the process, 6.0 g melamine was put in a crucible. The crucible was heated up to 550 °C with a heating rate of 2.3 °C/min and kept at 550 °C for 4 h. The product was cooled naturally, and the sample obtained was denoted as *bulk CN*.

*Preparation of N-doped graphitic carbon:* The N-doped carbon was also synthesized *via* a modified reference method for comparison.<sup>2</sup> Firstly, the graphite carbon was oxidized with 50 % HNO<sub>3</sub> of 5 h at room temperature, and then washed out water to removal excess acid and water-soluble products of oxidation. To introduce nitrogen groups, 10 g of the oxidized carbons were treated with a melamine suspension (6.67 g of melamine in 34 mL of ethanol) which was followed by a 5 h stirring at room temperature. The mixture was then boiled until the evaporation of the alcohol and dried at 120 °C for 12 h. The sample were then heated in nitrogen at 10 °C/min to 450 °C, and maintained at these temperatures for 30 min. The obtained product was denoted as N-GC.

#### Characterizations

The X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on a PANalytical diffractometer (X'PertPro, Panalytical Corp.) with an X'Celerator detector, using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at 45 kV, 40 mA. Fourier transformed infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer, and the samples were prepared as KBr pellets. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition and elements states of g-C<sub>3</sub>N<sub>4</sub> on a Thermo Scientific ESCALAB 250 spectrometer. The data were calibrated using the binding energy of C1s (284.6 eV) as the standard. Nitrogen adsorption-desorption isotherms were carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp.). The morphologies and microstructures of g-C<sub>3</sub>N<sub>4</sub> have been studied by scanning electron microscope (SEM) analysis (S-4800, Hitachi, Japan). HRTEM images of the as-prepared samples were obtained with a high-resolution transmission electron microscope (Tecnai G2 F20, operating at 200 kV). Raman spectra were recorded in a Renishaw invia Raman Microscope with a 325 nm laser excitation. Solid-state <sup>13</sup>C NMR spectra was recorded on a Bruker Advance IIIHD 500 spectrometer. Elemental analysis results were collected from a Vario EL. H<sub>2</sub>S in situ FT-IR spectra: Firstly, the sample (30 mg) was placed into the cell. The sample was pretreated at 210 °C with He for 1 h and the spectra were collected. Then

100 mL of  $H_2S$  was pumped into the cell, spectra were collected after that. The spectra were obtained at a resolution of 4.0 cm<sup>-1</sup> with 64 scans.

#### **Evaluation of catalytic activity**

All the tests were performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure. A 0.4 g catalyst (40-60 mesh) was placed in the central section of the reactor. The mixture gas containing 5000 ppm H<sub>2</sub>S, 2500 ppm O<sub>2</sub> and balance gas (N<sub>2</sub>) were fed into the reactor at 20 mL/min (WHSV = 3000 mL·g<sup>-1</sup>·h<sup>-1</sup>) and reacted in temperature range of 90-240 °C. After the reaction, the effluent stream was detected by a gas chromatograph (GC9720) equipped with a FPD and TCD. A condenser was located at the bottom of the reactor to trap the sulfur gas in effluent stream. Instantaneous fractional conversion of H<sub>2</sub>S, sulfur selectivity and sulfur yield were defined as follows:

 $H_2S \text{ conversion} = \frac{(H_2S)_{in} - (H_2S)_{out}}{(H_2S)_{in}}$ S selectivity =  $\frac{(H_2S)_{in} - (H_2S)_{out} - (SO_2)_{out}}{(H_2S)_{in} - (H_2S)_{out}}$ 

Sulfur yield =  $(H_2S \text{ conversion}) \times (S \text{ selectivity})$ 



Fig. S1. Proposed polymerization process of trithiocyanuric acid at high temperature.

Upon heating, trithiocyanuric acid partially decomposes to some intermediates such as NH<sub>3</sub> and sulfur-containing species, and then the NH<sub>3</sub> would react with trithiocyanuric acid to produce melam. Melam undergoes polymerization to melon and further to extended polymers.



Fig. S2. FT-IR spectra of bulk CN and CNM samples.

The FT-IR measurement has been employed to dissect the microstructure of the as-prepared samples. As shown in **Fig. S2**, both the bulk CN and CNM samples present typical IR patterns of graphitic carbon nitride. The absorption band located at

ca. 802 cm<sup>-1</sup> originates from the vibration of the triazine units, indicating the existence of the basic melon units with NH/NH<sub>2</sub> groups. The bands at 1240-1640 cm<sup>-1</sup> attributable to the stretching vibration of CN heterocycles such as C–N(–C)–C (full condensation) or C–NH–C (partial condensation). The broad peaks from 3000 to 3400 cm<sup>-1</sup> are contributed by N–H band and O–H stretches due to the free amino groups and adsorbed hydroxyl species, respectively. <sup>3</sup> These results demonstrate that CNM is endowed with intrinsic functional groups, such as –NH and –NH<sub>2</sub>, acting as potential activity sites for H<sub>2</sub>S reaction.



Fig. S3. Raman spectra of bulk CN and CNM samples.

As shown in **Fig. S3**, several characteristic peaks of CN at 468, 705, 754, 976, 1217, and 1296 cm<sup>-1</sup> are observed.<sup>4</sup> The peaks at 754 and 980 cm<sup>-1</sup> are assigned to the C–N–C bending vibration and breathing vibration of heptazine or s-triazine modes, whereas, the region of 1200-1700 cm<sup>-1</sup> is attributable to the stretching vibration of CN heterocycles.



Fig. S4. Solid-state <sup>13</sup>C NMR spectrum for CNM-600 sample.

 $^{13}$ C NMR also indicates the presence of an s-triazine structure in CN. As shown in **Fig. S3**, CNM-600 shows two remarkable peaks at approximately 157.08 and 165.38 ppm, which are assigned to CN<sub>3</sub> and CN<sub>2</sub>NH<sub>2</sub> groups, respectively.<sup>5</sup>



**Fig. S5.** XPS spectrum of CNM-600 sample (a) and the corresponding high-resolution XPS spectra of C 1s (b), N 1s (c), and S2p (d).

The composition of the CN and the chemical status of C and N elements in the sample have been characterized by XPS. **Fig. S5** shows the XPS spectrum of representative sample CNM-600. The survey scan XPS spectrum reveals the presence of C, N and O atoms in CNM-600. The O1s signal may be arising from the absorbed

 $H_2O$  molecules on the CN surface. The high-resolution XPS spectrum of C 1s shows two peaks at 287.7 eV and 284.6 eV. The peak at 287.7 eV originates from sp2-hybridized C in the aromatic ring, the other peak at 284.6 eV is attributed to graphitic C. High-resolution N 1s spectra can be deconvoluted into three peaks. The main peak at 398.2 eV is assigned to sp2 hybridized aromatic N in triazine rings. As for the peak at binding energies of 400.2 and 404.21 eV, which are attributable to the tertiary N bonded to C atoms in the form of N–(C)<sub>3</sub>/H–N–(C)<sub>2</sub> and charging effects, respectively.



Fig. S6. High-resolution XPS spectra of C1s in Bulk CN and CNM samples.



Fig. S7. N<sub>2</sub>-sorption isotherms and the corresponding BJH pore-size distribution of the bulk CN and CNM samples



Fig. S8. SEM images of bulk CN (a), CNM-500 (b), CNM-525 (c), CNM-550 (d), CNM-575 (e) and CNM-600 (f).

As shown in **Fig. S8**, the bulk CN displays a monolith-like morphology with big and rather dense stacked layers. As for the CNM samples, they differ significantly from the morphology of the bulk CN. The CNM-500 obtained at lower temperature also shows stacked layers structure, but some lamellar sheets can be observed on the surface. As the pyrolysis temperature increases, the CNM-525 is transformed into continuous thin nanosheets. Moreover, the sheets have been rolled up to lower the surface free energy. When the temperature is further increased to 600 °C, the resulting CNM-600 sample is further transformed to thinner, and fluffy structure. These nanoscale morphological alterations are more evident in the TEM images (Fig. S9), where the lamellar structure of CNM are defoliated into, silk-like structures and then to the thin chip-like nanosheets as the temperature increases. Looking carefully at the TEM pictures, the irregularity pores can be found in the sample. This is due to the generation of some gases such as (NH<sub>3</sub> etc.) and the volatilization of sulfur during the CN pyrocondensation process. The high temperature accelerates the volatilization of sulfur, supports the expansion of the stacking layers and facilitates the formation of CN nanosheets with smaller thickness.



Fig. S9. TEM images of CNM-500 (a), CNM-550 (b), CNM-600 (c).



Fig. S10. Catalytic performance of graphite carbon (GC), N-doped GC, commercial Fe<sub>2</sub>O<sub>3</sub> and CNM-600 samples at 180 °C. Reaction conditions: catalyst (0.4 g), H<sub>2</sub>S/O<sub>2</sub>/N<sub>2</sub>=0.5/0.25/99.25 (wt %), WHSV (3000 mL·g<sup>-1</sup>·h<sup>-1</sup>), Gas flow rate (20 mL·min<sup>-1</sup>).



Fig. S11. The sulfur recovered.



Fig. S12. S 2p high-resolution XPS spectrum of used CNM-600 sample.



**Fig. 13.** Durabilities of CNM samples at 180 °C. Reaction conditions: catalyst (0.4 g), H<sub>2</sub>S/O<sub>2</sub>/N<sub>2</sub>=0.5/0.25/99.25 (wt%), WHSV (3000 mL·g<sup>-1</sup>·h<sup>-1</sup>), Gas flow rate (20 mL·min<sup>-1</sup>).



Fig. S14. XRD patterns of CNM samples before and after catalytic reaction.



Fig. S15. XRD patterns of CNM-600 sample before and after catalytic reaction.



Fig. S16. IR spectra of CNM-600 sample before and after catalytic reaction.

samples							
Samples	C1s	N1s	Relative comp	C/N <sup>[c]</sup>			
	(atm. %) <sup>[a]</sup>	(atm. %)	carbo	ratio			
			P1	P2			
Bulk CN	40.22	59.01	3.90	36.32	0.62		
CNM-500	43.31	54.05	9.34	33.97	0.63		
CNM-525	40.74	55.62	5.82	34.92	0.63		
CNM-550	41.53	56.12	5.61	35.92	0.64		
CNM-575	43.49	51.51	9.97	33.52	0.65		
CNM-600	42.72	51.69	9.06	33.66	0.65		

 Table S1. Elemental composition and the C/N atomic ratio in Bulk CN and CNM samples

<sup>[a]</sup> atomic ratios of carbon and nitrogen in samples obtained from the XPS results.

<sup>[b]</sup> carbon percentages deconvoluted from the C1s XPS spectra.

<sup>[c]</sup> the ratio of C/N in bulk CN and CNM is calculated *via* carbon present in C-N bonds divided by nitrogen, according to the equation C/N=P2\*C1s/N1s.

Sumples propuled at anterent temperatures								
Sample	Yield	Н	S	C/N	Pore	SBET		
	(wt %)	(wt %)	(wt %)	rate	volume	(m²/g)		
					(cm <sup>3</sup> /g)			
Bulk CN	52.7	1.76	-	0.66	0.092	12.1		
CNM-500	26.5	2.36	-	0.66	0.194	36.7		
CNM-525	23.0	2.16	-	0.67	0.251	57.4		
CNM-550	20.2	2.06	-	0.68	0.362	75.2		
CNM-575	12.7	1.88	-	0.69	0.499	110.8		
CNM-600	8.2	1.69	-	0.69	0.453	114.1		

**Table S2**. Elemental composition and physical properties of bulk CN and CNM samples prepared at different temperatures

Table S3. Different catalysts used for selective oxidation of H<sub>2</sub>S to S

Feed	catalyst	GHSV h <sup>-1</sup>	Temp. ℃	Sulfur capacity	Sulfur yield %	ref
H <sub>2</sub> S,5000 ppm	CNM-600	3000	180		90.48	/
O2,2500 ppm	CIVIN-000					
H <sub>2</sub> S,3000ppm	Mn/active	3000	180	0.142		6
O2,3000ppm	carbon					0
H <sub>2</sub> S,1000 ppm	Macroscope		100		69	7
O <sub>2</sub> , 2.5%	N-CNTs	-	190		08	/
H <sub>2</sub> S/O <sub>2</sub> =1/2.5 with 30%	EarOr/SiC	2000	250		05	0
water	Fe2O3/SIC	3000	250		73	ð

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