

Electronic Supplementary Information (ESI)

Transforming chitosan into N-doped graphitic carbon electrocatalysts

EXPERIMENTAL SECTION

Chemicals. Chitosan was purchased from Aladdin Reagent Company, acetic acid, anhydrous ethanol, sulfur powders and potassium hydroxide (KOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial E-TEK Pt/C catalyst was purchased from Alfa Aesar. All the chemicals were used as received without further purification.

Synthesis of N-doped particulate carbon materials (C-900) via direct pyrolysis of chitosan. Certain amount of chitosan powder was added into a rail boat and placed in a tube furnace. This was followed by flushing the furnace with high purity nitrogen (99.99%) for 30 minutes before heating to 900 °C at a heating rate of 5 °C min⁻¹, and kept at 900 °C for 4 h. After that the furnace was cooled down to room temperature, the resultant products were stored in a sealed glass bottle for further use.

Synthesis of N-doped carbon nanoparticles (N-CNPs). In a typical synthesis process, 0.70 g chitosan powder was fully dissolved in 70 ml 2% acetic acid. The resultant solution was sealed into a Teflon-lined stainless steel autoclave (100 ml), which was then placed in a furnace for hydrothermal treatment at 180 °C for 12 h. After the autoclave was cooled down to room temperature, the obtained black suspension was centrifuged at 14000 rpm for 5 min, washed with deionized water three times, and freeze-dried. The resultant N-CNPs were used

for characterisations and pyrolysis conversion into nitrogen-doped graphitic carbon nanoparticles (N-GCNPs).

Synthesis of sulfur-nitrogen co-doped carbon nanoparticles (S, N-CNPs). In a typical synthesis process, 0.10 g sulfur powder was added into the above chitosan/acetic acid solution, stirred to disperse evenly. The mixture was then sealed into a Teflon-lined stainless steel autoclave (100 ml) for hydrothermal treatment at 180 °C for 12 h. After the autoclave was cooled down to room temperature, the obtained black suspension was transferred to a beaker with 50 ml CCl₄ and was magnetic stirred for 3 h to remove unreacted elemental sulfur. After a standing and layering process, the black suspension was centrifuged at 14000 rpm for 5 min, washed with anhydrous ethanol three times to remove residual CCl₄, then adequately washed with deionized water and freeze-dried. The resultant S, N-CNPs were used for characterisations and pyrolysis conversion into sulfur-nitrogen co-doped graphitic carbon nanoparticles (S, N-GCNPs).

Synthesis of nitrogen-doped graphitic carbon nanoparticles (N-GCNPs) and sulfur-nitrogen co-doped graphitic carbon nanoparticles (S, N-GCNPs). The resultant N-CNPs and S, N-CNPs were thermally converted into N-GCNPs and S, N-GCNPs, respectively, via a pyrolysis process in a tube furnace with high purity nitrogen protective ambient. The detailed procedure was: a suitable amount of N-CNPs or S, N-CNPs samples were added into a railboat and placed in a tube furnace. This was followed by flushing the furnace with high purity nitrogen (99.99%) for 30 minutes before heating to 900 °C at a heating rate of 5 °C min⁻¹, and kept at 900 °C for 4 h. After that the furnace was cooled down to room temperature, the resultant N-GCNPs or S, N-GCNPs samples were stored in a sealed

glass bottle for further use.

Physical and chemical characterization. Field emission scanning electron microscopy (FESEM) images were taken on a FESEM (Quanta 200FEG) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images were recorded by a high resolution TEM (JEOL 2010), operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Philips X-Pert Pro X-ray diffractometer with Cu K α radiation ($\lambda_{K\alpha 1} = 1.5418 \text{ \AA}$). Raman spectra were carried out on a LabRAM HR800 confocal microscope Raman system (Horiba Jobin Yvon) using an Ar ion laser operating at 632 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K $\alpha_{1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar 3020M).

Electrochemical evaluation. Electrochemical measurements were conducted on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) coupled with a PINE rotating disk electrode (RDE) system (from Pine Instruments Co. Ltd. USA). A standard three-electrode electrochemical system equipped with gas flow system was employed.

Prior to the surface coating, rotation ring-disk electrode (5mm in diameter) was polished with 5.0, 0.3 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for a few minutes, respectively. The cleaned electrode was dried with a high-purify nitrogen steam. A total of 20 μL of the products or commercial E-TEK Pt/C catalyst (2 mg catalyst/1ml deionized water) was dropped on the pretreated

electrode surface and dried at room temperature. In order to make the catalyst covered the entire electrode surface, another 20 μL of the catalysts was dropped on the pretreated electrode surface and dried at room temperature. After that, 10 μL Nafion (DuPont Corp., 0.05% in aqueous solution) was then placed on the surface of the above materials modified electrodes and dried at room temperature before electrochemical experiments.

The ORR performance of the catalysts was studied by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in an aqueous solution of 0.1 M KOH. CVs were measured at a scan rate of 50 mV s^{-1} . LSVs were measured at a scan rate of 10 mV s^{-1} under different disk rotation rates of 400, 625, 900, 1225 and 1600 rpm. All the potentials in this study were reported with respect to the Ag/AgCl reference electrode. The obtained current values were normalized to the mass of the catalyst used (i.e. given in mA mg^{-1}) for direct comparison between samples. For Koutecky-Levich analysis, the un-normalized currents obtained from measurements at varying rotation rates were used.

The number of electrons transferred per oxygen molecule was calculated by the Koutecky-Levich equation given below:¹

$$J^{-1} = J_k^{-1} + (B\omega^{1/2})^{-1} \quad (1)$$

$$B = 0.2nF(D_{O_2})^{2/3} \nu^{-1/6} C_{O_2} \quad (2)$$

Where J is the measured current density of the ORR, J_k is the kinetic current density, ω is the electrode rotating rate, B is the slope of K-L plots, n represents the number of electrons transferred per oxygen molecule, F is the Faraday constant ($F = 96485 \text{ C} \cdot \text{mol}^{-1}$), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \cdot \text{S}^{-1}$), ν is the kinetic viscosity ($0.01 \text{ cm}^2 \cdot \text{S}^{-1}$), C_{O_2} is the bulk concentration of O_2 ($1.2 \times$

$10^{-3} \text{ mol} \cdot \text{L}^{-1}$).² The constant 0.2 is adopted when the rotation speed is expressed in rpm.

Table S1. Elemental composition of the prepared carbon materials as obtained by XPS.

Sample	XPS analysis (at%)		
	C	N	S
N-CNPs	76.0	5.6	-
N-GCNPs	92.5	3.4	-
S, N-CNPs	71.5	4.1	2.4
S, N-GCNPs	91.1	3.4	1.4

Table S2. N₂ sorption-derived textural properties of the prepared carbon materials.

Sample	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore Size (nm)
C-900	198.29	0.097	1.9
N-CNPs	226.11	0.36	6.3
N-GCNPs	533.41	0.65	4.9
S, N-CNPs	396.98	0.59	6.0
S, N-GCNPs	579.52	0.76	5.3

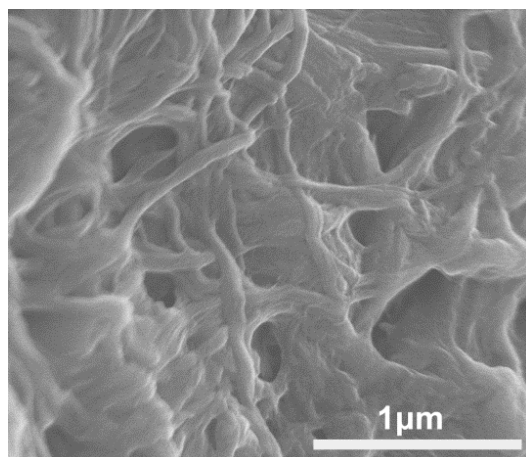
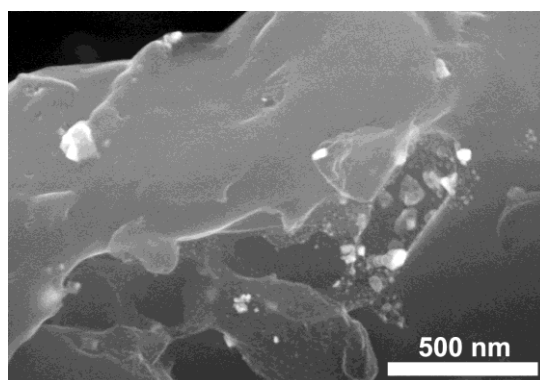
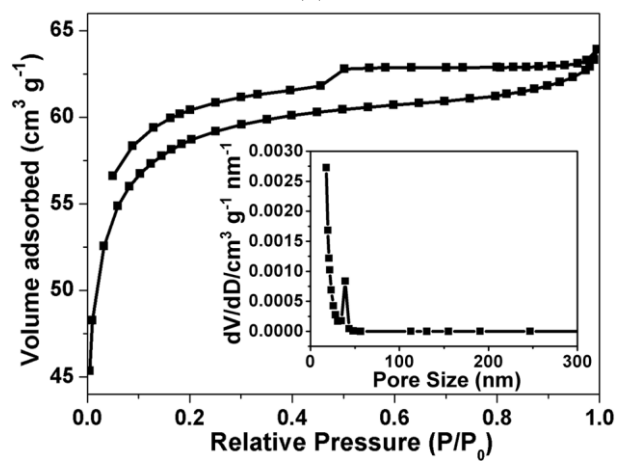


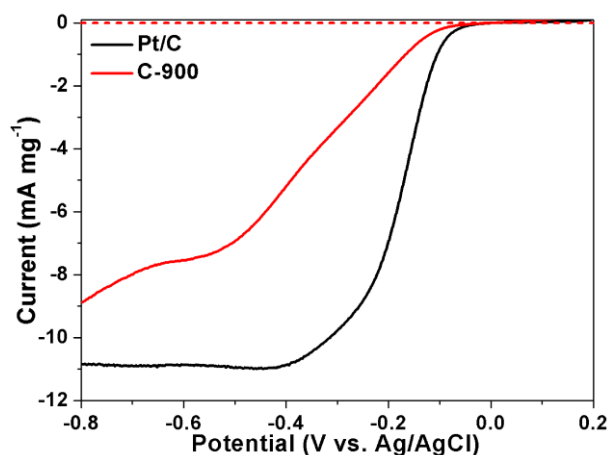
Fig. S1 SEM image of chitosan.



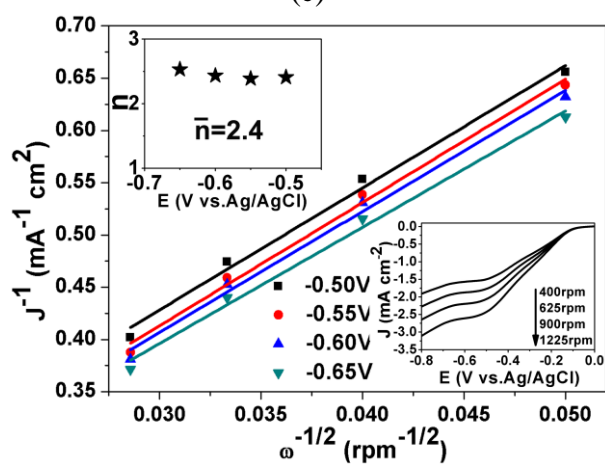
(a)



(b)



(c)



(d)

Fig. S2 (a) Carbon product (denoted as C-900) from direct pyrolysis at 900 °C. (b) Nitrogen sorption isotherms and pore size distribution (inset) of C-900. (c) LSVs of C-900 and Pt/C electrodes in an O₂-saturated 0.1 M KOH solution with a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. (d) Koutecky-Levich plots of C-900 (the bottom inset: corresponding LSVs, the top inset: calculated transferred electron numbers).

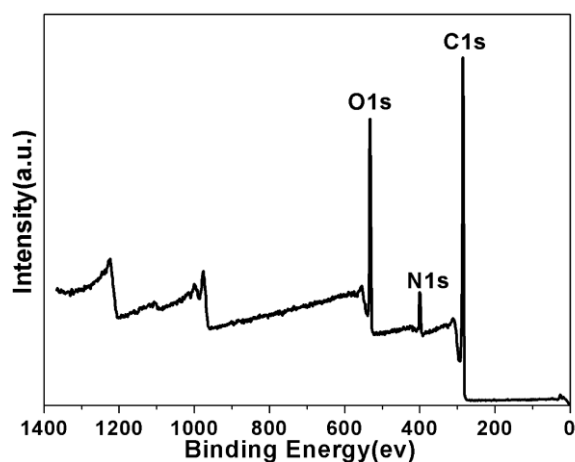


Fig. S3 XPS survey spectrum of N-CNPs.

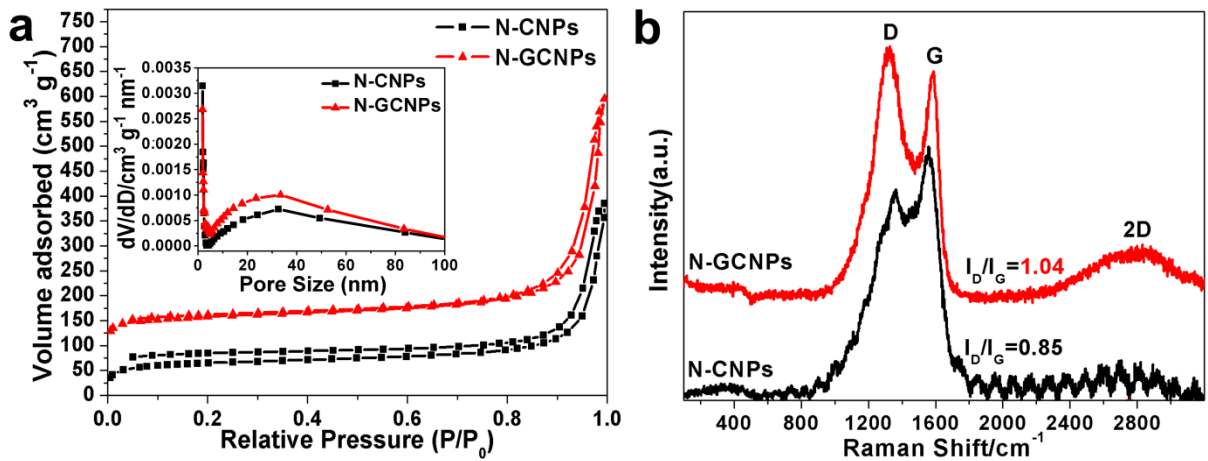


Fig. S4 (a) Nitrogen sorption isotherms and pore size distributions (inset) of N-CNPs and N-GCNPs. (b) Raman spectra of N-CNPs and N-GCNPs.

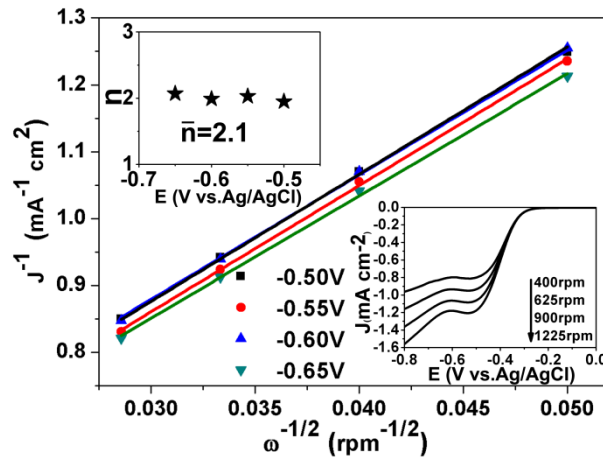


Fig. S5 Koutecky-Levich plots (the inset in bottom-right: corresponding LSVs, the inset in top-left: transferred electron number) of N-CNPs.

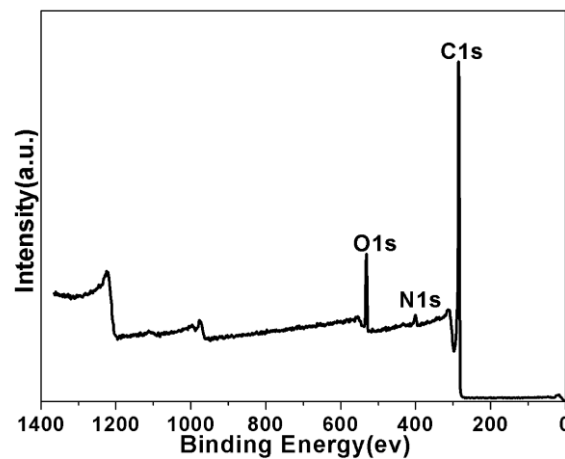


Fig. S6 XPS survey spectrum of N-GCNPs.

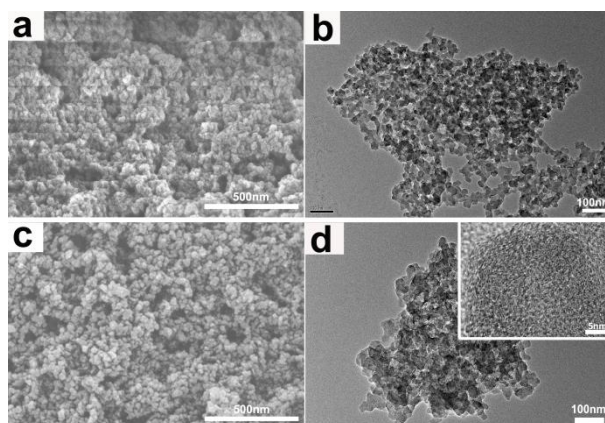


Fig. S7 (a) SEM and (b) TEM image of S, N-CNPs, (c) SEM and (d) TEM image (HRTEM image inset) of S, N-GCNPs.

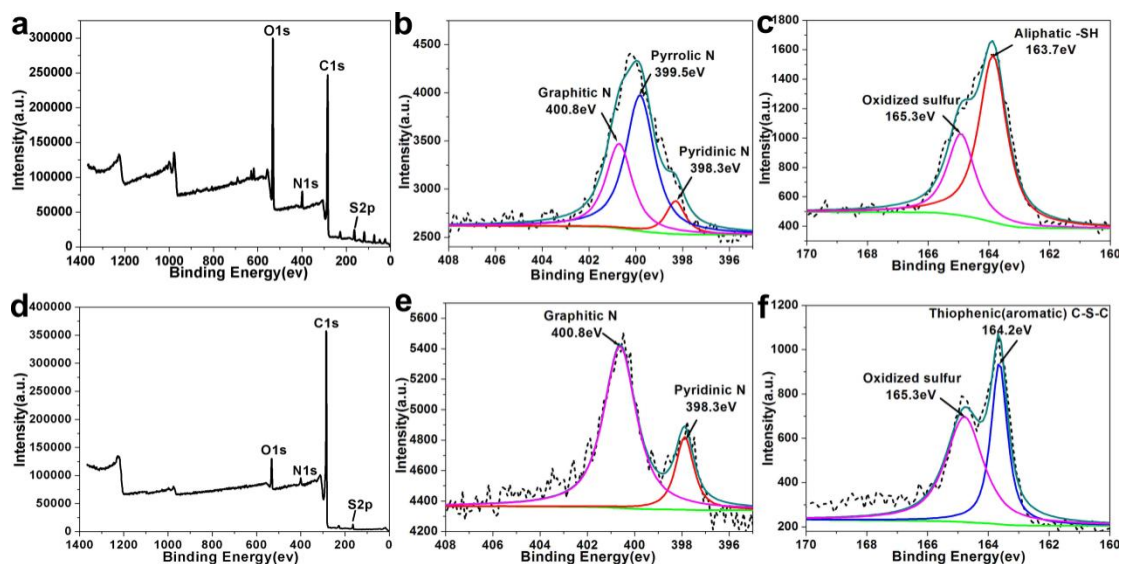


Fig. S8 (a) XPS survey spectrum, (b) and (c) High resolution spectra of N1s and S2p of S, N-CNPs, (d) XPS survey spectrum, (e) and (f) High resolution spectra of N1s and S2p of S, N-GCNPs.

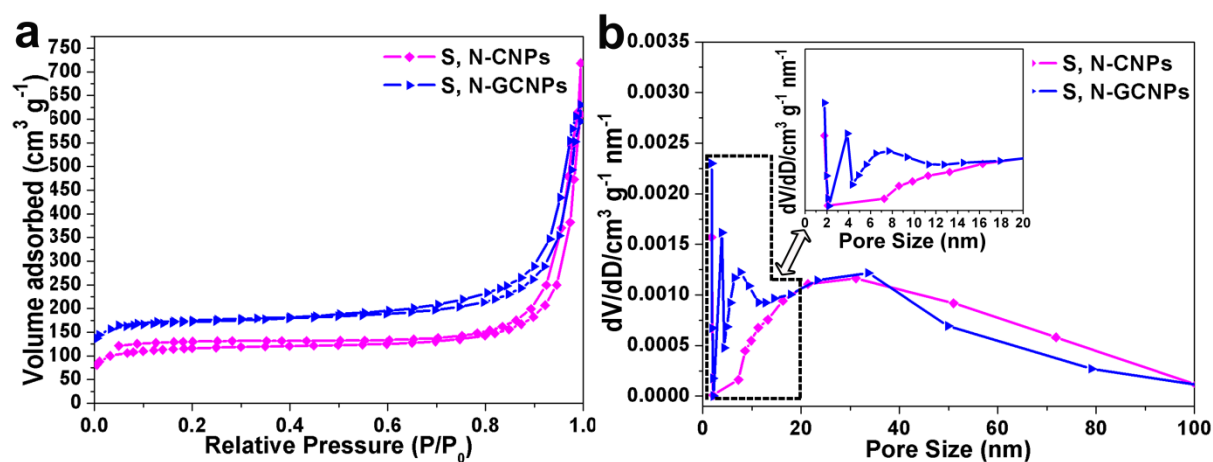


Fig. S9 (a) Nitrogen sorption isotherms and (b) pore size distributions of S, N-CNPs and S, N-GCNPs.

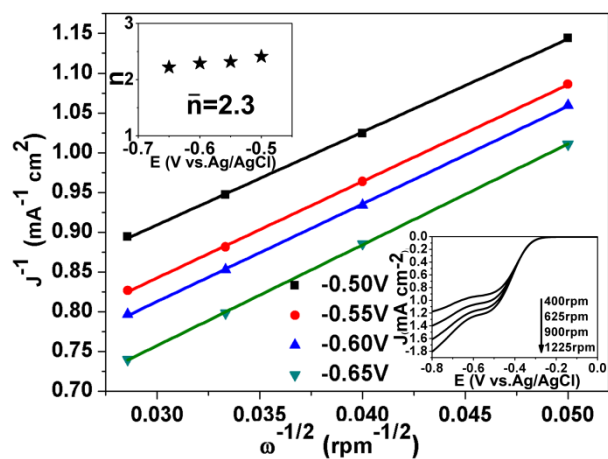


Fig. S10 Koutecky-Levich plots (the inset in bottom-right: corresponding LSVs, the inset in top-left: transferred electron number) of S, N-CNPs.

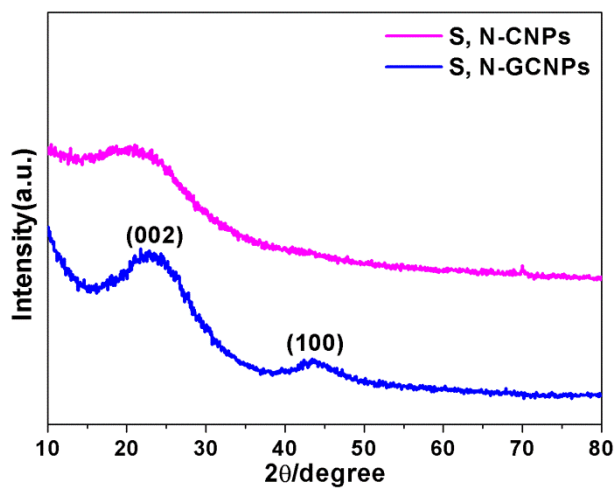


Fig. S11 XRD patterns of S, N-CNPs and S, N-GCNPs.

References:

- 1 A.J. Bard, L. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- 2 R. Davis, G. Horvath and C. Tobias, *Electrochim.Acta*, 1967, **12**, 287.