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Supplementary Information

Controlling Solubility: A Chemistry Approach toward Preparing Nitrogen-Doped Hollow Carbon Nanospheres

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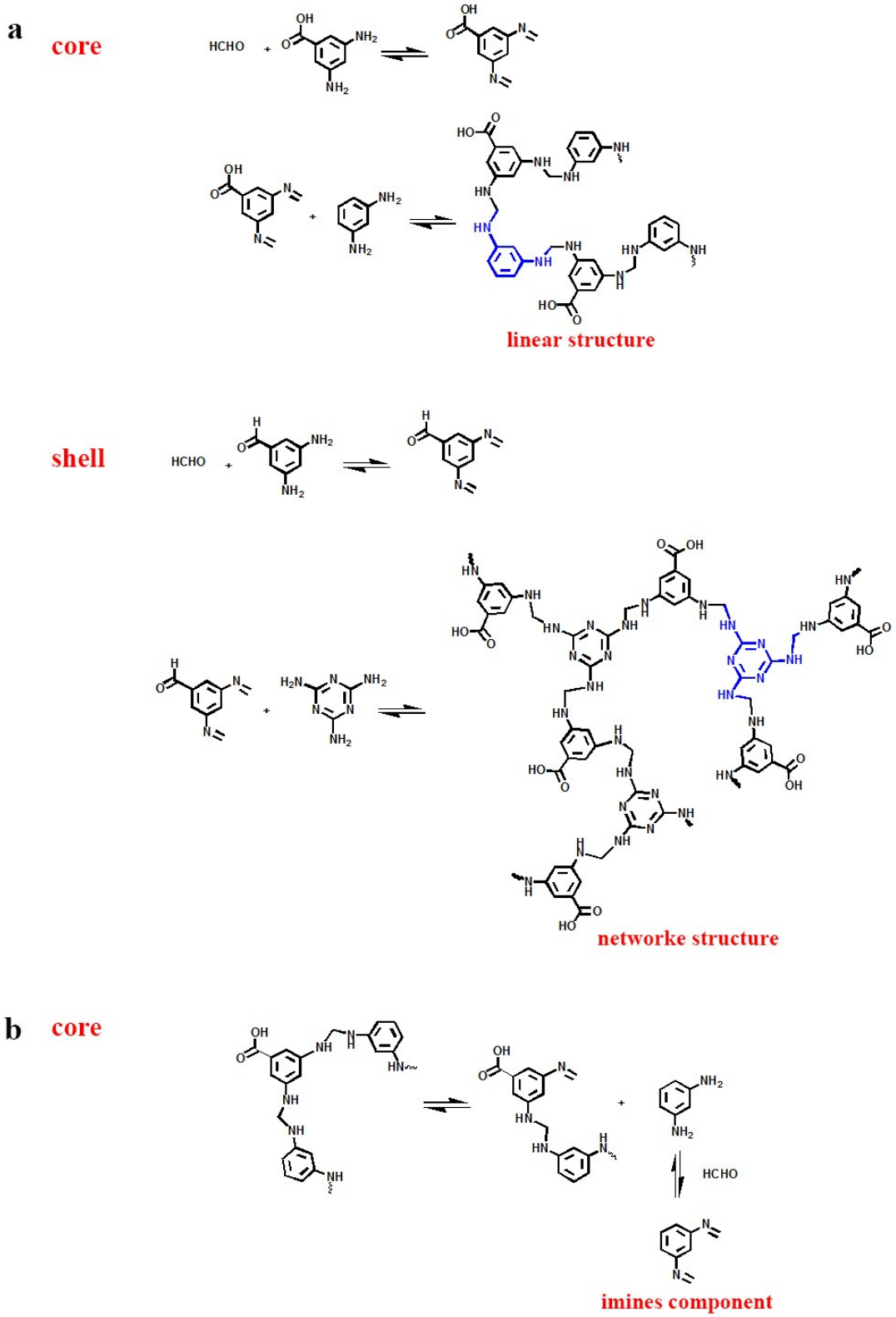

Fig. S1 Illustration of the forming and dissolving process of the polymer.

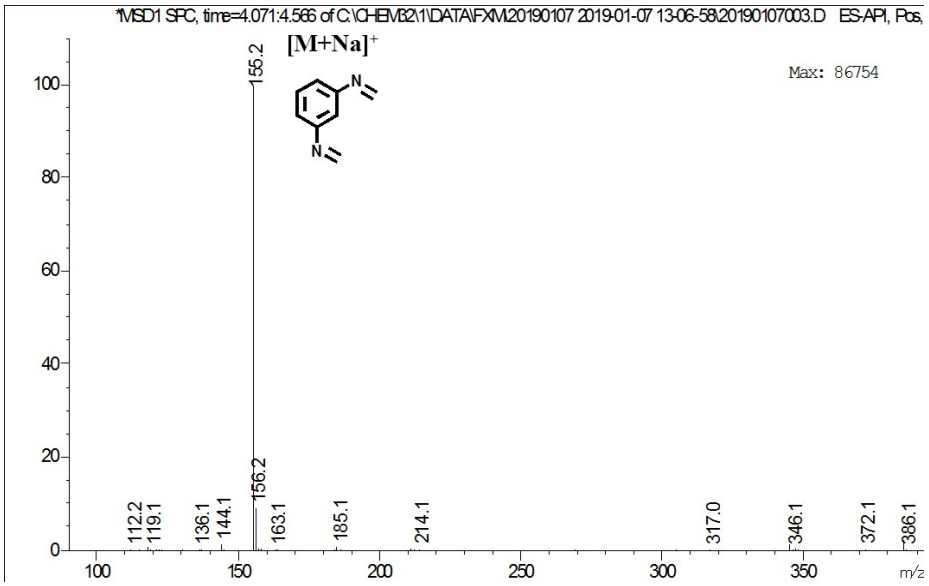

Fig. S2 ESI mass spectrum of the imine component from the inner polymer decomposition in formaldehyde solution.

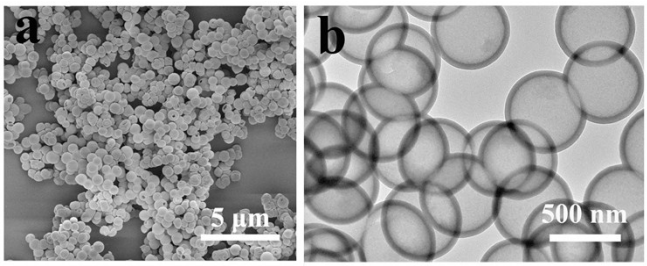

Fig. S3 SEM and TEM image of HPSs formed by using recovered liquid of formaldehyde treatment as reactant. The experiment parameters were same with HPSs, except that 2 mL formaldehyde solution (37%~40%) was replaced with 2 mL recovered liquid.

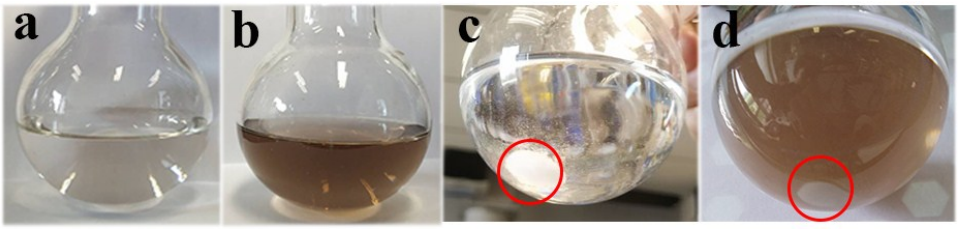

Fig. S4 Photographs of the states of reactants in acetone-water solvent before reaction: a) *m*-PD, b) DABA, c) melamine, d) *m*-PD, DABA and melamine dispersed in the solvent. The undissolved melamine can be observed at the flask bottom as marked in red circles.

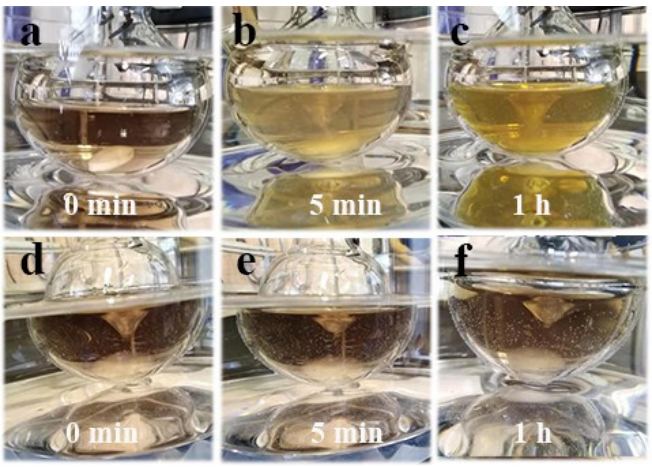

Fig. S5 Photographs recorded turbidity variation of reaction systems containing *m*-PD (a-c) or melamine (d-f). Both the solvents are pure water and dosages of other reactants are same.

The experiments are performed to better state the different reaction rates of formaldehyde and *m*-PD or melamine. First, we measured the absorption spectra of precursor solutions containing *m*-PD or melamine and colloidal suspensions of their products (Figure S6 a). The wavelength of 450 nm where reactants were almost no light absorption and the signals were corresponded to products was selected for turbidity measurements. Then the in situ optical monitoring was performed to see the different reaction rates. The result is as following, which indicate the *m*-PD presents a higher rate of reaction.[1]

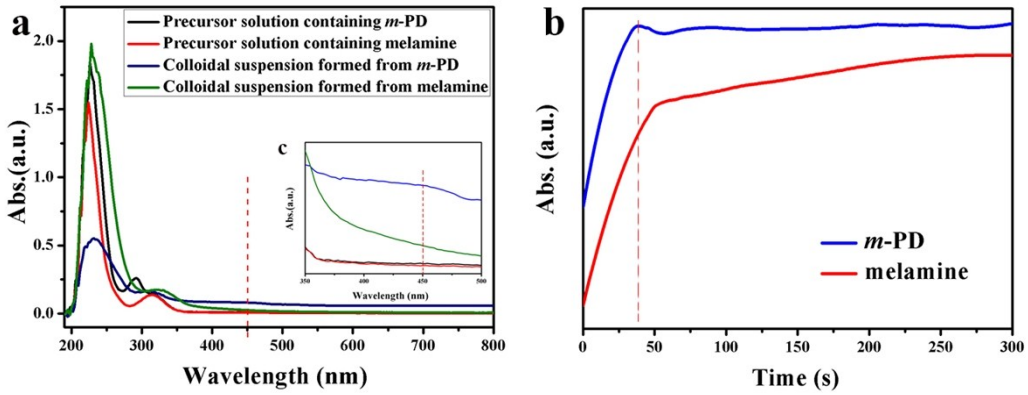

Fig. S6 a) Absorption spectra of solutions containing *m*-PD or melamine and their colloidal suspensions after reacted with formaldehyde. Inset is a magnification from 350 nm to 500 nm. b) A graph showing the change in absorbance over time using reactant including *m*-PD or melamine at the wavelength of 450 nm.

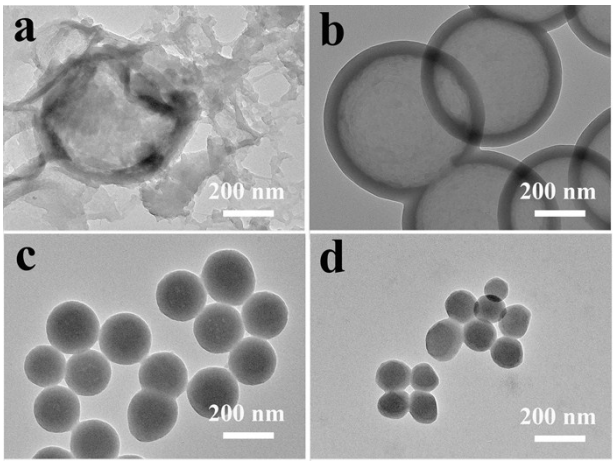

Fig. S7 TEM images of samples synthesized in mixture solvent of a) 2.5 mL water 47.5 mL acetone, b) 5 mL water 45 mL acetone, c) 10 mL water 40 mL acetone, and d) 50 mL water 0 mL acetone.

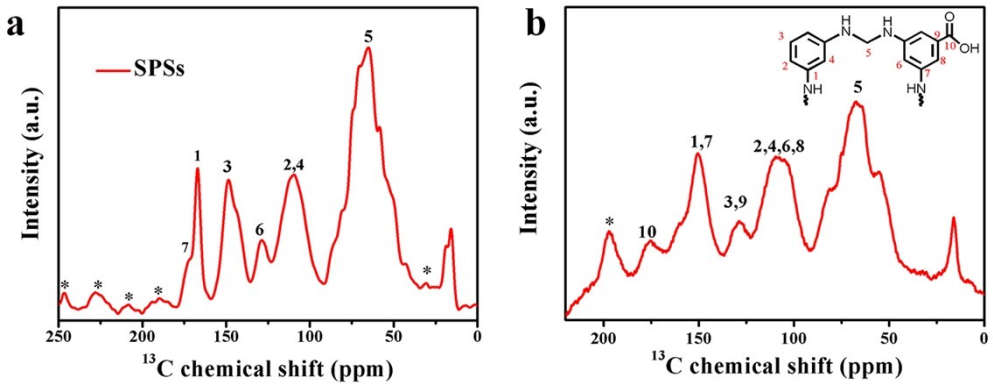

Fig. S8 ^{13}C CP-MAS NMR of SPSs and the polymer formed from reactants only containing *m*-PD and DABA.

The peak of 15 ppm in both SPSs and the polymer formed from *m*-PD and DABA was the methyl peak of the acetone, which was caused by fast reaction between *m*-PD, DABA and formaldehyde. In the inner of the two kind of polymer leaved a small amount of acetone.

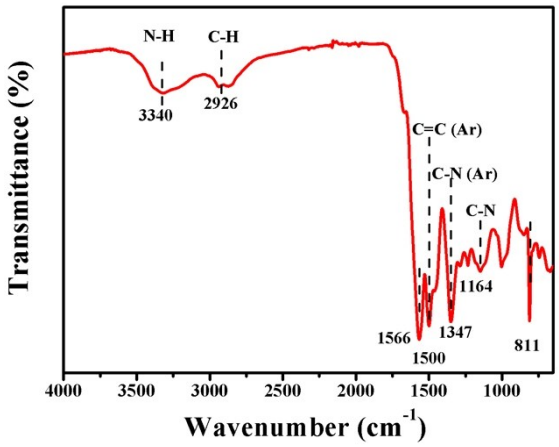

Fig. S9 FTIR spectra of SPSs.

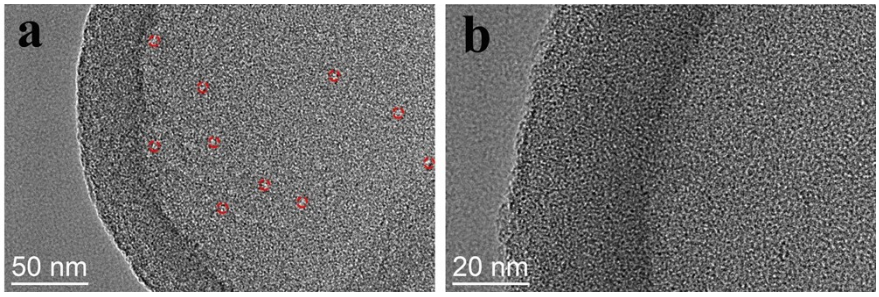

Fig. S10. a) TEM images of the HCSs-5 (the red circles indicate the mesopores in the sphere and the diameters of the pores are around 2 nm). b) HRTEM image of the HCSs-5

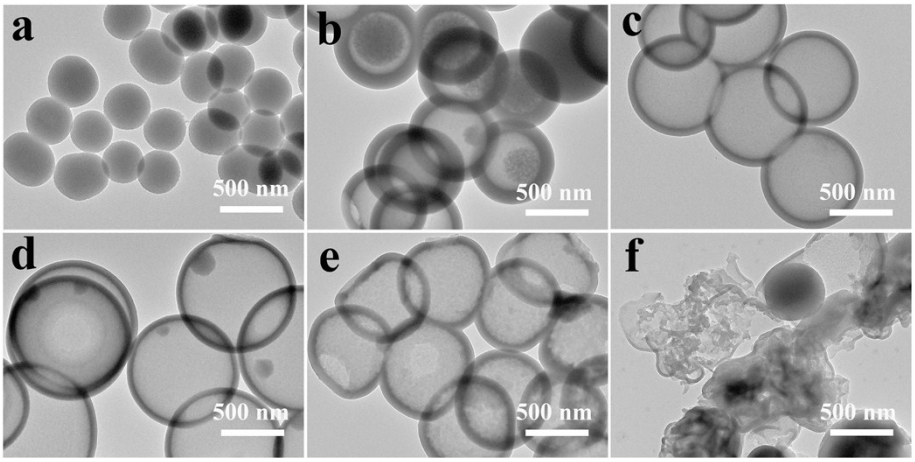

Fig. S11. TEM images of samples synthesized in different amounts of ammonia solution. a) 0 mL, b) 0.1 mL, c) 0.2 mL, d) 0.3 mL, e) 0.4 mL, and f) 0.8 mL.

The amounts of ammonia could affect the size of the spheres[2, 3], which can be confirmed from Fig. S11 (a-d). But excess ammonia dosage leaded to worse morphology of the spheres (Fig. S11 e, f).

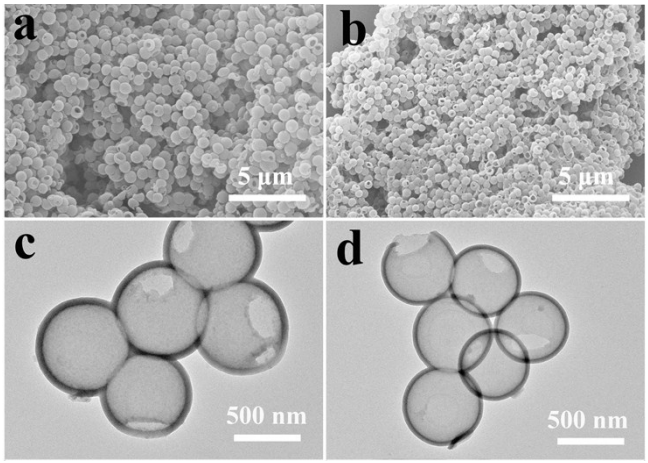

Fig. S12. SEM and TEM images of HPSs synthesized with different amounts of *m*-PD. (a and c) 0.108 g, (b and d) 0.027 g.

The sphere diameter can be changed by tuning the *m*-PD dosage and the controllable range is 530

nm to 710 nm.

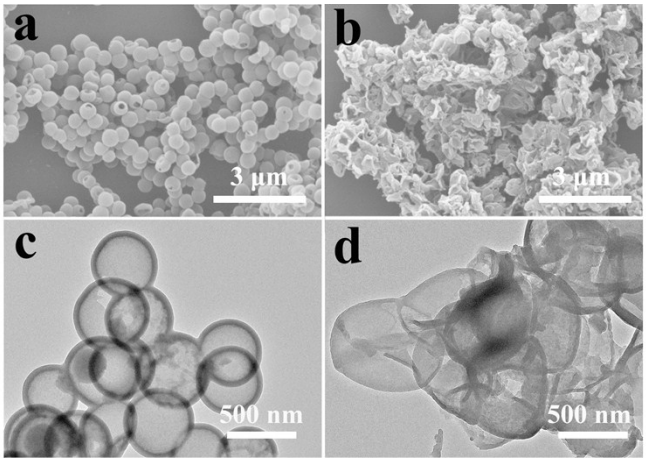

Fig. S13. SEM and TEM images of hollow samples synthesized with different amounts of melamine. (a and c) 0.128 g, (b and d) 0.032 g.

Increasing the melamine usage can increase the thickness and strength of hollow sphere shell (Fig. S13a, c). If the amount of melamine is insufficient, no stable shell can be formed (Fig. S13b, d), which indicated that the shell composition contains a polymer formed by the reaction of melamine.

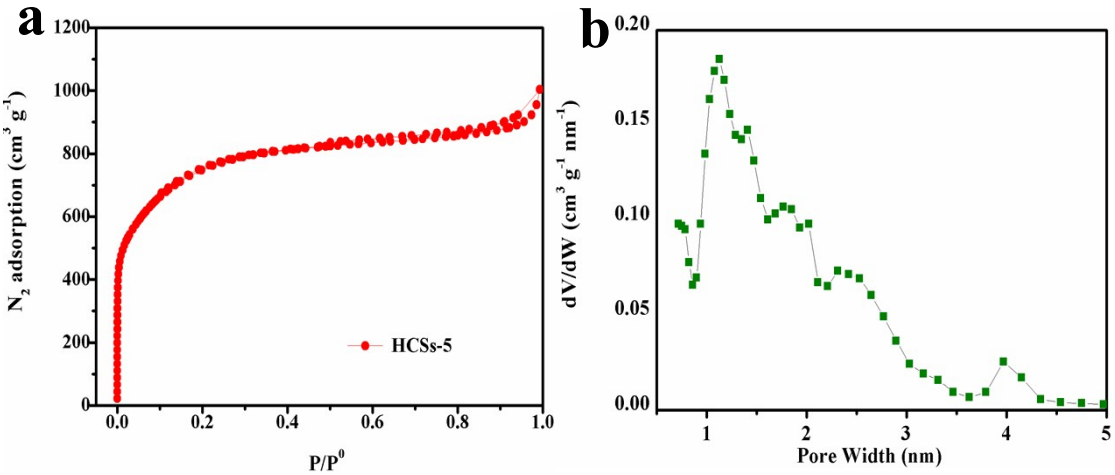

Fig. S14 N_2 sorption isotherms (a) and pore-size distribution (b) of HCSs-5-S.

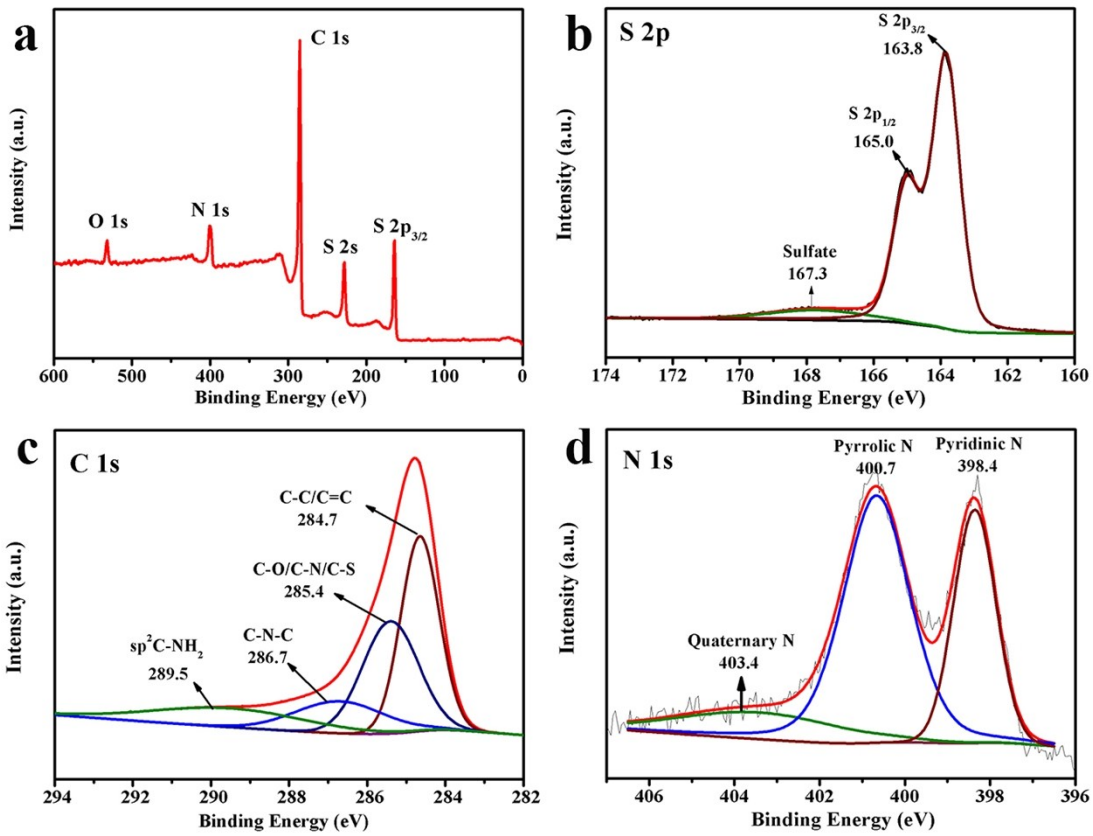

Fig. S15 XPS survey spectrum (a) and S_{2p}, C_{1s}, and N_{1s} spectra (b-d) of HCSs-S.

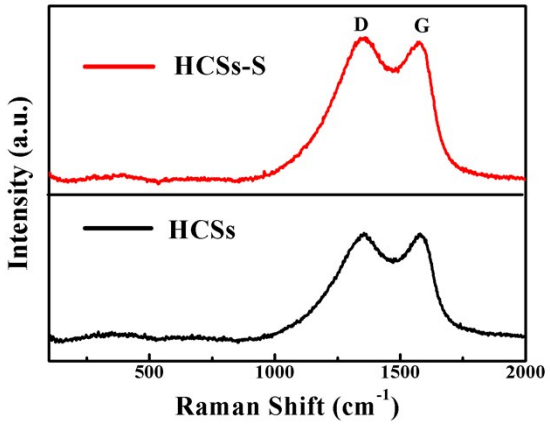

Fig. S16 Raman spectra of HCSs and HCSs-S.

Table S1. Elemental analyses of SPSs, HPSs and HCSs.

Sample	N [wt %]	C [wt %]	H [wt %]
SPSs	21.36	50.57	6.86
HPSs	26.99	49.85	6.25
HCSs	12.50	71.02	2.06

References

1. W. Guo, W. Xia, K. Cai, Y. Wu, B. Qiu, Z. Liang, C. Qu and R. Zou, *Small*, 2017, 13, 1702049.
2. J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Zhao and G. Q. M. Lu, *Angew. Chem., Int. Ed.*, 2011, 50, 5947-5951.
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