

Electronic Supplementary Information for

Template-free fabrication of nitrogen-doped hollow carbon spheres for high-performance supercapacitors based on a scalable homopolymer vesicle

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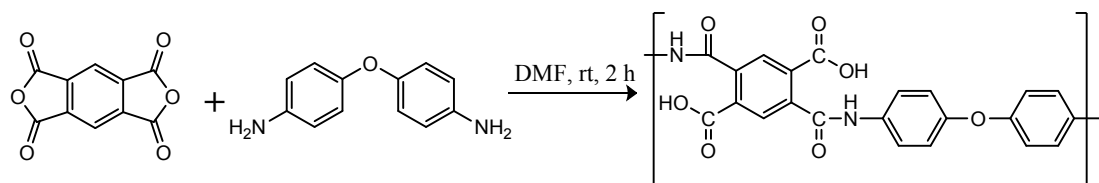
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Schemes and Figures

Scheme S1. Synthesis of PAA homopolymer.



Scheme S2. Imidization of PAA upon heating.

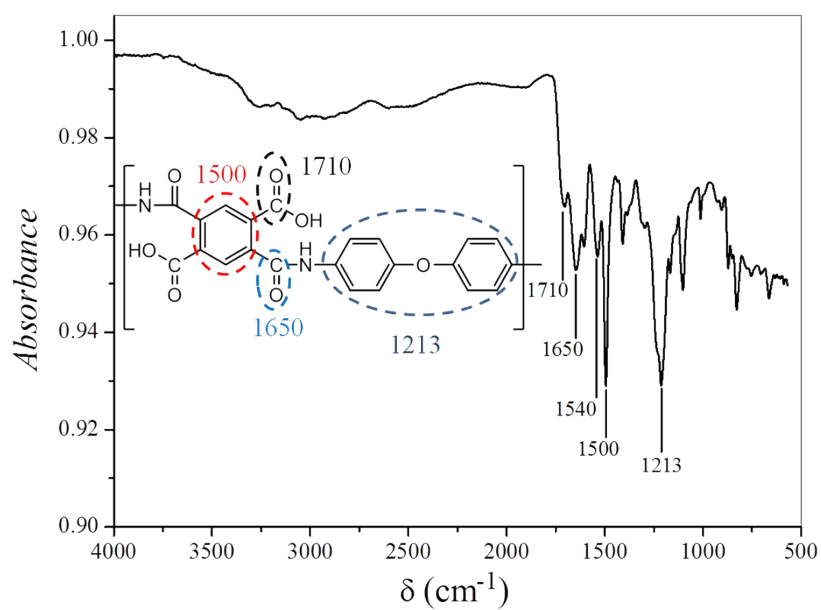
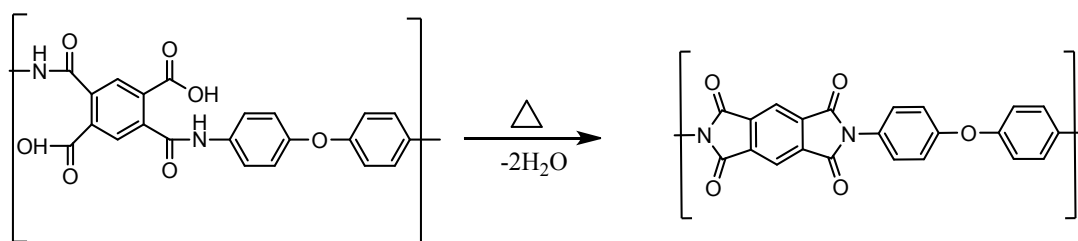


Fig. S1. FT-IR spectrum of PAA homopolymer.

The peak at 1710 cm^{-1} is ascribed to the stretching of the aromatic carboxyl ($\text{C}=\text{O}$) group. The peak at 1650 cm^{-1} is due to the stretching of the imide ($\text{C}=\text{O}$). The peak at 1540 cm^{-1} is because the stretching ($\text{C}-\text{N}$) and variable angle vibration (NH) of the imide. The peaks at 1500 cm^{-1} and 1213 cm^{-1} are related to the stretching of the symmetric benzene (C_6H_2) and the aromatic ether ($\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4$), respectively. ^1H NMR analysis in Fig. S2 further confirmed that PAA homopolymer was successfully synthesized as peaks a and b are assigned to the hydrogen of $-\text{CONH}-$ and $-\text{COOH}$, respectively.

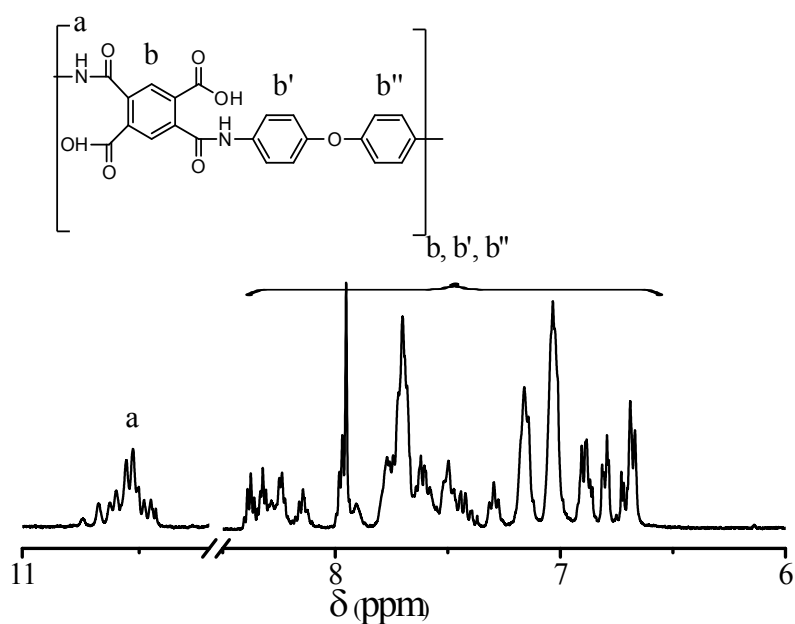


Fig. S2. ^1H NMR spectrum of PAA homopolymer in $\text{DMSO}-d_6$.

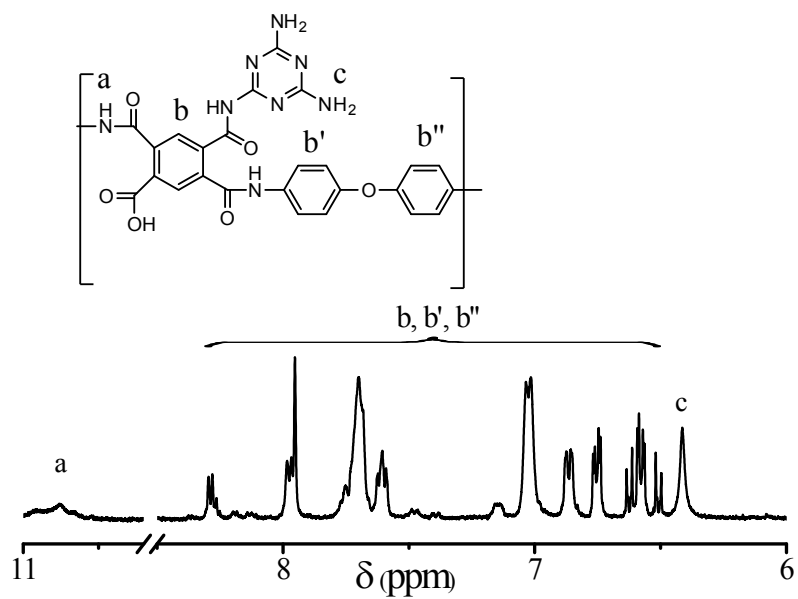


Fig. S3. ^1H NMR spectrum of PAA vesicles cross-linked by melamine in $\text{DMSO-}d_6$.

The molar ratio of melamine to carboxyl group is 0.25.

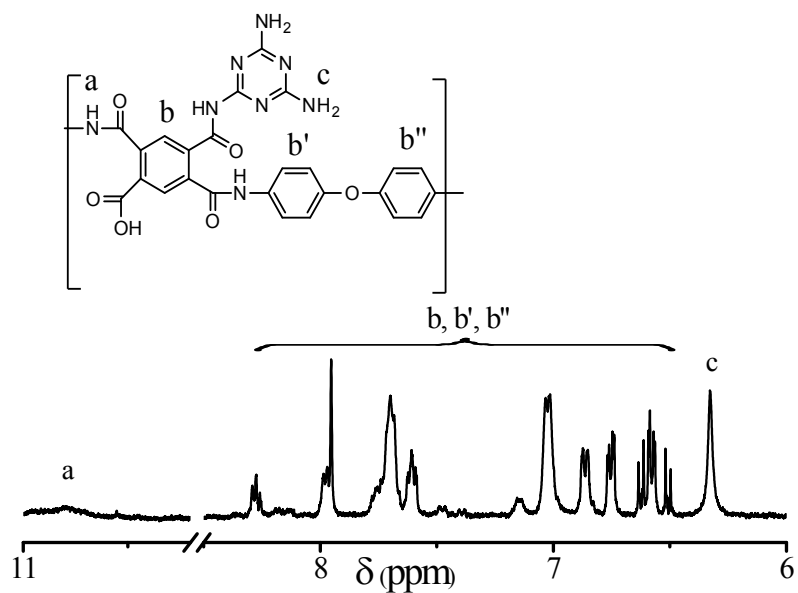


Fig. S4. ^1H NMR spectrum of PAA vesicles cross-linked by melamine in $\text{DMSO-}d_6$.

The molar ratio of melamine to carboxyl group is 0.5.

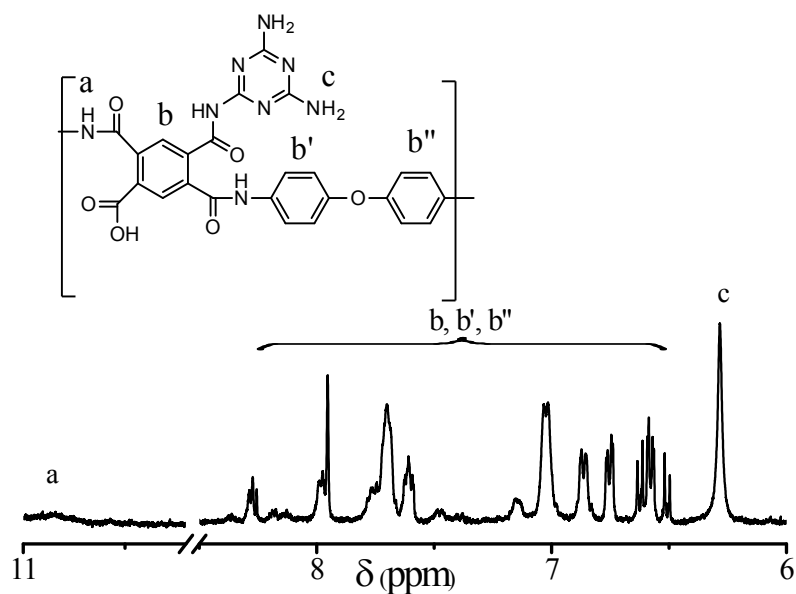


Fig. S5. ^1H NMR spectrum of PAA vesicles cross-linked by melamine in $\text{DMSO-}d_6$.

The molar ratio of melamine to carboxyl group is 1.0.

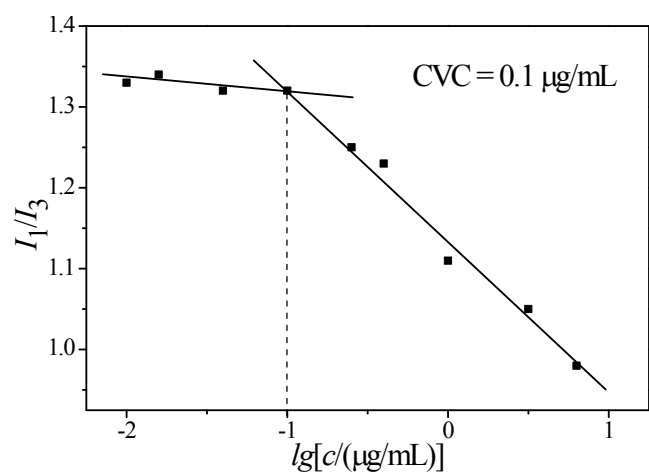


Fig. S6. Determination of the critical vesiculation concentration (CVC) of PAA.

The critical vesiculation concentration (CVC) of PAA homopolymer is $0.1 \mu\text{g/mL}$, which is much smaller than traditional block copolymers and homopolymers. As shown in Scheme S1, the novel structure of PAA homopolymer causes this phenomenon because the hydrophilic moieties are only carboxyl groups while the hydrophobic moieties are much more than the hydrophilic moieties. As a result, the solubility of

PAA homopolymer is extremely low in water, which means the homopolymer starts self-assembling at very low concentration.

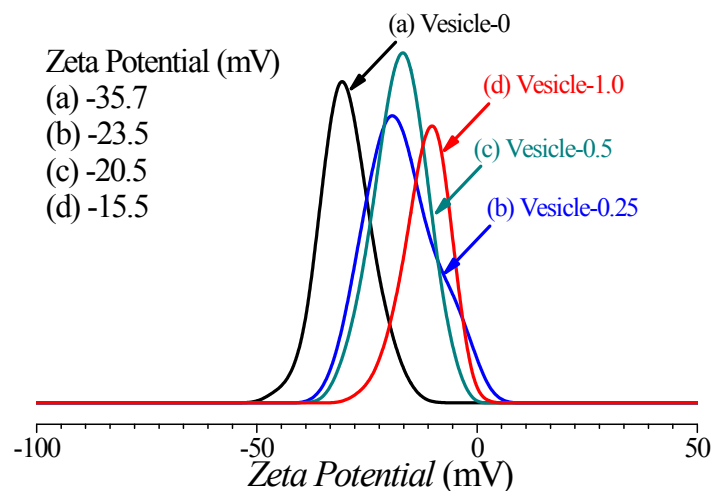


Fig. S7. Zeta potential of PAA vesicles without and with cross-linking by melamine.

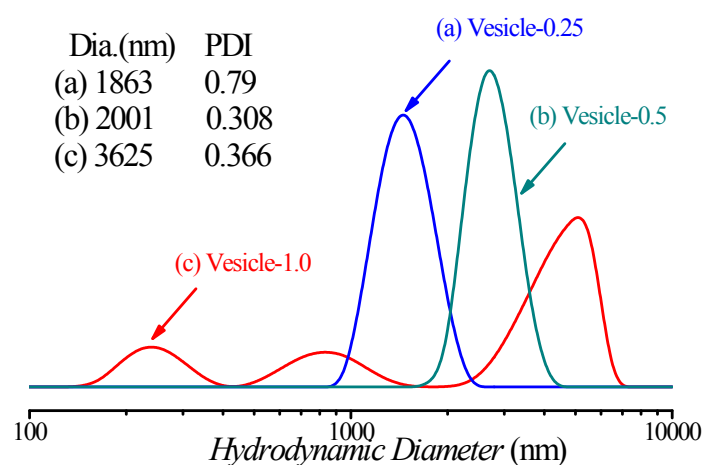


Fig. S8. DLS studies of PAA vesicles cross-linked by melamine before ultrasound treatment. The high PDI is because of the aggregation of vesicles. Curves a-c correspond to different molar ratios of melamine to carboxyl group (0.25, 0.5, 1.0), respectively.

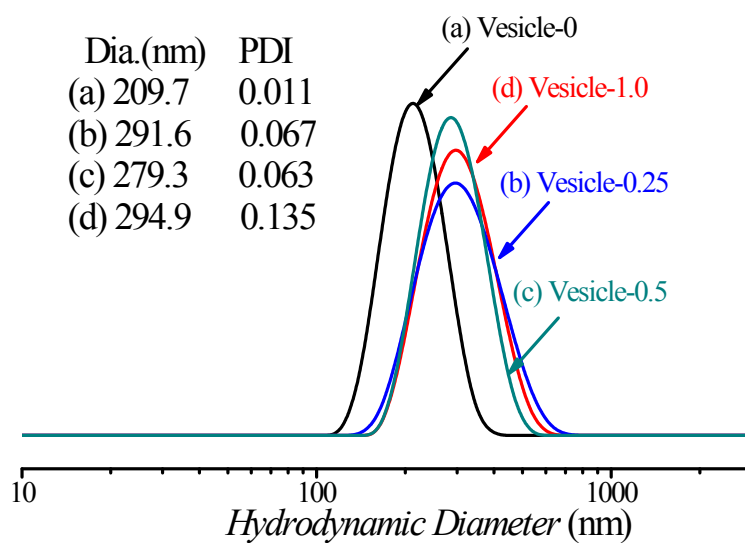


Fig. S9. DLS studies of PAA vesicles without and with cross-linking by melamine after ultrasound treatment for 2 min. Curves a-d correspond to different molar ratios of melamine to carboxyl group (0, 0.25, 0.5, 1.0), respectively.

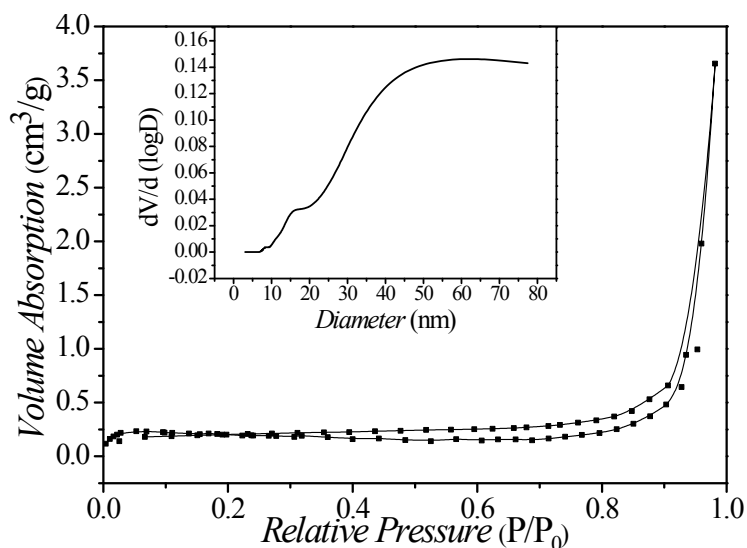


Fig. S10. Nitrogen adsorption-desorption isotherm and corresponding pore size distribution curves of PAA vesicles without cross-linking.

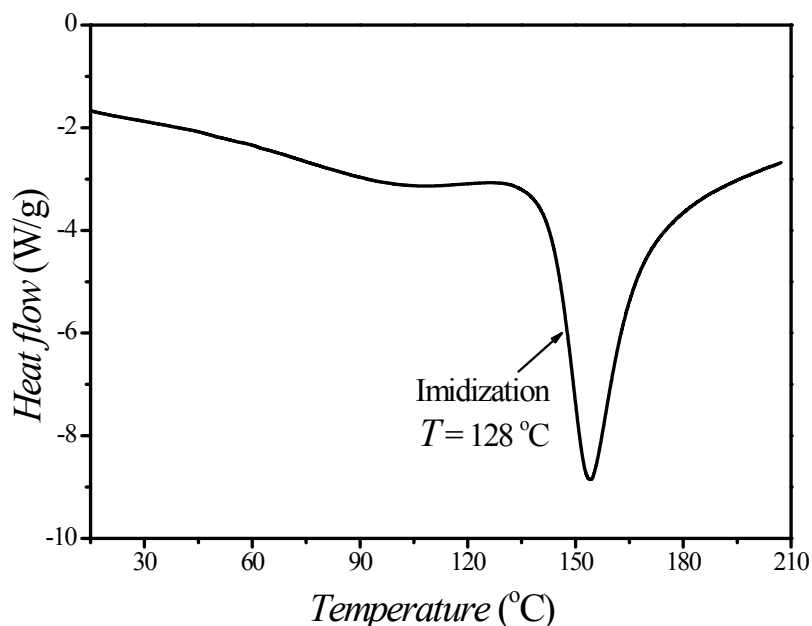


Fig. S11. DSC curve of PAA homopolymer.

During the carbonization process, when the temperature reaches 128 °C, the PAA homopolymer undergoes imidization reaction between amino and carboxyl groups and gives two equivalents of water (Scheme S2). With the increase of temperature, the imidization finishes and the carbonization process starts.

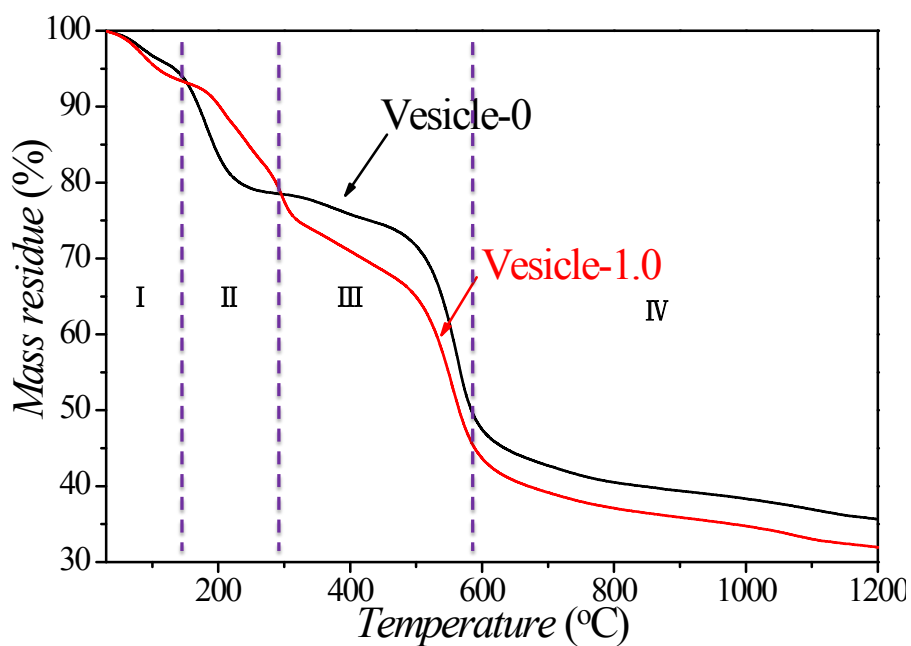


Fig. S12. TG curves of PAA vesicles (Vesicle-0 and Vesicle-1.0).

Either for Vesicle-0 or Vesicle-1.0, the chemical reactions are similar when heated in an inert atmosphere. PAA homopolymer vesicles undergo four stages at different temperatures to form inorganic hollow carbon spheres. As shown in Fig. S12, at the first stage, the sample will lose water and moisture to give dry PAA vesicles; while the temperature increases to above 128 °C, the imidization reaction between the repeat units takes place and gives two equivalents of water (Scheme S2 and Fig. S11). The imidization reaction finishes at nearly 300 °C, and about 80% of the mass of the samples remains. Continuing to increase the temperature, the carbonization process starts. At this stage, the sample will deoxidize and dehydrogenize to form carbon framework gradually. When the temperature reaches 600 °C, the carbonization procedure almost completes. 47.4% and 43.6% of the mass preserves of Vesicle-0 and Vesicle-1.0, respectively. Further increasing the temperature, the carbon framework begins to decompose and the mesoporous structure forms, which was discussed in the main text.

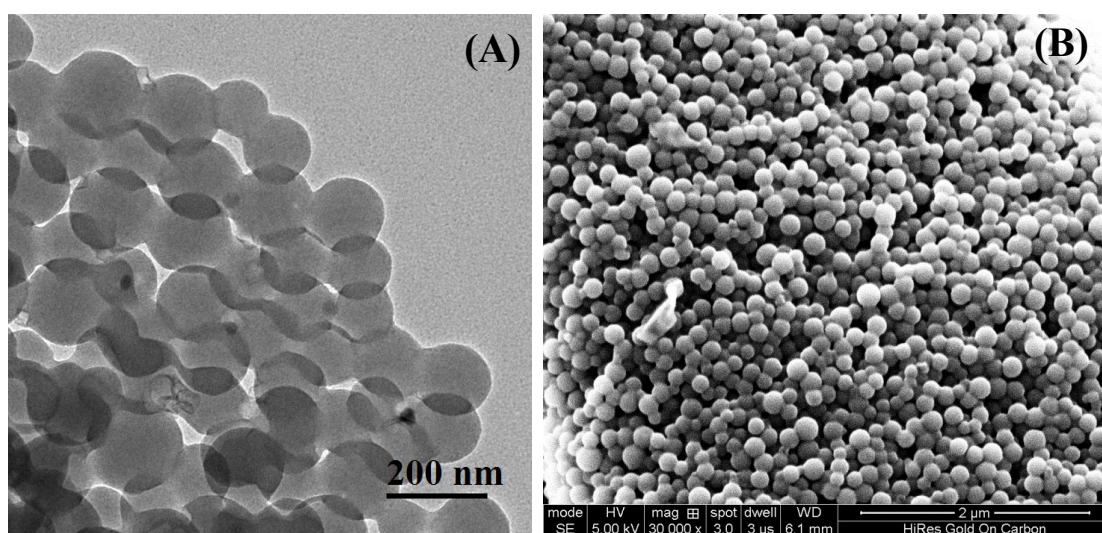


Fig. S13. (A) TEM and (B) corresponding SEM analysis of nitrogen-doped hollow carbon spheres (N-HCS-1.0).

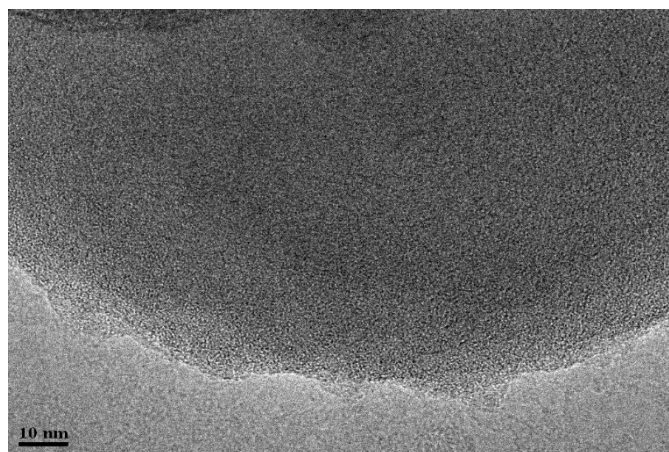


Fig. S14. High resolution TEM image of hollow carbon spheres (N-HCS-0).

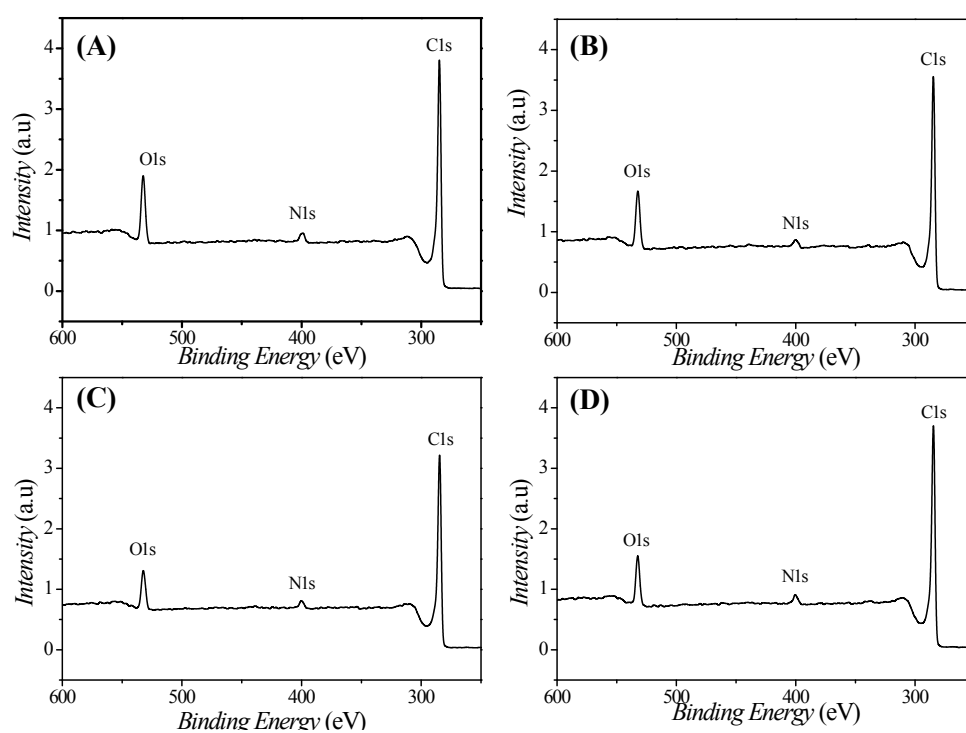


Fig. S15. XPS spectrum of nitrogen-doped hollow carbon spheres: A (N-HCS-0), B (N-HCS-0.25), C (N-HCS-0.5) and D (N-HCS-1.0).

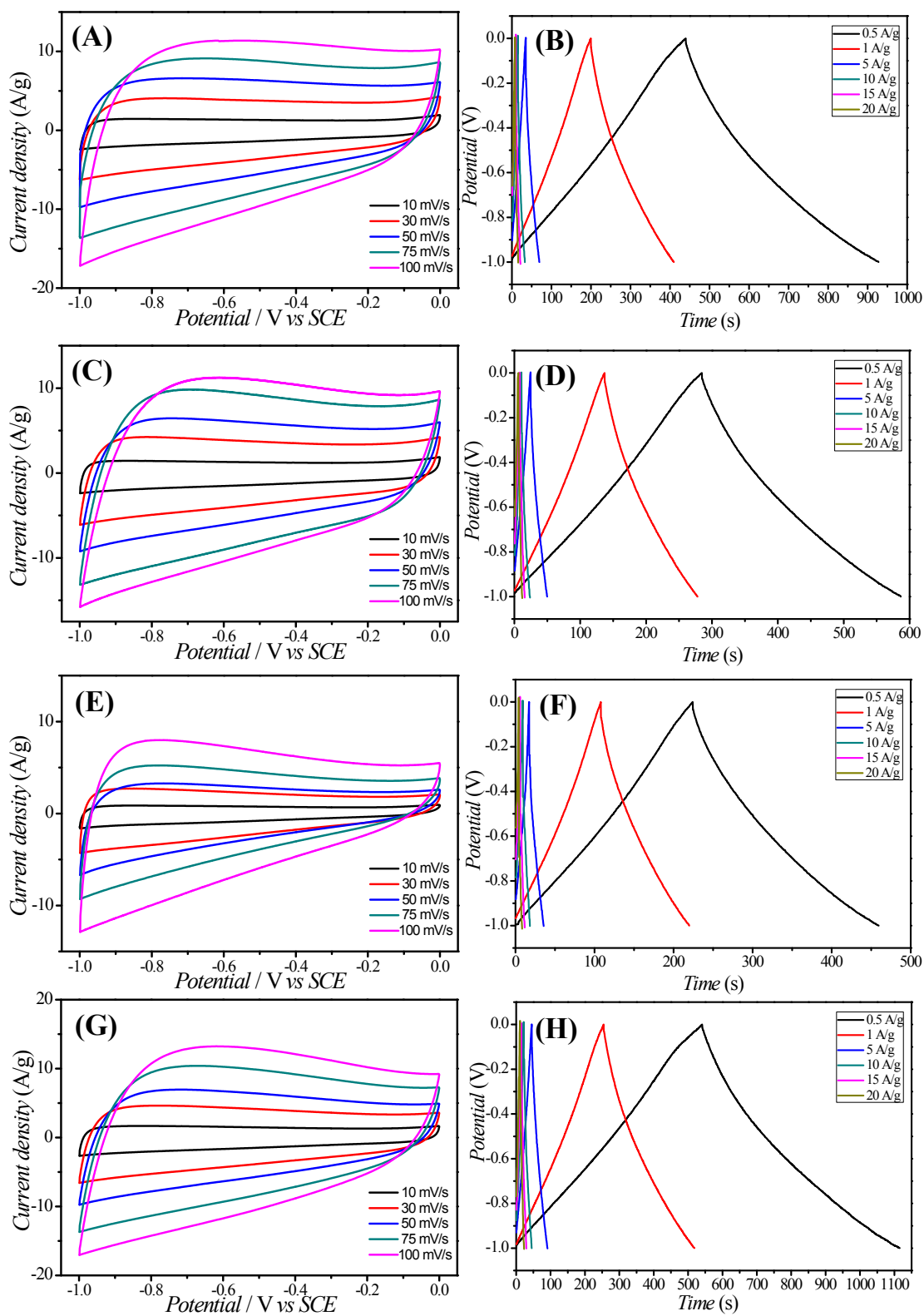


Fig. S16. CV curves at different scan rates and charge-discharge curves of N-HCSs at various current densities of (A and B) N-HCS-0, (C and D) N-HCS-0.25, (E and F) N-HCS-0.5 and (G and H) N-HCS-1.0.