Supporting Information for

Controlling the Compositional Chemistry in Single Nanoparticles for Functional Hollow Carbon Nanospheres

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EXPERIMENTAL SECTION

Synthesis of mesoporous HCNs. The mesoporous 3-AF resin HNs were first synthetized and then carbonized to mesoporous HCNs. The synthetic processes for mesoporous resin HNs was almost the same as resin HNs, but using the mixed solvent of ethanol/water (v/v 1:2), The detailed synthesis parameters for the mesoporous resin HNs are shown in Table S1. After carbonized under an Ar atmosphere, the mesoporous HCNs were obtained.

Sample	3-AP	H2O	Ethanol	НСНО	Acetone
	(g)	(ml)	(ml)	(ml)	(ml)
1S-HNs	0.1	30	/	0.1	20
2S-HNs	0.15	45	/	0.15	30
3S-HNs	0.32	96	/	0.32	64
4S-HNs	0.54	162	/	0.54	108
5S-HNs	0.6	180	/	0.6	120
6S-HNs	0.68	204	/	0.68	136
7S-HNs	0.7	210	/	0.7	140
Mesoporous 1S-HNs	0.1	20	10	0.1	20
Mesoporous 2S-HNs	0.15	30	15	0.15	30
Mesoporous 3S-HNs	0.32	64	32	0.32	64

Table S1. Synthesis parameters of the resin HNs and mesoporous resin HNs

Synthesis of yolk-shell carbon structure. In a typical experiment, 3-AP (o.6 g, 5.442 mmol) and formaldehyde solution (HCHO (37 wt%), o.6 ml, 7.986 mmol), were added into 40 ml deionized water with ammonia aqueous solution (NH4OH, 25 wt%) as catalyst at room temperature. The reacting solution was stirred continuously at room temperature for 30 min. Next, acetone was added into the solution to selectively remove the dissolvable part of the forming solid inhomogeneous nanospheres. After that, resin yolk-shell nanospheres were obtained and collected by centrifugation. Yolk-shell carbon nanospheres were obtained by heating the yolk-shell resin nanospheres under an Ar atmosphere.

Synthesis of composite structure of hollow Ag/carbon nanospheres. For a typical run, AgNO₃ (0.02g, 0.12 mmol), 3-AP (0.1g, 0.907 mmol) were added into 30 ml deionized water under magnetic stirring for 30min with ammonia aqueous solution (NH4OH, 25

wt%) as catalyst at room temperature. Then, formaldehyde solution (HCHO (37 wt%), o.1 ml, 1.331 mmol) was added and the stirring continued at room temperature for another 30 min. Next, acetone was added into the solution to removal the interior part and then collected by centrifugation. Next, hollow Ag/resin nanospheres formed after heating at 400 $^{\circ}$ C under a H2/Ar (v/v 5/95) atmosphere.

Synthesis of SiO2 @ carbon yolk-shell nanostructures. 0.1g SiO2 nanospheres with particle size around 350 nm synthesized by a classical Stöber methoed¹ were dispersed in 75 ml ethanol/water solution (v/v 1:2), and and then 3-AP (0.25g, 2.27 mmol), hexadecyl trimethyl ammonium Bromide (CTAB, 0.075g ,0.206 mmol), formaldehyde solution (HCHO (37 wt%), 0.25 ml, 3.327 mmol) were added to start the reaction with ammonia aqueous solution (NH4OH, 25 wt%) as catalyst. The reacting solution was stirred continuously at room temperature for 60 min. Next, acetone was added into the reacting solution to selectively remove the dissolvable part of the forming nanospheres. After that, SiO2 @ 3-AF resin yolk-shell nanospheres were obtained and collected by centrifugation.

Synthesis of tubular structure. For a typical experiment, 3-AP (0.1g, 0.907 mmol), CTAB (0.03 g, 0.082 mmol), formaldehyde solution (HCHO(37 wt%), 0.1 ml, 1.331 mmol) were added into 30 ml ethanol/water solution (v/v 1:29) with ammonia aqueous solution (NH4OH, 25 wt%) as catalyst and mixed with each other under magnetic stirring to start the reaction. The reacting solution was stirred continuously at room temperature for 90min. Next, acetone was added to selectively remove the dissolvable part of the forming nanorod. Then, tubular resin particles were obtained and collected by centrifugation. Tubular carbon nanorods were obtained after heating under an Ar atmosphere.

FTIR, 'H NMR, and GPC measurements. Measurement samples of interior parts and exterior parts of the solid 3-AF resin nanospheres for FTIR, 'H NMR and GPC were prepared as follows: the forming solid 3-AF resin nanospheres of 30min were separated from the mother liquid by centrifugation. Then the collected solid 3-AP resin nanospheres were washed five times by the deionized water and then re-dispersed into the deionized water. Next, acetone was added into the solution for 15min to dissolve the interior part of the solid 3-AF resin nanospheres (volume ratio of acetone/water was 2/3). After centrifugation, the exterior part (the hardened shell) and the interior part (still dissolve in the solution) were separated from each other. The exterior part was again washed five times by deionized water and then collected by centrifugation. Then, both the exterior parts and the solution containing the interior parts were frozen momentarily by the liquid nitrogen with a boiling point of -196 °C, and then dried by freeze-drying technique using freeze drier (FD-1A-50, Beijing Boyikang Laboratory Instruments Co.,Ltd) at a temperature of -50 °C until

the samples had constant weights. FTIR spectras were recorded by BRUKER IR microscope (TENSOR-27). 'H-NMR measurements were performed using Nuclear Magnetic Resonance Spectrometer (Bruker Avance 400) with N, N-dimethylformamide-d7 (DMF-d7) as solvent. GPC analyses were performed using a Water instrument (Water 1515) with a refractive index (RI) detector. N, N-dimethylformamide (DMF) was used to dissolve the measurement samples and also acted as mobile phase for analysis. Standard calibration was performed with polystyrene (PS) standards.

Computational details. To obtain the value of NBO charges of carbon atom in aromatic ring of the different phenolic monomers, the DFT calculations were first performed, and then the NBO calculations were further performed based on the results of DFT calculation. All DFT calculations were performed by using the Gaussian o9 suite of programs for the B3LYP functional^{2,3} in conjugation with the all-electron 6-31++G (d, p) basis set⁴. An ultrafine integration grid (99,590) was used for numerical integrations. All structures were fully optimized as gas phase. The NBO charges were calculated by using the NBO 3.1 program embedded in Gaussian o9⁵.



Figure S1. Controllable synthesis of hollow 3-AF resin nanospheres. (a-c), Shell thickness controlled by regulating the addition of acetone. The acetone/water volume ratios in (a-c) were 1/1,0.5/1, and 0.3/1,respectively. The corresponding shell thicknesses in a-c were 30 nm, 80nm, and 100nm respectively. (d-f), Size controlled by regulating the reaction temperature. The reacted temperatures in d-f were 32 °C, 25 °C , and 16 °C, respectively. The corresponding particle sizes in d-f were 180nm, 260nm, and 380nm, respectively.



Figure S2. Scheme for the synthesis of 2S-HNs. Starting from the acetone treatment of solid 3-AF nanospheres with inner compositional inhomogeneity (stage 1), resin 1S-HNs were prepared after acetone treatment (Stage 2). Then these as-prepared 1S-HNs used as the growth seeds were added

into the same growth environment for 3-AF polymerization. For the following reaction, newly-form 3-AF resin would grow around the pre-existing seeds due to favorable kinetics for a heterogeneous growth. Importantly, the newly-formed layer will also exhibit a similar pattern in compositional inhomogeneity as schemed in stage 3. After the acetone treatment, the dissolvable parts were removed and the 2S-HNs formed (stage 4).



Figure S₃. TEM images of a second-round-growth 3-AF resins nanospheres. The single-shelled hollow 3-AF nanospheres was used as seeds.



Figure S4. Engineering the shell-shell interspaces size of the resin 2S-HNs. By regulating the 3-AP amount in the second round of growth, the shell-shell interspaces size can engineer. The 3-AP amounts used in (a-c) are 1.35 times, 1.5 times and 2 times of that used in the synthesis of the 1S-HNs seeds, respectively. The corresponding shell-shell interspaces in (a-c) are 15nm, 30nm, and 60nm, respectively.



Figure S5. Morphological and structural analysis of MS-HCNs. a-d, TEM image of 1S-HCNs (a), 2S-HCNs (b), 3S-HCNs (c) and 4S-HCNs (d). e, HRTEM images of 1S-HCNs. f, XRD patterns of 1S-HCNs. The MS-HCNs were obtained by heating the resin MS-HNs at 1200 °C. The characterization results, including the absence of obvious lattice fringes in the high resolution TEM (HRTEM) image (e), the broad peaks in the X-ray diffraction (XRD) pattern (f) were in good agreement with each other, revealing the formation of hard carbon with a low graphitic conten⁶.



Figure S6. Raman spectrum of 1S-HCNs obtained at 1200 $^{\circ}$ C. Intensity ratio of D-band over G-band (I_D/I_G) is 1.0



Figure S7. TEM images of the forming 3-AF resin solid nanoparticles collected at different growth stages after starting the 3-AF polymerization and the shell evolution of the hollow structure after acetone treatment. (a), 35 sec; (b),1 min; (c), 2 min; (d),5 min; (e), 30 min; and (f), 24 h. The insets of (d), (e) and (f) show the shell evolution of the hollow structure after acetone treatment. The nanoparticles collected before 2 min were largely dissolvable in acetone without indissolvable shell. Scale bars of the inset of (d), (e) and (f), 100 nm.



Figure S8, TEM image of the 3-AF resin nanoshperes after the methanol treatment. No obvious shape change was observed for the 3-AF nanospheres due to the low dissolving capability of methanol towards oligomers.



Figure S9. Morphological of the forming nanospheres from resorcinol and 2-AP before and after acetone treatment. a-b, Morphological of the nanospheres of resorcinol before (a) and after (b) acetone treatment. c-d, Morphological of the nanospheres of 2-AP before (c) and after (d) acetone treatment.



Figure S10. TEM image of the forming nanospheres from 2,3-Diaminophenol. a, molecular structural formula. b-c, SEM and TEM image of the obtained 2,3-Diaminophenol- formaldehyde resin before acetone treatment, which showed irregular particles rather than spheres. d, TEM image of 2,3-Diaminophenol- formaldehyde resin after acetone treatment.



Figure S11. The innate inhomogeneity for 4-AF resin nanoparticles. obtained by increasing the catalyst concentration. (a), Morphological of the solid 4-AP resin nanoparticle. (b), hollow 4-AP resin nanospheres after the acetone treatment of the solid ones. Reaction between 4-AP and formaldehy here was sped up by increasing the ammonia concentration to enlarge the inner compositional difference. The addition amount of ammonia here is 0.2 ml (2.677 mmol) in 30 ml reacted solution, which is four times as much of that used in Figure. 3g, h.



Figure S12. Morphological and Pore structures of mesoporous 1S-HCNs. (a), TEM images of mesoporous 1S-HCNs obtained by heating the resin mesoporous 1S-HNs at 700 °C. (b), N_2 adsorption-desorption isotherms of as-prepared mesoporous 1S-HCNs. The specific surface area of the sample is 1053 m² g⁻¹.



Figure S13. Characterizations of Ag nanoparticles encapsulated in the 3-AF resin hollow nanospheres. (a), Low-magnification TEM. (b), Magnified TEM. (c), Elemental mappings images for Ag. (d), XRD patterns for Ag. The size of the Ag nanoparticles is 2~4 nm.



Figure S14. TEM image of SiO₂@3-AP resin yolk-shell nanostructure.



Figure S 15. Nanorods and tubular structure of 3-AP resin particles. (a), TEM image of resin nanorods; (b), tubular structure obtained by the acetone treatment of the prepared solid nanorods.

Table S₂, Molecular weight of exterior part and interior part of inhomogeneous 3-AF resin nanospheres based on the GPC test with polystyrene (PS) as calibrated standard. The interior parts dissolved by different volume ratio of acetone/water ($V_{acetone}/V_{water}$) were also tested and compared.

Sample (V _{acetone} /V _{water})	Mn	Mw	Polydispersity (Mw/Mn)
Exterior part (2/3)	26554	256364	9.65
Interior part (2/3)	9532	78292	8.21
Interior part (1/1)	16556	119793	7.24

Supplementary References

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