SUPPLEMENTARY INFORMATION

Synthesis of Raspberry-like Hollow Carbon Nanospheres with High Uniformity by Extension of the Stöber Method

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Experimental Section

Synthesis of Stöber spheres: In a typical procedure, 9 mL of ammonia aqueous solution (NH_4OH, 25 wt%) was dissolved in a mixture 16.25 mL of ethanol and 24.75 mL of water, stirred at room temperature for 5 mins to prepare the solution **A** and solution **B** was prepared by mixing 4.5 mL of TEOS in 45.5 mL ethanol and stirred at room temperature for 5 mins. The silica spheres were separated by centrifugation and rinsed thoroughly with water and ethanol.

Synthesis of silica@RF nanospheres: In a typical protocol, 200 mg 360 nm silica spheres were dispersed in a mixture of ethanol and water with a total volume of 28 mL; then 0.1 mL of ammonia aqueous solution (NH_4OH, 25 wt%) and 1 mL of 0.01 mol/L CTAB solution were added and stirred for more than 1 hour. Subsequently, 0.05 g of resorcinol was added and continually stirred for 30 mins. The 0.07 mL of formaldehyde solution was then added to the reaction solution and stirred for 24 h at 30 °C, and subsequently heated for 24 h at 100 °C under a static condition in a Teflon-lined autoclave. The silica@RF spheres were separated by centrifugation and washed three times with water.

Synthesis of hollow carbon nanospheres: The as-made silica@RF was heated at 5 °C /min from room temperature to 350 °C and held at this temperature for 1 h under a nitrogen flow. The temperature was then ramped at 5 °C /min to 600 °C and held at this temperature for 2 h. The pyrolyzed product was treated with aqueous 10% HF for 24 h to remove silica, thus generating HCCNs.

Enrichment tests: The as-prepared HCCNs show promising potential in the application of matrix-free LDI-MS detection of peptides. In a typical experiment, the carbon nanospheres were dispersed in ethanol at a concentration of 10 mg/mL and 1 μL of the slurry was

deposited on the plain steel plate. After drying under ambient condition, 0.2 μL of diluted molecule solutions (N-[1-(2,3-dioleoyloxy)-propyl]-N,N,N-trimethylammonium methyl chloride, DOTAP) were added on the nanospheres followed by MS analysis. For MS analysis, the samples were directly analysed on a Bruker Autoflex TOF/TOF III Smart beam. All mass spectra were obtained in the RP-HPC-Proteomics mode via an accumulation of 500 laser shots at 10 different sites under a laser intensity of 36% for data collection. Two standard peptides, Angiotensin II (M.W. 1046.5) and ACTH-Clip (M.W. 2465.7), were used for calibration to reduce variability.

Characterization: Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. The samples for TEM measurement were suspended in ethanol and supported onto holey carbon film on a Cu grid. Scanning electron microscopy (SEM) was taken with a JEOL-6400 electron microscopy operating at 8 kV. The surface area of the hollow carbon spheres was measured with the Brunauer−Emmett−Teller (BET) method using nitrogen adsorption and desorption isotherms through a Micrometrics ASAP 2020 system.

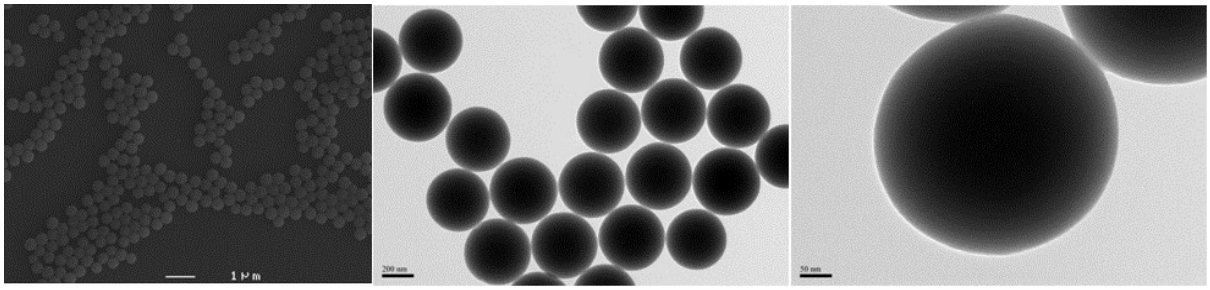

Figure S1. Typical large-scale SEM image and TEM images of silica nanospheres with an average size ~360 nm.

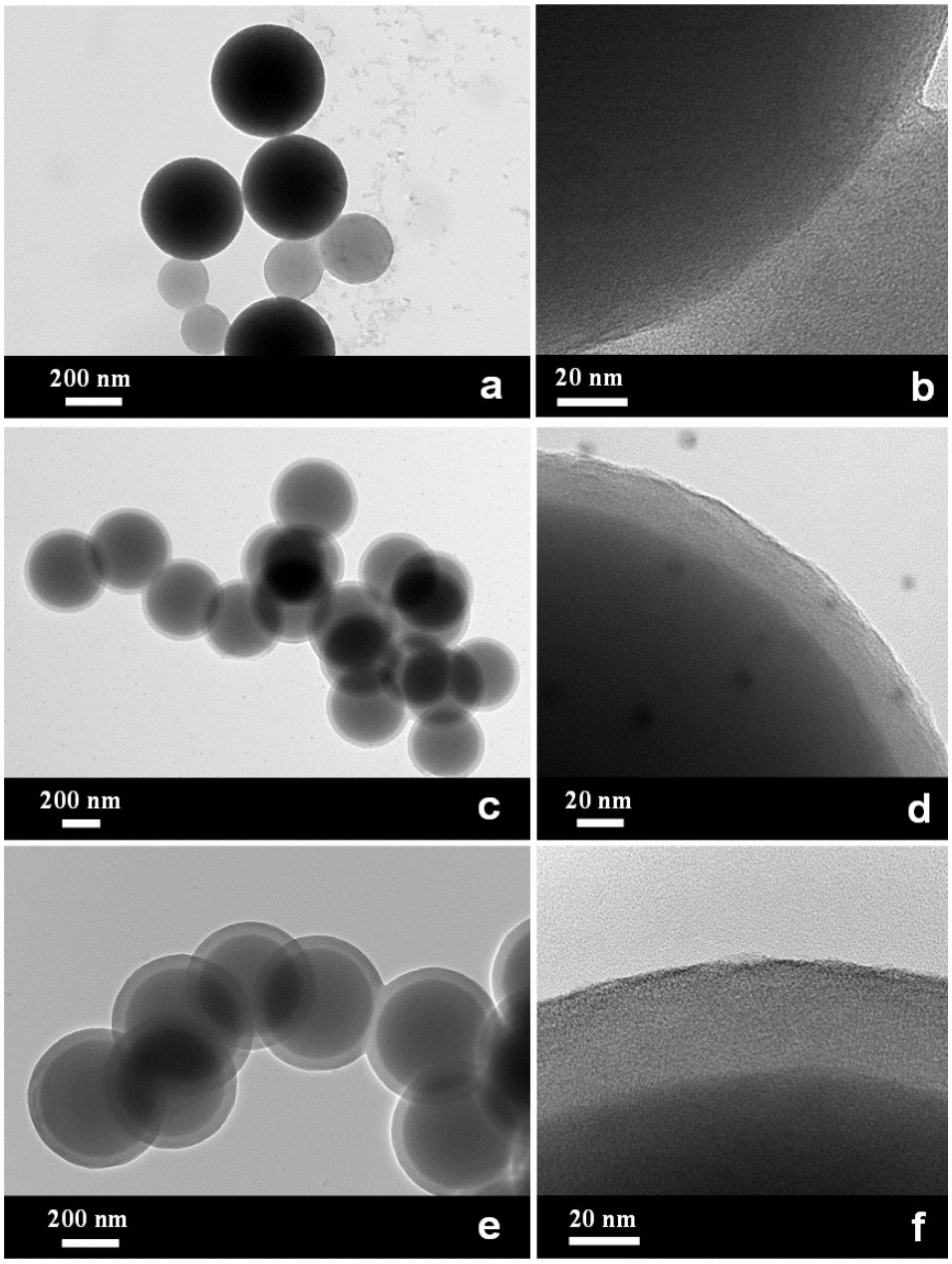

Figure S2. The effect of CTAB treatment to RF resin coating on the surface of silica. (a-b) no CTAB added; (c-d) 1 mL of CTAB added; and (e-f) 5 mL of CTAB added.

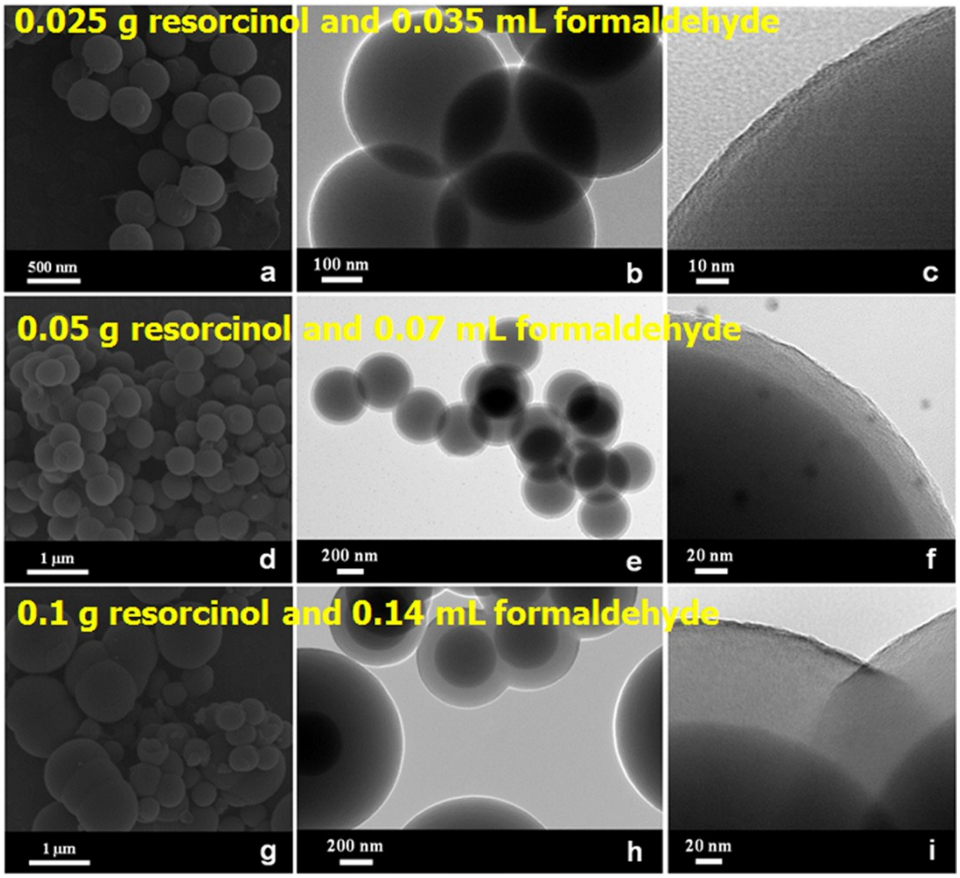

Figure S3. Shell thickness control by tuning the concentration of precursors. (a-c) shell thickness around 6 nm; (d-f) shell thickness around 20 nm; (g-i) shell thickness around 75 nm.

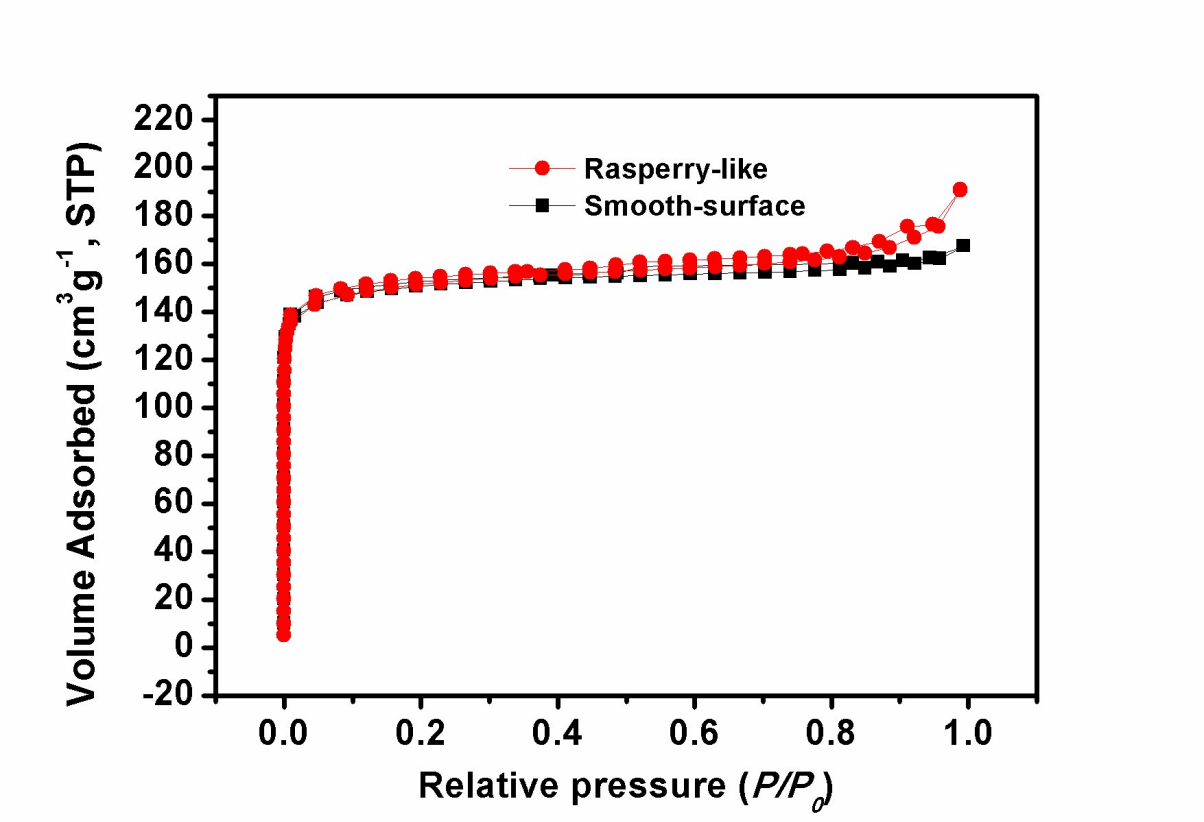

Figure S4. Nitrogen adsorption/desorption isotherms of the raspberry-like and smooth HCCNs.

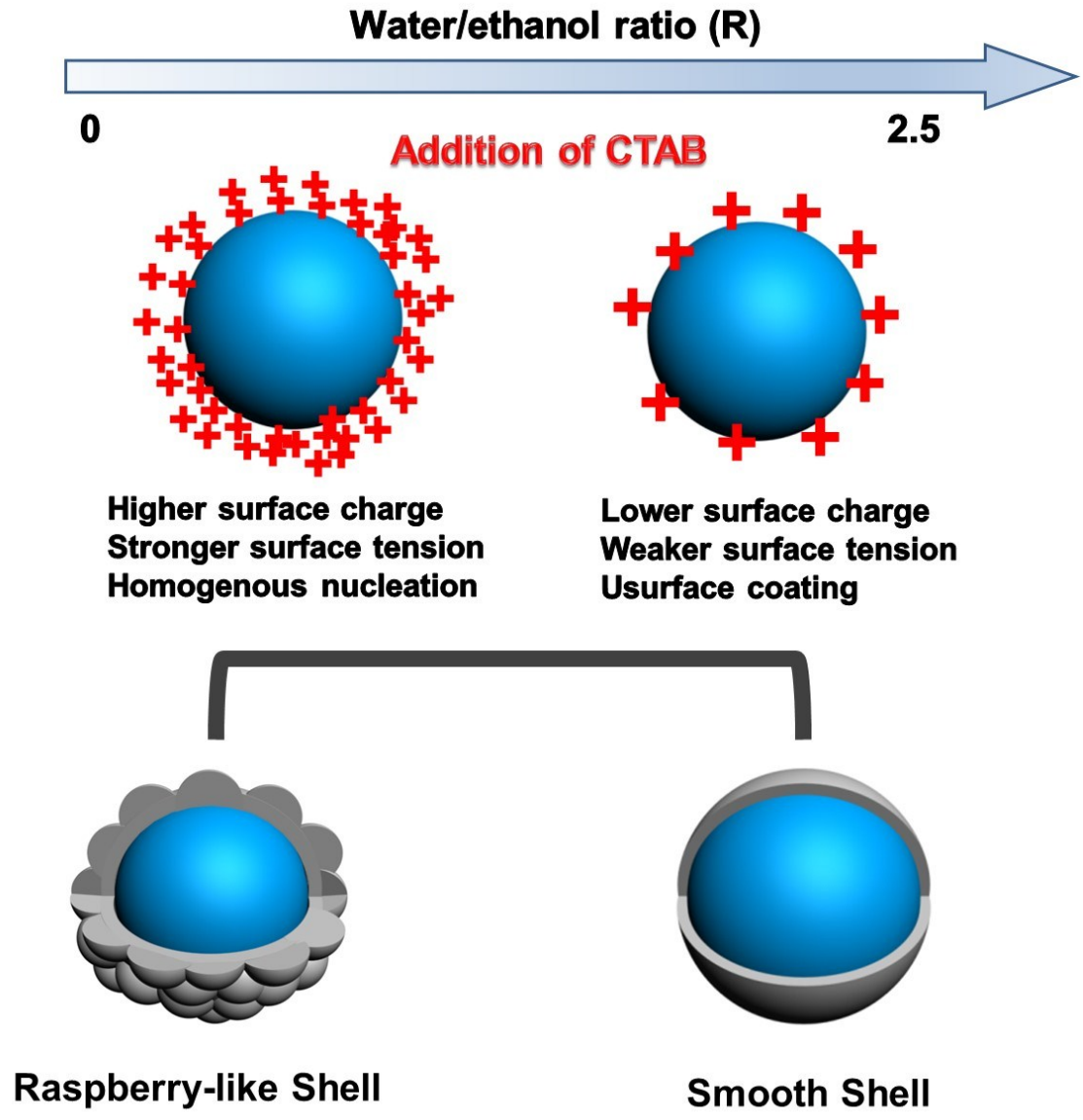

Figure S5. Proposed formation mechanism of RF coating process in mixture solution of water and ethanol with different ratios.