

Facile Synthesis of Monodisperse Bulk Boron- and Nitrogen- Doped Carbon Nano/Microspheres

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Experimental

Materials

3-Hydroxyphenylboronic acid and formaldehyde (37.0-40.0 wt %) were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous ethanol, sulfuric acid, and ammonia solution (25 wt %) was purchased from Beijing Chemical Reagent. Nafion solution (10 wt %) was purchased from Aldrich. All chemicals were used as received without any further purification. All the aqueous solutions were prepared with ultrapure water from a Millipore system.

Preparation of HPBAF Polymer Nano/Microspheres

Typically, ammonia, 3-hydroxyphenylboronic acid, water and/or ethanol were mixed in a flask equipped with a magnetic stirring bar. After mixing, formaldehyde solution was added into the reaction solution. The color of this solution was colorless. Subsequently, the mixture solution was heated at 120 °C for 12 h in a Teflon-lined autoclave. The polymer spheres were purified with distilled water by centrifugation at a speed of 12000 rpm for 2 times. The detailed synthesis parameters are given in Supporting Information (see Table S1).

Preparation of BNC Nano/Microspheres

The HPBAF polymer nano/microspheres were carbonized at 400 °C for 1 h at a heating rate of 1 °C/min and then heating at 800 °C for 4 h with a rate of 1 °C/min under nitrogen atmosphere. The cooling rate down to room temperature was 5 °C/min.

Characterization

The morphology of the samples was characterized by using a TECNAI G2 high-resolution transmission electron microscope (TEM) and a FEI/Philips XL30 ESEM FEG field-emission scanning electron microscope (SEM). The FTIR spectra were collected on a Bruker VERTEX 70 FTIR spectrometer (2 cm^{-1}), and the spectra were scanned over the range of $400\text{-}4000\text{ cm}^{-1}$. Thermogravimetric analysis (TGA) measurement was performed on a Mettler Toledo from room temperature to 800 °C at a heating rate of 10 °C/min under a constant flow of nitrogen. XPS measurements were conducted with a VG ESCALAB MKII spectrometer. The XPSPEAK software (Version 4.1) was used to deconvolute the narrow-scan XPS spectra of the B1s, C1s, and N1s of the samples, using adventitious carbon to calibrate the C1s binding energy (284.5 eV). ^{13}C NMR and ^{11}B NMR analyses were carried out on a Varian Infinity plus 400 spectrometer operating at a magnetic field strength of 9.4 T. Dynamic light scattering (DLS) measurement was carried out at 25 °C on a Malvern Zetasizer NanoZS Instrument (detection range: 3–3000 nm) equipped with an ALV-5000/EPP Multiple Tau Digital Correlator and a JDS Uniphase 1145P 22 mW He–Ne laser (632.8 nm wavelength). The scattering angle was 90°, and the intensity autocorrelation functions were analyzed by the CONTIN method. Nitrogen adsorption isotherm was measured at 77 K on a Micromeritics Tristar 3000 system with micropore analysis. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. Prior to measurements, the sample was outgassed at 120 °C for at least 6 h.

Electrode Preparation and Electrochemical Measurement

Electrochemical measurements were conducted on a computer-controlled potentiostat (CHI 660C, CH Instrument, China) with a three-electrode electrochemical cell. The standard three-electrode electrochemical cell was fabricated using glassy carbon with deposited sample as the working electrode, platinum wire as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. The working electrode was fabricated as follows: first, 5 mg of the bulk boron- and nitrogen-doped carbon spheres was added to 0.5 mL of DI water/isopropanol/nafion solution (1 wt %) (volume ratio = 38:5:7) and then subjected to ultrasonication for one hour. The suspension was dropped onto a glassy carbon electrode. All the electrochemical measurements were carried out at room temperature using a 1.0 M H₂SO₄ electrolyte. The potentials for electrochemical measurements were reported relative to an Ag/AgCl reference electrode and the potential window for cycling was confined between -0.2 and 0.8 V. The specific capacitance C_s was calculated according to the following equation using the discharge portion of the charge-discharge curves:

$$C_s = (I \times \Delta t) / (m \times \Delta V) = I / (m \times K)$$

where I , Δt , ΔV , m , and K are the applied current, discharge time, voltage change, the mass of active material, and the slope of the discharge curve, respectively.

Table S1. Sizes and synthesis parameters of HPBAF polymer colloidal nano/microspheres.

Sample	Water	Ethanol	3-Hydroxyphenylboronic Acid	Formaldehyde	Ammonia	Particle Size	
	mL	mL	mmol L ⁻¹	mmol L ⁻¹	mmol L ⁻¹	nm	
HPBAF-1	12	4	30	60	0	no	
HPBAF-2	12	4	30	60	8.85	sticking	
HPBAF-3	12	4	30	60	17.7	680	
HPBAF-4	12	4	30	60	26.6	1627	
HPBAF-5	12	4	30	60	44.3	1520	
HPBAF-6	12	4	30	60	88.5	1400	
HPBAF-7	12	4	30	60	133	845	
HPBAF-8	Effect	12	4	30	60	177	424
HPBAF-9	of	12	4	30	60	239	256
HPBAF-10	ammonia	12	4	30	60	354	101
HPBAF-11		12	4	30	60	708	96
HPBAF-12		16	0	30	60	0	126
HPBAF-13		16	0	30	60	0.885	256
HPBAF-14		16	0	30	60	8.85	615
HPBAF-15		16	0	30	60	44.3	964
HPBAF-16		16	0	30	60	88.5	172
HPBAF-17		16	0	30	60	177	156
HPBAF-18		16	0	30	60	354	92
HPBAF-19	Effect	12	4	9	18	88.5	no
HPBAF-20	of	12	4	60	120	88.5	1741
HPBAF-21	precursors	12	4	90	180	88.5	sticking

Note: the reaction volume is defined the whole volume of water and/or ethanol.

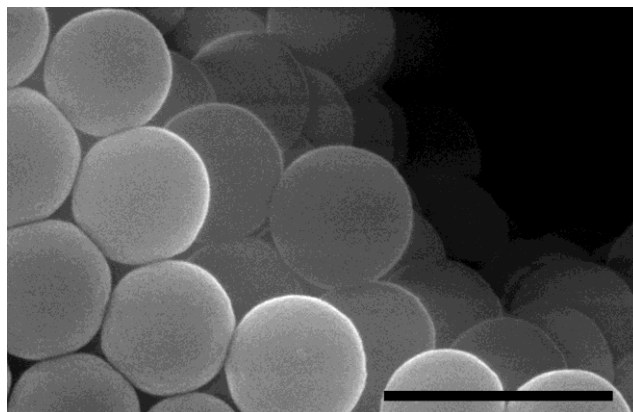


Fig. S1 A vertical plane of Fig. 1a; scale bar, 1 μm .

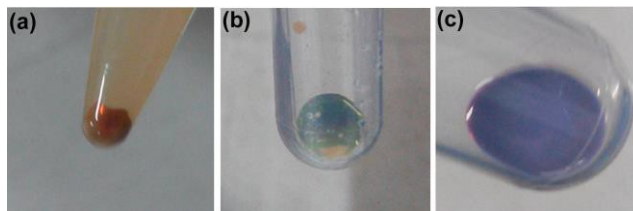


Fig. S2 Photograph of samples (a) HPBAF-14, (b) HPBAF-9, and (c) HPBAF-10 after centrifugation, respectively.

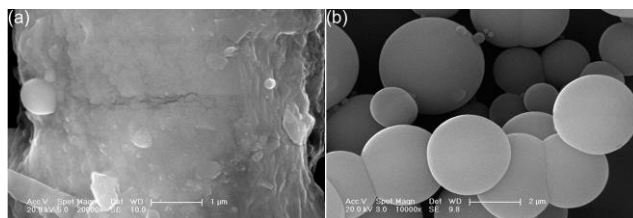


Fig. S3 SEM images of HPBAF polymer colloidal spheres synthesized by using different concentration of ammonia in the mixing solution (12 mL water and 4 mL ethanol): (a) 0 mmol L^{-1} (HPBAF-1) and (b) 8.85 mmol L^{-1} (HPBAF-2). 3-hydroxyphenylboronic acid, 30 mmol L^{-1} ; the molar ratio of 3-hydroxyphenylboronic acid /formaldehyde, 0.5.

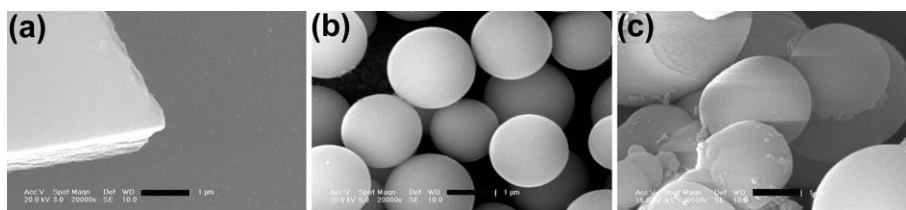


Fig. S4 SEM images of HPBAF resin colloidal spheres synthesized by using different concentration of 3-hydroxyphenylboronic acid: (a) 9 mmol L⁻¹ (HPBAF-19), (b) 60 mmol L⁻¹ (HPBAF-20), and (c) 90 mmol L⁻¹ (HPBAF-21). Ammonia, 88.5 mmol L⁻¹, the volume ratio of ethanol/water, 1/3; the molar ratio of 3-hydroxyphenylboronic acid /formaldehyde, 0.5. The scale bars are 1 μm.

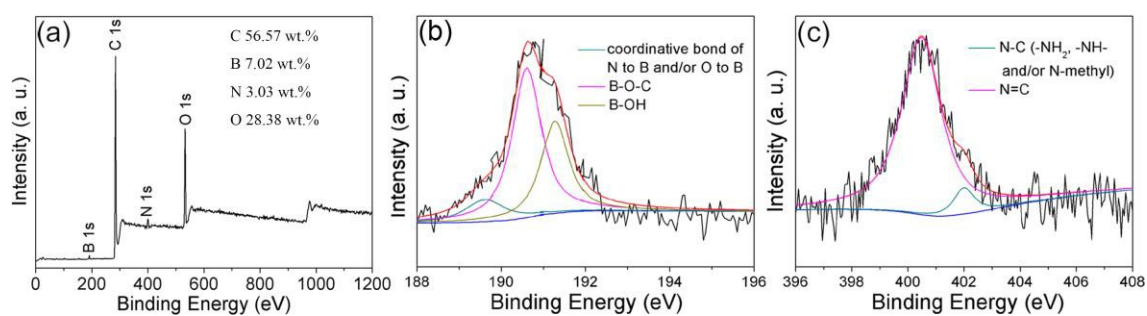


Fig. S5 X-ray photoelectron spectra of HPBAF-14: survey XPS spectrum (a), and high-resolution XPS spectra of (b) B1s and (c) N1s.

Table S2. Comparison of thermal stability of HPBAF spheres with that of other reported polymer resin spheres.

Resin polymer spheres	Temperature of pyrolysis	Yield of char	Reference
Resorcinol/ammonia/formaldehyde resin polymer spheres	800 °C	~ 53 %	[1]
Resorcinol/ 1,6-diaminohexane /formaldehyde resin polymer spheres	800 °C	~ 46 %	[2]
Melamine/formaldehyde resin polymer spheres	800 °C	~ 9 %	[3]
3-Hydroxyphenylboronic acid/ammonia/formaldehyde resin polymer spheres	800 °C	64 %	This work

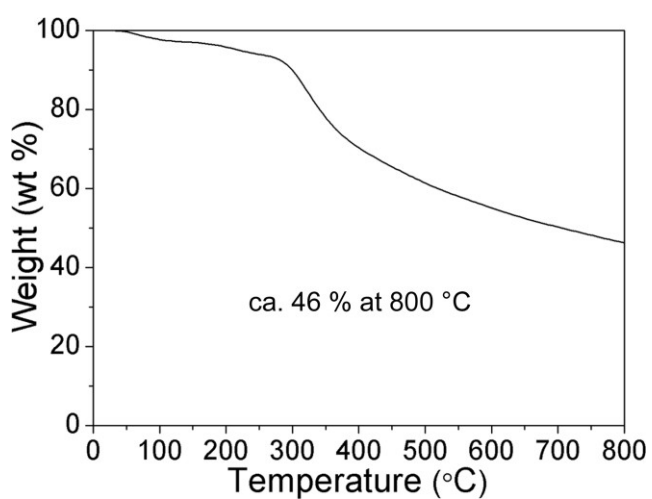


Fig. S6 TGA curve of 3-aminophenol-formaldehyde resin polymer spheres.^[4]

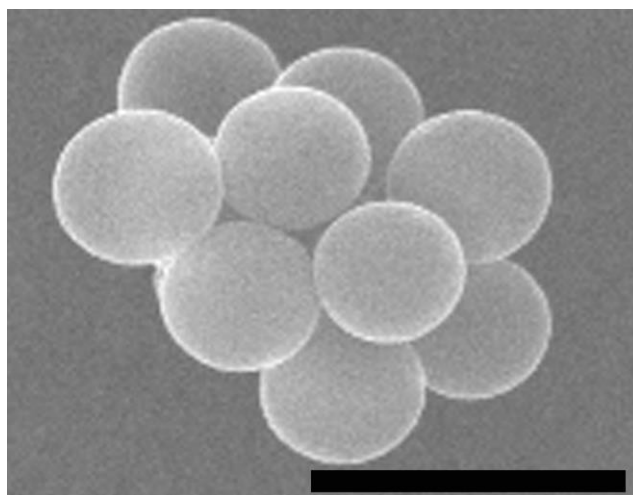


Fig. S7 SEM image of BNC-14 spheres; scale bar, 1 μm .

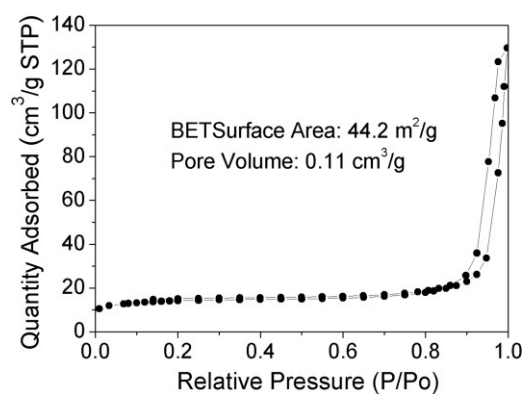


Fig. S8 N_2 adsorption/desorption isotherm of BNC-14 spheres.

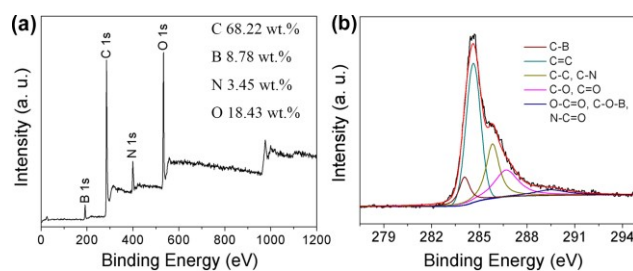


Fig. S9 X-ray photoelectron spectra of BNC-14: survey XPS spectrum (a), and high-resolution XPS spectrum of (b) C1s.

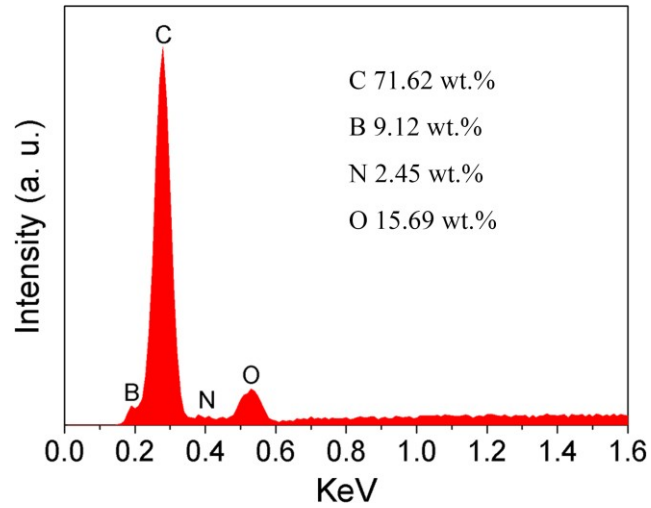


Fig. S10 EDX spectrum of B, C, N and O in BNC-14 spheres.

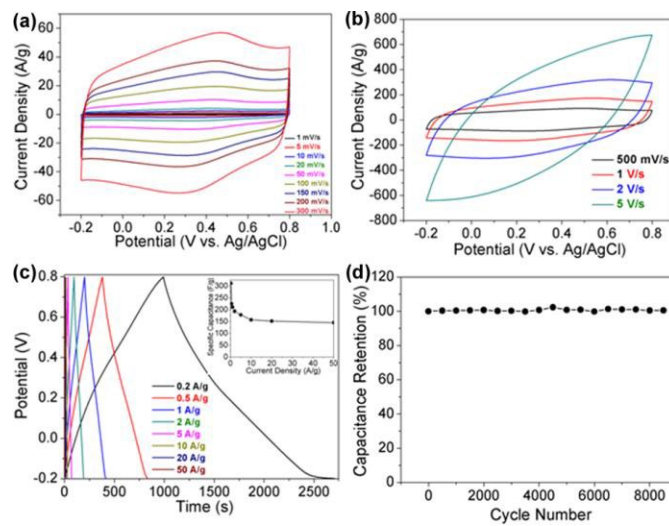


Fig. S11 Electrochemical capacitive behaviour of BNC-9 spheres in 1.0 M H_2SO_4 . Cyclic voltammograms at low (a) and high (b) voltage scanning rate. (c) Constant current charge-discharge curve. (d) Cyclic stability. Insert in c): Specific capacitance calculated from charge-discharge curve for different current densities.

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