

A Template-Free and Surfactant-Free Method for High-Yield Synthesis of Highly Monodisperse 3-Aminophenol–Formaldehyde Resin and Carbon Nano/Microspheres

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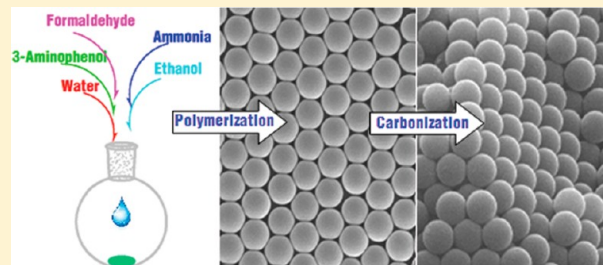
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S Supporting Information

ABSTRACT: A template-free and surfactant-free method for the synthesis of highly monodisperse phenol formaldehyde resin and corresponding carbon nano/microspheres with excellent size tunability has been developed for the first time after investigating a series of phenol derivatives, including 3-methylphenol, 1,3,5-trihydroxybenzene, 2-aminophenol, 3-aminophenol, and 4-aminophenol. The method is based on the polymerization reaction of 3-aminophenol and formaldehyde in the mixture solutions of water and ethanol to generate 3-aminophenol/formaldehyde (APF) resin colloidal spheres. The sizes of APF resin colloidal spheres are tunable in a very broad range from 80 nm up to 2500 nm by changing reaction conditions. The excellent thermal stability of APF resins allows the generation of monodisperse carbon spheres by the pyrolysis of APF resin spheres with high yields. Both APF resin spheres and corresponding carbon spheres are so monodisperse (polydispersity <3%) that can form three-dimensional periodic structures. The method has striking features of excellent monodispersity, very broad size tunability, high yield, smooth sphere surface, and easy preparation. This approach also holds great promise for the large-scale production of resin spheres and carbon spheres.



INTRODUCTION

Monodisperse colloidal nanospheres have broad applications, such as drug delivery,^{1–3} biodiagnostics,^{4–6} colloidal catalysts,^{7–12} and nanodevices.^{13–15} In addition, the self-assembly of colloidal nanospheres into structured assemblies has long been investigated because of the unique optical and material properties produced by such structures.^{16–23} As a result, tremendous attention has been paid to the development of various methods for the controllable synthesis of monodisperse spheres.²⁴ However, only limited types of polymer nano/microspheres have been synthesized with great success, such as polystyrene spheres,^{16,17,25} poly(methyl methacrylate) spheres,²⁶ and poly(hydroxyethyl methacrylate) spheres.²⁷ These polymer spheres cannot be converted to monodisperse carbon spheres because of their thermal instability.

Phenol formaldehyde resins are formed by a step-growth polymerization reaction of phenols with formaldehyde. They are the earliest commercial synthetic resins and are widely used in the production of circuit boards, pool balls, laboratory countertops, and as coatings and adhesives.^{28,29} Nanostructured

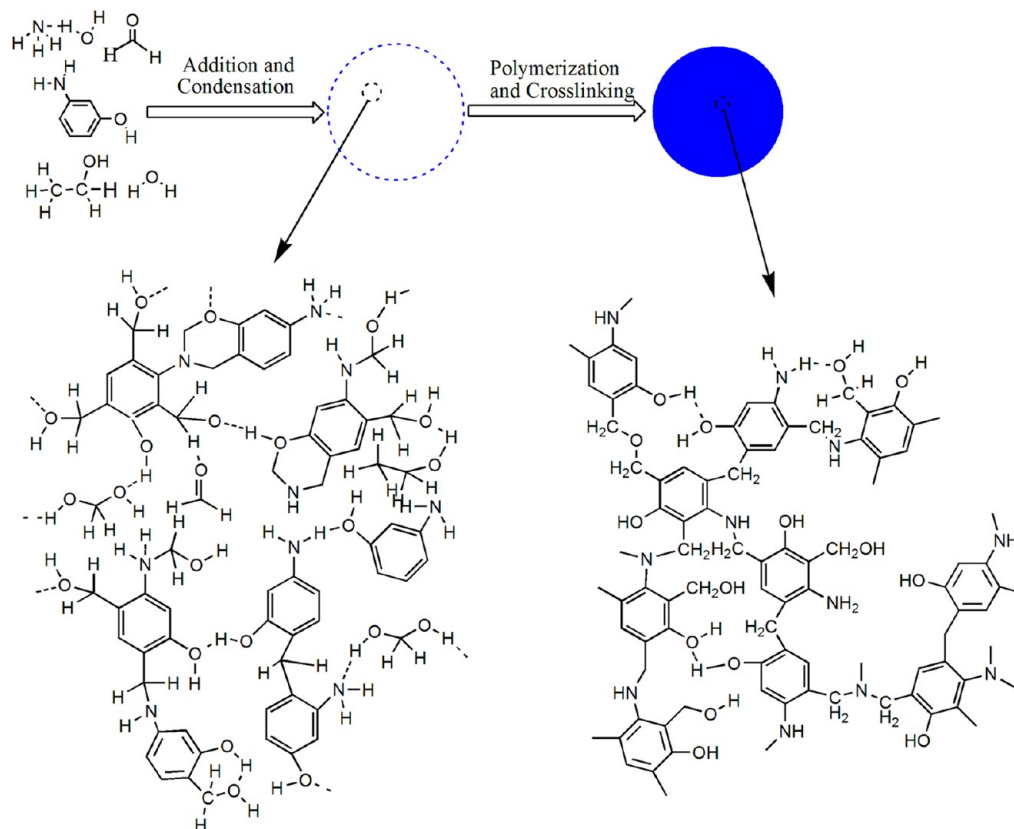
phenolic resins also exhibit good compatibility for biomedical applications, such as cellular delivery vehicles, cell targeting, and imaging.^{2,30,31} Because of their good thermal stability and high char yield, phenol formaldehyde resins have been used widely to prepare nanostructured carbon materials for various applications, such as adsorbents, supercapacitors, lithium-ion battery electrodes, drug delivery carriers, and as supports for catalysts.^{32–36} Compared with the synthesis of these common polymer spheres, the synthesis of highly monodisperse phenol formaldehyde resin spheres and corresponding carbon spheres has been achieved with limited success. Recently, a few breakthroughs for the synthesis of phenol formaldehyde resin colloidal nanospheres have been made.^{37,38} But these synthesis methods either require the use of template/surfactant, have a narrow size-tunability, or cannot produce smooth spheres with narrow size distribution. Moreover, only resorcinol has been

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Scheme 1. Formation Process of APF Resin Colloidal Spheres



used successfully for the preparation of monodisperse phenol formaldehyde resin colloidal nanospheres. It is helpful to investigate the feasibility to synthesize monodisperse phenol formaldehyde resin colloidal nanospheres with other phenol derivatives.

In this study, we report a template-free and surfactant-free method for the synthesis of highly monodisperse phenol formaldehyde resin and corresponding carbon nano/microspheres after investigating a series of phenol derivatives, including 3-methylphenol, 1,3,5-trihydroxybenzene, 2-aminophenol, 3-aminophenol, and 4-aminophenol. The method is based on the polymerization reaction of 3-aminophenol and formaldehyde in the mixture solutions of water and ethanol to generate 3-aminophenol/formaldehyde (APF) resin colloidal spheres. The sizes of APF resin colloidal spheres are tunable in a very broad range from 80 nm up to 2.5 μm by changing reaction conditions (Table S1 in Supporting Information). The excellent thermal stability of APF resins allows the generation of monodisperse APF-based carbon (CAPF) spheres by the pyrolysis of APF resin spheres with high yields. Both APF resin spheres and corresponding carbon spheres are so monodisperse (polydispersity <3%) that can form three-dimensional periodic structures.

EXPERIMENTAL PART

Materials. 3-Methylphenol, 1,3,5-trihydroxybenzene, 2-aminophenol, 3-aminophenol, 4-aminophenol, dihydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9%, metal basis), formaldehyde (37 wt %), and ammonia aqueous solution (25%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol and sulfuric acid were purchased from Beijing Chemical Reagent (Beijing, China). Nafion (10 wt %) was bought from Aldrich. All chemicals were used as received.

Preparation of 3-Aminophenol–Formaldehyde Resin and Carbon Nano/Microspheres. The detailed synthesis parameters are shown in Table S1. Typically, ammonia aqueous solution (NH_4OH , 25%) was mixed with 3-aminophenol in water/ethanol mixed solvent for 10 min at 30 $^\circ\text{C}$. After the addition of formaldehyde solution, the resulting mixed solution was stirred at 30 $^\circ\text{C}$ for 4 h and subsequently heated at 100 $^\circ\text{C}$ for 24 h in a Teflon-lined autoclave. The resin spheres were purified with distilled water by centrifugation at a speed of 8000 rpm for 2 times. Carbon spheres were obtained by heating APF resin spheres under a N_2 atmosphere at 410 $^\circ\text{C}$ for 1 h with a heating rate of 1 $^\circ\text{C}/\text{min}$ and then heating at 550 $^\circ\text{C}$ for 4 h with a rate of 1 $^\circ\text{C}/\text{min}$. The cooling rate down to room temperature was 5 $^\circ\text{C}/\text{min}$.

Characterization. Scanning electron microscopy (SEM) images were taken using an FEI XL30 ESEM FEG scanning electron microscope operated at 25 kV. Transmission electron microscopy (TEM) measurements were conducted on a Hitachi H-600 operated at 100 kV. The IR spectra were collected on a Bruker VERTEX 70 FTIR spectrometer. Dynamic light scattering (DLS) measurements were carried out at 25 $^\circ\text{C}$ 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 $^\circ$, 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 samples were outgassed at 120 $^\circ\text{C}$ for at least 6 h.

Electrochemical Measurements. 12 mg of CAPF-20 was added into a glycol solution containing 1.25 mM H_2PtCl_6 . The mixture was dispersed uniformly under ultrasonication. Then the mixture was heated at 120 $^\circ\text{C}$ for 6 h in a Teflon-lined autoclave. The obtained catalyst CAPF-20@Pt was thoroughly washed with deionized water and then dried at 60 $^\circ\text{C}$. The obtained CAPF-20@Pt was dispersed in 1 wt % Nafion solution and coated onto glassy carbon electrode

(GCE) via controlled drop-casting approach. Electrochemical measurements were performed using a CHI 660C electrochemical analyzer from CH Instruments by linear sweep voltammetry (LSV). CAPF-20@Pt-coated GCE, Ag/AgCl reference electrode (saturated KCl), and Au wire were used as working, reference, and counter electrodes, respectively. The oxygen reduction reaction (ORR) catalyzed by the CAPF-20@Pt catalysts was evaluated in both O₂-saturated and O₂-free (under a N₂ atmosphere) 0.5 M H₂SO₄ solutions at room temperature at a scan rate of 10 mV s⁻¹.

RESULTS AND DISCUSSION

Many phenol derivatives can be used for the syntheses of phenol–formaldehyde resins; therefore, some commonly used phenol derivatives, including 3-methylphenol, 1,3,5-trihydroxybenzene, 2-aminophenol, 3-aminophenol, and 4-aminophenol, were tested for preparing monodisperse phenol–formaldehyde resin colloidal nano/microspheres. 3-Methylphenol and 1,3,5-trihydroxybenzene cannot form colloidal spheres because of steric hindrance. 2-Aminophenol and 4-aminophenol cannot form monodisperse spheres (Figure S1), which is probably attributed to the instability of 2-aminophenol and 4-aminophenol in ammonia solutions. Only 3-aminophenol can form monodisperse phenol–formaldehyde resin colloidal spheres. Thus, we focused on the synthesis of monodisperse phenol–formaldehyde resin colloidal spheres using 3-aminophenol. The synthesis process of APF resin spheres is shown in Scheme 1. First, 3-aminophenol, formaldehyde, and ammonia react to form the mixtures of addition and condensation compounds, such as hydroxymethyl derivatives, benzoxazine derivatives, and oligomers.^{38–42} These generated compounds may form emulsion droplets and react further to produce monodisperse cross-linked resin colloidal spheres by the minimization of interfacial energy.^{42–44} The formation of resin colloidal spheres is very fast under mild conditions. As shown in Figure S2, the reaction solution become white and opaque within 300 s at 30 °C after the addition of formaldehyde into 3-aminophenol solution. Finally, the as-prepared colloidal sphere solution is hydrothermally treated to improve cross-linking degree through the condensation of hydroxymethyl derivatives to form methylene and methylene ether bridged compounds, the ring-opening polymerization of benzoxazine derivatives, and so on.^{38–40,42}

Figure 1 shows the SEM and TEM images of APF-20 (see Table S1) spheres. These spheres have regular spherical morphology and smooth surfaces. The colloidal spheres are so uniform that they can form three-dimensional periodic structures (Figure 1b).²⁰ The size distribution diagram of APF resin colloidal spheres acquired from more than 100 particles in the corresponding SEM image shows that the APF-20 spheres are monodisperse with a particle size of 528 nm and a size distribution of 1.1% (Figure S3). Meanwhile, the dynamic light scattering data also show that the colloidal spheres have very uniform sizes and disperse well (Figure 1d).

In order to rationalize the influence of different parameters in the formation of APF resin colloidal nano/microspheres systematically, the effects of the concentrations of ammonia and APF precursor as well as the volume ratio of water/ethanol are investigated. First, the diameters of APF resin colloidal spheres are tuned by changing the concentrations of ammonia. In the absence of ammonia, APF resin colloidal spheres adhere to each other due to the lack of static repulsion (Figure 2a) since the surfaces of emulsion droplets have no NH₄⁺. The addition of ammonia can effectively avoid the adhesion of spheres, improve the size distribution, and tune the sizes of

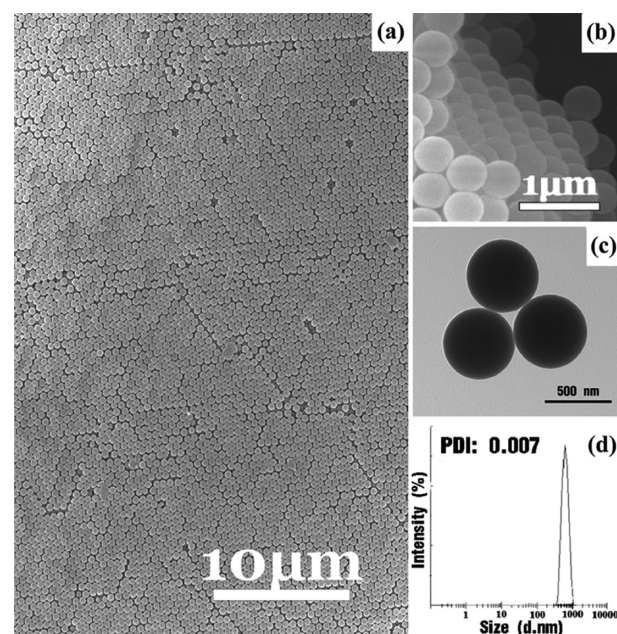


Figure 1. (a) Typical large area SEM image of APF resin colloidal spheres synthesized at water/ethanol volume ratio of 2.5, ammonia/3-aminophenol/formaldehyde molar ratios of 1/2/4, 3-aminophenol concentration of 98.1 mmol/L. (b) A vertical plane of (a). (c) The TEM image and (d) the DLS plot of APF-20.

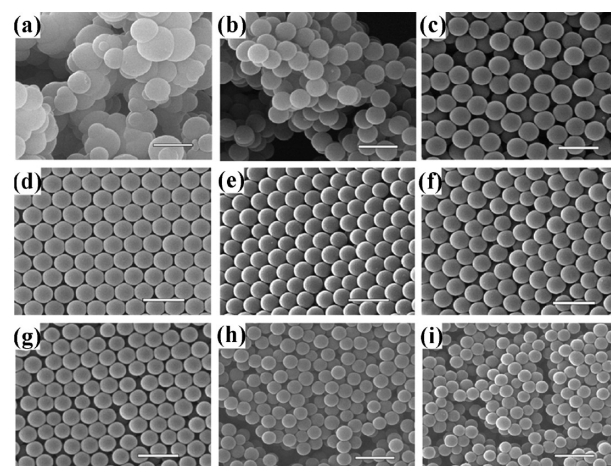


Figure 2. SEM of APF resin colloidal spheres synthesized by using different concentrations of ammonia: (a) 0, (b) 0.48, (c) 9.54, (d) 14.3, (e) 23.9, (f) 33.4, (g) 47.7, (h) 71.6, and (i) 143 mM. 3-Aminophenol, 32.7 mM; the molar ratio of 3-aminophenol/formaldehyde, 0.5; the volume ratio of ethanol/water, 0.4. The scale bars are 1 μm.

spheres. As shown in Figure 2 and Figure S4, the sphere sizes decrease from 510 nm (Figure 2b) to 297 nm (Figure S4a) with increasing ammonia concentrations from 0.48 to 143 mM (Figure S5). As the concentrations of ammonia increase, the colors of mixture solution change more rapidly, which indicates the increase in reaction rates. The increase in ammonia concentrations may facilitate the formation of more nuclei and thus decrease the sizes of spheres.³⁷ When the concentrations of ammonia are higher than 477 mM, the spheres obtained are no longer uniform (Figure S4b).

The concentrations of 3-aminophenol and formaldehyde also have a significant effect on the sizes of the APF resin colloidal

spheres. For the sake of convenience, the molar ratios of 3-aminophenol/formaldehyde were kept constant at 0.5. When the concentrations of 3-aminophenol are less than 3.27 mmol/L, no spheres are obtained because the concentration of precursors is less than critical micelle concentration, and no emulsion droplets were formed in the reaction system (Figure 3a).⁴⁵ When the concentrations of 3-aminophenol are adjusted

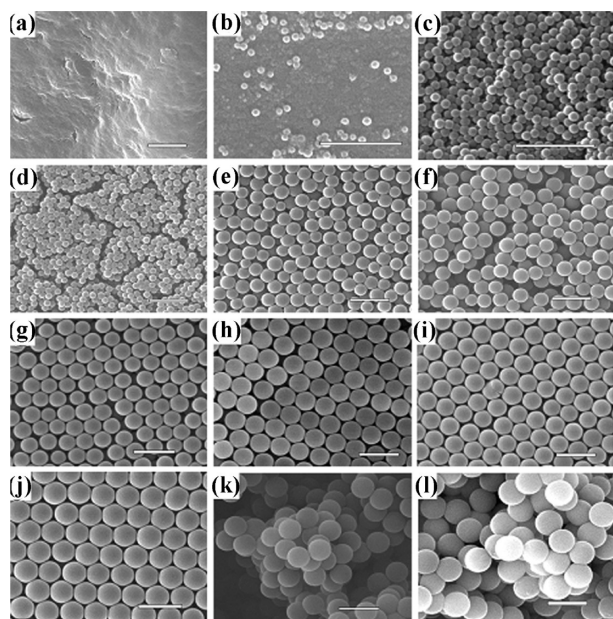


Figure 3. SEM of APF resin colloidal spheres synthesized by using different concentration of 3-aminophenol: (a) 3.27, (b) 4.91, (c) 6.54, (d) 9.81, (e) 16.4, (f) 22.9, (g) 32.7, (h) 49.1, (i) 65.4, (j) 98.1, (k) 131, and (l) 229 mM. Ammonia, 47.7 mM; the volume ratio of ethanol/water, 0.4; the molar ratio of 3-aminophenol/formaldehyde, 0.5. The scale bars are 1 μm .

from 4.91 to 160 mmol/L, the sphere sizes increase from 80 to 654 nm (Figure S6 and Figure 3b–l). Probably, the increase in precursor concentrations enhances polymerization rates, leading to the increase in emulsion droplet sizes and sphere sizes.

The volume ratio of water/ethanol has a remarkable effect on the sizes of spheres as well. When the volume ratios of water/ethanol decrease from 16.8/0 to 0/16.8, the sphere sizes increase from 280 nm up to about 2.5 μm (Figure S7 and Figure 4a–i). The decrease in water content increases the surface tension of the emulsion droplets,⁴⁶ resulting in the formation of smaller emulsion droplets and smaller APF resin colloid spheres.

Carbon spheres can be formed by the pyrolysis of APF resin colloidal spheres at 550 $^{\circ}\text{C}$ for 4 h under a N_2 atmosphere with a yield of 52–73%. Figure 5 shows the SEM image of the resin spheres APF-20 as well as the typical SEM images and TEM image of their corresponding carbonized spheres CAPF-20. The 15% linear shrinkage rate from parent spheres (528 nm) to carbon spheres (449 nm) suggests that the APF resin spheres shrink and lose water, NH_4^+ , alcohol, and functional groups during pyrolysis as confirmed by the FTIR spectra (Figure S8) of APF-20 and CAPF-20, respectively. These indicate that the polymer structure is uniformly converted to carbon. Noteworthy, all the CAPF-20 spheres still preserve smooth spherical morphology, high uniformity, and three-dimensional periodic structures (Figure S9 and Figure 5). Highly

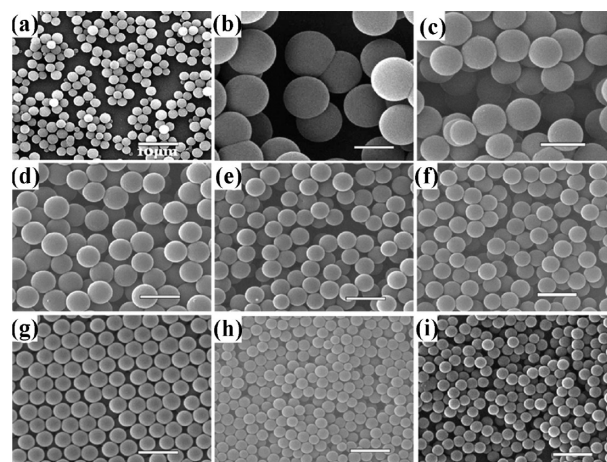


Figure 4. SEM of APF resin colloidal spheres synthesized by using different water/ethanol volume ratios: (a) 0/16.8, (b) 2/14.8, (c) 3/13.8, (d) 5/11.8, (e) 8.4/8.4, (f) 10/6.8, (g) 12/4.8, (h) 14/2.8, and (i) 16.8/0. 3-Aminophenol, 32.7 mM; ammonia, 47.7 mM; the molar ratio of 3-aminophenol/formaldehyde, 0.5. The scale bar in (a) is 10 μm ; other scale bars are 1 μm .

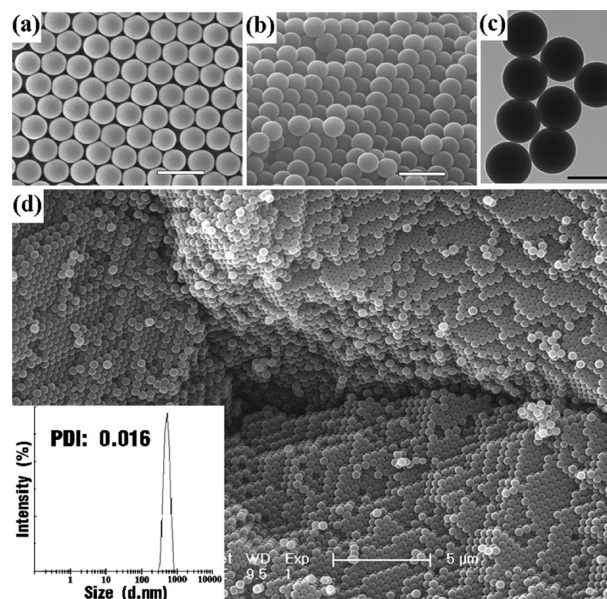


Figure 5. SEM images of (a) the monodisperse polymer spheres APF-20 and (b) their corresponding carbonized spheres CAPF-20, (c) TEM image of CAPF-20, and (d) typical large-scale SEM image of CAPF-20 (inset: the DLS curve of CAPF-20). The scale bars in (a, b) are 1 μm , the scale bar in (c) is 500 nm, and the scale bar in (d) is 5 μm .

monodisperse carbon spheres can also be obtained even the pyrolysis temperature is increased up to 650 $^{\circ}\text{C}$ (Figure S10) because of the highly cross-linked structures of APF resin. N_2 adsorption provides more quantitative information about the surface of carbon spheres. As shown in Figure S11, the Brunauer–Emmett–Teller (BET) surface area of CAPF-20 is 366 m^2/g and the total pore volume is $\sim 0.20 \text{ cm}^3/\text{g}$, making these microporous carbon spheres promising materials as catalyst supports, adsorbents, and so on. For example, Pt nanoparticles can be easily loaded on the surface of carbon spheres to form CAPF-20@Pt composites (Figure S12) and the as-prepared CAPF-20@Pt composites can effectively electro-

catalyze the reduction of oxygen (Figure S13), which shows that these carbon spheres have the potential to become a new kind of catalyst support materials and are suitable to be used in energy conversion and other related areas.

CONCLUSIONS

In summary, a template-free and surfactant-free method has been developed to synthesize highly uniform 3-aminophenol-formaldehyde resin colloidal nano/microspheres for the first time. The particle size of APF resin spheres can be tuned from 80 to ~2500 nm by varying the concentrations of ammonia and APF precursors as well as the volume ratios of water/ethanol. Because of the excellent thermal stability of APF resins, these spheres can be easily converted to corresponding monodisperse carbon spheres with spherical morphology, smooth surfaces, and large BET surface areas by carbonization. These polymer and carbon spheres are potentially important for applications in catalysis, drug delivery, building blocks for complex structures, electrochemistry, photonics, adsorption, and separation. This facile approach is extendable to prepare other polymer spheres and carbon spheres and holds great promise for the large-scale production of APF resin polymer and carbon spheres.

ASSOCIATED CONTENT

Supporting Information

Table of synthesis parameters, photographs for recording the color change of the reaction solution, particle size distribution of APF-20, SEM images of APF-10 and APF-11, effect of NH_4OH , precursor, and water/ethanol on the diameters of spheres, FTIR spectra of APF-20 and CAPF-20, large-scale SEM images of vertical plane of CAPF-5 and CAPF-20A, nitrogen adsorption-desorption isotherm of CAPF-20, characterization and electrochemical measurement of CAPF-20@Pt composite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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