



# A facile method of synthesizing uniform resin colloidal and microporous carbon spheres with high nitrogen content



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## ABSTRACT

3-Aminophenol/formaldehyde (AF) resin colloidal spheres with narrow size distribution and high nitrogen content are synthesized in the presence of urea. The obtained particles that indicated by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) are spherical morphology and uniform. It can be further carbonized into carbon spheres preserving high nitrogen percent. The particle size is tunable from 300 nm to 850 nm by appropriately varying the concentration of precursor or water/ethanol volume ratio. Even using the water as an only solvent, we can also obtain spherical particles with different size. Typically, the nitrogen percent in the obtained polymer and carbon particles is as high as 10.39 wt% and 8.95 wt%, respectively. The typical surface area of resulted carbon particles obtained from nitrogen adsorption measurement is  $459 \text{ m}^2 \text{ g}^{-1}$ . X-ray diffraction demonstrates the obtained carbon spheres are amorphous, which are expected to have practical application in the field of energy devices. The method can be considered as a low cost and facile method for mass production.

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## 1. Introduction

The colloidal sphere is always an extensive research subject in material chemistry and condensed-matter physics [1–3]. As a promising candidate, carbon based material has received burgeoning attention due to its potential applications in catalyst supports [4–7], drug delivery [8–10], cell imaging [11,12], adsorbents [13], as well as electrodes [14–16]. For these practical applications, the spherical carbon particles are of considerable interest. To date, although a variety of synthetic methods for spherical carbon particles including chemical vapor deposition [17,18], nanocasting [19,20], and pressure carbonization [21] have been developed [21], these methods are either complicated or need special equipments [22]. Furthermore, the resulting products are required further purified which are time-consuming and usually have a broad size distribution. Therefore, it is worthwhile to develop an economic method for the synthesis of carbon particles. Unfortunately, there are only a few successful methods reported for the synthesis of monodisperse carbon spheres with controllable size [22–26].

Phenolic resins have demonstrated to be the marvelous materials for the fabrication of carbon because of their good thermal stability and high yield of carbon conversion, which have attracted much attention [24,26–28]. Analogous to the hydrolysis and

condensation of silicon alkoxides in the synthesis of silica spheres, resorcinol–formaldehyde (RF) nanospheres can be synthesized through hydrolysis and condensation of resorcinol and formaldehyde in the presence of some basic catalysts. For example, Dong et al. [23] synthesized RF polymer spheres and the corresponding carbon nanospheres using *L*-lysine as catalyst. Similar to the Stöber method, the size of resultant polymer particles can be tuned by changing the mounts of catalyst and precursor/ $\text{H}_2\text{O}$  ratio. However, the distribution of obtained particles was broad and the particles often aggregate [23]. In addition, the experiments were conducted at about 333 K, which was higher than room temperature and thus it is energy-consuming. Later, Liu et al. [24] further invested the Stöber method for synthesizing resorcinol–formaldehyde resin polymer and carbon spheres. The resultant carbon particles have spherical morphology and a narrow distribution. However, the surfaces of the spheres were rough. For some sophisticated applications, spherical, monodisperse, smooth-surfaced carbon particles are highly required or would be advantageous [28]. Recently, Zhao and co-workers further modified the method by using 3-aminophenol in place of resorcinol reported [26]. The roughness of particle surfaces was decreased obviously.

In order to access a greater variety of different applications, heteroatom-doped carbon materials are vital candidates [16,29–32]. In this respect, it has been reported that nitrogen doping is a promising method or enhancing physical and chemical properties, such as high activity [4,7], capacity [33,34], and conductivity [35]. In

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most cases, nitrogen-doped carbons have been achieved by post-treatment of carbon products or using N-containing materials as precursors [36–38]. But these methods involve harsh experimental conditions or costly synthetic processes.

To our knowledge, there are few reports of synthesizing mono-disperse carbon spheres with high nitrogen content, and the resultant nitrogen carbon spheres either aggregates, with low nitrogen contents or have a broad distribution. Overall, developing a facile method for high nitrogen contents of carbon particles with an efficient catalyst is highly desirable.

When synthesizing particles, one of the important factors is the reasonable selection of catalyst since the catalyst will determine the structure, morphology and property of the obtained particles. The same as Stöber method for silica spheres fabrication, caustic and hazardous ammonia is the normal catalyst in the aforementioned reports for synthesizing phenolic resin polymer particles. The residual ammonia solution would be dangerous for the environment because ammonia is highly toxic to aquatic animals even at dilute concentration. In addition, from an industrial perspective, it is less feasible. The strong pungent smell of ammonia would be harmful to workers. Thus, it is urgent to explore a new catalyst for synthesizing resin polymer spheres.

In the past decade, amino acids derivatives have been applied to synthesize mesoporous materials and nanospheres [39–41]. In particular, by using *L*-lysine as catalyst, uniform silica nanospheres were synthesized successfully [41]. These give an access to the new nanosphere synthesis methods. Recently, monodisperse mesoporous silica nanospheres with tunable pore structure have been produced by an innovation synthetic method by using small organic amines (i.e. triethanolamine, triethyleneamine, and 2-amino-2-(hydroxymethyl) propane-1,3-diol) [42]. Inspired by these accomplishments, we thought some organic amines molecule can be used in preparing resin and carbon spheres with narrow size distribution and high nitrogen content.

In this work, we present a greener technology to synthesize monodisperse AF resin polymer and carbon spheres with high nitrogen content by using urea as catalyst. The monodisperse AF resin polymer particles can also be obtained using water as the only solvent. Both 3-aminophenol and urea are employed as N-containing precursor for the high-content nitrogen-doped AF resin polymer spheres. The obtained polymer spheres can be carbonized to carbon spheres preserving high nitrogen percent (8.95 wt%). The size of particles is tunable from 300 to 850 nm. We expect the present method can be a new avenue to synthesize carbon based materials with high heteroatom content and to explore the applications of carbon spheres.

## 2. Experimental section

### 2.1. Materials

Formaldehyde (37 wt%) and urea (ACS,  $\geq 99.5\%$  (T)) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ethanol was purchased from Beijing Chemical works (Beijing, China). 3-methylphenol was purchased from Xiya Reagent (Chengdu, China). Urea was dried under reduced pressure in vacuum oven at 40 °C for 2 days before use. All other chemicals were used as received. Distilled water was used throughout the work.

### 2.2. Synthesis of the 3-aminophenol/formaldehyde resin microspheres and carbon spheres

The uniform resin microspheres were synthesized in the presence of urea by using 3-aminophenol and formaldehyde solution as precursors. In a typical synthesis of 3-aminophenol/formaldehyde

(AF) resin spheres with 572 nm diameter, 3-aminophenol (180.0 mg, 98.1 mM) and urea (49.5 mg, 49.0 mM) were mixed in water/ethanol (12.0 ml/4.8 ml) mixing solvent at 30 °C. Following, the required amount of formaldehyde was added and the reaction system was kept stirring at 30 °C for another 6 h. The resulting spheres were collected by centrifugation at 6000 rpm for 5 min. Different sized particles can be obtained by varying molar ratios of the reagents. The detailed synthesis parameters are given in [Supporting Information \(SI\) \(Table S1\)](#).

To obtain carbon particles, the obtained AF resin polymer spheres were air-dried at 100 °C for 24 h and then the dried particles were heated under argon atmosphere at 410 °C for 1 h with a heating rate of 1 °C/min. Following, the temperature was raised to 600 °C with a heating rate of 1 °C/min and kept for 4 h. The cooling rate down to room temperature was 5 °C/min.

### 2.3. Characterization

Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 microscope (JEOL, Japan) operated at 100 kV. Field emission scanning Electron microscopy (FE-SEM) images were recorded on a FEI XL30 ESEM FEG electron microscopy operating at 25 kV. CHN elemental analysis was conducted on a VarioEL cube analyzer (Elementar Analysensysteme GmbH). Diffuse reflectance Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer. Before each FTIR measurement, the samples were carefully dehydrated under infrared lamp to avoid the influence of water. XRD analysis was conducted on a ray diffractometer with  $2\theta$  ranging from 10° to 90°. The nitrogen adsorption measurement was conducted on a Micromeritics Tristar 3000 system with micropore analysis at 77 K. Surface area was calculated using the Brunauer–Emmett–Teller (BET) method from nitrogen adsorption–desorption isotherms.

## 3. Results and discussion

### 3.1. Morphology of the prepared AF resin microspheres

[Fig. 1](#) shows the TEM and SEM images of typically prepared AF particles synthesized in the presence of urea. The obtained particles have regular spherical morphology with 572 nm diameter. The size distribution is very narrow with coefficient of variation  $C_v \sim 1.9\%$ , which is determined from more than 150 particles in TEM images using ImageJ software. The corresponding diagram is shown in [Fig. 1c](#). On the contrary, we cannot obtain any particles without urea. Thus, the urea plays an important role in the formation of AF particles. Different from normal strong alkaline solution, such as NaOH or KOH, urea solution is slightly alkaline at the synthetic conditions that can catalyze the polymerization of 3-aminophenol with formaldehyde feasibly. Similar to the reported ammonia-catalyzed resin spheres, the uniform AF resin polymer spheres mainly depend on the initial emulsion droplets [24]. In the presence of urea, the emulsion droplets are formed rapidly during stirring because of the hydrogen-bonding interactions between urea, water, ethanol, formaldehyde and 3-aminophenol. The protonated amino groups in urea supply the positive charges, avoiding the aggregation of particles. Following the addition of formaldehyde, the polymerization in the emulsion is initiated by  $\text{NH}_4^+$  located at the outer surface of the emulsion droplets. 3-Aminophenol reacts with formaldehyde quickly to form numerous hydroxymethyl substituted species, followed by cross-linking of these species. Some urea molecules may be encapsulated in the obtained AF resin spheres due to the hydrogen-bonding between  $-\text{NH}_2$  in urea and AF precursor, resulting in high nitrogen

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