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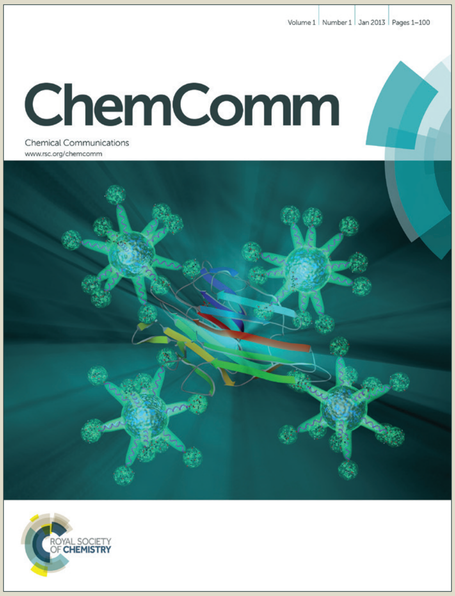

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Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Sustainable and scalable production of monodisperse and highly uniform colloidal carbonaceous spheres using sodium polyacrylate as dispersant

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Monodisperse, uniform colloidal carbonaceous spheres were fabricated by the hydrothermal treatment of glucose with the help of tiny amount of sodium polyacrylate (PAANa). This synthetic strategy is effective at high glucose concentration and scale-up experiments. The sphere size can be easily tuned by the reaction time, temperature and glucose concentration.

The discovery of fullerenes and carbon nanotubes boosted the interest in searching for shaped carbon materials. The shaped carbon materials include fibers,[1] spheres,[2] horns,[3] flasks,[4] carbon onions,[5] *etc*. Among them, spherically shaped carbon materials have been investigated for decades and widely applied in various fields such as chromatography,[6] catalyst supports,[7] reinforcement materials for rubber and so forth.

Diverse attempts such as chemical vapor deposition (CVD),[8] high pressure carbonization,[9] arc-discharge,[10] and the reduction of carbon dioxide[11] were applied to access carbon spheres. However, the extreme reaction conditions and complex instruments limit their use as general methods for mass production. Recently, the hydrothermal carbonization (HTC) of carbohydrates was regarded as a green and sustainable process for the synthesis of colloidal spherical carbon-based materials.[12] Carbon spheres can be obtained with following carbonization. Since the first report by Wang *et al* who produced carbonaceous microspheres by the HTC of sucrose,[13] great efforts have been made about the morphology control and characterization of colloidal carbonaceous spheres fabricated via HTC methods.[14] The key targets to make spherical materials are to ensure that they are monodisperse and that the size and the chemical properties of the external rim can be controlled.[2] The surface of HTC carbonaceous material can be readily tuned by heat treatment or following functionalization.[15] Therefore, achieving monodispersity and uniformity is the biggest challenge during the HTC process. In fact, the HTC carbonaceous spheres are always interconnected and irregular.[12b, 14b] According to most previous reports, monodisperse carbonaceous spheres were only produced at specific reaction conditions (either low concentration or special temperature) generally with poor uniformity.[16] Only a few successful strategies have now been proposed to maintain monodispersity of the HTC colloidal carbonaceous spheres. For example, Li *et al* synthesized monodisperse, uniform colloidal carbonaceous spheres with glucose concentration between 0.5 M and 1 M.[12a] A two-step HTC approach was applied by Chen&Li *et al* to fabricate monodisperse carbonaceous spheres with high uniformity. However, the sugar concentration needs to be under 0.4 M to keep monodisperse.[17] Soft drink was even used as the starting reactant to make uniform carbonaceous spheres.[18] Apart from the high cost, the fixed composition limited the condition regulation. Therefore, how to develop a facile, sustainable, and scalable one-pot HTC approach for the generation of monodisperse colloidal carbonaceous spheres with nice uniformity is still in great desire.

Herein, we display a facile one-pot HTC method to produce absolutely monodisperse, uniform colloidal carbonaceous spheres (MDCSs) with the help of tiny amount of PAANa (< 0.1 wt% of the glucose). The monodispersity and uniformity can even be realized at glucose concentration as high as 400 g/L. This synthetic strategy is also applicable in scale-up experiments. The sphere sizes can be simply adjusted by the reaction time, temperature and sugar concentration.

The SEM images in Fig. 1 show the morphology of the HTC products of glucose with and without PAANa. Consisted with previous reports, a high temperature (*e.g.*, over 180 °C) in classical HTC process led to the burst nucleation and durative polycondensation of glucose molecules, finally developing irregular and highly crosslinked carbonaceous clusters (Fig. 1a).[12b, 19] In contrast, the PAANa-assisted HTC of glucose resulted in the monodisperse, uniform carbonaceous spheres (Fig. 1b). In the whole SEM

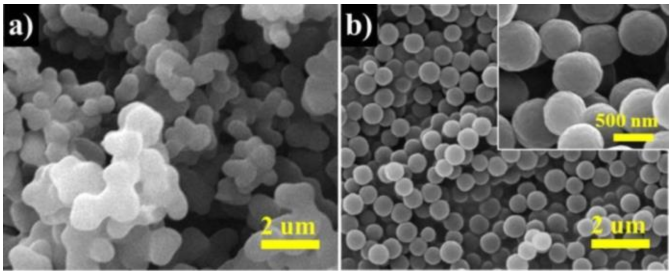

Fig. 1 SEM images of the products prepared from HTC of glucose without (a) and with 15 mg (b) PAANa at 180 °C.

observations, the prepared spheres are completely monodisepersed with uniform size (550 – 750 nm). There is no particle with other shapes or carbon fragment in the sample. It indicates that PAANa perfectly suppresses the crosslinking of neighboring spheres. The high-magnification image demonstrates that the sphere rims are rough with some flaws (Fig. 1b, inset), different from those prepared by traditional HTC process, which may be caused by the uneven adsorption of PAANa on the sphere surface.

The IR spectra of the MDCSs and the carbonaceous cluster obtained by traditional HTC are identical (Fig. 2). The bands at 3470 cm^{-1} and 1100 cm^{-1} are attributed to the O–H (hydroxyl or carboxyl) stretching vibration and C–OH bending vibrations. The two peaks at 2920 and 2840 cm^{-1} are ascribed to the stretching vibration of the aliphatic C–H. The bands in the region between 1700 and 1600 cm^{-1} are related to C=O and C=C stretching vibrations, respectively. The bands at 875–750 cm^{-1} are attributed to aromatic C–H out-of-plane bending vibrations.[15a] The similarity of the two IR responses indicates that the PAANa-assisted HTC of glucose undergoes the same dehydration-polymerization/aromatization process with the one without PAANa.[14d, 20]

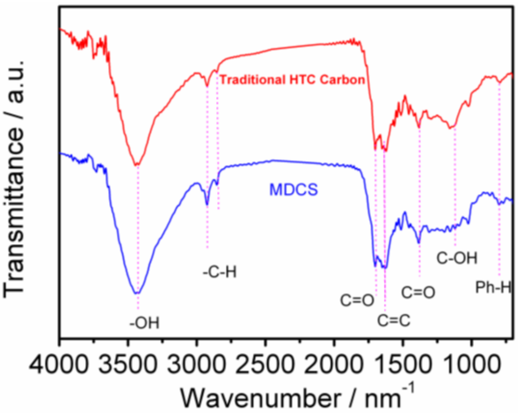

Fig. 2 Infrared spectra of carbonaceous material from traditional HTC of glucose and MDCSs prepared with PAANa-assisted HTC method.

Different amounts of PAANa were applied to investigate the influence on the morphology change (Fig. S1). When only 10 mg of PAANa was employed, the obtained spheres was uniform however slightly crosslinked (Fig. S1a). The spheres became totally monodisperse when the PAANa dosage was increased to 15~20 mg (Fig. S1b, S1c). Further increase of the PAANa to 40 mg led to the nonuniformity (Fig. S1d). The sample consisted of two types of spheres. One was the relatively large one about 1 μm, another was the smaller one in the range of 200-400 nm. PAA anion ("PAA" for short) is known as an dispersant to regulate the rheological properties and stability of concentrated particulate suspensions[21] or to control the crystallization of water scale.[22] The PAA can interact with solid particles and thus reduce the surface energy.[23] However, no example of PAANa-assisted method was reported for the fabrication of carbon materials. According to our experimental results, the PAANa shows great impact on the dispersity of the HTC carbonaceous spheres. Zeta potentials were measured to give some enlightenment for the formation mechanism of the MDCSs. The HTC process without PAANa was carried out and stopped after 2 hours to produce carbon seed. Then the seed colloidal solution was evenly divided into four parts and added different dose of PAANa. As shown in Fig. 3a, the zeta potential becomes more negative once adding PAANa and rises with the increasing PAANa dosage. It indicates that the surface of the carbon seeds becomes more negatively charged, thus offering stronger electrostatic repulsion between the particles. If small dosage of PAANa was added (*e.g.*, 15 mg), the glucose can move to the surface smoothly and the carbon seeds would grow regularly to uniform spheres.[24] When more PAANa was applied (40 mg or more), the increased adsorbed layers and thickness fully block the surface and arrest growth, so that new nucleation occurs. These new particles are likely to grow into bigger spheres because the free PAA concentration in solution is much lower than that at the beginning (as most is adsorbed on the initially nucleated particles). As a consequence, the resulting product shows polydispersity (Fig. 3b).

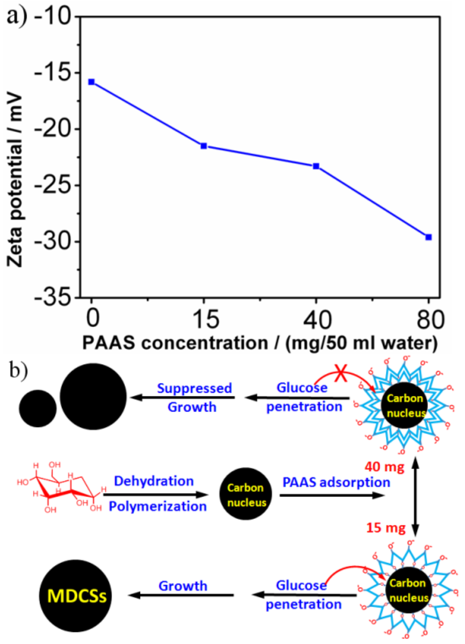

Fig. 3 Zeta potential of the colloidal carbon seeds with different dosage of PAANa (a) and the formation mechanism of the MDCSs (b).

Hydrothermal time and temperature are two main factors affecting the product morphology. As shown in Table 1, the spheres size increases with the extension of dwell time. The mean diameter of the MDCSs are 618, 814 and 898 nm after 8 h, 12 h and 24 h of reaction, respectively (Entry 1,2,3, Table 1). This is in line with the growth mechanism of the spheres. After nucleation, the glucose continues diffusing to the nucleus surface and grows isotropically.[24] Therefore, the sphere size increases with the reaction time. The change of temperature from 180 °C to 190 °C dose little effect on the sphere size. Nevertheless, the mean size rises from approximate 620 nm to 810 nm when the temperature is raised to 200 °C (Entry 1,4,5, Table 1), which results from the faster polymerization and aromatization. The carbon

Table 1 The average sizes of the spheres obtained at different conditions

Entry	Temperature/ °C	Time /h	C_{glu}/ (g/50ml water)	Average size/ nm
1	190	8	12	618
2	190	12	12	814
3	190	24	12	898
4	180	8	12	632
5	200	8	12	810
6	190	8	8	474
7	190	8	20	977

Reaction conditions: with 15 mg of PAANa spheres are all monodisperse under all these condition (Fig. S2,S3). In most previous HTC protocols, the monodispersity and uniformity were only achieved at either low sugar concentration or short reaction time, which lead to low production yields.[12b, 24] The unreacted saccharide is difficult to recover and reuse, causing the waste of raw materials. Generally, 1 M of glucose is the maximum concentration to access monodisperse colloidal carbonaceous spheres. We tried to get monodisperse colloidal spheres at the reported successful concentration (4 g glucose in 40 ml water) without using PAANa.[12a] However, the dispersity of the obtained carbonaceous spheres is relatively poor and more importantly the repeatability of the experiments is also bad (Fig. S4). Our experiments show that the introduction of PAANa perfectly solved these problems. The PAANa-assisted HTC process can be operated at glucose concentrations as high as 2 M (20 g/ 50 mL) with excellent repeatability (Fig. 4). The obtained spheres are still monodisperse and uniform. The spheres size increases from 474 nm to 618 nm and 977 nm when the glucose concentration is changed from 8 g/50 mL to 12 g/50 mL and 20 g/50 mL, respectively (Entry 1,6,7, Table 1). The dynamic light scattering (DLS) curves show only one intensive peak for all the MDCSs samples, demonstrating high uniformity (Fig. S5). What's more important to note, the final production mass of the PAANa-assisted HTC process is even larger than those produced by traditional PAANa-free HTC protocols (Table S1). This may due to that PAANa suppresses the crosslinking of the carbonaceous nucleus, which leads to more nucleuses growing at the same time. The PAANa-assisted HTC method also turned out to be effective in scale-up experiment. The reaction with 120 g of glucose and 150 mg of PAANa can also proceed to form MDCSs (Fig. S6). The successes in high concentration and scale-up experiments make it promising for industrial production of carbonaceous spheres.

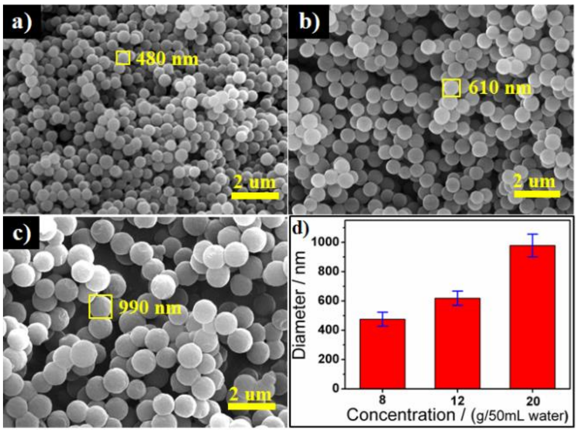

Fig. 4 SEM images of MDCSs prepared with glucose concentration of 8 g/50 mL (a), 12 g/50 mL (b), 20 g/50 mL (c) at 190 ^{o}C over 8 hours and corresponding average sizes (d).

For the production of monodisperse and uniform carbon spheres, the obtained carbonaceous spheres were directly carbonized in N_2 atmosphere. After calcined at 600 ^{o}C for 4 h, the resulting carbon yield is 59 %. Yields up to 56 % and 50 % were also achieved after 1 hour of carbonization at 800 ^{o}C and 900 ^{o}C, respectively (Table S2). The spherical shape with monodispersity and uniformity was perfectly reserved (Fig. S7a-c). Rich microporosity was developed in the carbon spheres after calcination (Fig. S8). The degree of graphitization could be simply adjusted by the carbonization temperature. The structural order of the carbons was characterized by X-ray diffraction (XRD) analysis. Fig. S7d shows that the peak centered at 19.8^{o} which is attributed to the 002 interlayer reflection shifts to 22.9^{o} after calcination, suggesting the decrease in the interlayer spacing.[25] A peak at 43.8 ^{o} appears upon calcination and becomes more pronounced with the increasing temperature. This peak can be assigned to the 100 in-plane scattering and its enhancement demonstrates better carbonization of carbon spheres.[26] The temperature variation can regulate the content of oxygen functional group, BET surface area, and pore volume of the spheres as well (Table S3). The MDCSs can also be employed as sacrificial template agents for porous materials (Fig. S9).

In summary, monodisperse and uniform colloidal carbonaceous spheres were successfully fabricated with a facile hydrothermal process at high glucose concentrations with a small dosage of PAANa. The adsorption of PAANa on the carbonaceous nucleus suppressed the crosslinking, which led to the monodispersity. The spheres size was uniform and could be easily adjusted by the variation of the reaction time, temperature and glucose concentration. The product yield was improved compared to traditional additive-free hydrothermal process. It provides a sustainable and facile way for the production of carbon spheres on a large scale.

Financial support from the National Natural Science Foundation of China (21376208 & U1162124), the Zhejiang Provincial Natural Science Foundation for Distinguished Young Scholars of China (R13B030002), the Specialized Research Fund for the Doctoral Program of Higher Education (J20130060), the Fundamental Research Funds for the Central Universities, the Program for Zhejiang Leading Team of S&T Innovation, and the Partner Group Program of the Zhejiang University and the Max-Planck Society are greatly appreciated.

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Electronic supplementary information (ESI) available: [Representative experimental procedures, SEM images, Elemental analysis, production yield]. See DOI: 10.1039/c000000x/

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