

Metal salts assisted thermoplastic polymer NIPAM in-situ carbonization on porous silica microspheres surface

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Abstract

The unique structure of porous Silica@Carbon (Sil@C) microspheres not only can provide larger surface area and active site, but also have the characteristics of high mechanical strength and easy modification. However, the preparation of different carbon-shell morphology microspheres and controllable operation of surface area via using polymers as carbon source was still a challenge. Herein, we report a simple method to in-situ fixation a series of different morphology graphitized carbon shell (rosa roxburghii, bulk, and carbon sphere shapes) on porous silica microspheres surface. The heat released by metal salts at high temperature will not only prepare graphitized carbon with different morphology on silica surface, but also facilitate the in-situ carbonization of thermoplastic polymer on the surface of cabinet without entering silica internal pores. This experimental method provided an experimental theoretical basis to prepared Sil@C microspheres with controllability of carbon-shell morphology and surface area.

Introduction

Carbon materials (CMs) were widely applied to various fields, such as wastewater treatment [1-3], gas storage and separation [4-6], electrode catalysis [7-9], supercapacitor, and batteries manufacturing [10-14], that attribution to its advantage including changeable morphology, easy to modify, rich surface functional group, etc. The excellent properties of CMs were height correlation to itself morphology, resulted in a variety of CMs morphology, such as activated carbon [15], graphite [16], graphene [17], fullerene [18], carbon nanotubes [19], carbon microspheres [20-24], carbon quantum dots [25] and so on. So far, the strategies for preparing CMs with different morphologies can be summarized as follows: one was high-temperature carbonization or chemical physical peeling the specific morphologies materials [26,27], the other was small molecule chemical synthesis [28,29], and the third was chemical physical assisted method of amorphous materials [30-33]. However, the mechanism of preparing different types of CMs by chemical physical assisted method was not very clear. Metal salt assisted amorphous carbon source was a common method to prepare CMs with different morphologies [34,35]. However, the research at this stage can only prove that transition metal salt was conducive to improve the stability of carbon source in the carbonization process [26], and cannot explain the difference of morphology between the formed CMs. On the other hand, when synthetic polymers are used as carbon sources to prepare CMs with various morphologies, thermosetting polymers were used in most cases. The reason was thermoplastic polymers would collapse and shrink during carbonization and cannot maintain their original morphology. Nevertheless, the synthesis of thermosetting polymers with specific morphology was not simple, the preparation steps were cumbersome and complex, and special monomers should be used, these were limiting polymers as carbon sources to prepare CMs.

In this work, firstly, polymer monomer N-isopropylacrylamide (NIPAM) and crosslinker pentaerythritol triacrylate (PETA) were in-situ polymerized on the porous silica microspheres surface to obtain a layer thermoplastic polymer had coated core-shell microspheres, then graphitized carbon shells with different morphologies (rosa roxburghii, bulk, and carbon microsphere shapes) were prepared by in-situ carbonization of thermoplastic polymers assisted by metal salts. The shell morphology has no

correlation with the thermoplastic polymer morphology itself, which greatly simplifies the preparation process. It was worth noting that the thermoplastic polymer was assisted by the additional heat release of metal salts in the high-temperature carbonization process, so that the thermoplastic polymer will not collapse and block the pores of porous silica microspheres in the high-temperature carbonization process, but will only carbonize in-situ on the surface. In addition, the surface area of prepared material has a positive correlation with the heat released by metal salt, in the process of high temperature carbonization, the more heat released by metal salt, the larger surface area of prepared material.

Reagents And Experimental Reagents And Instruments

The detail of reagents and instruments saw in supporting information.

Synthesis of porous Sil@C microspheres

As shown in Fig. 1a, the preparation of porous Sil@C composites microspheres with different morphology can be divided into two simple steps: (1) coating polymer NIPAM on bare porous silica microspheres surface, which were referring to our group previous works (denoted as NIPAM@Sil) [36-38], (2) high temperature carbonization in the presence of different metal salts (named as Sil@C). Experimental details saw in supporting information experimental section.

Results And Discussions

Direct carbonized NIPAM@Sil without metal salt assistance

After NIPAM in-situ polymerization on bare silica surface, scanning electron microscopy (SEM) images have showed that an irregular polymer layer formed on NIPAM@Sil surface and a slight adhesion phenomenon between the microspheres (Fig. S1a-d). When the NIPAM@Sil was carbonized at 500 °C without the assistance of metal salt, the polymer coating on surface bare silica basically disappeared, but there were still some residues on silica microspheres surface, and the color changes from white to black (Fig. S2), indicated that NIPAM not completely pyrolyzed but formed carbon at 500 °C. In addition, the surface area and pore volume of Sil@C decreased sharply compared with bare silica and NIPAM@Sil. As a result, the carbonation process was deduced as follow: (1) the morphology of thermoplastic polymer on silica microspheres surface was collapsed under high temperature environment, (2) all the collapsed polymers occupied the pore of porous silica microspheres, (3) the graphitized carbon formed by thermoplastic polymer occupied the pores of porous silica microspheres.

Effects of NiCl₂assisted carbonization and carbonization temperature

Thermogravimetric analysis (TGA) decomposition results have shown that compared to bare silica with no significant mass loss, NIPAM@Sil had 11.97% mass loss at about 400 °C. The Sil@C was black (Fig. S2b) and there were residues on silica microspheres surface (Fig. S1e, f), indicated that the NIPAM at 400 °C was not pyrolysis completely. As shown in Fig. S3a and b, when NiCl₂ was introduced to carbonization process, adhesion phenomenon of NIPAM@Sil has disappeared and collapsed accompanied with about 30 nm carbon microspheres formed on bare silica surface (noted as Sil@C(NiCl₂)). Moreover, the number of carbon microsphere decreased sharply with the increase of carbonization temperature (Fig. S3a-f). The transmission electron microscopy (TEM) images also showed a sharp decline in carbon microspheres with carbonation temperatures rising (Fig. S4). Notably, with the increase of carbonization temperature, the color of Sil@C(NiCl₂) has changed from black to gray, which shown that the more complete the pyrolysis of NIPAM with the increase of temperature, and 500 °C was the more appropriate carbonization temperature.

Furthermore, compared to bare silica, broad and overlapping D (1351 cm⁻¹) and G (1587 cm⁻¹) bands were registered in the first order Raman spectra for Sil@C and Sil@C(NiCl₂) (Fig. 2b). These two overlapping bands were identified as poorly organized carbons: (i) 1351 cm⁻¹ assigned to disordered crystal graphitized carbon or sp³-rich phase, and (ii) 1587 cm⁻¹ ascribed to amorphous sp²-bonded forms of carbon [39,40]. Compared with the fourier transform infrared spectroscopy (FT-IR) of bare silica and NIPAM@Sil, FT-IR spectrum of Sil@C(NiCl₂) has shown the stronger absorptions of 3300-3400 cm⁻¹ and absorptions of 1630 cm⁻¹ belonged to the carboxyl (Fig. S6a) [37]. X-ray photoelectron spectroscopy (XPS) of Sil@C and Sil@C(NiCl₂) revealed stronger existence of C 1s peak (~287.8 eV) and weaker SiO₂ peak (~103.5 eV) compared with bare silica and NIPAM@Sil (Fig. S6b). The high-resolution C 1s XPS of Sil@C and Sil@C(NiCl₂) can be deconvoluted three individual peaks assignable to the graphitic C (284.5 and 285.2 eV) and O=C-O (289.6 eV) (Fig. S6c, d) [41-43]. In particular, as Fig. 2c and d shown that the surface area and pore size of Sil@C(NiCl₂) only had a small reduction compared with NIPAM@Sil, but had larger surface area and smaller pore size than Sil@C. The surface area and pore size of Sil@C(NiCl₂) very close to non-carbonized NIPAM@Sil, this shown that with the assistance of NiCl₂ in the carbonization process, NIPAM almost only carbonized on silica surface of and not collapsed and shrunk into the silica microspheres inside pores.

Effects of different metal salts on assisted carbonization process

In order to verify that the in-situ carbonization of NIPAM on silica surface by NiCl₂ was not an accident. Six other metal salts, including Na₂CO₃, NaCl, Na₂SO₄, NiCO₃, NiSO₄ and CoCl₂, were selected to assisted carbonize NIPAM@Sil under 500 °C. Only Na₂CO₃, NiCO₃ and NaCl could forming a specific morphology of graphite carbon, including rosa roxburghii and bulk, on porous silica microspheres surface, respectively (Fig. 3a, b, e). However, other metal salts cannot remain graphite carbon on porous silica microspheres

surface, which were same like bare porous silica microspheres surface (Fig. 3c, d and f). Though the colors of Sil@C(Na₂CO₃), Sil@C(NiCO₃) and Sil@C(NaCl) were black with graphitic carbon (Fig. S7), the other metal salts assisted carbonized process was yellow or closer to white (Fig. S8). Thus, it can be speculated that some metal salts may lead to NIPAM instability during carbonization. In addition, compared with NiCl₂ assisted NIPAM to formed carbon microspheres on silica microspheres during carbonization, different metal salts were used for assisted carbonization to formed different morphologies, which may be related to the corresponding catalytic properties of metal salts.

Different metal salt assisted on NIPAM@Sil carbonization mechanism

NiCl₂ assisted carbonization not only generated carbon microspheres on silica surface, but also avoided the collapse of polymer into silica internal pores. Moreover, different metal salts including Na₂CO₃, NaCl, Na₂SO₄, NiCO₃, NiSO₄ and CoCl₂ assisted carbonized NIPAM@Sil process was compared with the surface area, pore diameter. As shown in Fig. 4a, b and Table S5, different metal salts assisted carbonization Sil@C with different surface areas and pore sizes which indicated that metal salts had played an important role in maintaining the in-situ carbonization of thermoplastic polymer NIPAM on porous silica microspheres surface, and this maintenance ability must be related to metal salts properties. Without the assistance of metal salt NIPAM@Sil during carbonization, NIPAM will collapse and enter the internal pores of silica, while with the assistance of NiCl₂, it was basically carbonized in-situ only on silica surface, which mean that in the whole carbonization heating process, thermoplastic NIPAM will preferentially collapse at NiCl₂ around and then be carbonized. Bare silica and NIPAM@Sil without obvious thermal effect in the heating process (Fig. S9a, b), that was no additional heat supply except the heat provided by the instrument. The differential scanning calorimetry (DSC) results of seven metal salts have shown that all of metal salts had obvious exothermic peaks higher than 150 °C, which directly explained the auxiliary pair of metal salts for NIPAM@Sil carbonization, in addition to the heat provided by the instrument, there was a certain amount of heat released by the metal salt itself (Fig. S9). For the integration of these exothermic peaks, the emission of each metal salt was different, ranging from 2.7 to 677.9 J g⁻¹. An interesting phenomenon was that the more heat the metal salt releases in the process of auxiliary carbonization, the larger the surface area of Sil@C. During the heating process, Na₂CO₃ only released 2.7 J g⁻¹ heat, which leads to the weak ability of Na₂CO₃ to maintain the in-situ carbonization of NIPAM on silica surface, and the surface area of Sil@C(Na₂CO₃) (76.47 m² g⁻¹) was only a little larger than that of Sil@C (53.48 m² g⁻¹). What was more noteworthy was that the flake graphitized carbon grown directly from silica microspheres pores can be directly captured by SEM (Fig. S7a), which shown that NIPAM would collapsed and enter the internal silica microspheres pores during heating. In addition, it was not that the more heat released by the metal salt was more conducive to the in-situ carbonization of NIPAM on silica the surface. NiSO₄ released 677.9 J g⁻¹ heat, which promoted the more complete pyrolysis of NIPAM, resulting in the surface area of Sil@C(NiSO₄) (392.60 m² g⁻¹) closer to the bare silica

(370.72 m² g⁻¹) rather than NIPAM@Sil (289.37 m² g⁻¹) and the color closer to white. Based on the above phenomena, it can be seen that it was precisely because the metal salt assists in the heat release in the carbonization process that thermoplastic polymer preferentially carbonates after collapse near the metal salt, and the more heat released, the stronger the ability to maintain the in-situ carbonization of thermoplastic polymer.

Conclusions

In summary, Sil@C composites microspheres with series carbon morphologies (rosa roxburghii, bulk, and carbon sphere shapes) was successful prepared by in-situ carbonized the thermoplastic polymer NIPAM on porous silica microspheres surface. Direct carbonization of thermoplastic polymers will lead to polymer collapse and occupy the internal pores of porous silica, which is not conducive to the preparation of materials with high surface area. Metal salts were introduced to assist the carbonization of thermoplastic polymer NIPAM, which can not only prepare carbon materials with different morphologies on silica surface, but also maintain the in-situ carbonization of NIPAM. It was proved that the relationship between the heat released by metal salts and the ability to maintain in-situ carbonized NIPAM on silica surface: the maintenance ability was relatively weak at low heat, medium heat was conducive to maintain the carbonization in situ, and high heat was not conducive to the carbonization stability of NIPAM. This strategy provided a theoretical and experimental basis for the preparation of CMs with different morphologies and surface areas using thermoplastic polymers.

Declarations

Acknowledgments

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Declaration of competing interest

The authors declare no competing financial interest.

Author Contributions Statement

Chao Fan: Visualization, Software, Data curation, Investigation, Writing-original draft, Writing-review & editing. Xiaojing Liang: Writing-review & editing, Conceptualization, Supervision. All authors reviewed the manuscript.

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Figures



Figure 1

Synthetic scheme of porous Sil@C microspheres

Figure 2

(a) TGA for Bare silica and NIPAM@Sil. (b) Raman spectra for bare silica, Sil@C and Sil@C(NiCl₂). (c, d) Nitrogen adsorption and desorption isotherms at 77 K and pore size distributions for Bare silica, NIPAM@Sil, Sil@C and Sil@C(NiCl₂).

Figure 3

The SEM images of different metal salt assisted carbonize the NIPAM@Sil. (a) Sil@C(Na₂CO₃), (b) Sil@C(NiCO₃), (c) Sil@C(Na₂SO₄), (d) Sil@C(NiSO₄), (e) Sil@C(NaCl) and (d) Sil@C(CoCl₂). Scale bar: 1 μm.

Figure 4

(a, b) Nitrogen adsorption and desorption isotherms at 77 K and pore size distributions for different Sil@C with different metal salt assisted carbonization process. (c) The surface areas of different Sil@C with different metal salt assisted carbonization process. (d) The DSC analysis of different metal salts total heat released.

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