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Direct synthesis of hierarchical porous polymer nanoparticles from nitrile monomers and its application for methylene blue adsorption

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Abstract

Microporous covalent triazine-based frameworks (CTFs) have been widely used as adsorbents, separation and catalysts in the past few years, but the confined microporous network often induces diffusion limitations of molecules to and from the active sites. Here, we present a general bottom-up synthetic strategy to produce hierarchical porous polymer nanoparticles by cyclotrimerization of 1,4-dicyanobenzene in molten ZnCl2. Controlling the ratio of monomer to molten salts is the key to prepare hierarchical porous polymer nanoparticles by ionothermal methods, and uniform nanoparticles with particle size of 100–400 nm can be facilely synthesized at a low monomer/ZnCl2 molar ratios. The resulting hierarchical porous polymer nanoparticles exhibit great adsorption capacity of methylene blue. The enhancement is ascribed to enhanced mass transfer of the molecules and easy access to the active sites as a result of the short diffusion lengths of hierarchical porous polymer nanoparticles. This method is simple and efficient for the preparation of size-controllable hierarchical porous polymer nanoparticles from nitrile monomers, which is conducive to expand its application in adsorption, catalysis and other related fields.

1. Introduction

Porous organic polymers (POPs), which combine chemical stability with wide synthetic diversity, have attracted tremendous attention for their potential applications in adsorption, separation, light harvesting, sensing, catalysis, energy storage and conversion [1]. The field of POPs with a well-defined pore size including polymers of intrinsic microporosity (PIMs) [2], hyper-crosslinked polymers (HCPs) [3], conjugated microporous polymers (CMPs) [4, 5] and covalent organic frameworks (COFs) [6, 7] have been developed over the last decades. A large number of studies have been carried out on the structures, synthesis methods and applications of this kind of porous materials, and they has become one of the major research fields of material chemistry [8–10].

Covalent triazine frameworks (CTFs) is a new class of covalent porous polymers with regular microporous structure, which has been developed by trimerization of aromatic nitriles in molten ZnCl2 [11]. In the past few years, CTFs have attracted more and more attentions due to their large surface area, well-defined microporosity, high chemical and thermal stability, as well as chemical and structural tunability [12–16]. CTFs have been emerged as promising candidates for application as adsorbents owing to their high specific surface area and pore volume, a variety of pollutants such as methyl orange [17], methylene blue [18], Rhodamine B (Rhb) [19], 4,4’-(Propane-2,2-diyl)diphenol [20], humic acid [21] and some surfactants [22]. The outstanding adsorption capacities of benzene and aromatic compounds CTFs have showed is due to the presence of hydrogen bonding, electrostatic attraction and π–π interaction [23, 24]. However, CTFs are mostly microporous polymers (pore sizes <2 nm), which was unfavorable for the mass transfer in adsorption and separation. Since the first report of microporous CTFs in 2008, methods to tune the morphology, pore size and particle size of the microporous
CTFs materials have been proposed to enhance mass transfer of the guest molecule in the microporous framework [25, 26]. By varying precursor with different length of organic linkers, the pore size distribution and surface area of these CTFs materials can be tuned in some extent. Controllable synthesis of hierarchical porous CTFs with microporous and mesoporous structures have attracted great attention due to the enhanced accessibility of active sites. With a two-step high temperature approach, hierarchical porous CTFs materials with plenty of accessible mesopores can be facilely synthesized and show greatly enhanced catalytic performance in the cycloaddition of CO2 to cyclic carbonates [27]. Different synthetic approaches have been developed to synthesize CTFs materials, but most of which resulted in micrometer sized CTFs particles. As an alternative approach, decreasing the particle size to the nanoscale can also enhance mass transfer as a result of the short diffusion lengths, which was favorable for their application as adsorbents or catalysts [28]. Still, synthesis of hierarchical porous CTFs nanoparticles remains to be a great challenge.

In this paper, hierarchical porous polymer nanoparticles were synthesized with a careful control of the monomer/ZnCl2 ratios. Monodisperse hierarchical porous nanoparticles could be synthesized with low monomer/ZnCl2 ratio under the ionothermal conditions. Compared with micron-sized CTF-1, hierarchical porous nanoparticles exhibit better adsorption capacity of methylene blue. This bottom-up procedure is a general approach for preparation of size-controllable hierarchical porous nanoparticles from nitrile monomers.

2. Experimental section

2.1. Materials
1,4-dicyanobenzene (DCB) and zinc chloride (ZnCl2) (≥98%) were products of Alfa-Aesar. HCl and ethanol were purchased from Aladdin.

2.2. Methods
In a typical experiment, a mixture of DCB and ZnCl2 with different molar ratios were mechanically milled by Retsch PM400 planetary ball mill. The obtained mixture was placed into a quartz ampule inside a glove box filled and then flame-sealed. The sealed ampule was put into a furnace and heated at 400 °C for 40 h. After the reaction, the ampoule was crushed after cooling to room temperature, and the solid block was thoroughly ground. In order to remove ZnCl2, the reaction mixture was washed thoroughly with diluted HCl and water. And then the resulting black powder was filtered, washed with water and ethanol and dried at 100 °C for 12 h. The product was named as CTF-1-n, where n was the molar ratios of ZnCl2/DCB.

2.3. Characterization
Transmission electron microscopy (TEM) images were tested on a JEOL 2000EX electronic microscope, and the operating voltage was 120 kV. Scanning electron microscopy (SEM) images were detected by Phenom LE Scanning Electron Microscope. X’Pert Pro (PANAnalytical) diffractometer with Cu Kα radiation was used to record x-ray diffraction (XRD) patterns. Elemental element composition was carried out on a Vario EL elemental analyzer. 13C CP-MAS was measured by Bruker Avance 400 spectrometer operating at 100.6 MHz. The samples were degassed at 90 °C for 1 h and 180 °C for 6 h before analysis. The surface area was calculated by BET method based on adsorption data in the partial pressure (P/Po) range 0.04 to 0.2, the total pore volume was determined based on the amount of nitrogen adsorbed at a relative pressure of 0.99, and the micropore surface area and the micropore volume were calculated via t-plot analysis. Thermogravimetric analysis (TGA) measurements were carried out on a TGA Q500 thermal analysis system with a heating rate of 10 K min−1.

2.4. Adsorption capacity test of methylene blue
100 ml of methylene blue (MB) with the concentration of 25 mg l−1 were stirred at ambient conditions. 25 mg of adsorbent was added to this solution to detect their adsorption capacity. The absorbance of the solution was determined by Spectrophotometer (Metash UV5500, Shanghai, China), and the concentration of residual methylene blue in solution under different adsorption time was deduced by MB standard curve. The determination process of MB concentration was described in supporting information (available online at stacks.iop.org/MRX/8/035001/mmedia).

The adsorption capacity of methylene blue on adsorbent is expressed by q (mg g−1), and q = (c0-cf)V/m. In this equation, c0 (mg l−1) is the initial concentration of MB in the solution, cf (mg l−1) is the concentration of MB at time t (h). V (L) is the volume of the solution, m (g) is the mass of the adsorbent used.
3. Results and discussion

A series of CTF-1-n samples were synthesized by polymerizing a mixture of DCB and ZnCl$_2$ with different DCB/ZnCl$_2$ molar ratios in quartz ampules at 400 °C for 40 h. The morphology of the products were characterized by TEM and SEM. As shown in figure 1(a), bulk CTF-1 sample show the irregularly shape with grain size ranging from 5 to 50 μm, which agrees well with previous reports. Some irregular micrometer sized particles can be found for the CTF-1-10, which were smaller than that of CTF-1 (figure 1(b)). Besides irregular

![Figure 1. TEM images of (a) CTF-1, (b) CTF-1-10, (c) CTF-1-20, (d) CTF-1-30, (e) CTF-1-40 and (f) CTF-1-50.](image1)

![Figure 2. Average uniform particle size distributions of CTF-1-40 and CTF-1-50.](image2)
micrometer sized particles, some individual nanometer sized particles can be observed for CTF-1-20 and CTF-1-30 samples (figures 1(c) and (d)), which proved The fraction of nanometer sized particles in the obtained materials increases remarkably along with the decrease of DCB/ZnCl₂ ratios. Further reduce the concentration of DCB in molten salt, highly dispersed nanoparticles become the major products in CTF-1-40 and CTF-1-50 (figures 1(e), (f)). As can be seen from the TEM images, the content of molten salt determines the morphology of the products. SEM images showed similar results. CTF-1-40 and CTF-1-50 contained some agglomerated particles with size ranging from 300 to 500 nm (figure S2). Compared with CTF-1-40, the particle size of CTF-1-50 is more uniform. The energy-dispersive x-ray spectroscopy (EDX) mapping images revealed that C, N and O elements were uniformly dispersed in the entire products (figure S3). Furthermore, the data in table S2 showed that most of ZnCl₂ in the system was removed after washing the products with water and ethanol.

Considering the yield and size range, we choose nanometer sized CTF-1-40 and CTF-1-50 as the research object to further analyze their structures and properties. The particle size distributions of CTF-1-40 and CTF-1-50 were measured by Nanoplus-3 nanoparticle size analyze. As shown in figure 2, the particle size of the sample was in the range of 100–400 nm. The average uniform particle size of CTF-1-40 was 259 nm. The size of nanoparticles could be varied by changing the DCB/ZnCl₂ molar ratio. Decreasing the DCB/ZnCl₂ molar ratio resulted in an obvious decrease of average particle size. The average diameter decreased from 259 nm to 225 nm with the DCB/ZnCl₂ molar ratio decreased from 0.025 to 0.02, which indicated that the particle size of the products could be able to conveniently tune through the control of the monomer concentration.

A series of characterizations were detected to observe the structural changes of the obtained nanoparticles. Figure 3(a) showed XRD patterns of CTF-1, CTF-1-40 and CTF-1-50. Consistent with the previous reports, two diffraction peaks centered at around 7.4 and 25.7° were detected in the XRD pattern of CTF-1. The peak at 25.7° was a characteristic interlayer stacking (002) peak of conjugated interlayer aromatic sheets with an interlayer spacing of 3.4 Å, while the characteristic peak of the in-plane reflection (100) was centered at 7.4°. Compared with that of the CTF-1, the crystallinity of CTF-1-40 and CTF-1-50 nanoparticles were poor. Furthermore, the disappearance of (100) characteristic peak reflected the poor long-range order of CTF-1-40 and CTF-1-50 nanoparticles.

The functional groups on the surface of the products were characterized by FTIR spectroscopy (figure 3(b)). A weak band around 2225 cm⁻¹ due to the stretching vibration of residual and terminal CN were detected in all products. Similar to CTF-1, the strong bands at 1400 cm⁻¹ were detected in CTF-1-40 and CTF-1-50, which
assigned to skeleton vibration of the aromatic rings in monomers. FTIR spectrum of the CTF-1 showed strong absorption band at 1517 and 1349 cm\(^{-1}\), corresponding to the aromatic C-N stretching band characteristic of the triazine units. And the band at 805 cm\(^{-1}\) was attributed to the breathing mode of the triazine units. However, these bands were disappeared in the FTIR spectra of CTF-1-40 and CTF-1-50. It was indicated that when the content of molten salt in the system is large, it was not conducive to the formation of triazine skeleton by cyano polymerization.\(^{13}\) C CP-MAS solid state NMR spectroscopy were characterized to deeply understand the local chemical structure of the products (figure 3(c)). Three resonances at \(\delta = 169, 138\) and 116 ppm corresponded to the sp\(^2\) and sp\(^3\) carbons of the CTF-1 framework, indicating the presence of aromatic and triazine units in CTF-1. Additionally, besides the three expected peaks, a very small peak at 116 ppm originate from terminal and residual cyano groups could be detected in the\(^{13}\)C CP/MAS NMR spectra of CTF-1. The types of carbon species decreased with the decrease of nitrogen content in the system. Only one broad peak centered at 127 ppm was detected in CTF-1-40 and CTF-1-50, which contained some undistinguished carbon species. The thermal stability of the products were affected by their particle size, TGA measurements revealed that CTF-1 was more stable than CTF-1-40 and CTF-1-50 (figure 3(d)).

The chemical composition of CTF-1, CTF-1-40 and CTF-1-50 were characterized by Vario EL elemental analyzer (table S3). The chemical composition of conventional CTF-1 (C\(_3\)N\(_4\).52H\(_{1.88}\)) implied the partial depletion of the nitrogen of DCB monomer in molten ZnCl\(_2\). Decrease of DCB/ZnCl\(_2\) molar ratios leaded a remarkable decrease of nitrogen content for CTF-1-40 and CTF-1-50. The C/N molar ratio of CTF-1-40 and CTF-1-50 were much higher than that of CTF-1(1.0), which indicated that the triazine ring in the framework is eliminated due to partial carbonization during the polymerization.

Furthermore, elemental analysis indicated that no significant diminution of the hydrogen content for CTF-1-40 and CTF-1-50 nanoparticles. The CTF-1-40 and CTF-1-50 (~1.7–1.9 wt.%) showed similar H contents with that of the conventional CTF-1 (~1.88 wt.%), and all the H content of the products were close to that of the DCB monomer. The above characterizations show that adjusting the concentration of molten salt in the system may lead to the change of their composition and structures.

The porous structure of CTF-1, CTF-1-40 and CTF-1-50 could be nicely followed and quantified by N\(_2\) sorption experiments. N\(_2\) adsorption/desorption isotherm indicated that CTF-1 had type-I isotherm, indicating there were highly micropores in the structure of CTF-1 (figure 4). In contrast to microporous CTF-1, type-IV isotherms with hysteresis loops were observed for CTF-1-40 and CTF-1-50, indicating there were a lot of mesopores in the structure of them. The corresponding quantitative data were summarized in table 1. Compared with CTF-1, CTF-1-40 yielded higher BET specific surface area and total pore volume. However, When the DCB/ZnCl\(_2\) molar ratios decreased to 0.02, the specific surface area of CTF-1-50 decreased to 789.07 m\(^2\) g\(^{-1}\). As it can be noted from table 1, a significant reduction in the micropore volume can be observed for CTF-1-40 and CTF-1-50, which indicated that the micropore system of the CTF-1 was changed.

Development of a distinct mesoporosity in the nanoparticles was demonstrated by a significant increase in the mesopore volume. As reported, molten salts in the system was acted as both solvent and template.\(^{29}\) Owing to the existence of a large number of molten ZnCl\(_2\), DCB with low concentration randomly polymerized in the system to form irregular porous polymers. And mesoporous structure may be formed after removal of ZnCl\(_2\).
Therefore, CTF-1-40 and CTF-1-50 was a kind of hierarchical porous polymer nanoparticles with both micropore and mesopore.

On the basis of the above results and literature precedents, a possible mechanism for the formation of CTF-1-40 in molten ZnCl₂ is summarized in figure 5. The synthesis of polymers in molten ZnCl₂ has been
described in detail elsewhere, and the molten ZnCl$_2$ may act as solvent and trimerization catalyst. In principle, the trimerization of dicyano compounds has to be carried out in molten ZnCl$_2$ at high temperatures to enable the formation of extended and periodic CTF networks. However, when decrease the concentration of DCB in the system, -CN groups in DCB may be eliminated from the aromatic ring and polymerized with the adjacent aromatic ring by coupling [30, 31].

At a very low concentration of DCB, the products are well dispersed in the molten ZnCl$_2$ and spatially well-separated in the matrix of the molten ZnCl$_2$. As a result, according to the large viscosity of molten ZnCl$_2$, it is not easy for the nanoparticles to agglomerate, and thus free-standing or randomly aggregated CTF-1-40 nanoparticles can be obtained.

To assess the effect of particle size on the adsorption capacity, CTF-1, CTF-1-40 and CTF-1-50 were utilized to methylene blue in solution. As shown in figure 6, CTF-1-40 and CTF-1-50 had better MB adsorption capacity than that of CTF-1. CTF-1-40 with highest BET specific surface area and total pore volume showed the highest adsorption capacity. Although the specific surface area of CTF-1-50 was smaller than that of CTF-1, it had a higher adsorption capacity for MB. This phenomenon was attributed to the existence of a large number of mesoporous structures in CTF-1-50 nanoparticles. The existence of mesoporous structure enhances the ability of mass transfer of the molecules, and MB molecules were easy to access to the adsorption sites, and the diffusion length of molecules in CTF-1-40 and CTF-1-50 nanoparticles was reduced.

4. Conclusions

In summary, we have synthesized size-controllable hierarchical porous CTF-1-40 and CTF-1-50 nanoparticles by cyclotrimerization of DCB in molten ZnCl$_2$ through a general innothermal synthetic strategy. We demonstrate that the precise control of the DCB/ZnCl$_2$ molar ratios provides an avenue to tune the particle size of CTFs, and the nanoparticles can be facilely synthesized at a low DCB/ZnCl$_2$ molar ratios in the range of 0.02 ~ 0.025. The resulting CTF-1-40 and CTF-1-50 nanoparticles display particle size in the range of 100 ~ 400 nm, high surface area and pore volume. CTF-1-40 and CTF-1-50 nanoparticles reveals high adsorption capability of methylene blue owing to the short diffusion lengths in the nanostructure. This bottom-up method can efficiently polymerize nitrile monomers to form size-controllable hierarchical porous nanoparticles, which is expected to open up application prospects in adsorption, catalysis and other fields.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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