Freeze-drying of “pearl milk tea”: A general strategy for controllable synthesis of porous materials

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Porous materials have been widely used in many fields, but the large-scale synthesis of materials with controlled pore sizes, pore volumes, and wall thicknesses remains a considerable challenge. Thus, the controllable synthesis of porous materials is of key general importance. Herein, we demonstrate the “pearl milk tea” freeze-drying method to form porous materials with controllable pore characteristics, which is realized by rapidly freezing the uniformly distributed template-containing precursor solution, followed by freeze-drying and suitable calcination. This general and convenient method has been successfully applied to synthesize various porous phosphate and oxide materials using different templates. The method is promising for the development of tunable porous materials for numerous applications of energy, environment, and catalysis, etc.

Porous materials with unique porous structures and high surface areas have been widely used in many fields such as energy, catalysis, adsorption, separation, etc1–9. Currently, porous materials are typically obtained via template-assisted processes, during which the hard-templating (polymer- or silica-based colloidal crystals, anodic aluminum oxide and other porous solids) or soft-templating (surfactants, block copolymers) techniques are often used5–12. Although various advanced porous materials have been reported, the large-scale synthesis of materials with controlled pore sizes, pore volumes, and wall thicknesses remains a considerable challenge5–13. Therefore, synthesis strategies that enable the production of porous materials with controlled pore characteristics are of key general importance. Herein, we report a convenient “pearl milk tea” freeze-drying approach to synthesize porous materials with precisely tunable porous characteristics. The generality of our approach is demonstrated by describing the controllable synthesis of various porous phosphate, oxide, and composite materials.

The formation of porous materials by freeze-drying “pearl milk tea” is generally involved three steps, as schematically shown in Fig. 1. First, the raw materials and templates are dispersed and mixed into a small amount of solvent (water or some organic solvent) to form the precursor solution of “pearl milk tea”, where the template corresponds to the pearl. Second, the “pearl milk tea” is rapidly frozen and subsequently freeze-dried in vacuum to immobilize the template in the solid precursor and remove the solvent by sublimation. Third, the solid precursor is slowly calcined at a relatively low temperature to further condense the precursor, and it is subsequently annealed at a higher temperature to remove the templates and obtain the target porous materials. With this strategy, the pore size of the produced porous material is determined by the size of the applied template, whereas the pore distance and wall thickness are tuned using the ratio of template (namely, the concentration of template in the precursor). Thus, the porosity can be finely controlled. For widely used methods such as the colloidal crystal template process, the templates must be packed into a highly ordered film before infiltrating the precursor solution into the voids among the packed templates5–12. Therefore, although highly ordered reverse replica porous materials can be obtained using the colloidal crystal template method, the controllability of the pore distance, porosity and the large-scale production are partly restricted. The reason for this restriction is the constantly closest packing geometry of the colloidal template beads with a specific size9, as shown in Supplementary Figure S1. In contrast, in the current approach, the template beads (pearl) are initially freely dispersed in the precursor solution (milk tea) before they are suddenly frozen and solidified. Parameters such as the distance between the template beads and the template-to-precursor ratio can be easily controlled to finely and widely control the porous characteristics of the product.

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**Results**

Olivine lithium iron phosphate (LiFePO₄) is an important positive electrode material of rechargeable lithium-ion batteries and is used in various applications such as portable electronic devices and electric vehicles\(^{14-18}\). Thus, LiFePO₄ was selected as an example to demonstrate the effectiveness of this method. First, polymethyl methacrylate (PMMA), which has been widely used in the aforementioned colloidal crystal template process, was introduced. In a typical synthesis, PMMA templates with a uniform bead size were prepared by emulsion polymerization according to the literature\(^{12}\). Then, 4.04 g of iron nitrate, 1.02 g of lithium acetate and 0.68 mL of phosphoric acid were dissolved into a certain amount of distilled water, and the PMMA template was added. The mixture was stirred for 2 h to form the “pearl milk tea”, which was subsequently rapidly frozen using liquid nitrogen (−196 °C) and freeze-dried in a vacuum freezing dryer for 72 h. The solidified dry precursor was heated at 5°C/min to 220°C and maintained at this temperature for 3 h to further condense the inorganic precursor. Then, it was heated at the same rate to 600°C and maintained for another 3 h in a reductive atmosphere of 90% argon and 10% hydrogen.

Figure 2a shows the SEM image of the PMMA template, which is a spherical particle with a uniform diameter of 100 nm. After they were well dispersed in the precursor solution, rapidly frozen and freeze-dried, the PMMA beads were uniformly mounted and immobilized in the solidified precursor, as shown in Fig. 2b. Upon the removal of the templates by calcination, the obtained materials replicated the size and morphology of the template and had a highly porous structure (Fig. 2c). The pores were notably uniform, and the pore size was approximately 100 nm, which is similar to the diameter of the applied template. X-ray diffraction studies indicate that the dried precursor remained amorphous and that the sample crystallized into a pure-phase olivine structure after annealing (Fig. 2d).

The porous characteristics of the olivine LiFePO₄ material can be conventionally tuned by the experiment parameters. For example, the porosity, pore distance and wall thickness could be easily controlled by adjusting the template concentration (mass concentration of template to the target product, similarly hereinafter). Figure 3 displays the SEM images of the LiFePO₄ products when the concentration of the applied template gradually increased from 25% to 80%. The pores were approximately 100 nm in size (similar to the diameter of the used templates) and were homogeneously distributed in these materials because of the uniform distribution of templates in the solidified precursor. When the template concentration increased from 25% to 80%, the surface area of the obtained materials remarkably increased from 18.59 to 94.58 m²/g, the porosity increased from 0.13 to 0.28 cm³/g (Supplementary Figure S2a), and the average pore wall thickness decreased from ~300 to 60 nm. The XRD patterns in Supplementary Figure S2b indicate that all of the materials crystallized into pure-phase olivine LiFePO₄ (consistent with the standard diffraction card No: 01-083-2092). In addition, the PMMA templates with various bead sizes were synthesized by emulsion polymerization (30–200 nm, as shown in the SEM images in Supplementary Figure S3). When these templates were applied, porous LiFePO₄ with various pore sizes of approximately 30, 50, 100, 130, 180 and 200 nm were obtained, as shown in Supplementary Figure S4, and the crystal structures were verified using XRD measurements (Supplementary Figure S5).

Importantly, this versatile method can be used to create porous structures in many different materials to tailor their physical, chemical, electrical and other properties. Similar to LiFePO₄, porous olivine structural LiMPO₄ (M = Mn, Co, and Ni), which is a promising positive electrode material with high potential and high theoretical energy density for lithium-ion batteries\(^{15-18}\), can be conveniently prepared using this “pearl milk tea” freeze-drying method by simply replacing iron nitrate with Mn, Co, or Ni containing nitrate. As shown in Supplementary Figure S6a-d, porous LiMnPO₄, LiCoPO₄, LiNiPO₄, and LiFeₓMn₁₋ₓPO₄ with pore diameters of approximately 100, 100, 150, and 100 nm, respectively, and an average wall thickness of 80–500 nm were easily prepared using PMMA templates with various diameters and concentrations (see the XRD results in Supplementary Figure S7). Such control of the electrode material is notably useful because the porous characteristics are relative to the electrode surface area, the electrode/electrolyte interface, the charge transfer ability and, consequently, the high-rate power capability\(^{14-16}\).

In addition to the phosphates, porous oxides can be effectively prepared using this synthesis strategy, as demonstrated by the successful synthesis of two important functional materials: TiO₂ and Li₄Ti₅O₁₂\(^{18-21}\). In
this case, the choice of solvent is important because most soluble organic titanates (e.g., tetrabutyl titanate) and titanium-containing inorganic salts (e.g., TiCl4) tend to completely hydrolyze in water and form discrete nanoparticles. When tetrabutyl titanate is used as the source material and tertiary butyl alcohol, a widely used organic agent for the freeze-drying technique, is used as the solvent, the frozen precursor melts again during the subsequent freeze-drying process, probably because of the exchange of butyl and tertiary butyl and the low freezing point of the produced butyl alcohol. Nevertheless, the use of titanium sulfate and tertiary butyl alcohol enables the successful synthesis of porous TiO2 and Li4Ti5O12 (with added Li salts) when using this method. As shown in Supplementary Figure S6e,f, uniformly distributed pores were created throughout both samples (see the XRD results in Supplementary Figure S8a,b). These results indicate that the “pearl milk tea” freeze-drying method can also be applied to organic-solvent systems.

To further investigate the generality of the “pearl milk tea” freeze-drying method, other widely used templates such as SiO2, polystyrene (PS), and polypyrrole (PPy) were applied and studied. Figure 4 displays typical SEM images of the applied templates, dry solid precursors, and calcined products of porous LiFePO4 using 100 nm PPy (Fig. 4a–c), porous MnO2 using 300 nm SiO2 (Fig. 4d–f), and porous MnO2 using 400 nm PS (Fig. 4g–i) (see the XRD results in Supplementary Figure S8c,d). Similar to PMMA, the PPy and PS templates were easily removed during the annealing process, but an additional etching process with HF solution after annealing was required when the SiO2 template was used because of its strong thermal stability. These phenomena and processes to the case of the PMMA template were clearly observed. These templates also helped produce homogeneously distributed porous materials, and the porous characteristics were highly related to the size and ratio of the applied templates.
Discussion

The microscopic reaction mechanisms of the “pearl milk tea” freeze-drying method are proposed as follows. Initially, both templates and ions (cation and anion) from the source materials are dissolved and homogeneously dispersed in a certain amount of solvent to form the sol-like tea (Fig. 1a). After their rapid freezing and subsequent freeze-drying in vacuum, the inorganic species may cross-link and form a continuous network among and surrounding the dispersive templates. For the process in an organic solvent, a small quantity of crosslinking agent (cellulose or PVP) is required to assist the oligomer and network formation; otherwise, only discrete nanoparticles are obtained. At this stage, no clear crystallization occurs, as verified by the XRD pattern of the almost amorphous structure (Fig. 2d(i)). When calcination is performed at a low temperature, the inorganic networks further condense to a firmer solid and subsequently crystallize into the final porous structure after the templates are removed by annealing at high temperature (however, the SiO₂ template requires a further etching process).

Figure 3. SEM images of porous LiFePO₄ materials synthesized with PMMA templates of various concentrations. (a) 25 wt. %; (b) 33 wt. %; (c) 50 wt. %; (d) 67 wt. %; (e) 75 wt. %; (f) 80 wt. %. For all samples, the pores are approximately 100 nm in size, which is similar to the diameter of the applied template, and the average pore wall thickness decreases with the increase in template concentration.
The precise control of the porous structure (including the porosity, pore architecture, and pore size, etc.) in porous materials is significant for their properties and performance. Currently, porous materials are mainly synthesized using soft-templating, hard-templating and non-templating methods. The soft-templating approach typically uses a surfactant as the structure-directing agent, and the specific precursor and surfactant combinations must be appropriately selected. It is also difficult to obtain ordered and crystalline porous materials when the surfactant removal temperature is low because the crystallization of the inorganic phase at a higher temperature without support can destroy the desired porous structure. For the hard-templating method, rigid structures such as anodic aluminum oxide membranes and silica- or polymer-based colloidal crystal films are pre-synthesized. Although highly crystallized and ordered porous materials can be obtained by using these templates, the wide controllability of pore characteristics and large-scale production are partly restricted. Compared to templating techniques, non-templating methods such as sol-gel and hydrothermal syntheses are usually simpler in procedure. However, the porous architectures and ordering of the material are hardly controlled, and broader pore-size distributions are often obtained. In comparison, the present “pearl milk tea” freeze-drying method combines the advantages of the templating synthesis and the freeze-drying technology, and highly crystallized pore architectures of materials can be effectively and precisely controlled. Moreover, the preparation of a highly ordered template framework similar to hard-templating is avoided, which simplifies the synthesis process and is suitable for the large-scale production of porous materials.
Conclusion
In summary, we have demonstrated the “pearl milk tea” freeze-drying method to form porous materials with controllable pore characteristics such as the pore size, wall thickness, surface area and porosity. The unique strategy is realized by rapidly freezing the uniformly distributed template-containing precursor solution, followed by freeze-drying and suitable calcination. This method has been successfully applied to synthesize multi-element phosphates (LiFePO₄, LiMPO₄ (M = Mn, Co, Ni), and LiFeₓMn₁₋ₓPO₄), multi-metal and single-metal oxides (LiₓTiₓO₁₂, TiO₂, MnO₂) porous materials with controllable pore characteristics using various templates (PMMA, PS, PPy, and SiO₂) in either water or organic-solvent-based systems. Porous materials with even smaller pore sizes (e.g., sub-nano scale) may also be controllably synthesized using the current methodology, if the proper sub-nano template materials are selected and applied. Therefore, we believe that this general and convenient strategy can lead to rapid advancements in the development of various precisely tunable porous materials for numerous energy, environment, and catalysis applications.

Methods
Synthesis of PMMA template. The PMMA template was synthesized using an emulsion polymerization method according to the literature. Sodium dodecyl sulfate (SDS) was used as the surfactant, and potassium peroxydisulfate (KPS) was used as the initiator. First, SDS was dissolved in distilled water at room temperature, and methyl methacrylate (MMA) was added before the solution was heated to the preset temperature. Then, the KPS solution was added drop-wise, and the reaction continued for 4 h at the same temperature. The solution began to turn opaque when the PMMA polymerization started; finally, a milky white colloidal solution formed. The templates were washed and collected by centrifugation and re-dispersed in the solvent. By carefully adjusting the synthesis conditions, a series of PMMA templates with various particle diameters (30–200 nm) were successfully synthesized, as summarized in Supplementary Table S1.

Synthesis of PPy template. Polypyrrole (PPy) nanoparticles were synthesized in a water-soluble polymer/metal cation system according to a previous report. Briefly, 2.58 g of polyvinyl alcohol (PVA) was dissolved in 204 mL of distilled water with stirring, and 1.54 g of FeCl₃ was added. After a few minutes, pyrrole monomer was introduced, and the molar ratio of FeCl₃ to pyrrole was set as 2.3. The solution turned black within a few minutes and was continuously stirred for 3 h. The PPy nanoparticles were washed several times with distilled water to remove the impurities and collected by suction filtration.

Synthesis of PS template. The polystyrene (PS) template was synthesized by emulsion polymerization as described in the literature. First, 5 mL of styrene was dissolved in 150 mL of distilled water. The solution was heated to 70 °C, and an aqueous solution of 0.25 M K₂S₂O₈ was subsequently added to initialize the polymerization. The mixture was kept at 70 °C for 4 h, filtrated and washed to obtain the PS template.

Synthesis of SiO₂ template. The SiO₂ template was synthesized according to the literature. First, 9 mL of ammonia, 16 mL of ethanol and 25 mL of distilled water were mixed, and another solution of 4.5 mL tetraethyl orthosilicate (TEOS) and 45.5 mL ethanol was added. Then, the solution mixture was retained in an ice water bath for 6 h to obtain the suspension of SiO₂ spheres. Finally, the products were centrifuged and washed with ethanol several times.

Synthesis of porous LiFePO₄. To prepare porous LiFePO₄ samples, iron nitrate, lithium acetate, and phosphoric acid were used as the source materials. In a typical synthesis, 4.04 g of iron nitrate was first dissolved into 1.6 mL of distilled water; then, 1.02 g of lithium acetate and 0.68 mL of phosphoric acid were added, and the solution was stirred for 3 h to ensure homogeneity. Then, a specific amount of PMMA template was added, and the mixture was stirred for another 2 h. The mixture was subsequently rapidly frozen using liquid nitrogen and dried in a vacuum freezing dryer for 72 h. The dried samples were slowly heated to 220 °C, maintained at this temperature for 3 h to further condense the inorganic precursor, heated to 600 °C and maintained at this temperature for another 3 h. Various amounts of PMMA templates and templates with different diameters were used to tune the porous characteristics of the product. The samples were calcined in a reductive atmosphere (90% argon and 10% hydrogen) to ensure that Fe (III) was completely reduced to Fe (II) species. Porous LiFePO₄ sample was prepared with the PPy template. The synthesis processes were similar to those with PMMA, but the PPy template was used.

Synthesis of porous LiMPO₄ (M = Mn, Co, Ni) and LiMn₀.₅Fe₀.₅PO₄. The synthesis processes of porous LiMPO₄ (M = Mn, Co, Ni) and LiMn₀.₅Fe₀.₅PO₄ were identical to those of LiFePO₄, except Fe(NO₃)₃·9H₂O was replaced by Mn(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O or their combination.

Synthesis of porous LiₓTiₓO₁₂ and TiO₂. First, 0.2 g of ethyl cellulose was dissolved into 20 mL of tertiary butyl alcohol, and 6.0 g of Ti(SO₄)₂ and 2.1 g of LiH₂PO₄ were added. Then, the solution was heated to 50 °C and stirred for 3 h to ensure the homogeneity. Subsequently, 2.3 g of PMMA template was added to this solution, and the mixture was stirred for another 2 h. The mixture was rapidly frozen using liquid nitrogen and dried in a vacuum freezing dryer for 72 h. Then, the sample was heated at 5 °C/min to 220 °C and held at this temperature for 3 h to further condense the inorganic precursor. Subsequently, the sample was heated at the same rate to 800 °C and remained at this temperature for 16 h. The final product was obtained after natural cooling to room temperature. For porous TiO₂, the synthesis process was similar to that of LiₓTiₓO₁₂, except for the absence of LiH₂PO₄.

Synthesis of porous MnO₂. Porous MnO₂ materials were synthesized with both PS and SiO₂ templates. For the PS template, typically, 0.20 g of PVP and 12.55 g of Mn(NO₃)₂·4H₂O were first dissolved in 10 mL tertiary butyl alcohol, and 6.0 g of Ti(SO₄)₂ and 2.1 g of LiH₂PO₄ were added. Then, the solution was heated to 50 °C and maintained at this temperature for 16 h. The final product was obtained after natural cooling to room temperature.
butyl alcohol, and 1.45 g of PS was added. The mixture was stirred for 4 h, rapidly frozen using liquid nitrogen, and dried in the vacuum freezing dryer for 72 h. Finally, porous MnO₂ was obtained after calcination in air at 400 °C for 3 h. For the SiO₂ template, all procedures were similar, except the SiO₂ template was used instead of PS. Because of the thermal stability of SiO₂, a diluted hydrofluoric acid was used to etch away the templates after the thermal treatments. Porous MnO₂ was finally obtained after washing with distilled water and drying in a vacuum drying oven.

**Characterization.** X-ray powder diffraction (XRD) was used to identify the purity and crystallinity of the samples, and the diffraction data were collected using an Xpert Pro MPD diffractometer with Cu Kα radiation (λ = 0.15418 nm) and 20 angles from 20° to 80°. SEM investigations were conducted using a scanning electron microscope (SEM, PHILIPS XL30 TMP) with an acceleration voltage of 15 kV. The nitrogen sorption isotherms were measured on Autosorb-1-MP/LP at the boiling point of liquid nitrogen, and the specific surface area was calculated using the multipoint Brunauer-Emmett-Teller (BET) method.

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**Author Contributions**

Y.K.Z. and X.H.T. conceived and designed the experiments, analyzed the results and wrote the manuscript. X.H.T., P.C.W., M.H. and G.D.D. performed the experiments and analyzed the results. All authors discussed the results and commented on the manuscript.
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