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Shaped crystalline aggregates of comb-like polyethyleneimine for biomimetic synthesis of inorganic silica materials

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ABSTRACT

Biomimetic synthesis of shaped functional inorganic materials is still a hot issue. In this work, we investigated the influence of crystallization conditions on formation of crystalline aggregates from comb-like polyethyleneimine (cPEI). A range of well-controlled polymeric aggregates rich in basic amine groups were prepared through a crystallization-driven self-assembly of cPEI under varied conditions such as different crystallization media (including solvent type and composition) and temperature, as well as the presence of metal cations of different valence. Meanwhile, these crystalline aggregates were applied as catalytic templates to replicate silica with corresponding structures and shapes. The cPEI templates and the templated silica products were mainly subjected to scanning electron microscope (SEM) observation, Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) measurements. The results indicated that cPEI was a very effective template component for the construction of specially structured silica materials being due to the special crystallites growing behavior of cPEI.

1. Introduction

Construction of functional inorganic materials having multiple shape and hierarchical structure has been attracting considerable interest in the fields of materials science and biomedical applications [1–5]. For example, well-controlled silica materials with various nanostructures, *e.g.*, sheet-like [5–7], fibrous/tubular [5,8–10], (hollow) spherical nano-objects [5,11–15], and several micrometer-sized hierarchical structures [16–23], have been reported. In terms of synthesis approach, template-directed biomimetic technology using various polyamine (or polypeptide)-bearing self-organizers as catalytic template has been widely developed to prepare the shaped inorganic oxides such as silica and titania because of the simple procedure and very mild conditions, for example, in water medium and at room temperature, in which the amine groups of polyamine play a key role in effectively promoting hydrolytic condensation of the precursors such as tetramethoxysilane or chelated titanate to produce silica or titania; meanwhile, the shape can also be duplicated from the organic template to the corresponding inorganic matter [24]. Namely the template itself can act as catalyst to control the biomineralization reaction temporally and spatially. Therefore, bio-template design and construction becomes a vital factor for development of inorganic functional materials with novel morphology and structure.

Polyethyleneimine (PEI) as a unique polyamine is composed of many secondary amine groups in its macromolecular backbone [20,21]. It is insoluble in aqueous media at room temperature but can well dissolve in hot water (above 60 °C) and crystallize during cooling process, and self-assemble to form shaped crystalline aggregates with distinctive structures. Such polyamine aggregates via crystallization-driven self-assembly are versatile catalytic templates for biomimetic mineralization. In our previous report [16–24], lots of hierarchical templated amorphous silica structures such as nanowires, fibrous bundles, nanofiber-based networks and platelets were prepared employing linear PEI or star-like PEI as a mediator with a change of the crystallization conditions (*e.g.*, media type and composition, or introduction of small molecular additive such as metal ions and organic guest, *etc.*) [17,18,20]. It is demonstrated that the shape and fine structure of crystalline PEI aggregates strongly depend on not only the physical property of crystallization media but also the macromolecular architecture. We have studied the templating role of the aggregates from linear PEI and six-arm star-like PEI formed under same conditions [18,20]. For example, nanofiber-packed dendritic silica was obtained in the presence of pre-organizers of linear PEI in water/methanol (50/50 in volume) medium, while the fan-like structured silica was formed

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in star-like PEI system under same condition. Moreover, the shapes can be well duplicated from PEI crystalline aggregates to the corresponding silica in silicification process.

Inspired by this, we recently synthesized a novel type of PEI, *i.e.*, comb-like PEI (denoted as cPEI) [25], which consists of polystyrene main chain and densely-grafted linear PEI side chains. Herein, we aim to systematically investigate the crystallization-driven self-assembling behavior of the cPEI under varying conditions by which produce more novel structured crystalline aggregates that were used as catalytic templates for silicification, i.e., hydrolytic polycondensation of tetramethoxysilane to obtain corresponding structured silica controlled by cPEI crystallization conditions.

2. Results and discussion

2.1. Synthesis of cPEI with different composition

Three comb-like polyethyleneimines (cPEI)s with different side chain and/or main chain composition, *i.e.*, P(CMS-*g*-$PEI_{69})_{64}$, P(CMS-*g*-$PEI_{69})_{127}$, and P(CMS-*g*-$PEI_{121})_{127}$ which is denoted as cPEI1, cPEI2 and cPEI3, respectively, were synthesized according to our previously reported method [25]. The characteristics of these samples are shown in Table 1. Both the cPEI1 and cPEI2 had the same polymeric degree in side chains. In contrast, the cPEI3 containing the same main chain length with that of cPEI2 is also designed.

2.2. Formation of cPEI aggregates and their templating role in silicification

Following a typical procedure (shown in Scheme 1) for crystallization-driven self-assembly of PEI in our group, at first, a certain amount of cPEI polymer was added into aqueous solution and then heated to about 80 °C to give a clear solution. As the temperature decreases to room temperature gradually, the former solution system becomes white turbid, which means that the crystalline cPEI aggregates with a larger size are formed during the cooling process. Then silica deposition was performed by mixing tetramethoxysilane (TMOS) and the pre-organizers of cPEI at room temperature. The final white powders were collected by centrifugation and characterized by scanning electron microscopy (SEM). Here we mainly discussed the influence of the crystalline aggregates obtained from certain conditions such as cPEI concentration, polymer composition, the type and component of medium (water, water/methanol, water/acetone and water/DMF), metal-ion additive (K^+, Cu^{2+}, Fe^{3+}) and temperature on the shape and structure of the final silica which was replicatively produced on the cPEI crystalline aggregates.

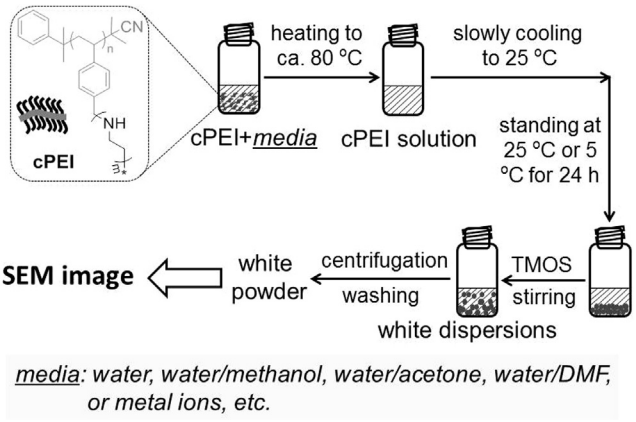
2.2.1. Concentration of cPEI

It is well-known that concentration of templates is one of the important factors in crystallization-driven self-assembly process. It can direct and influence the morphology and even fine structure of self-organizers. Therefore, we first discussed the self-assembly

Table 1
Characteristics of cPEIs used as the template sources.

Entry	Sample[a]	M_n (kg mol^{-1})[b]
cPEI1	P(CMS-*g*-$PEI_{69})_{64}$	356.3
cPEI2	P(CMS-*g*-$PEI_{69})_{127}$	707.1
cPEI3	P(CMS-*g*-$PEI_{121})_{127}$	1228.9

[a] Each EI unit of comb polymers contains two crystal water.
[b] The molecular weight of cPEI was calculated according to ^{1}H NMR data of the crude polymerization products.



Scheme 1. Schematic illustration of the preparation of cPEI crystalline aggregates and multiply shaped silica products employing cPEI aggregates as catalytic templates.

behavior of cPEI1 with the concentration of 0.25, 0.50, 0.75, and 1.0 wt% in water/methanol (50/50 in volume) medium, respectively. As can be seen in Fig. 1, SEM images showed the different morphologies with an adjustment of cPEI1 concentration. For the system containing 0.25 wt% of cPEI1, silica chips with irregular morphology were obtained (Fig. 1a, e). As the concentration increased to 0.5 wt%, the well-controlled micrometer-sized silica hybrids of nanolamella-based double-wing fan (DWF) arrays were formed (Fig. 1b, f). Also, with the higher concentration of 0.75 wt% (Fig. 1c and g) and 1.0 wt% (Fig. 1d and h), the nanolamella-based DWF shape still existed, but it tended to form much longer and more narrow structure. Since methanol is a good solvent for cPEI at room temperature, thus the crystallization of cPEI can be suppressed in the presence of methanol. In the mixed medium with high volume fraction of methanol, when the cPEI concentration is 0.25 wt%, it is difficult to crystallize to form regular aggregates under such a low concentration of cPEI. As the increase of polymer concentration, silica product having a regular morphology was obtained, indicating that its good crystallization behavior negates the negative effect caused by solubilization when the cPEI concentration is above 0.5 wt%. Therefore, we selected the cPEI concentration of 0.5 wt% in the following experiment.

2.2.2. Composition of cPEI

We investigated three cPEIs with different side chain and/or main chain length, respectively. As shown in Fig. 1b, f and Fig. 2, it can be seen that the silica hybrids from cPEI1 and cPEI3 appeared as the same DWF shape in water/methanol (50v/50v), whereas, that of cPEI2 revealed a relatively irregular DWF morphology with a smaller size, namely the cPEIs with a similar ratio between main chain and side chain showed a better crystallization performance.

2.2.3. Self-assembling media

As mentioned in our previous reports concerning linear and star-like PEI system, the type and composition of crystallization media play a key role in adjusting the morphology of pre-organizers in the crystallization process. For example, shaped silicas with varied morphology were given in the presence of pre-organizers formed in neat water, water/methanol, water/acetone, and water/DMF medium systems, in which methanol, acetone and DMF are typical water-miscible solvents, but these organic solvents have different dissolving ability for PEI, *i.e.*, methanol is a good solvent, acetone is a non-solvent, but DMF is a poor solvent for PEI [20,25]. For comparison, herein we investigated the self-assembly behavior of cPEI in same medium system with that of linear and