Amino-functionalized polymethylmethacrylate-co-polyethyleneimine (PMMA-co-PEI) as a template to fabricate nano-silica

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Abstract
Polymer template method is a general and facile to fabricate nano-structural matters. Some amphiphilic polymers or co-polymers were used as templates to synthesize nano-silica. In this contribution, polymethacrylate (PMMA) employed was a commercial hydrophobic acrylate polymer and grafted with a strong hydrophilic polyethyleneimine (PEI, a densely amino-groups polymer) via aminolysis reaction, which was monitored and identified by means of FT-IR. The aminolysis reaction was optimized and the suitable reaction time was 12 h at 110 °C. The obtained copolymer, PMMA-co-PEI was applied as a template to prepare nano-silica spheres that was characterized by a scanning electron microscope (SEM). When the dosage was 1 wt% of purified PMMA-co-PEI, the resultant nano-silica had uniform particle size, and average diameter of 311 nm. When the dosage of PMMA-co-PEI was increased to 2 wt% or 4 wt%, the resultant particles became bigger and inclined to aggregate. Nano-silica afforded by this template method will be a promising material in application of catalysis, energy, biology and chromatographic analysis and the copolymer of PMMA-co-PEI will be a template for producing metal oxide nano-spheres.

1. Introduction

Polyamines are low-molecular-weight compounds or polymers with multiple amino groups, such as, ethylenediamine, diethylenetriamine, triethylenetetramine and polyethyleneimine (PEI). Due to the alkalinity of amino groups and the coordination complexation of nitrogen atoms, the polyamines polymers are often used in the preparation of nanomaterials [1], gene delivery system [2–5], removal of heavy metal ions [6, 7], water treatment [8, 9], etc. Polyethyleneimine is hard to be applied in medium or non-polar organic systems because of their strong hydrogen bonding and hydrophilicity. It is also difficult to stabilize micelles independently in aqueous solution systems and prepare stable nanostructured materials.

Other modified polyamines with hydrophobic backbone have been paid more and more attention. An aminated styrene was afforded by the process of nitration, reduction, Michael addition, aminolysis reactions [10]. The obtained amino-styrene was employed as a template for the synthesis of silver nanoparticles. Chen et al prepared a polyaniline through aminolysis of polycrylonitrile and the resultant polyaniline was used to remove heavy metal chromium (VI) [11]. Chemical surface modification of polyethylene terephthalate (PET) fibers by aminolysis and grafting of carbohydrates was conducted [12]. And PET resin waste could be recycled by aminolysis to give some useful amino compounds [13, 14]. As described by Pavlinec et al PMMA beads was cross-linked by diamines via aminolysis reaction [15].

Silicon is the most abundant element in the natural world except for oxygen. It mainly exists in the form of silicon oxide (silica). Silica is widely used in ceramics, metallurgy, construction, chemical industry, machinery, electronics, coatings, medicine, etc. With the development of nanotechnology, low-dimensional nano-silica and its nanostructures have shown promising applications in catalysis [16, 17], energy [18], biology [19] and...
A commercial PMMA powder (molecular weight of 350,000 g mol\(^{-1}\)) containing primary, secondary and tertiary amino groups randomly, N-methyl pyrrolidone (NMP), tetraethoxyl silicon (TEOS), ethanol (EtOH), tetrahydrofuran (THF) and n-hexane (n-Hex) were of analytical grade and purchased from Aladdin Co., Ltd, which were not purified further prior to use. Deionized water was afforded by a reverse osmosis water purifier, UPH-IV-60L.

### 2. Experimental

#### 2.1. Materials

A commercial PMMA (molecular weight of 350,000 g mol\(^{-1}\)) powder, polyethyleneimine (PEI, Mw: 600 g mol\(^{-1}\)) containing primary, secondary and tertiary amino groups randomly, N-methyl pyrrolidone (NMP), tetraethoxyl silicon (TEOS), ethanol (EtOH), tetrahydrofuran (THF) and n-hexane (n-Hex) were of analytical grade and purchased from Aladdin Co., Ltd, which were not purified further prior to use. Deionized water was afforded by a reverse osmosis water purifier, UPH-IV-60L.

#### 2.2. Synthesis of aminated PMMA (PMMA-co-PEI)

5.0 g of PMMA, 5.0 g of PEI, 42.0 g of NMP were added in a 100 ml flask. The reaction solution was stirred by a magnetic stirrer and heated to 110 °C in an oil bath. 12 h later, the reaction was terminated and cooled to room temperature.

The crude reaction solution with no further treatment was used directly to synthesize microspheres of silica. And as control, the reaction solution was post-treated by precipitation to remove NMP and some small molecules. 0.4 g of solution (solid content, N.V.: 20 wt%) added into 5 ml of co-solvents of tetrahydrofuran and n-hexane (THF/n-Hex = 1/2, v/v) for precipitation, and standing for 1 h, the sticky precipitate was obtained. After dried in vacuum oven at 40 °C, 0.07 g of sticky liquid was given with yield of 87% and employed as template to synthesize silica particles as well.

#### 2.3. Synthesis of nano-silica

The obtained PMMA-co-PEI solution (solid content, N.V.: 20 wt%) was diluted by deionized water, and the solution of EtOH and TEOS added to prepare nano-silica. As shown in table 1, the dosages of PMMA-co-PEI and purified PMMA-co-PEI were optimized mainly. For example (Run 1), 0.4 g of PMMA-co-PEI solution was added into a 25 ml flask equipped with a magnetic stirrer, and when stirring, 3.6 of water, 3.5 g EtOH added in turn. 0.5 h later, 0.5 g of TEOS charged into this flask. Continued to stir at room temperature (~20 °C) for 5 h, the silica sol was given, and the silica particle could be taken out by demulsification or high-speed centrifugation. After PMMA-co-PEI purified, the procedure as similar as the former was employed to prepare nano silica (Run 4–6, table 1).

### Table 1. The recipe of preparing nano-silica with PMMA-co-PEI used as a template.

| Run. | PMMA-co-PEI (Reaction solution)/g | Purified PMMA-co-PEI/g | H\(_2\)O/g | EtOH/g | TEOS/g |
|------|----------------------------------|------------------------|-----------|--------|--------|
| 1    | 0.4                              | —                      | 3.6       | 3.5    | 0.5    |
| 2    | 0.8                              | —                      | 3.2       | 3.5    | 0.5    |
| 3    | 1.6                              | —                      | 2.4       | 3.5    | 0.5    |
| 4    | 0.4                              | 0.07                   | 3.5       | 3.5    | 0.5    |
| 5    | 0.8                              | 0.15                   | 3.5       | 3.5    | 0.5    |
| 6    | 1.6                              | 0.32                   | 3.5       | 3.5    | 0.5    |
2.4. Characterization

The aminolysis reaction of PMMA by PEI was characterized and identified by means of Fourier transform infrared spectroscopy (FTIR, Nicolet AVATAR 370DTGS) with liquid membrane. The morphologies of obtained nano-silica were observed by means of a scanning electron microscope (SEM, Phenom Pro, Netherlands, 10 kV accelerating voltage).

3. Results and discussion

3.1. Synthesis and characterization of aminated PMMA

The aminolysis reaction was affected mainly by temperature, time and pH value \[15\]. In the aminolysis reaction of PMMA and PEI used NMP as solvent, the conversion and process was monitored qualitatively by dispersity or solubility of reaction products in water. At the beginning, the PMMA was not grafted enough PEI chain, and easy to precipitate when the reaction solution dropped into water. After 8 h later, there was no precipitate when the reaction solution was dropped into water. While the reaction time was extended to 12 h, there was some insoluble products in the bottom of reaction flask, which indicated more side reactions taken place, and over cross-linking PMMA-co-PEI by-products produced, shown in the scheme 1.

The sample of reaction solution was taken, and solvent evaporated out to give crude product identified by means of FT-IR, shown in figure 1. After dried in vacuum oven at 40 °C, the precipitate of PMMA-co-PEI by cosolvent of THF/n-hexane was characterized (figure 1).

The absorption peaks at 2995 and 2950 cm\(^{-1}\) were assigned to -CH\(_3\) of PMMA, and the peak at 1730 cm\(^{-1}\) was a stretching vibration of C=O of ester (–COO–) \[29\]. After aminolysis reaction, the new peak at 1677 cm\(^{-1}\) was appeared in the IR spectra of PMMA-co-PEI and its precipitate (purified PMMA-co-PEI), which was assigned to C=O (–CONH–) of resultant amide. The absorption bands at about 3428 cm\(^{-1}\) can be assigned to amino groups (–NH\(_2\), –NH) originated from PEI.

3.2. Preparation of nano-silica using PMMA-co-PEI as a template

The recipe of fabricating nano-silica was shown in table 1, and the effect of PMMA-co-PEI without purification on average diameter of nano-silica spheres shown in table 2 and figure 2. The as-prepared nano-silica spheres was growing larger in average diameter when the dosage of PMMA-co-PEI increased from 1 wt% to 2 wt%. The particle size distribution width was narrower when 1 wt% PMMA-co-PEI used, compared with figures 2(b) and (d). And obviously, there were two or three particles aggregated in figure 2 when 2 wt% PMMA-co-PEI employed, which caused wide particle size distribution. While the dosage of PMMA-co-PEI was raised to 4 wt%, large amount of resultant nano-silica particles gathered together to form aggregates, as shown in figures 2(e) and (f).

The purified PMMA-co-PEI was used as template and the effect of its content on average diameter of silica spheres also investigated. As shown in table 3 and figure 3. The dosages of purified PMMA-co-PEI was like those shown in table 2 and the average diameters of as-prepared silica microspheres also became larger with the dosage increasing but much smaller when similar dosage used. 2 wt% of PMM-co-PEI gave nano silica with 557 nm
and purified one afforded 353 nm (table 3). Compared with figures 2(d) and 3(d), the particle size distribution width of the later was narrower. However, the polydisperse index (PDI) was reduced with dosage of PMMA-co-PEI increasing. More interestingly, the resultant nano silica via purified PMMA-co-PEI had irregular spheres when the dosages were lower than 2 wt% (figures 3(a) and (c)), and they would go regular when the dosage up to 4 wt% (figure 3(e)). The purification process via precipitation of THF/n-hex cosolvent removed the high polar solvent of NMP and some lower molecular weight molecules, which maybe resulted easily in aggregating, i.e., colloidal stability was broken down.

### 4. Conclusion

A template method is general and facile to fabricate nano-structural matters. In this study, a copolymer, PMMA-co-PEI were synthesized firstly and identified by means of FT-IR. The ester of PMMA was aminolized successfully to form amide and the reaction affected mainly by reaction temperature and reaction time. The crude PMMA-co-PEI and those given via precipitation of cosolvent of THF/n-hex were employed to synthesize nano-silica. The particle sizes of as-prepared nano-silica became lager with the dosage of PMMA-co-PEI increasing. The purified PMMA-co-PEI gave silica microspheres with much smaller size and narrower distribution. And interestingly, the spheres given by purified PMMA-co-PEI were irregular when dosage lower than 2 wt%, which would be explored further in the future. This work suggested a template method to afford nano-silica having controllable particle size and narrow particle size distribution width, which will be applied in chromatographic separation, environment, catalysis, etc.
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Figure 2. The morphologies of obtained nano-silica and particle size distribution. (a): 1 wt% of PMMA-co-PEI and (b): particle size distribution; (c): 2 wt% of PMMA-co-PEI and (d): particle size distribution; (e) and (f): PMMA-co-PEI, 4%, magnification is 5,000 ×, 30,000 ×, respectively.

Table 3. The effect of dosage of purified PMMA-co-PEI on average diameter of nano-silica.

| Run | PMMA-co-PEI, wt% | TEOS, wt% | Solv., wt% | Aver. Diam., nm | PDI |
|-----|------------------|-----------|------------|-----------------|-----|
| 1   | 0.9              | 6.6       | 92.5       | 311             | 0.64|
| 2   | 2                | 6.5       | 91.5       | 353             | 0.34|
| 3   | 4                | 6.4       | 89.5       | 761             | 0.24|
Data availability

The data to support the findings of this study is available from the corresponding authors upon request.
Conflicts of interest

There are no conflicts of interest related to this paper.

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