Preparation and characterization of PPy-CD nanospheres with a coreshell nanostructure

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ABSTRACT

A facile strategy for fabricating the polypyrrole-β-cycledextrin (PPy-CD) nanospheres with a unique coreshell structure was presented in this paper. The prepared nanospheres have a uniform nano-size with a narrow size distribution. The PPy-CD nanospheres were successfully synthesized via a simple ultrasonic treatment by mixing pyrrole and β-cycledextrin (β-CD) in the ethanol/aqueous solution at room temperature, and $FeCl_3$ was added as an oxidant. With the aid of $FeCl_3$, a continuous polypyrrole (PPy) layer was formed on the surface of β-CD through the oxidative polymerization of pyrrole. These PPy-CD nanospheres were extensively characterized by scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). It was found that the prepared PPy-CD nanospheres have a clear coreshell nanostructure.

Keywords: nanospheres, coreshell structure, inclusion complex, molecular template

1 INTRODUCTION

The delivery of unique nanospheres has aroused wide attention due to the potential applications in optical,[1] electrical,[2] magnetic,[3] and biological devices.[4] Special attention has recently been paid to the methods for controlling the size and distribution of polymer nanospheres, because the size and distribution of nanospheres would significantly influence the application of nanospheres in the advanced devices.[5-7] Even though nanospheres have commonly been produced by the template polymerization and supramolecular self-assembly, effective controlling the size or structure of polymer nanospheres has remained a challenging task. For this reason, diverse synthetic ways to prepare nano-sized polymer spheres have been continuously developed. To prepare polymer nanospheres, smaller templates (e.g. gold nanoparticles) or other methods (e.g. in situ polymerization on template particles) have to be used instead. However, the techniques mentioned above can only be used to prepare hollow spheres with a specific size range. Thus, developing effective strategies to fabricate stable nanosphere with controllable size is still an ongoing challenge. The purpose of this study is to fabricate PPy-CD nanospheres with a narrow size distribution via oxidative polymerization of pyrrole in the presence of β-CD. The β-CD plays the roles of both stabilizer and template material, and introduces hydrophobic cavity. The β-CDs cavities were shown to serve as molecular templates, in which pyrrole monomer molecules anchor and initiate the oxidative polymerization of pyrrole.

2 EXPERIMENTAL

The PPy-CD nanospheres were produced by simply adding the pyrrole monomer to β-CD aqueous solution, and add iron (III) chloride as the oxidant. A representative polymerization for the nanospheres was as follows: β-CD was added into 100 mL aqueous solution in a 150 mL glass flask under constant stirring for 30 min. Then, 10 mmol pyrrole was injected to the β-CD solution and stirred vigorously for 30 min. $FeCl_3$ (2.28 g, 10 mmol) was dissolved in 100 mL ethanol to prepare an oxidant solution. The two solutions were then carefully transferred to a beaker. During the mixing process, the solution color changed from transparent to dark green, indicating that the polymerization takes place instantaneously. The polymerization was continued for about 24 h at 25 ^oC. The resulted solution was filtered and washed with sufficient hot water for one hour to wash out the remained β-CD and ferric trichloride. Finally, the PPy-CD nanospheres were obtained by precipitating with acetone and drying in the vacuum at 40 ^oC for 24 h. Pure PPy particles were prepared in the similar method but in the absence of β-CD.

3 RESULTS AND DISCUSSION

3.1 Formation of PPy-CD Spheres

In general, PPy can be prepared via oxidative polymerization of pyrrole involving different highly reactive intermediates. Furthermore, the pyrrole/CD complex can be polymerized in aqueous solution under oxidative conditions by adding the iron(III) chloride as an oxidants. The overall procedure for producing PPy-CD nanospheres involved several steps, as illustrated in Figure 1. The first step was the formation of pyrrole/β-CD inclusion complex in aqueous solution. β-CD was chosen as the molecular template because it can include the pyrrole monomer into its hydrophobic cavity, and can be as the molecules anchor and can initiate a desired reaction.[8] The subsequent step involved the formation of a PPy polymeric shell on β-CD surface. It was found that pyrrole preferred to polymerize around β-CD to form a PPy-CD nanosphere. β-CD cavity can be isolated in aqueous solution. When pyrrole molecules seeded in these well-separated β-CD cavities, the chemical oxidation growth of PPy was initiated. Then, the well defined PPy-CD nanospheres were obtained.

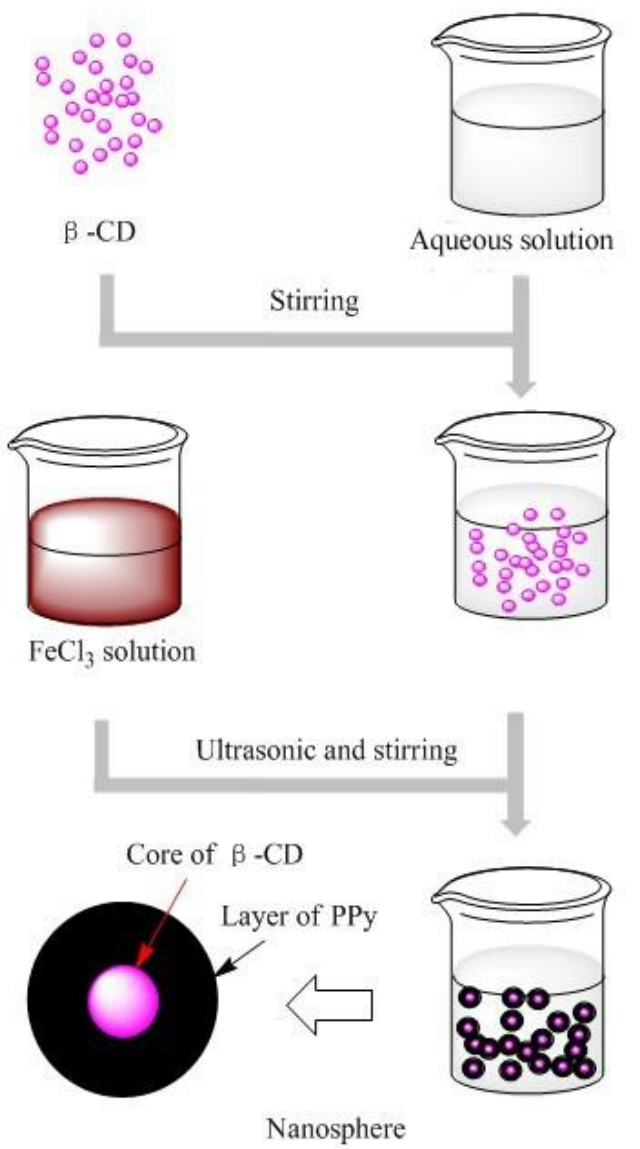

Figure 1. Schematic illustration of the process to fabricate the PPy-CD nanospheres

3.2 Morphology of PPy-CD spheres

The morphologies of the prepared PPy particles and PPy-CD nanospheres were studied by SEM. Figure 2(b) showed the typical SEM images of PPy-CD nanospheres synthesized in 100 ml ethanol at 25 ℃ for 24 h by using a $FeCl_3$/pyrrole molar ratio of 1:1. The SEM images clearly show different organization modes. The PPy-CD system seems to be a more organized system (Figure 2(b))., while the PPy particles show irregular structures (Figure 2(a)). The SEM image of the PPy-CD nanospheres also illustrated that the nanospheres were uniform and the average diameter was 400 nm in size. In the case of β-CD absence, only irregular structures of PPy were obtained.

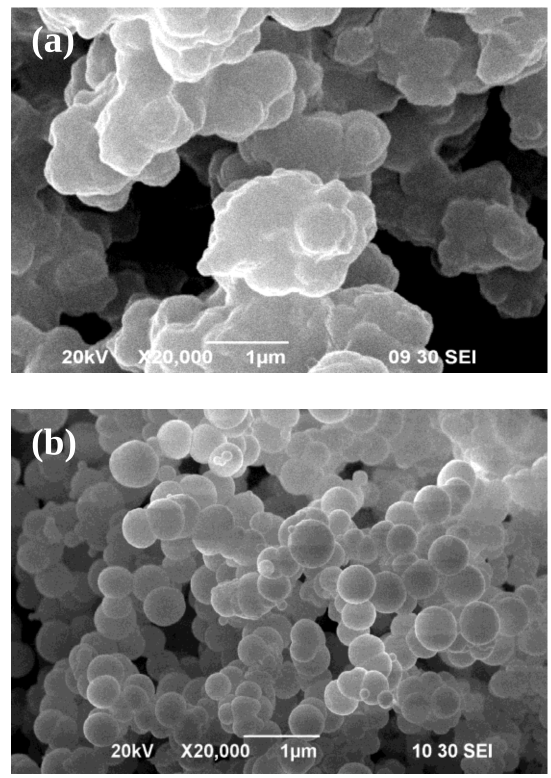

Figure 2. Scanning electron micrographs of (a) Typical SEM image of PPy particles, and (b) PPy-CD nanospheres.

Samples for TEM measurement were dispersed in aqueous solution undergoing a treatment with the sonication process. Representative TEM images of the as-prepared PPy-CD nanospheres were shown in Figure 3. Figure 3(a) shows that PPy particles prepared in the absence of β-CD had the agglomeration morphology. Apparently, Figure 3(b) shows the structure of PPy-CD nanospheres were more oriented and organized than that of PPy particles. Moreover, well defined nanospheres which contained the dark contrast PPy shell and the light contrast β-CD core were readily observed. It indicated that the β-CD as an anchor agent played an important role during polymerization of PPy.

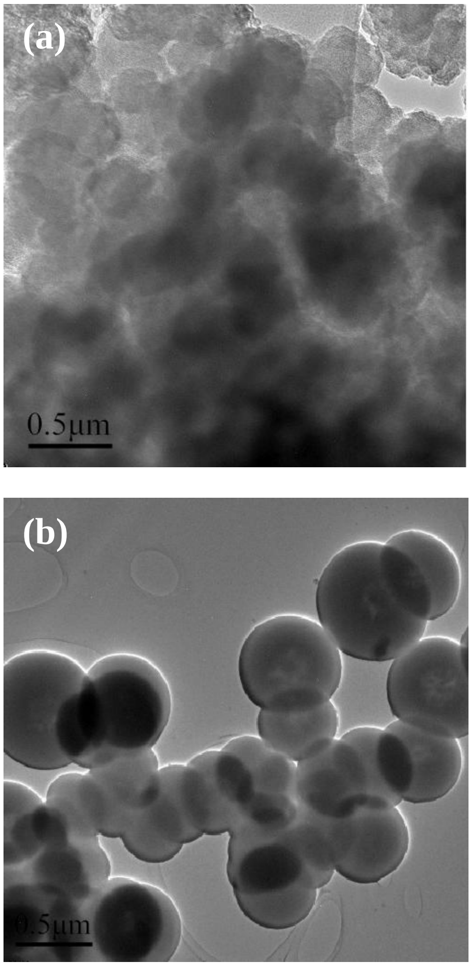

Figure 3. TEM images of (a) PPy particles, and (b) PPy-CD nanospheres

The polymerization of pyrrole around β-CD to form a PPy-CD nanosphere is of major interest when introducting β-CD into the reacting system. In the first step, the β-CD molecules formed the inclusion complex with the pyrrole monomers in aqueous solution. And then, the cavity of β-CD might provide active sites and induce the growth of PPy chains. With the growing of PPy chains, several β-CD molecules will form inclusion complexes with the PPy chain to complete the coating of PPy layers, leading to the formation of PPy-CD spheres. Moreover, β-CD acted as a useful stabilizer to promote a strong interaction between the β-CD and the PPy matrix, the interaction of β-CD and PPy could strengthen the binding force between polymer chains and finally optimize the configuration of polymer.

4 CONCLUSIONS

The PPy-CD nanospheres with the average diameter of 400 nm and highly stability have been successfully fabricated via a one-step polymerization of pyrrole in the presence of β-CD as the molecular template and by using $FeCl_3$ as an oxidant. TEM studies revealed that the prepared PPy-CD nanospheres have a clear coreshell nanostructure. The β-CD as an anchor agent played an important role during polymerization of PPy. Several β-CD molecules will form inclusion complexes with the PPy chain to complete the coating of PPy layers on the β-CD surface, leading to the formation of the PPy-CD nanospheres.

Acknowledgments

We gratefully acknowledge the grants from the Hong Kong innovation technology funding (ITS/003/09) and The Hong Kong Polytechnic University (A-PK10) to support this work.

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