Novel Micro/Nanostructures of Polyaniline in the Presence of Different Amino Acids via a Self-assembly Process

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Novel micro/nanostructures of polyaniline were synthesized via a self-assembly method in the presence of different amino acids, such as tryptophan, lysine, and aspartic acid. It was found that the morphologies, including spinous microspheres, smooth nanospheres, and nanosticks/tubes determined by SEM and TEM images, were related to the kind of different amino acids. The structures of the products were measured by FT-IR spectra and UV–vis spectra.

In the past decades, conducting polymers have been widely studied due to their unique physical and chemical properties.[1] Particularly polyaniline attracted much attention because of its low cost, easy synthesis, good processibility, unique properties which are easily controlled by oxidation and protonation, excellent environmental stability, and potential application in electronic devices.[2] Recently, special attention had been paid on micro/nanostructures of polyaniline which were produced with various strategies such as templates, surfactants, interface polymerization, self-assembly method,[3] and so on, in both chemical and material fields. Wan et al. had prepared PANI microstructure by the self-assembly method, i.e., template-free method to obtain the functionalized composites with electric, optic, and magnetic properties.[4]

As one of conducting polymers, polyaniline can change from an insulating state to a conducting state after doping treatment. Therefore, the electrically conductive form of PANI is usually prepared by chemical polymerization of aniline using an oxidant such as ammonium persulfate (APS) in strong acidic solutions.[5] A purple-colored solution leading to a non-conducting brown precipitate has been prepared when aniline was oxidized in solutions buffered above pH 4. Unbuffered solutions have been used in which the reaction started at a higher pH value, followed by a drop in pH as protons were liberated from the oxidation of aniline, and the pH fell to values of 2 or less. Under these conditions, nanotubes, nanospheres, and nanowires have been observed to form using a wide range of weak acids,[6–9] or even in an initial alkaline condition.[10]

Herein, we succeeded in synthesizing multi-morphologies of polyaniline micro/nanostructures by oxidative polymerization of aniline (An) in amino acids aqueous solution without any external physical or chemical templates and additives. Spinous microspheres, smooth nanospheres and nanosticks/tubes were obtained successfully. In this work, a series of amino acids such as lysine, aspartic acid, and tryptophan were used for their weak acidity and possible biological applications. All of them have extra functional groups such as –COOH, $–NH_2$, or heterocyclic groups besides the –COOH and $–NH_2$ in the same carbon atom. The –COOH group in the amino acids may act as the doping function. The experimental details of the synthesis are described in Supporting Information.[11] It was found that the morphologies, determined by SEM and TEM, were related to different kind of amino acids.

Typical SEM images of PANI nanostructures prepared in the presence of different amino acids are shown in Figure 1. As can be seen, PANI micro/nanostructures produced are nanosticks and micro/nanospheres. The products doped with lysine are hollow microspheres with rough surfaces, and their average sizes are in the range of 2.0–2.5 μm. And doped with tryptophan, hollow smooth nanospheres are observed with diameters of 450–700 nm. Nevertheless, the product doped with aspartic acid was nanosticks with diameters of 250–900 nm. Through the TEM images (Figure 2), it can be seen that the hollow spheres of PANI–tryptophan have smooth surfaces, while microspheres of PANI–lysine with nanometer-sized aciculae are gained. There are some hollow nanotubes in PANI–aspartic acid besides dominating nanosticks.

The UV–vis spectra of the material formed in amino acids solutions were shown in Figure 3. Polyaniline gained in lysine and aspartic acid solutions had strong peak at 378 nm, some 40–60 nm higher than bands due to π–π^* transitions in pure PANI samples, with a further peak seen at 273 nm. These lie in the same position as bands ascribed to substituted benzoquinones formed during aniline oxidation.[9] However, the product prepared in tryptophan solution showed much weaker absorption at around 390 nm. A more detailed UV–vis study is now in progress.

Both typical characteristic bands of PANI and amino acids were observed in the FT-IR spectra, as shown in Figure 4. Peaks

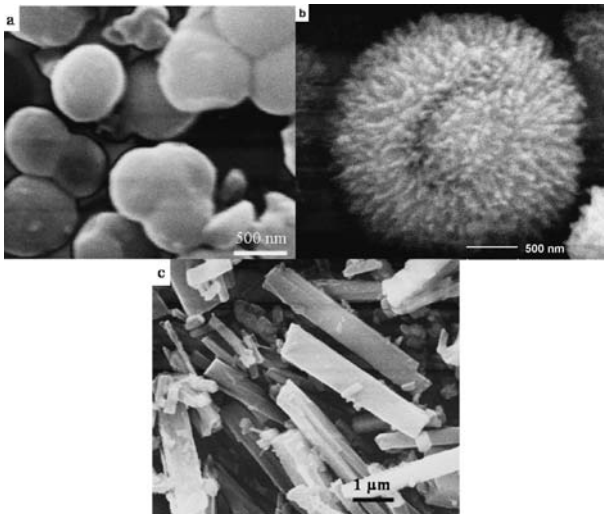

Figure 1. Typical SEM images of the representative samples. They were synthesized with different amino acids: (a) tryptophan; (b) lysine; (c) aspartic acid.

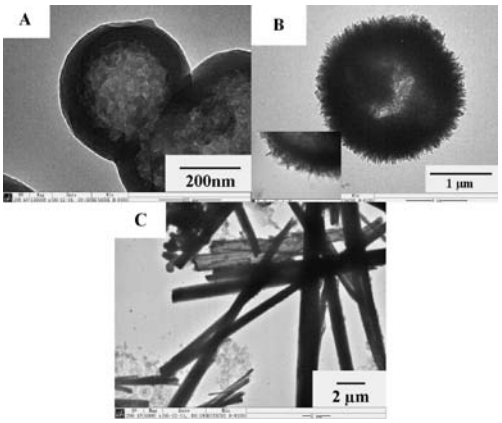

Figure 2. Typical TEM images of the samples in the presence of different amino acids: (A) tryptophan; (B) lysine; (C) aspartic acid.

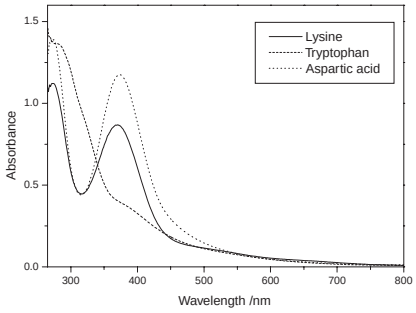

Figure 3. UV–vis spectra of samples in the presence of different amino acids.

at around 1500 and 1580 cm^{-1} were ascribed to PANI C=C stretching vibration of benzenoid and quinoid rings, respectively, and at 1145 cm^{-1} to a C–H bending vibration. The peaks at 825 and 1345 cm^{-1} were due to PANI C–H out-of-plane bending and C–N stretching vibration, respectively. The absorptions at 3430 and 3250 cm^{-1} were corresponding to the N–H stretching vibration.

A possible mechanism for the formation of PANI micro/nanostructures was proposed. The hydrogen bonding between –COOH group of the amino acid and $–NH_2$ group of PANI played an important role in self-assembly of PANI micro/nanostructures. According to previous reports,[12] the aniline–amino acids salt serves as the "soft template" to form nanotubes or nanofibers of PANI. In aspartic acid solution, the initial pH was below 7, the nanosticks and nanotubes were obtained. But in lysine and tryptophan solutions, the initial pH was around 7 or above, spherical micelles formed by the monomer were regarded as the "soft templates" of the hollow spheres.[13] So spheres formed in the start. With the polymerization proceeding, the aniline–lysine salt serves as the "soft template" to form one-dimension structure. Finally, microspheres with nanometer-sized acicular surfaces were obtained. But the aniline–tryptophan salt could not direct to form the aciculas. That is probably due to the steric hindrance of tryptophan. The further mechanism study is under way.

In summary, we succeeded in synthesizing multi-morphologies of polyaniline micro/nanostructures by oxidative polymerization of aniline (An) in amino acids aqueous solution without any external physical or chemical templates and additives. Spinous microspheres, smooth nanospheres and nanosticks were obtained successfully. A possible mechanism for the formation of PANI micro/nanostructures was proposed.

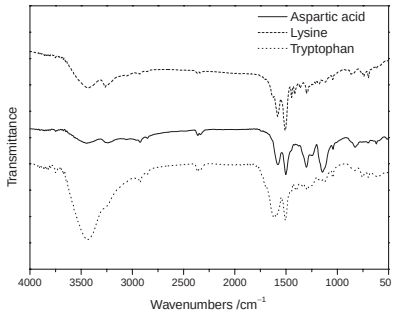

Figure 4. FT-IR spectra of samples in the presence of different amino acids.

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