

## Fabrication of Polyaniline/Ethylcellulose Composite Microspheres by Microencapsulation

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Polyaniline/ethylcellulose composite microspheres were prepared through microencapsulation technique via a modified emulsion–solvent evaporation method. The core was gained through the polymerization of aniline, while the shell was formed by the solidification of ethylcellulose under the condition of the evaporation of organic solvent.

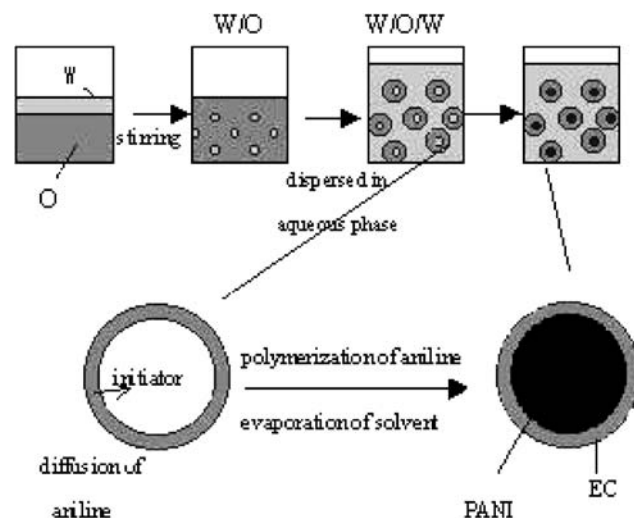
In recent years, functional composite microspheres have increasingly attracted interest because of their potential applications in catalysis,<sup>1</sup> optical device,<sup>2</sup> separation,<sup>3</sup> artificial cells,<sup>4</sup> chemical and biological sensing,<sup>5</sup> etc. At present, preparation of composite microspheres typically involves physicochemical and chemical methods such as layer-by-layer (LBL) method,<sup>6</sup> chemical deposition<sup>7</sup> and emulsion polymerization.<sup>8</sup> Some types of composite microspheres with well size distributions have been prepared by these methods. And the diameters of these microspheres are usually several microns. However, well-dispersed large composite microspheres with several tens of microns have rarely been reported in the literature. And these methods may be only fit to the preparation of some special types of composite microspheres, and some may need many complicated procedures. For example, in the LBL method, it usually uses the polymer or silica colloids as the template, which modifies the surface of the colloids by polyelectrolytes and then coats other functional materials. It is a good way to prepare well-dispersed composite microspheres and control the thickness of shell by the times of coating. But the species of template are limited, which may restrict the components of composite microspheres. So it is necessary to develop other new methods to prepare more types of composite microspheres, and make the procedures simpler or obtain well-dispersed microspheres with large diameter. Microencapsulation is a well-known process in which tiny particles or droplets are covered by a coating or a membrane. There are many methods for microencapsulation, such as emulsion–solvent evaporation, coacervation phase separation, interfacial polymerization, spray coating, multiorifice centrifugal process, and air suspension.<sup>9</sup> The microencapsulation concept was originally used in the ink formulation for carbonless copy paper<sup>10</sup> and has been successfully applied for encapsulation of active agents such as drugs, pesticides and dyes to protect the encapsulated material from environmental conditions or to release the active agent in a sustained and controlled manner into the surrounding medium.<sup>11</sup> However, so far as, little attention has been focused on preparation of functional composite microspheres by microencapsulation.

In this paper, it first reports the preparation of composite microspheres with the diameter of several tens of microns using microencapsulation technique via a modified emulsion–solvent evaporation process. In the traditional emulsion–solvent evaporation method, the polymer particles prepared in advance were directly as the core material.<sup>12</sup> To be different from the traditional emulsion–solvent evaporation method, during the course of the formation of shell, the core was gained via an in situ polymerization of

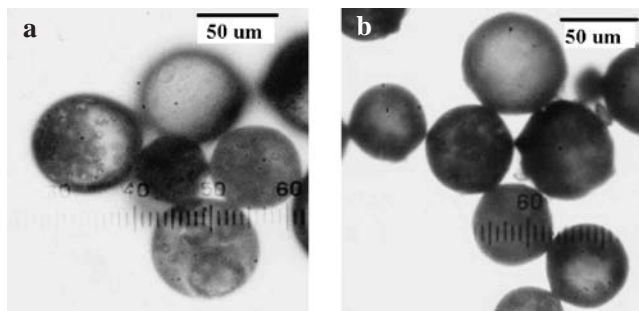
monomer in the emulsion at the same time. Compared with many other methods to prepare composite microspheres, it can easily prepare well-dispersed composite microspheres with large diameter. And it is a simple way that the microspheres can be obtained in one step instead of many steps. Because of the different formation mechanisms, this method can be used to prepare many composite microspheres that cannot be obtained by other methods. Here, ethylcellulose (EC) was chosen as shell material and polyaniline (PANI) as core material.

The composite microspheres were prepared in a water-in-oil-in-water (W/O/W) emulsion. Scheme 1 shows the formation mechanism of PANI/EC composite microspheres. In the oil phase, there are three sorts of materials: monomer of the core material (aniline), organic solvent ( $\text{CH}_2\text{Cl}_2$ ) and shell material (EC). After adding the aqueous solution containing the initiator (ammonium persulfate) into the oil phase, water-in-oil (W/O) emulsion could be obtained. Pouring the W/O emulsion into mass aqueous solution containing gelatin as the emulsifier will lead to form the W/O spherical droplets in the solution. Then aniline will diffuse into the internal aqueous phase from the oil phase, and the cores are gained through the polymerization of aniline in the internal aqueous phase. Simultaneously, the evaporation of  $\text{CH}_2\text{Cl}_2$  from the surface of spherical droplets makes the interfacial precipitation of EC on to the surface of the PANI.

Microscopic image of the EC microcapsules prepared by the same method without the addition of aniline and initiator is shown in Figure 1a. It can be seen that the EC microcapsules are all in spherical shape, and multicore structure can also be observed. The diameter of the microcapsules is about several tens of microns, and the centre of the microcapsules is transparent. Figure 1b shows the microscopic image of the PANI/EC composite microspheres. The shape of composite particles is still spherical like the EC mi-



**Scheme 1.** Scheme for the formation mechanism of PANI/EC composite microspheres.

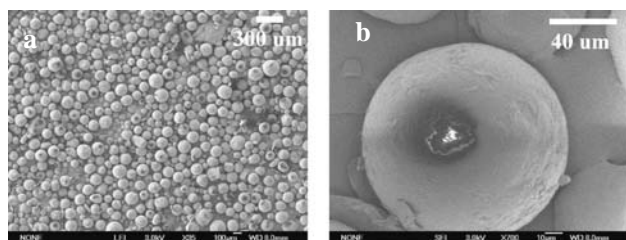


**Figure 1.** Microscopic images of (a) EC microcapsules; (b) PANI/EC composite microspheres.

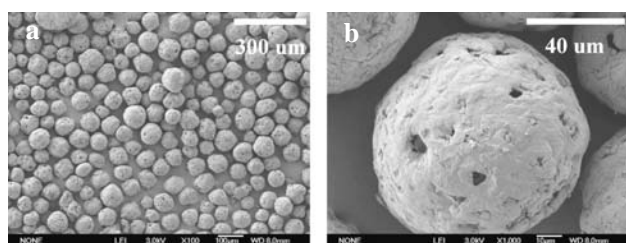
microcapsules. The size of the particles is similar to that of the EC microcapsules, but the centre of the microspheres is darker than that of the EC microcapsules. It indicates that PANI particles were wrapped in the interior of microspheres, which will be further confirmed by the FTIR spectrum.

The SEM images of the EC microcapsules are shown in Figure 2. Figure 2a is the low-magnification image, it can be seen that the EC microcapsules have a fairly narrow size distribution. Figure 2b shows a typical hollow EC microcapsule with a hole, and the surface of shell is smooth. Figure 3 shows the SEM images of the PANI/EC composite microspheres. Figure 3a indicates that PANI/EC composite microspheres are rather uniform, and the surface of shell is rough. As shown in Figure 3b, there are some pores on the microsphere. The difference in the rough degree of the shell between EC microcapsule and PANI/EC composite microsphere can be explained by the formation mechanism of composite microspheres: The core and shell were formed separately in the aqueous and oil phases of the W/O spherical droplet. When the polymerization of aniline was continuously proceeding, the PANI particles were gained. Because the W/O droplet is a soft template, the shape of the PANI particles formed in the aqueous phase of the droplet is not regular. So the interfacial precipitation of EC onto the irregular particles were not uniform, the surface of the shell was rough and had many pores.

The coating thickness of EC shell in the PANI/EC microsphere was 5.6 μm. It was calculated with the help of TGA dia-



**Figure 2.** SEM images of EC microcapsules.



**Figure 3.** SEM images of PANI/EC composite microspheres.

grams, using the second plateau observed in thermograms at 410 °C with the assumption that all particles were of the same thickness with perfect coating.<sup>13</sup> The PANI/EC composite microspheres were characterized by the FTIR and UV-vis. When the composite microspheres were not ground, the characteristic absorption peaks of PANI are not obvious in the FTIR spectrum. But after the composite microspheres being ground, there is an appearance of strong characteristic absorption peaks of PANI. The bands at 1490 and 1150 cm<sup>-1</sup> were assigned to the stretching vibration of benzenoid ring and bending vibration of C-H bonds on aromatic rings of PANI, respectively. This can be explained as follows: PANI particles as the cores were wrapped in the interior of the EC shells. Being ground, EC shells were destroyed and PANI particles were released from the interior of microspheres. The UV-vis analysis of EC microcapsules and PANI/EC composite microspheres in THF was carried out on a 756MC UV-vis spectrophotometer. Contrasts to the spectrum of EC microcapsules, there are two obvious absorption peaks in the spectrum of PANI/EC composite microspheres. The absorption peaks at 300 and 600 nm were due to the  $\pi \rightarrow \pi^*$  transition of the benzenoid ring and the exciton transition of the quinoid ring of PANI. They are both the UV-vis characteristic absorption peaks of PANI.

In summary, the uniform polyaniline/ethylcellulose composite microspheres with the diameter of several tens of microns were successfully prepared by microencapsulation via a modified emulsion-solvent evaporation method. The appearance of the obvious characteristic absorption peaks of PANI in FTIR and UV-Vis spectra indicated that PANI particles were wrapped in the interior of microspheres. It is believed that the high specific area, good stability of this kind of composite microspheres may make them valuable in such applications as electronics and separation. And also it is expected that this convenient preparation route to PANI/EC composite microspheres may be readily extended to the fabrication of composite microspheres of other functional materials.

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