



Synthesis and Characterization of Self-Assembled Porous Microspheres of Poly(*o*-chloroaniline)

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Self-assembled porous microspheres poly(*o*-chloroaniline) have been fabricated by simple oxidative polymerization of *o*-chloroaniline with camphor-sulfonic acid as dopant acid and ammonium persulfate as oxidant. In the synthesis system, formation of micelles of camphor-sulfonic acid in aqueous solution is a key factor in fabrication of porous microspheres of poly(*o*-chloroaniline). The conducting poly(*o*-chloroaniline) microspheres were characterized by means of Fourier transform infrared spectroscopy, UV-visible spectroscopy, X-ray diffraction and scanning electron microscopy. A mechanism has been proposed to explain the formation of poly(*o*-chloroaniline) microsphere which was supported by UV-visible spectroscopy and SEM data.

Keywords: Porous microspheres, Poly(*o*-chloroaniline), Self-assembly.

INTRODUCTION

Microspheres of conducting polymers have attracted much attention because of unique physical and chemical properties¹⁻³. Recently, micro or nanospheres have shown a number of promising applications in fields of controlled drug release, stationary phases for separation, chemical sensor and biosensors and microencapsulation⁴⁻⁶. These versatile applications of porous microspheres of conducting polymers made it an interesting and important subject in the field of material science⁷⁻⁹. Microspheres are generally synthesized by using spherical particle as templates^{10,11}. Self-assembly method, using 'soft templates' such as micelles, attracts much attention for producing porous micro or nanospheres of conducting polymers.

This approach is an inexpensive and simple as it does not involve the required pre- and post-synthesis procedures to prepare and remove the 'hard' templates^{12,13}. Wan *et al.*^{14,15} prepared microspheres of polyaniline (PANI) by self-assembly method with salicylic acid and naphthalene-2-sulphonic acid as dopants. Travas-Sejdic reported self-assembly of microspheres of poly(*o*-methoxyaniline) with *p*-toluene sulphonic acid and poly(methyl vinyl ether)maleic acid as dopant acids and found that the size and morphology of the spheres were dependent on the weight ratio of dopant acid to monomer^{16,17}. Hollow spheres of PANI can also be produced from 'alkali-

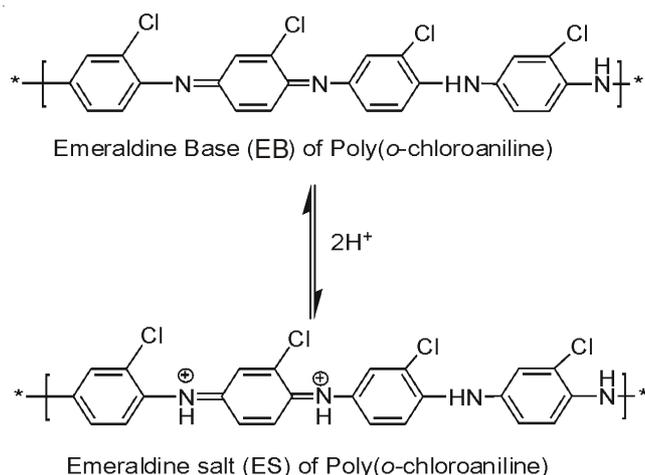
guided' synthesis in which ammonium persulfate (APS) was used to oxidize aniline in alkaline medium of sodium hydroxide or ammonium hydroxide¹⁸. Herein, we report the synthesis of porous microspheres of poly(*o*-chloroaniline) (POC) in aqueous medium by using camphor-sulfonic acid as oxidant. In the synthesis of microspheres, the camphor-sulfonic acid was employed to acts as dopant acid and at the same time the formation of its micelles in aqueous solution play a vital role in fabrication of porous microspheres. To the best of our knowledge, this is the first report to synthesize porous microspheres of poly(*o*-chloroaniline).

EXPERIMENTAL

o-Chloroaniline and ammonium persulfate were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). DDDPA was purchased from Tokyo Chemical Industries (TCI, Shanghai, China). Camphor-sulfonic acids were purchased from Aladdin Chemical Reagent Corporation (Shanghai, China). Methyl orange was obtained from Tianjin Chemicals (Tianjin, China). All the chemicals were of analytical grade and used as received. Distilled water was used throughout the present work.

Synthesis of poly(*o*-chloroaniline) microspheres: In a typical procedure, *o*-chloroaniline (0.48 mmol) was dissolved in 2.5 mL of D-camphor-sulfonic acid (3 M), with addition of DDDPA (0.02 mmol). This mixture solution, being referred to

as solution A, was warmed to 60 °C for 1 min and cooled down to room temperature (25 °C). A solution of the oxidant (solution B) was prepared by dissolving camphor-sulfonic acid (0.48 mmol) into 2.5 mL of 3M D-camphor-sulfonic acid solution. Solution B was rapidly added into solution A and then subjected to vigorous stirring for 30 s. After the polymerization reaction was conducted for 4 h, the crude product was washed with water and methanol several times. The cleaned product was dried in oven at 60 °C for 24 h and used for further analysis. The schematic for the preparation of poly(*o*-chloroaniline) microsphere is presented in **Scheme-I**.



Scheme-I: Schematic formula of EB and its transformation to ES by protonation

Instrumentation: UV-visible absorption spectra of the polymers were recorded on a UV-visible spectrometer (Varian Cary 50). FT-IR spectra were recorded using an IR spectrophotometer (Bruker Vertex 70) between 4000 and 400 cm^{-1} . The samples were prepared in the pellet form by using spectroscopic grade KBr powder. The morphological images of polymers were observed with scanning electron microscope (SEM, Hitachi S-4800, Japan).

RESULTS AND DISCUSSION

Structural characterization: Morphology of the prepared poly(*o*-chloroaniline) microspheres was observed on SEM (Fig. 1). It is clear from these images that the products showed the porous micro-spherical morphology. The size of the microspheres was about 10 μm in diameter and the diameters of the porous pores in the microspheres were more than 500 nm.

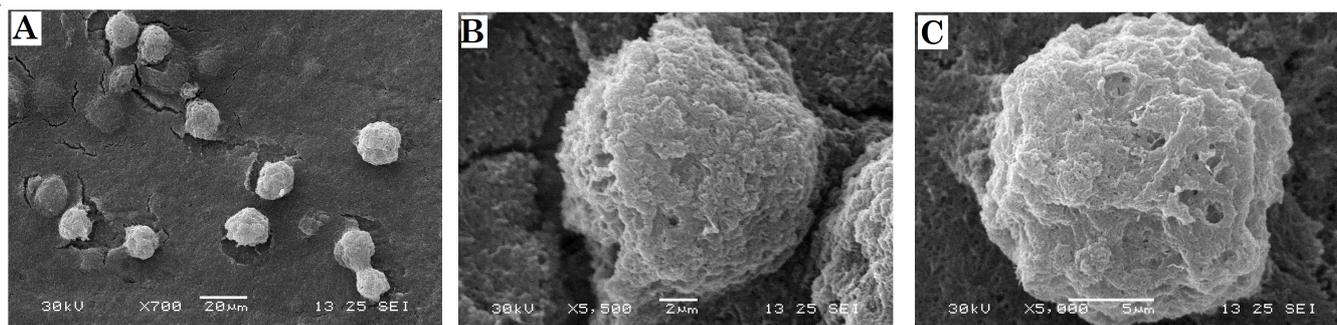


Fig. 1. SEM images of poly(*o*-chloroaniline) synthesized by using D-camphor-sulfonic acid as dopant

Fig. 2 shows the UV-visible absorption spectra of as prepared and de-doped poly(*o*-chloroaniline), being similar to the reported observations for polyaniline¹⁹⁻²², the spectrum of the as-prepared poly(*o*-chloroaniline) shows the absorptions around 900 nm and 400 nm ascribed to the π - π^* transition of the polarons, indicating that poly(*o*-chloroaniline) is in its doped state^{21,23}.

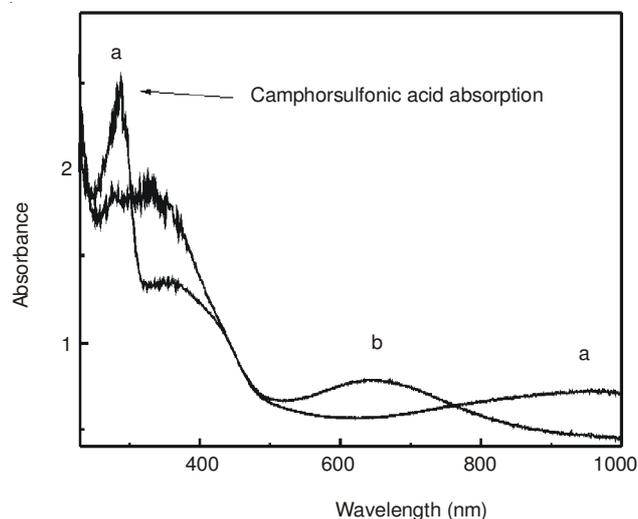
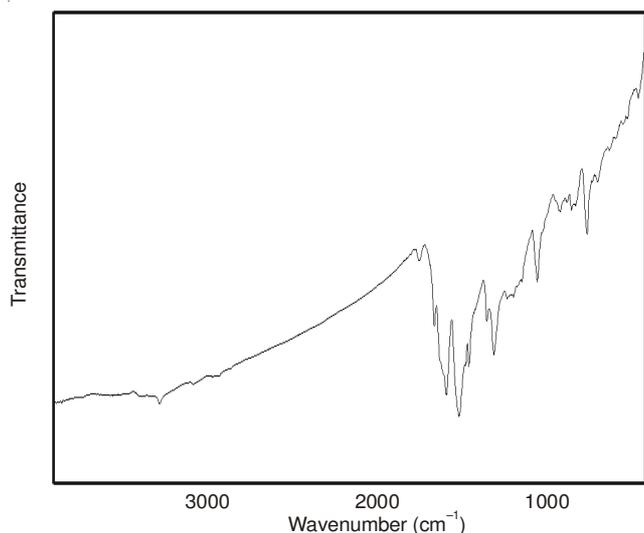
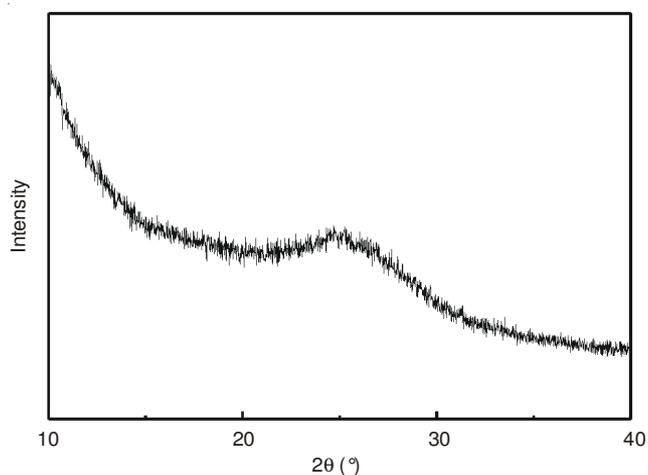


Fig. 2. UV-visible spectra of (a) as-prepared and (b) dedoped poly(*o*-chloroaniline)

FTIR spectrum of poly(*o*-chloroaniline) (Fig. 3) gives two bands at about 1502 and 1577 cm^{-1} , which can be assigned to the non-symmetric C_6 ring modes. The higher frequency vibration at 1577 cm^{-1} has a major contribution from the quinoid rings, while the lower frequency mode at 1502 cm^{-1} shows the presence of the benzenoid ring units. The presence of these two bands clearly shows that the polymers are composed of the amine and imine units. The bands around 1300 cm^{-1} originate from C-N stretching of secondary aromatic amine^{22,23}. The band at 1179 cm^{-1} and that around 837-810 cm^{-1} are primarily due to C-H in plane bending vibrations and aromatic C-H bending²⁴. The bands at 1338-1297 and 700 cm^{-1} are associated with the presence of chloro-moieties in the polymer backbone²⁵.

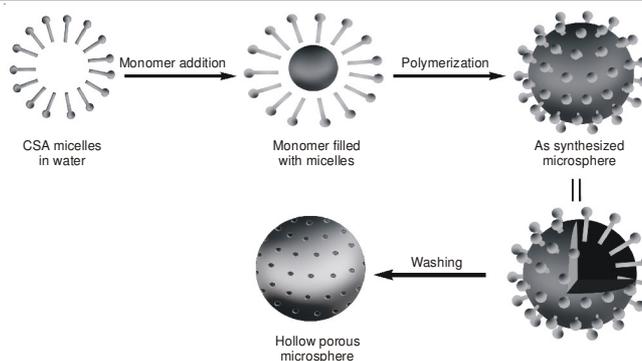
The poly(*o*-chloroaniline) porous microspheres are amorphous and only one broad peak centered at $2\theta = 25^\circ$ may be ascribed to the periodicity parallel to the polymer chain^{26,27}. The XRD pattern of the poly(*o*-chloroaniline) porous microsphere is presented in Fig. 4.

Fig. 3. FTIR spectrum of poly(*o*-chloroaniline) porous microspheresFig. 4. XRD pattern of poly(*o*-chloroaniline) porous microspheres

Mechanism for the formation of porous microspheres of poly(*o*-chloroaniline):

Several mechanisms have been proposed for the formation of porous or hollow spheres of conducting polymers^{13,14,17}. Han *et al.*¹³ suggested that when monomer is added to the aqueous solution, droplets of the monomer are formed in the bulk, which act as templates towards the formation of hollow spheres. After addition of oxidant (camphor-sulfonic acid), the polymerization takes place at the interface of droplets due to hydrophilicity of camphor-sulfonic acid. The monomers would diffuse from interior to exterior of droplet to form hollow structures. Similar mechanism was reported by Sui *et al.*¹⁷, who suggested that micelles composed of poly(methyl vinyl ether-paltmaleic acid) and monomer are formed and with the progress of polymerization monomers being contained in the interior of micelles would diffuse out to the surface leaving a hole inside, which results in the formation of hollow spheres.

In our experiments, when camphor-sulfonic acid is mixed in water, it forms micelles and further mixing with monomer these micelles fill the monomer droplets as shown in Fig. 5. After the addition of camphor-sulfonic acid, two types of polymerizations led to the formation of porous spheres. The first

Fig. 5. Schematic illustration of formation of porous microspheres of poly(*o*-chloroaniline)

one occurs among the monomers in the same micelle (intra micelle) and the second one takes place between the monomers in different micelles (inter micelle). In our previous work, we proposed an "electrical double model" for one dimensional growth of PANI nanofibers²⁸. According to this model, PANI fibers formed at the early stages of polymerization become positively charged due to the protonation of N atom of amine and partial oxidation of PANI chain being surrounded by anions, resulting in the formation of a structure of electric double layers at the interface between the nanofibers seed and solution. The positive charges on the chains of PANI repel the reactive species, which prevents the lateral growth and favors the elongation growth of PANI chains *via* the polymerization at head-sides. This growth pattern of PANI chain in one direction enables it to elongate, giving better fibrillar morphology. But here in the case of *o*-chloroaniline, the presence of chloro group withdraws electron density from the ring and gets negatively charged, which repels the dopant anions and consequently the strength of the electrical double layer gets weakened. This results in the inhibition of one directional growth of the polymer chain. Moreover, the steric hindrance posed by Cl⁻ causes a twist which induces the polymer chain to grow in a circular fashion, entrapping the camphor-sulfonic acid micelle, giving a porous spherical structure^{29,30}. After the polymerization is completed, camphor-sulfonic acid remains in the pores, which can be removed by simple dilution or washing by centrifugation. During washing or diluting by water, the camphor-sulfonic acid molecules diffuse out of the pores, giving microspheres a porous shape. The SEM image (Fig. 6) of as-prepared microspheres contains camphor-sulfonic acid in it, which is also demonstrated by UV-visible spectrum (Fig. 2).

Conclusion

In this study, porous microspheres of poly(*o*-chloroaniline) were synthesized *via* self-assembly process wherein camphor-sulfonic acid played a key role in framing hollow porous morphology. It has been concluded that the formation of micelles of camphor-sulfonic acid in aqueous solution is a key factor in the fabrication of porous microspheres of poly(*o*-chloroaniline). The poly(*o*-chloroaniline) microspheres were characterized by means of FTIR, UV-visible spectroscopy, X-ray diffraction, and SEM analysis. The mechanism proposed for the formation of microspheres was supported by the SEM and UV-visible spectroscopic data.

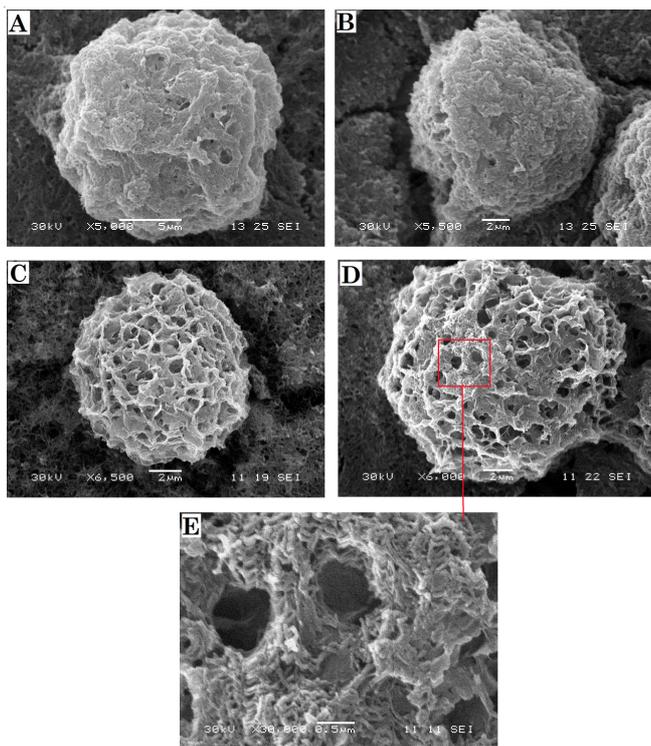


Fig. 6. SEM images of poly(*o*-chloroaniline) microspheres: (A) as synthesized and (B) after being washed with distilled water

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