

# Polymerization of pyrrole on a polyelectrolyte hollow-capsule microreactor

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## Abstract

'Caved-in' and spherical polypyrrole (PPy) capsules were successfully prepared by direct polymerization of pyrrole on polyelectrolyte hollow-capsule microreactors at different conditions. This microreactor was formed by alternate layer-by-layer (LbL) adsorption of chitosan (CS) and poly(sodium 4-styrenesulfonate) (PSS) on polystyrene (PS) colloidal particle and followed by removing the PS core with tetrahydrofuran (THF). The integrity and self-sustaining of the microreactor could be ensured through the chemical cross-linking of CS in multilayers with glutaraldehyde before the removing of PS. The direct polymerization of pyrrole on the microreactor, either polycations or polyanions at the outmost layer, can be achieved according to hydrogen bonding effect or electrostatic interaction. Participation of inorganic salts plays a significant role on morphology controllable of intact hollow polypyrrole capsules.

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*Keywords:* Polypyrrole; Chitosan; Poly(sodium 4-styrenesulfonate)

## 1. Introduction

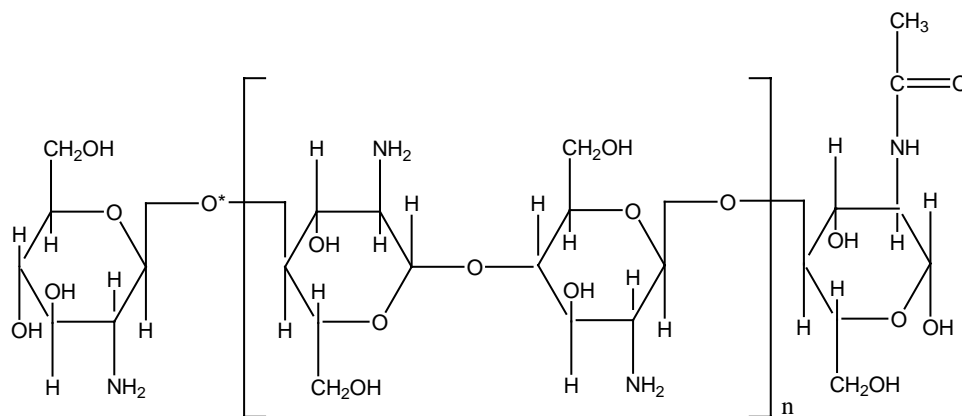
Nano or microscale hollow spheres of functional materials have attracted increasing interest because of their diverse potential application such as in drug delivery, cell and enzyme transplantation, gene therapy, separation in biomedicine, and as contrast agents in diagnostics [1]. The most commonly used strategy for the preparation of such hollow spheres include a stepwise sacrificial core process, i.e. first gaining the removable cores, then covering the shell, and finally removing the core template by using a variety of chemical and physical methods, such as calcinations or solvent etching [2].

Conducting polymers are emerging as a promising material for synthesis of nanostructured materials and devices [3] because they exhibit electrical, electronic, magnetic, and optical properties similar to metals or semiconductors while retaining their flexibility, ease of processing, and modifiable electrical conductivity [4]. Conducting polymer nanoparticles have been applied in electrorheological studies, catalysis reaction and analytical separation, proposed as diagnostics [5]. Conducting polymeric hollow spheres have recently been cited as novel types of carriers and nanoreactors with designed

properties, which should enable many applications such as the controlled release of drugs or gene therapy. Hollow spheres of conducting polymers were usually obtained by above mentioned template method [6]. However, the use of sacrificial cores as the template results in the non-uniformity of the conducting polymers shell and makes the removal of the colloid templates without breaking the conducting polymers shell difficult. Another approach to prepare hollow spheres of conducting polymers is through self-assembly. For instance, Wan et al. described the synthesis of polyaniline (PANI) hollow microspheres on an aniline emulsion template [7]. Chan et al. prepared hollow PANI spheres in the presence of amphiphilic triblock copolymer micelles [8]. Also, a novel one-step method to fabricate hollow nanometer-sized polypyrrole capsules with controllable shell thickness in the presence of chitosan has been developed in our lab [9]. However, self-assembly method is only suitable for special system.

Lately, electrostatic layer-by-layer (LbL) assembly technique has been successfully applied to prepare hollow capsules of defined composition, size and geometry. Caruso and co-workers pioneered the research on the preparation of inorganic hollow capsules [10] for spatially restricted inorganic synthesis and farther reported an approach to fabricate conductive core-shell particles by alternating self-deposition of polyaniline (PANI) and poly(styrenesulfonate sodium salt) (PSS) onto polystyrene (PS) colloidal particles [11]. Conductive hollow polyaniline (PANI) particles were obtained by

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Scheme 1. Chemical structure of Chitosan.

Shi et al. at the same period. They utilized PE multilayers preformed onto micrometer-sized melamine formaldehyde (MF) particles as a reaction vessel to form uniform PANI coatings and intact hollow PANI capsules by dissolving the MF core particles in acidic solutions [12]. At the same time, they emphasized that high-quality hollow PANI capsules can only be obtained by decomposing the MF cores after aniline polymerization because of the low strength of hollow PE capsules. Up to now, the reports relating to direct polymerization on PE hollow capsules are scarce and only a limited number of reports have appeared that demonstrate that polymerization inside hollow capsules could provide new opportunities for tuning the properties of the products [13].

In this article, we report our results concerning direct polymerization of pyrrole on polyelectrolyte hollow-capsule microreactors. This study overcomes a key synthetic challenge in the control of the integrity and self-sustaining of spherical polypyrrole capsules by cross-linking of polyelectrolyte multilayers. Besides, poly(styrenesulfonate sodium salt) (PSS), another charged polyelectrolyte component is chitosan (CS) (Scheme 1), instead of the common used poly(allylamine hydrochloride) (PAH). This improvement provides several advantages over the PAH/PSS system, such as the ability of both CS and PSS interact with pyrrole monomers, the possibility of cross-linking of CS layer with some reagents for increasing the strength of multilayers, the un-requirement of removing the template, and the reliability for obtaining intact hollow conductive polypyrrole spheres without broken PPy shells. On the other hand, polyelectrolyte hollow-capsule microreactor can be used for the targeted encapsulation of drugs before PPy deposition, which may improve the functionality of conducting polymers [14].

## 2. Experiment

### 2.1. Materials

Poly(sodium 4-styrenesulfonate) (PSS,  $M_w$  70,000) was obtained from Aldrich. Pyrrole (Aldrich) was distilled twice under reduced pressure, stored under nitrogen and refrigerated in the dark. The degree of deacetylation of chitosan (Nantong

Shuanglin Biological Product Inc. Jiangsu Province, China) was about 85%. All other chemicals were analytical grade reagents and used as produced.

### 2.2. Preparation of polystyrene particles

The negatively charged polystyrene (PS) particles were produced by emulsifier-free emulsion polymerization with potassium persulfate (KPS) as initiator in water under the conditions of mass ratio: styrene:  $H_2O$ : KPS (potassium persulfate)=1:15:0.023; reaction temperature of 70 °C; reaction time of 24 h; constant stirring rate of 120 rpm; and inert  $N_2$  protection.

### 2.3. Multilayer assembly on PS spheres (LbL deposition)

PS nanospheres were first coated with several PE layers by utilizing the previously reported LbL self-assembly procedure [15]. The requirements for multilayer build-up and colloidal stability were found to be conditions of pH lower than 4.0 and 11.0 for CS and PSS adsorption solution, respectively. So all PE solutions used had pH=3.8. Stock solutions of PSS and CS, both at 10 mg/mL concentration (with different content of NaCl), were prepared in aqueous solution of pH=3.8. 1g of PS particles were added into 10 mL above-mentioned solutions. After 30-min, the excess polymer in the supernatant fraction was removed by centrifugation (12,000 rpm, 15 min), and the pellet was redispersed in the forementioned solutions by shaking (gently ultrasonic if necessary). Successive repetition of this step was used to form polyelectrolyte multilayers. After a desired number of coatings were reached, the PS solution was centrifuged twice and redispersed in deionized water.

### 2.4. Preparation of intact PE hollow-capsules

PS particles coated with different PE layer numbers, were separately exposed to glutaraldehyde (GA) aqueous solution (25 wt%). The system was stirred for 30 min and centrifugation before exposure to THF. After dissolution in THF for 1 h the

hollow PE capsules were obtained by centrifugation and dispersed in aqueous solution.

### 2.5. Polymerization of pyrrole on the PE hollow-capsule

Pyrrole monomer (70  $\mu\text{L}$ , 1 mmol) and  $\text{FeCl}_3$  (0.162 g, 1 mmol) was added into 20 mL aqueous solutions with 0.2 g  $\text{PE}_n\text{-PS}$  particles or corresponding PE hollow-capsules. The polymerization was carried out for 24 h under  $\text{N}_2$  at room temperature. The resulting solution was then filtered and the residue was washed with water and ethanol several times. Finally, precipitates were dried under vacuum at 60  $^\circ\text{C}$  for more than 24 h.

### 2.6. Instrumentation

The morphologies were measured by scanning electron microscopy (SEM, JSM-6300 and Energy dispersive spectrometer EDS accessory for elemental measurement, Kevex-Sigma) and transmission electron microscopy (TEM, JEM-200CX). Transmission electron microscope operated at 100 kV.  $\zeta$ -Potentials were measurement on 90 PLUS Particle Size Analyzer instrument. Fourier-transform infrared spectra (FTIR) of the samples were recorded on a Bruker VECTOR22 spectrometer. Conductivity measurements were made on compressed pellets of the powder using conventional four-point probe technique at ambient temperatures.

## 3. Results and discussion

### 3.1. CS/PSS multilayer assembly on PS spheres

In order to follow the assembly deposition process, the  $\zeta$ -potential of polystyrene particles was recorded as a function of pH. The negative potential of PS particles in Fig. 1 was attributed to fragment of  $\text{SO}_4^-$  at the end of PS chains coming from initiator (potassium persulfate KPS) [16]. Since, chitosan dissolved in acidic aqueous solution, all adsorption experiment was performed in aqueous solution at  $\text{pH} = 3.8$ . The polystyrene

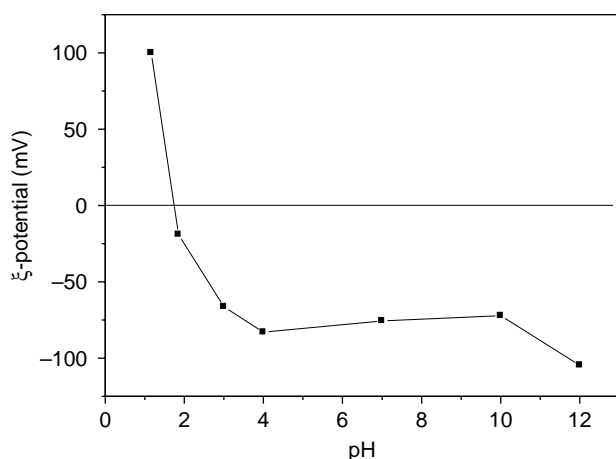


Fig. 1.  $\zeta$ -Potential of PS particles at different pH.

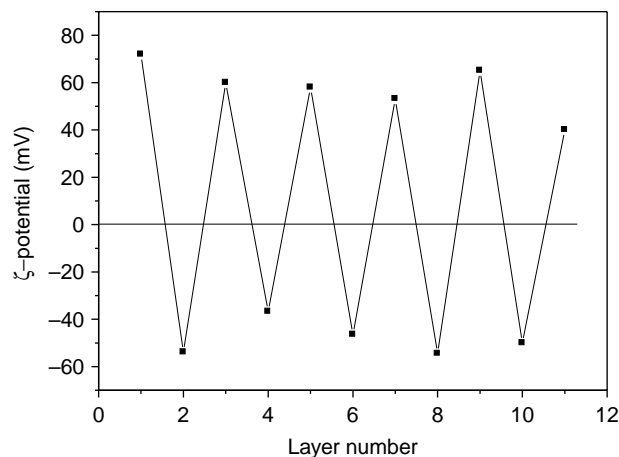


Fig. 2.  $\zeta$ -Potential of the CS/PSS-coated PS particles as a function of the number of layers deposited. The odd layer numbers correspond to CS deposition, and the even layer numbers to PSS deposited. The  $\zeta$ -potential measurements were performed in Milli-Q water at  $\text{pH} 3.8$ .

particles were coated first with a layer of CS, followed by a layer of PSS. Subsequently, the particles were coated alternately with CS and PSS.  $\zeta$ -potential measurements showed that the  $\zeta$ -potential alternated in sign between positive and negative values depending on whether CS or PSS was the outermost layer, respectively, suggesting successful polyelectrolyte multilayer growth (Fig. 2).

Direct visualization of CS/PSS coated PS particles was provided by TEM measurements. Fig. 3 shows the TEM micrograph of an uncoated PS colloid (average diameter 400 nm, inset), and (CS/PSS)<sub>16</sub> coated PS particle. The coated particles showed increased surface roughness while the PS particle exhibited a smooth surface (inset). But the PE multilayer film cannot be clearly distinguished because of the similar contrast between the PE and PS core under the electron beam. The particle diameter increased from about 400 to 430 nm as a result of coating, yielding a thickness of about 30 nm for the 16 PE layers film. This corresponds to an average thickness of about 2 nm for each PE layer, a value in good agreement with previous data [17].

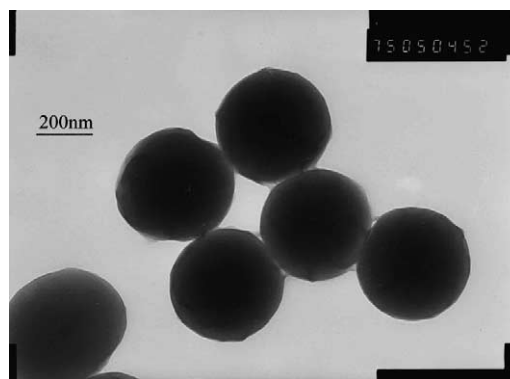


Fig. 3. TEM images of PS particles with a diameter of 400 nm coated with 16 layers of CS/PSS. The PS particles used as templates have a diameter of 400 nm (inset).

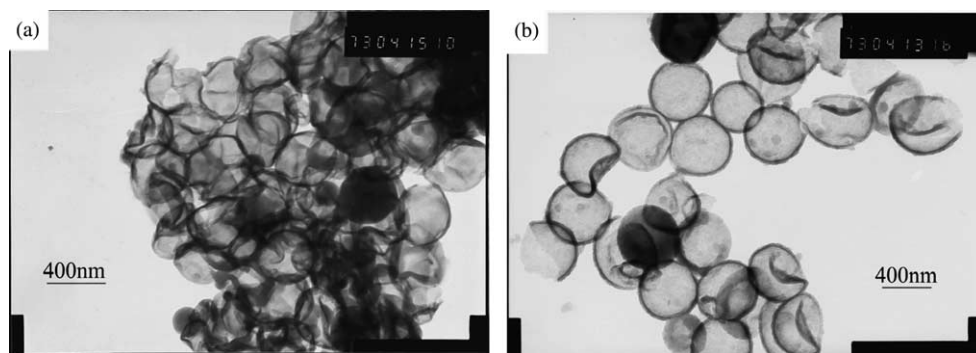


Fig. 4. TEM micrographs of the hollow PPy capsules obtained after removing PS core and drying on a copper grid. Left: PS was not coated with PE layers; right: PS was coated with six layers of PE multilayers.

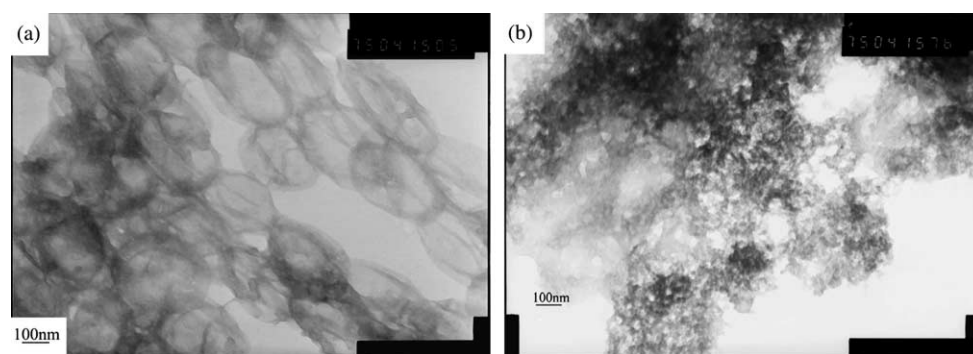


Fig. 5. TEM images of the (CS/PSS)<sub>9</sub> hollow PE capsules. (a) 400 nm PS particles coated with (CS/PSS)<sub>9</sub> layers and exposure to THF for 30 min after cross-linking with glutaraldehyde. (b) Without cross-linking.

### 3.2. PPy deposition on surface of PS particles coated with CS/PSS multilayer

PPy deposition was firstly performed on the surface of PS particles coated with PE multilayer. To examine the influence of both the thickness of the PE multilayer film and the nature of the outermost surface charge on the polymerization process of pyrrole, PS colloids coated with 0, 5 and 6 layers, were employed as templates. It is taken by surprise that PPy can be successfully coated on all of them in spite of the outermost surface charge of PS particles. To the best of our knowledge, situation of the polycation component in PE multilayer for fabrication of conducting polymers has never before been reported. Only the negative charges on colloidal particles facilitate the formation of uniform conductive polymer thin films [18]. In our designed CS/PSS multilayer, besides the effective deposition of PPy on polyanion PSS layer due to the electrostatic interaction, successful anchoring a layer of PPy on polycation CS layer can be attribute to the hydrogen bonding interaction between CS and pyrrole [19]. Hollow PPy spheres could be obtained simply by dissolution of PS cores with THF. It can be seen from Fig. 4, however, that solid particles with PS and a large amount of broken PPy shells were observed even after intensive solvent treatment for 4 days. This phenomenon implies that the capsules become less penetrates for the dissolving exudation of polystyrene cores after the polymerization of polypyrrole. Left image of Fig. 4 shows the almost broken and deformed PPy shells because of the very

thin PPy shells. As the number of PE layers increases, the PPy shells are getting thicker (see the right image of Fig. 4); however, the circumstances of PPy shells with both broken and deformed have not been improved much.

### 3.3. Formation of the polyelectrolyte hollow-capsule

To prevent high amounts of broken PPy capsules attempts have been made to fabricate hollow PPy spheres with preformed PE hollow-capsule as template. Preformed PE

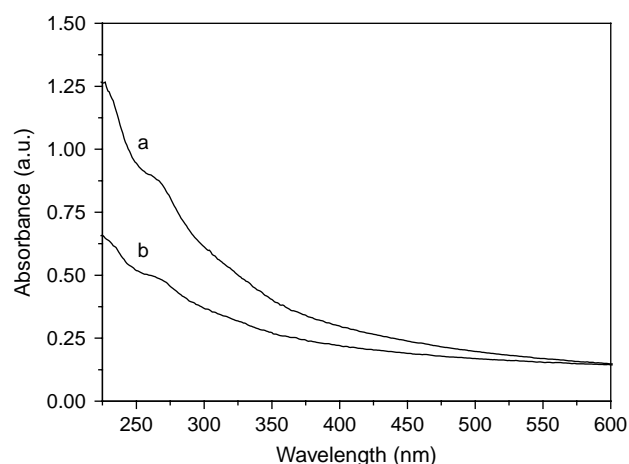


Fig. 6. UV-vis spectra of PE capsules (a): cross-linking; (b): without cross-linking.

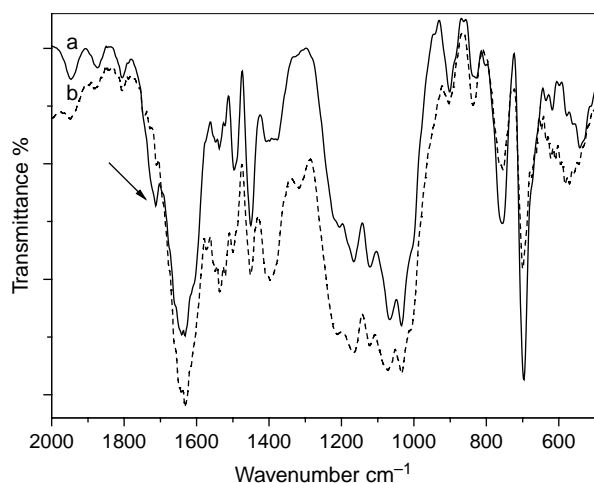


Fig. 7. FTIR of PE capsules (a): with cross-linking; (b): without cross-linking.

hollow-capsules were difficult to fabricate since swelling of PS in THF leads to a large volume increase that is directly responsible for capsules fractures. It is possible to improve the PE hollow-capsule self-sustaining ability by cross-linking of just one of components in the multilayer [20]. Glutaraldehyde has been used more frequently as a cross-linking reagent, since it is less expensive, non-toxic, and highly soluble in aqueous solution. Cross-linking chitosan with glutaraldehyde has been used to improve the strength of chitosan film [21]. In this work, we chose chitosan as polycations in the PE layers and made a try to cross-link CS before dissolution of PS in THF in order to improve the strength of PE capsules [22]. After coating the templates with the polyelectrolyte layers, a solution of glutaraldehyde were added to the dispersion before THF was added. It can be seen from Fig. 5 that after cross-linking intact

(CS/PSS)<sub>9</sub> capsules can be obtained. A noticeable decrease in diameter of the polymer hollow capsules (about 380 nm) was observed, compared with the PS particles (400 nm). This could be due to the effect of drying, as a result of which the polymer hollow capsules forms creases and folds in the shells as they collapse [23]. Reaction between the aldehyde and the amine groups will produce  $\text{-C=N-}$  bonds (Schiff base) on the capsule wall, which could exhibit absorbance in the UV region. UV-vis spectra in Fig. 6 illustrated an increased broad absorbance in the region of 250–350 nm, confirming the presence of cross-linking structure [24]. Fig. 7 showed FTIR spectra of PE hollow-capsules with and without cross-linked. For the PE hollow-capsules cross-linked with glutaraldehyde, peaks at  $1713 \text{ cm}^{-1}$  ( $\text{-C=N-}$ ) appear, suggesting a cross-linked structure of CS as a result of the reaction between  $\text{-CHO}$  groups of glutaraldehyde and  $\text{-NH}_2$  and  $\text{-HNCH}_3$  groups of chitosan [24].

### 3.4. Polymerization of pyrrole on the polyelectrolyte hollow-capsule

A schematic representation of the LbL approach applied to spherical particles to form hollow polypyrrole capsules is illustrated in Fig. 8.

Zhou et al. have carried out a FI-QCM (the flow-injection QCM) experiment to demonstrate the aniline monomers can rapidly be attracted to the surface of PE eggshell structures and subsequently slowly incorporated into the interior of PE shells [25]. In our study system, Py monomers can infiltrate into the PE multiplayer capsules and polymerize there. As shown in Fig. 9 large numbers of hollow polypyrrole spheres were obtained, implying that polymerization of pyrrole occurred on

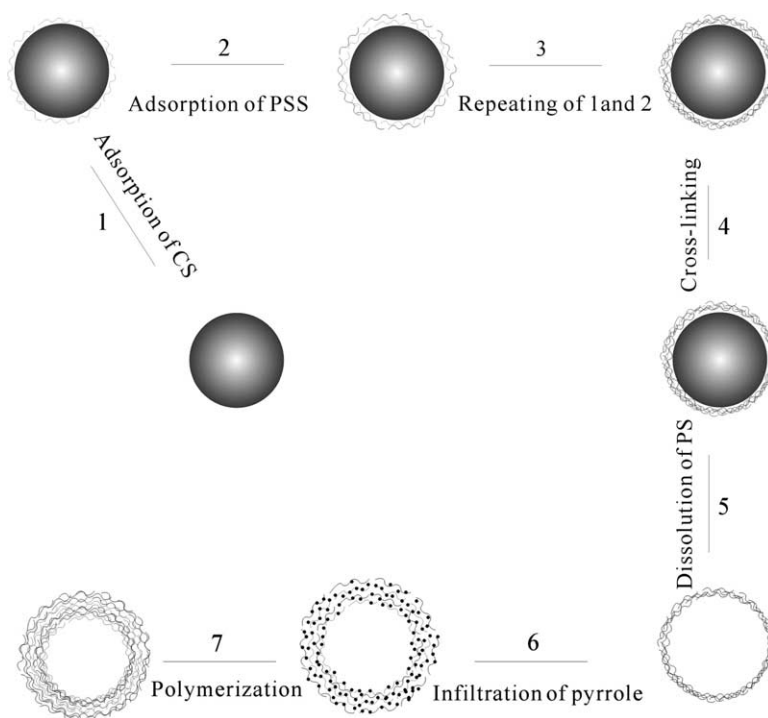


Fig. 8. Schematic illustrations of PE capsules preparation and deposition of PPy on the PE shell.

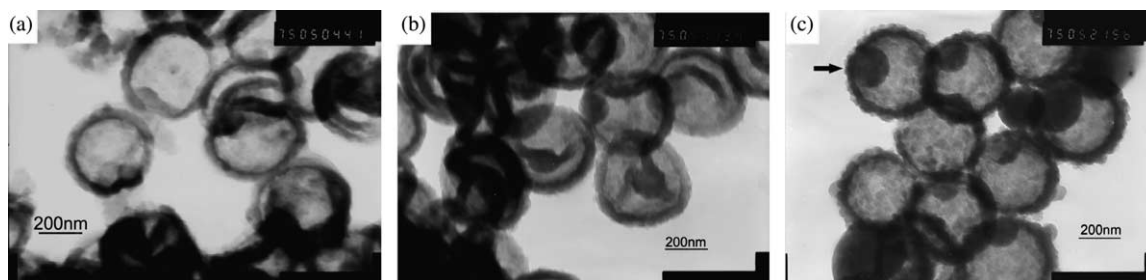


Fig. 9. TEM micrographs of Hollow PPy particles polymerization with hollow (CS/PSS)<sub>9</sub> capsules as microreactors (a): No salts; (b): 0.05 M NaCl; (c): 0.2 M NaCl.

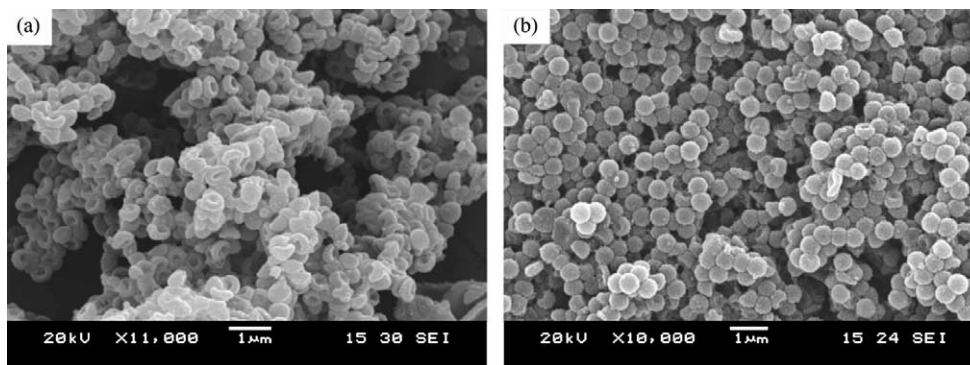


Fig. 10. SEM image of (a): 'caved-in' polypyrrole particles; (b): spherical polypyrrole particles.

the hollow-capsule microreactor instead of inside the hollow-capsule microreactor. Moreover, polymerization of pyrrole did not take place in the medium since granular polypyrrole did not be found in the aqueous solutions. The diameter of hollow spheres of polypyrrole (340–360 nm) is smaller than the diameter of the original PE hollow-capsules (360–380 nm) and the shell thickness (40–60 nm) is bigger than the original PE layers thickness (20 nm). It appears that the PPy deposition within the PE thin shell yielded an expansion of the eggshell structure. The charge and polarity of outmost layer seems not influence the formation of PPy capsules. The integrity of the hollow polypyrrole spheres fabricated depends just on the cross-linking and the layer number of assembled polyelectrolyte multilayers.

Because it is difficult to control the process of the alternate layer-by-layer adsorption of CS and PSS under the case of absence of inorganic salts, controlled amounts of salt are necessary due to its screening effect. On the other hand, with the increase of concentration of salts to 1 M, CS chains became so rigid that it cannot be dissolved absolutely in aqueous solutions. The appropriate concentration of the inorganic salts for the adsorption process is 0.1 M. From Fig. 9(a), we can see that intact PPy capsules, collapse PPy capsules and broken PPy capsules all appeared. It is concluded that the morphology of PPy capsules was controlled difficultly without participation of inorganic salts. It is well known that inorganic salts such as NaCl can weaken the influence of charge on the chitosan chains. Due to the screening effect of added salt, the presence of low amounts of salt reduces electrostatic interactions, thus leading to higher chain flexibilities and enabling rearrangement processes [26]. In this article, at lower ionic strength of NaCl

(0.05 M) 'caved-in' capsules of polypyrrole were observed (Fig. 9(b)). Their shapes (TEM image of Fig. 10(a)) are very similar to that of erythrocytes. Increasing of concentration of NaCl to 0.2 M, the macromolecular chains became more flexible compared with that in 0.05 M NaCl. After cross-linking, PE hollow-capsules with less permeability and higher strength were obtained, from which PS cannot be dissolved completely. Fig. 9(c) provides the clear image evidence of intact hollow polypyrrole capsules with some PS. Creases and folds in the shells disappeared possibly as a result of the stiffening of the PE hollow-capsules (TEM image of Fig. 10(b)). So, by tuning the quantity of inorganic salt added

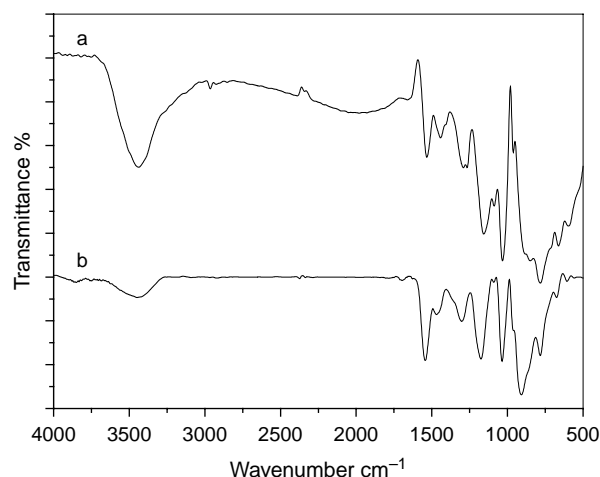


Fig. 11. FTIR spectra of (a): granular PPy; (b): hollow PPy spheres.

the morphology of intact hollow polypyrrole capsules can be controlled effectively.

### 3.5. Characterization of the hollow PPy capsules

The molecular structure of the PPy capsules was characterized by Fourier-transform infrared spectroscopy (FTIR) (Fig. 11). No obvious difference was found in the FTIR spectra of the PPy capsules from those of granular PPy obtained by common methods. The characteristic bands of the PPy samples were the pyrrole ring fundamental vibration at  $1534\text{ cm}^{-1}$ , C–N stretching vibration in the ring at  $1455\text{ cm}^{-1}$ , the =C–H in-plane vibration at  $1303$  and  $1040\text{ cm}^{-1}$ , and the =C–H in plane vibration at  $1171\text{ cm}^{-1}$  [27]. Because of presence of the PE layers in the PPy capsules, the conductivity value ( $5\text{ S cm}^{-1}$ ) is slightly lower than the granular PPy obtained by common method ( $16\text{ S cm}^{-1}$ ).

## 4. Conclusions

In conclusion, it has been demonstrated that the PE hollow-capsules composed of CS and PSS can be used as a microreactors to prepare hollow spheres of polypyrrole. The main essence of this strategy consisted in (1) improved strength of PE capsules by cross-linking of chitosan and participation of inorganic salts and (2) interaction of both CS and PSS with pyrrole monomers, which ensured the fabrication of hollow polypyrrole spheres. This method is a versatile water-based technique, thereby permitting the construction of intact hollow conductive spheres.

## Acknowledgements

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