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Synthesis of novel sunflower-like silica/polypyrrole nanocomposites via self-assembly polymerization

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Abstract

Novel sunflower-like organic–inorganic composites consisting of spherical silica and smaller conductive polypyrrole particles were successfully prepared through an in situ self-assembly polymerization process by choosing chitosan as a modifying agent of silica surface. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) showed that on the surface of individual silica particle polypyrrole nanoparticles were anchored perfectly. The sunflower-like silica–polypyrrole composites exhibited conductivity of 8 S cm^{-1} and colloid stability because of the special surface morphology. Adsorbed chitosan chain may play a dual-role of both providing the active sites for formation of the polypyrrole particles on silica and acting as a stabilizer of the silica–polypyrrole particles. Hydrogen-bonding interaction between the acetylamino group of chitosan and hydrogen atom on nitrogen of polypyrrole is a determining parameter in the former case.

Keywords: Conducting polymers; Polypyrrole; Chitosan

1. Introduction

Conducting polymers are extensively studied in recent years because they offer reasonably high conductivity that can be reversibly modulated over 15 orders of magnitude by controlling the dopant type and level [1]. Nevertheless, conducting polymers are difficult to be processed because of their insolubility in common solvents and infusibility. Consequently, much effort has been directed toward improving the tractability of conductive polymers using new methods [2]. Since 1986, various research groups have reported the preparation of colloidal dispersions of several conducting polymers, particularly polyaniline and polypyrrole (Ppy) [3]. In principle, these particles represent a more processable, and hence more useful, form of the conducting polymers. One of the new interests in the generation of colloidal conducting polymers is the preparation conducting colloidal particles consisting of inorganic core particles homogeneously covered with ultrathin films of conducting polymers because of the optical and electrical properties of these materials differing from their individual nanoparticles or macroscopic mixture [4]. Armes and co-workers have carried out pioneer studies on stable colloidal conducting polymer nanocomposites using a technique for encapsulating colloidal metal oxide nanoparticles with Ppy or polyaniline [5]. Techniques for the preparation of composites containing conducting polymers have been recently reviewed [6].

In this field, silica is the most commonly used inorganic support due to two main reasons. First, synthesis of monodispersed silica particles is quite easy to perform and well documented in the literature [7]. Second, various potential applications of silica-based systems are involved: gas–liquid chromatography, paintings, catalyst supports, etc. [8]. On the other hand, among conducting polymers, Ppy is one of the most extensively studied materials due to its good environmental stability, high conductivity and biocompatibility [9]. However, since silica is initially hydrophilic, it is very difficult to form the hydrophobic Ppy shell on silica by direct surface polymerization. Only 'raspberry' like composite was possibly available in this case. A high-resolution TEM picture obtained by Gill et al. was the first report to reveal this unusual 'raspberry' like morphology where the composite particles were aggregates of the original small silica particles held together by the conducting polymer component which acted as a 'binder' [10]. The XPS data revealed that the surface was silica rich rather than conducting polymer rich [10]. These

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very special surface characteristics provided them with prolonged colloidal stability comparably to the pure silica sol. But the conductivity of the composites was as low as 10^{-3}–10^{-4} S cm^{-1} since the surface is silica rich.

To increase the conductivity of the composites, silica should be coated completely with conductive polymer. For this purpose, the hydrophilic surface of silica needs to be modified to allow anchoring and polymerization of hydrophobic pyrrole monomer. Aminopropyl silane (aminopropyltrimethoxysilane, APS) coupling agent has been used to pretreat the silica before Ppy polymerization and silica–Ppy composites with Ppy-rich surface were obtained [11]. But the conductivity of the composites is still very low (10^{-2} S cm^{-1}) for some silica still exists on the surface of composites. On the other hand, the use of surfactants and macromolecule adsorbed onto solid surfaces as a medium for the formation of ultrathin polymer films has been reported [12,13]. To grow Ppy on the surface of substrates using adsorbed layer as templates, pyrrole monomers should be diffused into the layer or condensed onto the layer before polymerization. Hao et al. reported that monodispersed silica pretreated with poly(*N*-vinylpyrrolidone) can be covered by polypyrrole [14]. Core–shell composite was got, but the conductivity and the colloidal stability were not reported. Recently, Shi et al. assembled polyelectrolyte multilayers onto colloidal particles for the subsequent conducting polymer deposition by the layer-by-layer (LbL) self-assembly technique [15]. Using this method the common problem of particle aggregation upon deposition of conducting polymers could be overcome by localizing polymerization of the monomer within the polyelectrolyte multilayers. Although the colloid stability of the resulted particles was improved significantly [16], the conductivity value is still very low (2.2×10^{-3} S cm^{-1}) because of the non-conductive outmost polyelectrolyte multilayers.

In the present work, we aim to report new results along these lines on the synthesis of a novel sunflower-like conducting polymer–inorganic composite. For the first time, a natural biomacromolecule-chitosan was chosen as an adsorbent to alter the surface properties of silica. The acetylamino group in chitosan was considered to form hydrogen bonding with hydrogen atom on nitrogen of Ppy and ensures the fixed-site growing of polypyrrole on silica. Anchoring Ppy particles uniformly on silica to obtain novel surface morphology can optimize the colloidal stability and conductivity of the silica–Ppy composite particle. Such sunflower-like silica–Ppy composites have not been reported yet.

2. Experimental sections

2.1. Materials

Pyrrole (Aldrich) monomer was distilled under reduced pressure. Tetraethoxysilane (TEOS), Aminopropyltrimethoxysilane (APS) and a 25% aqueous solution of ammonia (Huakang Product Inc. Jiangsu Province, China) were purchased in their reagent grades and used without further purification. The degree of deacetylation of chitosan (Nantong Shuanglin Biological Product Inc. Jiangsu Province, China) was about 85%. Hydroxyethyl cellulose (HEC) 4000 was procured from Feinbiochemica Heidelberg.

2.2. Methods

2.2.1. Synthesis of 500 nm silica particles

The method employed for the synthesis of 500 nm silica particles was similar to the one described in Stober's work [7]. In a typical procedure, absolute ethanol (50 ml) and 22 ml of the aqueous solution of ammonia were introduced in a three neck round flask of 250 ml equipped with a refrigerating system. The mixture was stirred to homogenize. A solution of 5 ml of TEOS diluted in 20 ml of absolute ethanol was prepared separately and introduced continuously and slowly. Reaction occurred at room temperature under continuous stirring and lasted for 12 h.

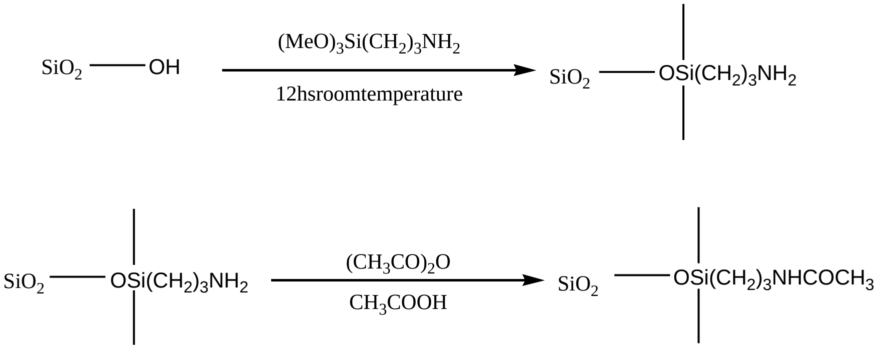
2.2.2. Silica suspensions treatment

The separation of the ammonia and ethanol was achieved by dialysis. The silica suspensions were dialyzed against water until neutral pH. The suspensions were concentrated and their final concentration was determined by measuring the mass of a dried extract.

2.2.3. Composite synthesis

Adsorption method. Polymerization of pyrrole was performed in the presence of the silica particles after adsorption of hydrophilic chitosan or HEC macromolecule. A stock solution of the macromolecule was added to the silica suspension in deionized water. The macromolecule concentration was chosen such as to saturate the silica surface. Adsorption was performed at room temperature and allowed to equilibrate for at least 24 h. After that, the excess chitosan or HEC was removed by three centrifugation (12,000 rmp)/dispersion/washing cycles. Pretreated silica was then dispersed in distilled water and pyrrole monomer and $FeCl_3$ ($FeCl_3$/pyrrole molar ratio = 2.33) were introduced. The mixture was stirred at room temperature for 24 h. The resulted composite was collected by centrifugation and dried in vacuo for 24 h. This method was called adsorption method.

Deposition method. Chitosan was also deposited on the surface of silica by another treatment process: chitosan was dissolved first under stirring in 2% acetate aqueous (pH = 4) followed by introduction of silica (silica/chitosan mass ratio = 1:1/1:0.5/1:0.1/1:0.07) to the solution. 4 M sodium hydroxide aqueous solution was then added dropwise to the abovementioned mixture under stirring. Chitosan could be deposited completely on the surface of silica by adjusting the pH value of the solution to 13. The product was centrifuged (4000 rmp) and washed with water until the pH value of the supernatant became 7. Pretreated silica was then dispersed in distilled water and pyrrole monomer and $FeCl_3$ ($FeCl_3$/pyrrole molar ratio = 2.33) were introduced. The mixture was stirred at room temperature for 24 h. Finally, silica–Ppy particles were obtained by precipitating with acetone and drying in vacuum at 40 °C for 24 h.



Scheme 1. Modification of silica surface by acetylamino group.

2.2.4. Modification of silica surface by acetylamino group

At first, silica surface was modified with amino group according to the method shown in Scheme 1. The amount of coupling agent aminopropyltrimethoxysilane (APS) was assumed to be nominally 0.1%. After reacting in APS–ethanol solution with continuously stirring at room temperature for 12 h, the silica suspension was purified through dialysis against water until neutral pH of the suspension was reached. The product was called as silica–APS.

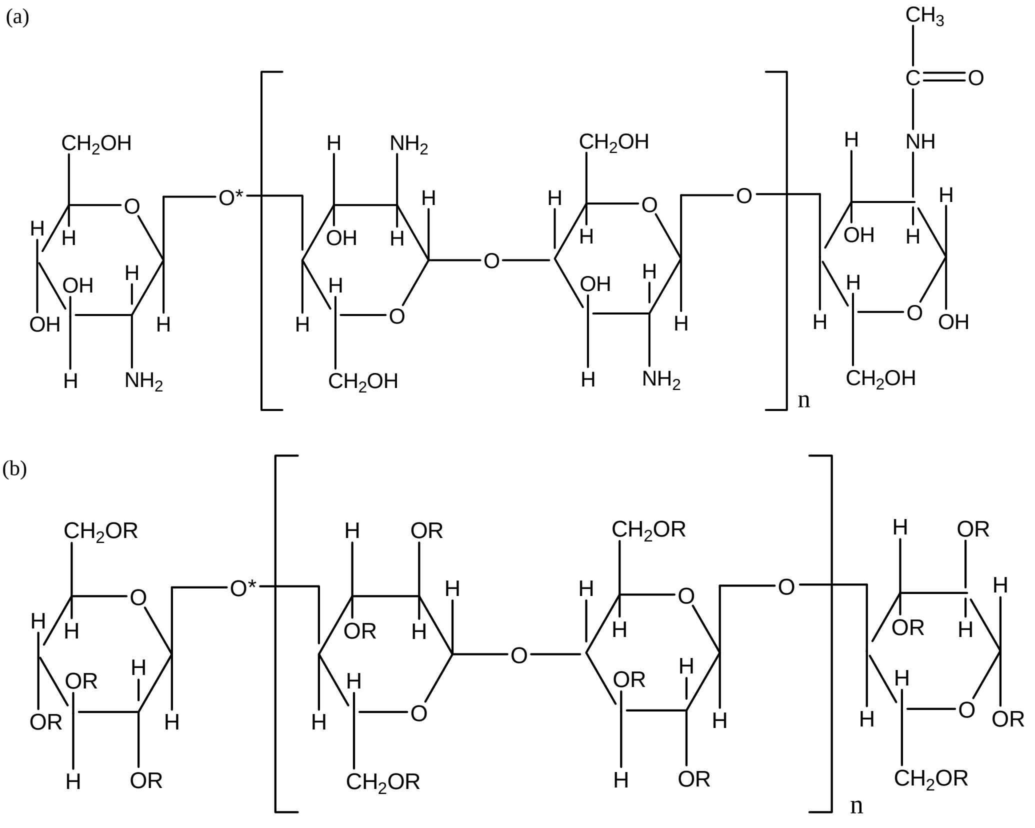
Then, 0.2 g of silica–APS particles were transferred in 10 ml acetic acid, and 5 ml of acetic anhydride was subsequently dropped into the mixture. After stirring at room temperature for 4 h, the silica particles in the mixture were separated and dispersed in water by three centrifugation/dispersion cycles. Finally, acetylamino-modified silica was obtained.

2.3. Instruments and measurements

Transmission electron microscopy (TEM) experiments were performed with a JSM-6300 microscope. The samples were prepared as follows: one drop of the dilute suspension of silica–Ppy colloid was deposited on a copper grid coated with a carbon membrane. Scanning electron microscopy (SEM) observations were performed with a JSM-5900 scanning electron microscope. The specimens were gold-coated prior to examination. Fourier-transform infrared spectra (FTIR) of the samples were recorded on a Bruker VECTOR22 spectrometer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument at a heating rate of 10 °C min^{-1} in air. The conductivities of compressed pellets of the silica–Ppy composite were determined using standard four-point probe techniques at room temperature.

3. Results and discussion

The chemical structures of the two types of macromolecules used as modifying agent in this work were given in Scheme 2. Rare studies concern the adsorption of chitosan [(1-4)-2-amino-2-deoxy-β-D-glucan] on silica. Chitosan chains are expected to be adsorbed on silica particles via two types of interaction: (1) electrostatic attraction between negative charges ($-\mathrm{SiO}^-$) on silica particles and positive charges ($-\mathrm{NH}_3^+$) on chitosan molecules and (2) attraction mediated by hydrogen bonds between hydroxyl and/or amino groups of chitosan and silanol groups of silica [17]. In this article, chitosan was deposited on the surface of silica by two different ways, that is, adsorption method and deposition method (Section 2). In the former case, adsorbed chitosan molecules were expected to have a loop-train-tail conformation on silica particles [17], and the excess chitosan was removed by centrifugation. In the latter case, chitosan could be deposited completely on the surface of silica by adjusting the pH value of the solution to 13 and thicker and loose chitosan layer was obtained [18]. Morphologies of the silica–Ppy composites obtained under the experimental conditions mentioned above are shown in Fig. 1. TEM images of sunflower-like silica–Ppy composites based on 500 nm silica particles are displayed clearly (Fig. 1(a) and (b)). Each silica sphere is surrounded by smaller conductive polypyrrole nanoparticles with diameter of about 130 nm, which seems to be strongly attached to the silica surface as confirmed by SEM image in Fig. 1(c) and (d). For the silica–Ppy composite obtained in both cases of adsorption and deposition, such sunflower-like morphology can all be observed. But different surface property was exhibited depending on the thickness of chitosan on silica. In adsorption method, adsorbed chitosan layer was thin and tight on/in which Py monomers diffused and polymerized, resulting in silica–Ppy composites with Ppy-rich surface. The colloidal stability may be due to the chitosan chains existing between the interspaces of polypyrrole particles. Conductivity measurements supply more supporting evidence for this result as can be seen is Table 1. The composites showed a high conductivity of 8 S cm^{-1} compared with the reported similar composite system because the composites surface is polypyrrole rich and non-conductive chitosan chains hide between interspaces of polypyrrole. The experimental condition in deposition method was a little different from that in adsorption method of the reactants. When the mass ratio of silica to chitosan was chosen as 1:0.5–1:0.1, sunflower-like composite with a much better colloidal stability was obtained which cannot be collected by centrifugation (12,000 rmp for 30 min) other than by adding acetone. This phenomenon can be explained as that pyrrole monomers can diffuse and polymerize within the thicker and loose chitosan layer formed on silica in the deposition method. It is the steric hindrance stabilization of



R=H or $(CH_2\text{-}CH_2\text{-}O)_m\text{-}CH_2\text{-}CH_2OH$

Scheme 2. Chemical structure of (a) chitosan; (b) HEC.

thicker chitosan on silica that endowed the sunflower-like silica–Ppy composite with excellent colloidal stability but lower conductivity (10^{-2} S cm^{-1}). The formation process of the two kinds of sunflower-like composites is schematically presented in Scheme 3.

It is noteworthy, that there was no sunflower-like composite formed when the mass ratio of silica to chitosan was chosen as 1:0.07 in deposition method (TEM image omitted here). It may be taken as a result that the adsorbed chitosan layer cannot provide enough active sites to initiate the pyrrole monomers diffused in the adsorbed layer. Interestingly, cotton-like silica–Ppy composite was available when the mass ratio of silica to chitosan was increased to 1:1, as illustrated in Fig. 1(e) and Scheme 3. In this case a lot of pyrrole monomers diffuse into the much thicker layer of chitosan and polymerize there.

It also can be furthermore, seen from TEM images that only a few free Ppy particles formed along with the sunflower-like particles, indicating that the polymerization of monomer took place predominately in or at the chitosan layer adsorbed on silica. In other words, the polymerization process is highly favored on the silica surface.

Usually, electrostatic interactions, hydrogen bonding, and covalent bonding are some of the associating forces between the coat and the substrate. In our case, hydrogen-bonding interaction between the acetylamino groups of chitosan and hydrogen atom on nitrogen of Ppy chain was assumed to take place at the surface of silica, thereby, anchoring the Ppy particle on the surface of silica.

In order to investigate the exact formation mechanism of sunflower-like silica–Ppy on the surface of colloidal silica, HEC that has similar molecular structure with chitosan except no amino and acetylamino groups (Scheme 2) was deliberately adsorbed on silica. In case of HEC, the adsorption is caused by interaction of ether groups in the hydroxyethyl side groups and silanol (Si–OH) surface sites [19]. As illustrated in TEM image of Fig. 2(a) there was no sunflower-like silica–Ppy particle formed. It has been concluded that there is no interaction between HEC and Ppy chain so that pyrrole monomer could not diffuse into adsorbed layer on silica. Compared with ether group, amino or acetylamino group in chitosan may play a role in the formation of the sunflower-like morphology. Amino modified silica has already been used to prepare silica–Ppy nanocomposites [11]. However, these resulting composites are usually composed of congerieses with aggregated silica nanoparticles and deposited Ppy. Therefore, amino group is not the key factor to influence the sunflower-like morphology.

To confirm that the presence of the acetylamino groups in chitosan is essential to the interaction between adsorbed layer and Ppy chains, modified silica on which acetylamino groups

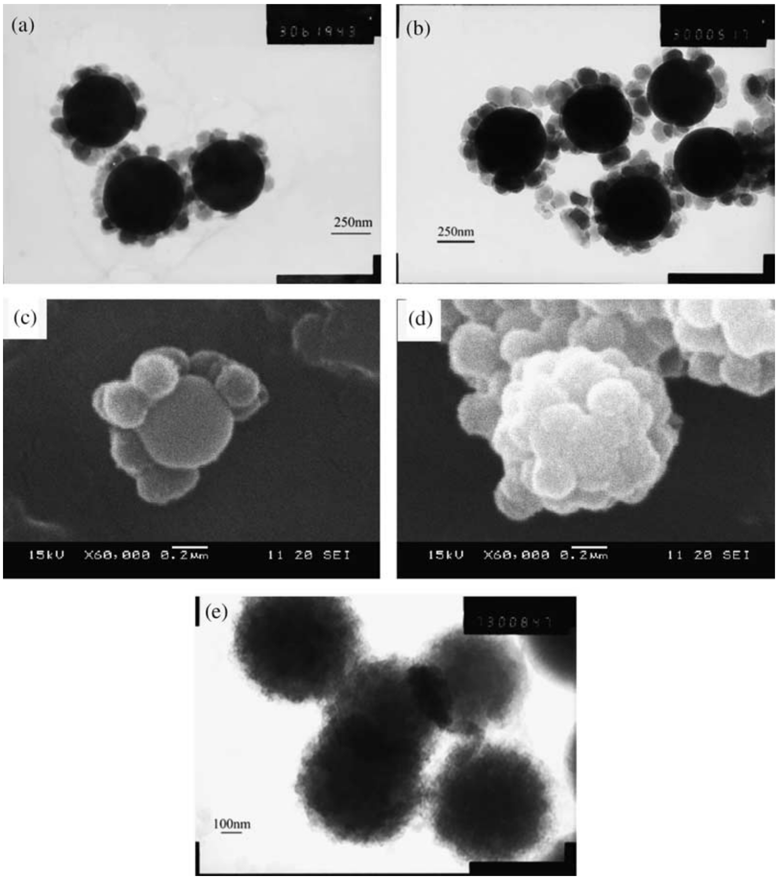


Fig. 1. TEM (a, b, e) images of silica–Ppy composites (a) silica was modified with chitosan by adsorption method; (b) silica was modified with chitosan by deposition method (silica/chitosan mass ratio = 1:0.1); (e) silica was modified with chitosan by deposition method (silica/chitosan mass ratio = 1:1). SEM images (c, d) of sunflower-like silica–Ppy composites.

were attached was also used to prepare silica–Ppy composites (Scheme 1). Silica–Ppy core–shell morphology was obtained as illustrated in Fig. 3. Obviously, acetylamino groups provide active sites on the silica so as to induce the growing Ppy chains.

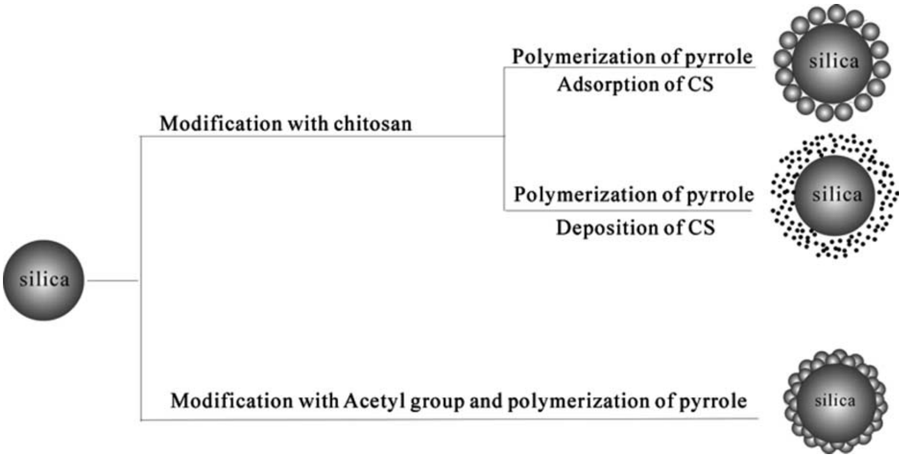
It is worthwhile, to notice here that only 15% acetylamino groups was left on the chitosan chain, so the density of acetylamino groups on the surface of silica is not as much as that in the acetylamino-directly-modified silica. Pyrrole monomer has a tendency to diffuse into the chitosan adsorption layer and polymerize on the surface of silica. Chitosan chain may play a dual-role of both offering the active sites for formation of the polypyrrole particles on silica and acting as a stabilizer of the silica–Ppy particles. Low content of acetylamino groups in chitosan adsorbed on silica offer fewer active sites, thus polypyrrole nanoparticles were mainly obtained on the surface of silica. When higher density of acetylamino groups was provided, too many pyrrole nuclei formed at the same time, and finally core/shell morphology was obtained in the case of acetylamino-modified silica.

3.1. Structural characterization and properties

The FT-IR spectrum of silica–Ppy composites was shown in Fig. 4. The peaks related to PPy, the pyrrole ring fundamental vibration at 1534 cm^{-1}, C–N stretching vibration in the ring at 1455 cm^{-1}, the =C–H in-plane vibration at 1303 and 1040 cm^{-1}, and the =C–H in plane vibration at 1171 cm^{-1} appeared [20]. The FT-IR similarity between the Ppy homopolymer powder and silica–Ppy composite further confirms that Ppy was successfully formed on the surface of the silica particles. In addition, the silica–Ppy composites exhibit a strong peak at 1100 cm^{-1}, which can be attributed to Si–O–Si at the silica surface [21]. The intensity of this peak is much stronger in the case of silica–Ppy admixture (Fig. 4(D)) for Ppy did not cover the silica surface, whereas the weak analogous peak for the surface-flower like composite, may due

Table 1
Summary of the conductivity and colloid stability of silica–Ppy composites

Morphology of composite	Method	Conductivity (S cm^{-1})	Colloid stability
Sunflower-like	Adsorption of CS on silica surface	8×10^{0}	Common
Sunflower-like	Deposition of CS on silica surface (mass ratio of silica to chitosan was 1:0.5–1:0.1)	10^{-2}	High
Cotton-like	Deposition of CS on silica surface (mass ratio of silica to chitosan was 1:1)	10^{-3}	High
Core–shell	Modification of silica surface by acetylamine group	10^{1}	No
None	Modification of silica surface by HEC	10^{-3}	No



Scheme 3. Schematic illustration of cross-section of the formation process of sunflower-like and core–shell silica–Ppy composites.

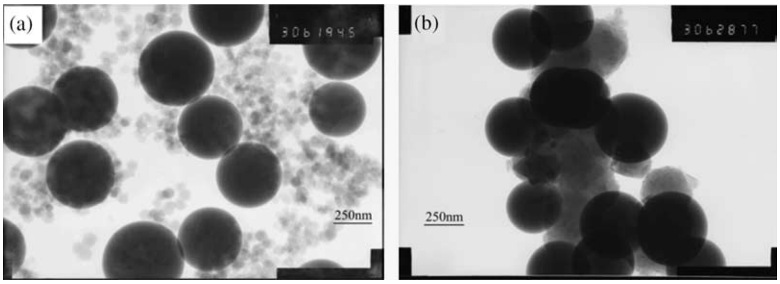


Fig. 2. TEM images of silica–Ppy composites (a) silica was modified with HEC; (b) silica was not modified.

to the bare surface of silica particles or the interspace of polypyrrole nanoparticles on silica (Fig. 4(A)–(C)). Also, the peak of 2922 and 2881 cm^{-1} in Fig. 4(A) may contribute to chitosan chain, which implied that chitosan chain existed on the surface of composite particle.

Results of the thermogravimetric analysis are shown in Fig. 5 where it can be seen that the decomposition temperature of the sunflower-like silica–Ppy composites is higher than that of the silica–Ppy mixture. This result could be interpreted by the strong bonding interaction between polypyrrole particles and silica surface in sunflower-like nanocomposites. The TGA curves of silica–Ppy composites show a two-step weight loss. The weight loss (about 10%) in the first step below 100 °C is attributed to the loss of residual moisture. The second step starting around 260 °C, corresponds the Ppy degradation

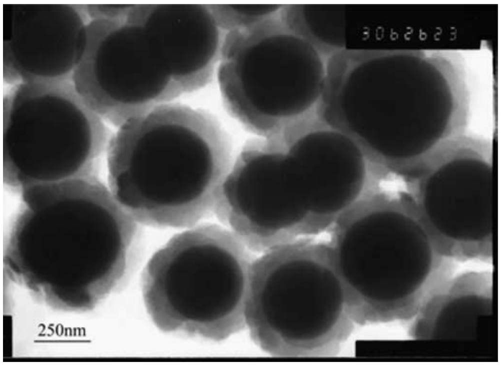


Fig. 3. TEM images of core–shell silica–Ppy composite. Silica was modified with acetylamine group.

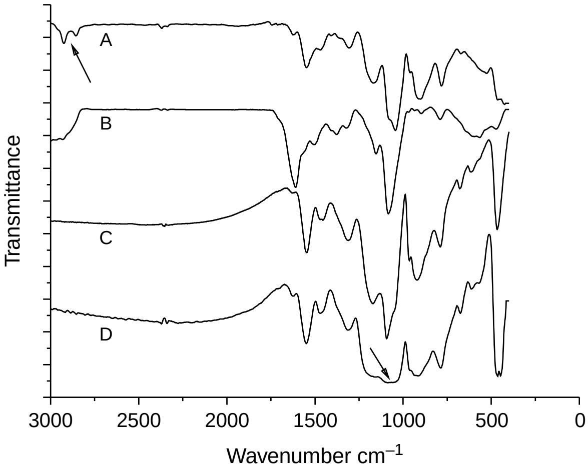


Fig. 4. FTIR of silica–Ppy composite (A) silica was modified with deposition of CS (mass ratio of silica/CS = 1:1); (B) silica was modified with deposition of CS (mass ratio of silica/CS = 10:1); (C) silica was modified with adsorption of CS; (D) silica was modified with HEC.

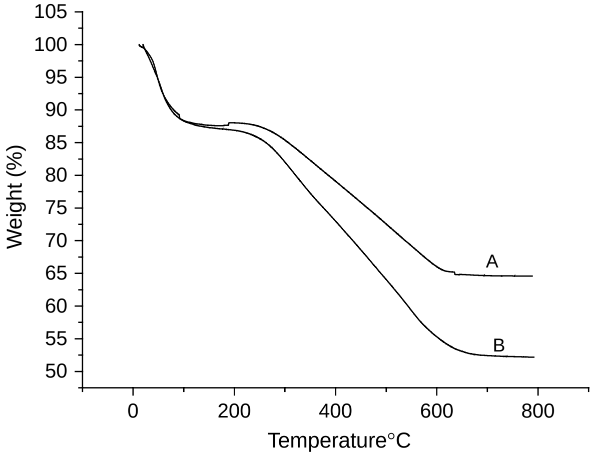


Fig. 5. TGA curves of silica–Ppy composites (A) sunflower-like silica–Ppy composite (silica modified with chitosan); (B) mixture of silica and Ppy (silica modified with HEC).

(about 36%). Residual sample mass after 700 °C is belong to silica (about 54%).

4. Conclusion

In summary, we managed to synthesize novel sunflower-like silica–Ppy composites. Well-defined silica spheres were first prepared via a base-catalyzed sol–gel process. Then the adsorption of chitosan was achieved on the silica surface to provide active sites for further in situ self-assembly polymerization of pyrrole monomer. Evidence is given that the final morphology of the composites is strongly dependent on the presence of the adsorbed chitosan. Chitosan ensures the formation of Ppy particles on the silica surface. The sunflower-like silica–Ppy nanocomposites exhibited high conductivity of $8\ \mathrm{S\ cm^{-1}}$ at room temperature as well as colloid stability because of the special morphology of composites. Increasing the thickness of the adsorbed chitosan layer can modulate the surface property of the silica–Ppy composites to give much prolonged colloid stability but low conductivity. These conductive composites have potential applications in a wide variety of areas such as conductive paint, wave absorbent, and air aerosol and so on.

Further, experiments are currently in progress in order to study the phenomenon at different organic or inorganic particles. Influence of experimental conditions such as the deacetylation and molecular weight of chitosan on the surface morphology and the property of silica–Ppy composites will be studied in detail.

Acknowledgements

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