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Facile Fabrication of Monolayered Hollow Submicrospheres of PANI on Surfaces of Modified Polymer Films

Wenbin Zhong,[1,2] *Yongxin Wang,*[1,2] *Yan Yan,*[1,2] *Wantai Yang**[1,2]

Summary: A novel strategy was developed in order to prepare monolayered polyaniline (PANI) submicrospheres on polymer substrates. The strategy involved two main steps, i.e., photografting of acrylate acid (AA) onto the surface of a polypropylene (PP) film, and subsequent oxidative polymerization of aniline on the grafted surface. It was found that the PANI monolayered hollow submicrospheres were immobilized on the surface of the PP film when the molar ratio of AA to aniline was about 1:1.6. A possible formation mechanism of the hollow PANI submicrosphere iss discussed.

Keywords: hollow submicrospheres; monolayer; polyaniline; surface self-assembly

Introduction

In recent years, there has been growing interest in the fabrication of hollow spheres with nanometer to micrometer dimension because of their wide applications in encapsulation, drug delivery, artificial cells, catalysts, and fillers owing to their low density, large specific area, stability, and surface permeability. Although many methods have been reported to synthesize hollow spheres, commonly the fabrication of hollow microspheres needs a template, including solid templates (for example, SiO_2,[1] and polymer beads,[2,3] etc.) and soft templates (such as colloids[4] or emulsions[5] etc.). In the template methods, the desirable materials are precipitated or polymerized on the surface of the template to form a core–shell structure, and the template is then removed by thermal or chemical post-treatment to obtain the hollow sphere. However, no matter what methods are used, they are all labor-intensive processes and should be carefully operated to avoid the degradation of the shells when the template is removed. Thus a simple and easily removed template is essential to prepare hollow sphere materials.

Polyaniline (PANI), as an important conducting polymer, has received considerable interest and has been extensively studied over several decades due to its relatively facile processability, electrical conductivity, and environmental stability. Different morphologies of PANI have been prepared by a variety of chemical oxidation synthesis methods.[6] Recently, the preparation of PANI nanofibers was reported by Kaner et al. with a liquid–liquid interfacial polymerization method.[7] Manohar et al. also reported the synthesis of PANI nanofibers by the method of ‘nanofiber seeding’.[8] As to the preparation of PANI hollow spheres, many methods have also been reported. Niu et al. reported the preparation of PANI hollow spheres by a template method, whose process was described as follows: monodisperse polystyrene particles were pre-functionalized with sulfone groups by sulfonic acid, and then aniline monomers absorbed on the sulfonated polystyrene cores were polymerized to form a core–shell structure, finally PANI hollow spheres were success-

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[1] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
Fax: (+86) 10-6441-6338;
E-mail:yangwt@mail.buct.edu.cn

[2] Department of Polymer Science, Beijing University of Chemical Technology, Beijing, 100029, P. R. China

fully fabricated by dissolving the polystyrene core.[2] A hollow octahedral PANI structure has been synthesized by using octahedral cuprous oxide as a sacrificial template.[9] Recently, methods to prepare PANI hollow microspheres using an easily removed emulsion template or by assembling with salicylic acid as dopant have been reported.[10]

It is desirable to put nanometer- or micro/nanometer-structured PANI onto insulting substrates and integrate them into useful devices. Some studies towards this have been reported. For example, oriented PANI nanowires have been fabricated with absorbed surfactants as templates on an atomically flat surface.[11] PANI nanowires have been fabricated on silicon surfaces with DNA templates.[12] Liang et al. and Liu et al. reported the template-free synthesis of large arrays of uniform and oriented PANI nanowires (with diameters much smaller than 100 nm) by electrochemical methods on a variety of substrates (Pt, Si, Au, carbon, silica).[13] Sawall et al. reported the surface grafting of PANI nanofibers on Au surfaces by an interfacial polymerization method.[14] As we know, polymeric materials are important and widely used because of their light weight, flexibility, shock resistance, and low cost.[15] The immobilization of PANI on the surfaces of polymer substrates has attracted growing attention in recent years.[16] In a previous report, we successfully built micro/nanostructured PANIs that included spherical particles, wires, and ribbons that were tethered on organic polymer substrates by a two step strategy.[17] This paper is a continuation of the work of the previous report, and herein, we show that with the same strategy (Figure 1), hollow PANI monolayer submicrospheres could be grown on the surface of a PP film when the molar ratio of AA to aniline was about 1:1.6. The special composite film with a tethered monolayer of PANI hollow spheres, and the feasibility and facility in the fabricating process reported here, are novel and meaningful for material science and technology.

Experimental Part

Materials

Commercially cast PP films 30 μm in thickness were cut into rectangular shapes 3.0 cm × 5.0 cm in size, and were then extracted by acetone for about 36 h to remove impurities and additives before use. Aniline and acrylic acid (AA) were distilled under reduced pressure. Acetone, ammonium persulfate (APS), benzophenone (BP), and methanol were all of analytical grade and used without further purification.

Measurement

Field emission scanning electron microscopy (FESEM, JEOL JSM-6700 F) was used to observe the surface features of the

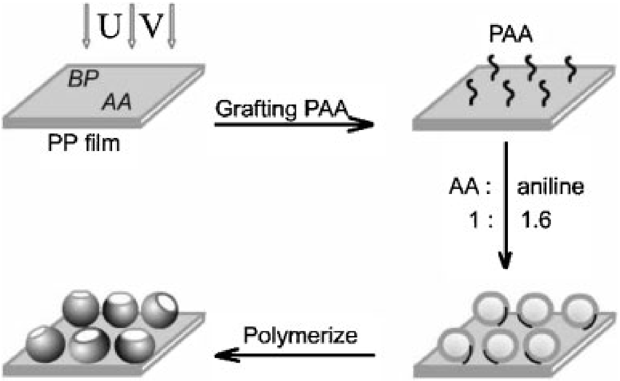

Figure 1.
Illustration of the process to fabricate the monolayered PANI hollow microspheres on the surface of a PP film.

resultant films and the PANI formed in solution. The morphologies of the PANI particles in aqueous solution were observed by transmission electron microscopy (TEM, H-800, Hitachi). The electrical conductivity was measured by a two-probe method under laboratory conditions with a 2400 digital source meter (Keithley). The distributions of grafted chains on the surfaces of PP-*g*-PAA and PP-*g*-PAA/PANI films were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). ATR-FTIR spectra were recorded on a Nicolet NEXUS 670 with a variable angle horizontal ATR accessory, on which a 45° rectangle ZnSe crystal was used. The UV-visible spectra of the PP-*g*-PAA/PANI films were recorded on a GBC CINTRA 20.

Preparation of a Monolayered PANI Hollow Submicrospheres on the PP Film Surface

The process mainly involved two steps, i.e., the grafting of PP films with AA and then oxidative polymerization of the aniline monomer on the surface of the PP-*g*-PAA films. In a typical experiment, grafting of the PAA on the PP film's surface using BP as a photoinitiator was carried out and purified as reported by Yang and coworker.[18] The PP-*g*-PAA films prepared were immersed into 300 mL of deionized water that contained 4.5 mL of AA and 9.6 mL of aniline. After stirring for 12 h, an aqueous solution of APS (as oxidant, the molar ratio of APS/aniline was 1:1) was added into the above solution (after having been placed in an ice bath for 2 h) in one portion. The reaction was allowed to proceed for 12 h at 0–5 °C. Finally, the composite film was splashed with water and then washed with deionized water and methanol three times, respectively. The composite films were dried under vacuum at 30 °C for 24 h.

Results and Discussion

The morphologies of the PANI/PP composite films are shown in Figure 2–d. It is clear that the surface of PP film is covered with many PANI spheres, and a majority of them have a diameter of about 800 nm. Some broken spheres disclose their hollow structure and the thick wall, about 150 nm (Figure 2b). Meanwhile, it is apparent that the number of PANI hollow spheres increases with the grafting percentage (the weight ratio of grafted PAA to PP-*g*-PAA) of PAA from 0.8 wt.-% to 1.5 wt.-% (Figure 2c,d). However, the shape of the PANI particles looks like 'disc' like, not spherical, when the grafting percentage of PAA is 1.5 wt.-%. It is found that PANI monolayer hollow spheres can be well formed on the surface when the grafting percentage of PAA is lower than 1.3 wt.-%. These results probably indicate that the PAA grafted on the surface of the PP film might serve as 'anchors'. The PANI monolayer hollow submicrospheres are tied to the surface of the PP films by these anchors.

The ATR-FTIR spectrum of the composite films with monolayered PANI hollow submicrospheres is shown in Figure 3. As controls, the spectra of a PP blank film and a PP film grafted with PAA are also shown. Comparing these spectra, besides all the characteristic bands assigned to the grafted PAA (for example, the C=O stretching vibration of carboxylic groups at about 1710 cm^{-1}), the characteristic bands of PANI at the 1581 cm^{-1} (assigned as the C=C stretching vibration of the quinoid rings) and 1489 cm^{-1} (C=C stretching vibration of the benzenoid rings)[19] definitely show that PANI is tethered on the PP films. The result is similar to that of the PP film's surface immobilized with micro/nanostructured PANI.[17]

From the UV-visible absorption spectra of PANI, it can be seen that a shoulder peak at about 420 nm and a broad peak at 800 nm with a tail assigned to the polaron transition (Figure 4a), are typical protonation characterization, identical to that of the emeraldine salt form of PANI.[20] These results are similar to the spectrum of helical PANI nanocomposites synthesized with PAA/10-camphorsulfonic acid (CSA)/aniline.[6m] When the PANI was dedoped (Figure 4b),

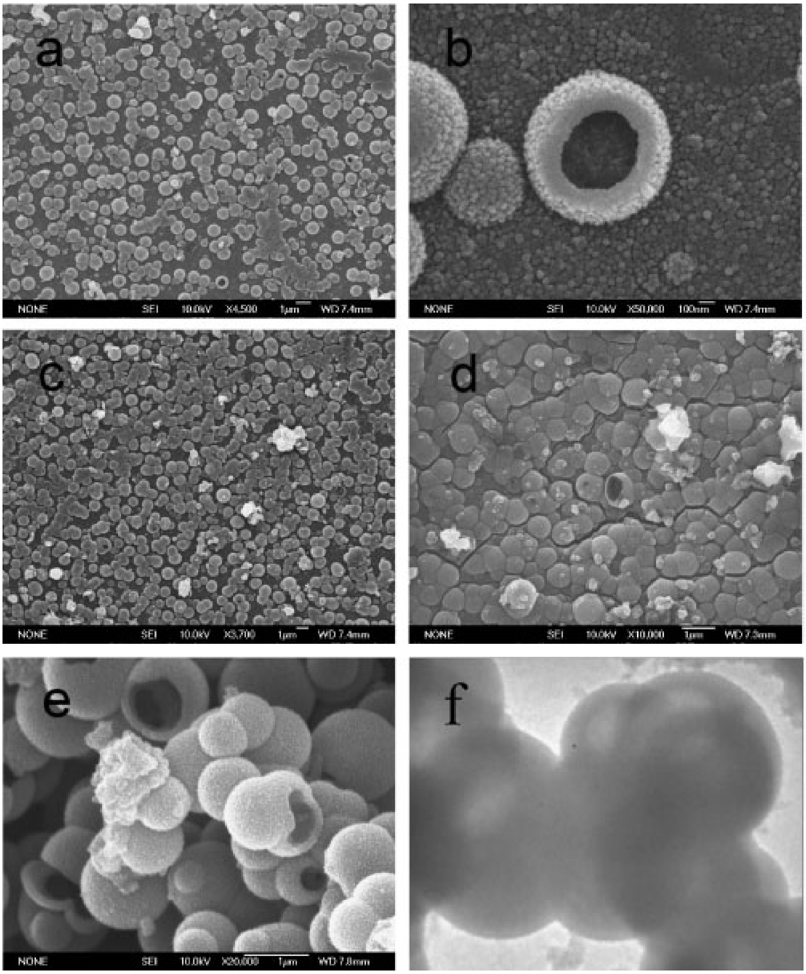

Figure 2.

FESEM images (a, b, c and d) of PANI hollow spheres on the surface of the PP film, reaction condition: AA = 0.22 M, AA/aniline/APS = 1:1.6:1.6. a, b) grafting percent of PP-*g*-PAA is 0.8 wt.-%, c) grafting percentage of PP-*g*-PAA is 1.1wt.-%, d) grafting percentage of PP-*g*-PAA is 1.5 wt.-%; e and f) FESEM and TEM image of PANI hollow spheres obtained in solution after removing PP/PANI composite film.

only two peaks at 320 nm and 630 nm can be observed in their UV-visible absorption spectra of the PANI, which are the same as that of the emeraldine base form of PANI. These results suggest that the PANI can be doped with PAA and AA, and furthermore dedoped with ammonium hydroxide. The UV-visible absorption spectra of PANI consists with that reported by Huang at al.[7a] The conductivity of the composite conductive films with submicrometer monolayered PANI hollow spheres is 1.1×10^{-2} S/cm (grafting percent of PP-g-PAA is 1.1%, AA/aniline/APS = 1:1.6:1.6). The result is also similar to the conductivity of helical PANI/PAA/CSA nanocompsoite.[6m]

In order to further understand the forming mechanism of the formation of the PANI hollow spheres, the morphologies of PANI in aqueous solution were observed by FESEM and TEM. In Figure 2e, some broken spheres with a wall thickness of about 150 nm reveal their hollow structure, which matched well with the results observed on the surface of the PP film (Figure 2a–d). Although the contrast of the

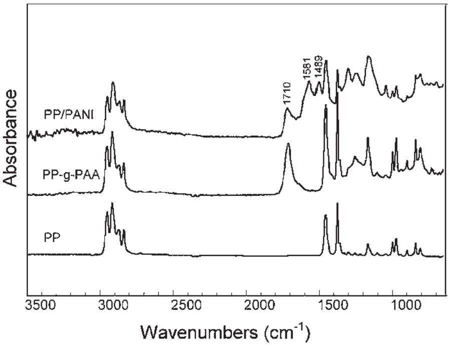

Figure 3.
ATR-FTIR absorbance spectra of a PP film, a PP-*g*-PAA film, and a PP composite film tethered with monolayered PANI hollow sphere.

TEM image of PANI is not great enough due to the thickness of the wall (150 nm), it still can be determined that the PANI spheres are hollow.

In addition, it is found that when the molar ratio of AA to aniline is 1:2.5, both PANI hollow spheres and PANI rods could be observed by FESEM. When the molar ratio of AA to aniline decreased to 1:1.6 and the concentration of AA changed from 0.14 to 0.31 M, only PANI hollow spheres on the surface of the PP film were observed. However, PANI hollow spheres tethered onto the surface of the PP film could not be found when the ratio of aniline/AA was lower than 1.4, which has previously been reported by our group.[17b]

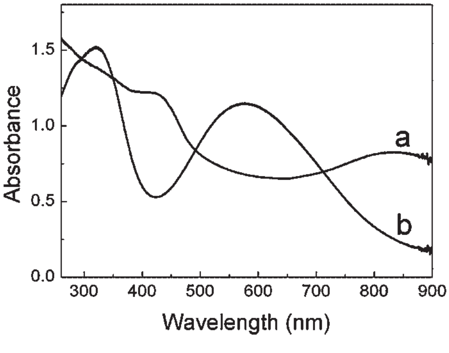

Figure 4.
UV-visible spectra of microstructured PANI conductive composite film: a) untreated and b) treated with ammonium hydroxide.

Zhang et al. have reported that PANI hollow microspheres could be synthesized when the salicylic acid/aniline ratio is ranged from 0.5 to 1.0. The formation mechanism for the PANI hollow sphere is proposed to be a result of the hydrogen-bonding interaction of the –OH group of salicylic acid with the amine of the PANI, which might be a driving force to self-assembly of the hollow spheres.[10b] In the AA/aniline system, PANI hollow microspheres formed by hydrogen bonds acting as a driving force might be impossible for the differently structured AA with salicylic acid. In our previous work, PANI nanowires have been immobilized on the surface of PP with a PAA/SDS (sodium dodecyl sulfate)/aniline system. PAA might play an important role in the formation of PANI nanowires.[17a] PANI with a controllable shape such as spherical particles, wires, and ribbons have been fabricated with the system of AA/aniline.[17b] Thus the mechanism of formation of the PANI hollow spheres with the system of AA/aniline might be a little different. It is thought that AA as a dopant for PANI, is composed of a hydrophobic alkyl group and a hydrophilic carboxylic group, in analogy to a surfactant such as SDS, which can form spheres, cylinders, and bilayers.[21] Here the AA might form micelles. Moreover, the structural units of the PAA chains grafted onto the surface of the PP films might also participate in AA micelle formation. When aniline is added, it probably reacts with the carboxylic groups so that the micelles with aniline are formed. Meanwhile, part of these micelles might be fixed on the surface of the PP films considering the PAA grafted on the surfaces. Free aniline and AA (and PAA)/anilinium probably take the shape of a droplet, where aniline serves as the core and AA/anilinium act as the shell.[10a] Simultaneously, the PAA chains grafted on the surface probably join in the formation of the core–shell structure considering the fact that the number of PANI monolayer hollow spheres increased with the PAA grafting percentage, thus the core–shell particles were fixed on the surface of the PP film. When APS is added, the polymerization would occur on the surface of the droplet to form the hollow spheres. Because the APS is soluble, it is almost impossible for it to diffuse into the droplets to oxidize aniline.[22] From the SEM images of the hollow spheres(Figure 2b), it can be seen that the surface of the hollow spheres is rough. This result indicates that the oxidation reaction occurs on the side of the water phase of the aniline/water droplets. The mechanism of formation of the PANI hollow spheres is strongly supported by the synthesis of poly(*o*-toluidine) hollow spheres using the droplets of *o*-toluidine in aqueous solution as a template during the polymerization process.[23] The formation mechanism of the PANI hollow spheres is similar to the platinum nanoshell synthesized using a tin-lipoporphyrin photocatalyst to initiate the reduction of platinum onto the surface of benzene nanodroplets in water.[24]

In summary, PANI monolayer hollow spheres were fixed on the surface of a PP film, the majority with a diameter of about 800 nm. The conditions to fabricate the PANI monolayer hollow spheres were systematically investigated. The formation mechanism of the PANI hollow spheres was speculated: the free aniline probably served as the core and the AA/anilinium acted as the shell, and the surface pregrafted PAA might also join in the formation of the shell structure. The proposed method provides a wider, easy, and repeatable route to prepare PANI monolayer hollow spheres.

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