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## COMMUNICATION

# Preparation of Multi-Shelled Conductive Polymer Hollow Microspheres by Using Fe<sub>3</sub>O<sub>4</sub> Hollow Spheres as Sacrificial Templates

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**Multi-shelled conductive polymer hollow microspheres were successfully generated by using Fe<sub>3</sub>O<sub>4</sub> hollow sphere as sacrificial template via a programmed reaction temperature process. Moreover, the multi-shelled PEDOT exhibited superb microwave absorbing performance.**

Hollow microspheres have gained tremendous attention as catalysts support,<sup>1</sup> electrode materials,<sup>2</sup> drug delivery agent,<sup>3</sup> sensors,<sup>4</sup> Li-ion batteries<sup>5</sup> and many others<sup>6</sup> because of their unique properties including controllable internal structure, high surface area, low density and desirable permeability. More recently, extensive studies have been devoted to synthesis of hollow spheres with multiple shells, which are expected to have better performances in chemical sensing,<sup>7</sup> microwave absorbing<sup>8</sup> and dye-sensitized solar cell applications.<sup>9</sup> So far, the fabrication of multi-shelled hollow structures is mainly based on inorganic materials. For example, multi-shelled Cu<sub>2</sub>O hollow microspheres were prepared via a cetyltrimethylammonium bromide (CTAB) vesicle templating route.<sup>10</sup> A facile method for synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> multi-shelled hollow spheres by spray drying has been developed,<sup>11</sup> or in more general, the number of shells of metal oxide hollow microspheres could be controlled by the utilization of carbonaceous microspheres as template.<sup>12</sup> These preparative methods, however, always involve a high temperature calcination processing or suit for each specific inorganic material and therefore difficult to applied for the preparation of organic materials. Nevertheless, it can be expected that such materials, for instance polymeric multi-shelled hollow spheres, would have more attractive characteristics compared to the metal ones, such as lower density, better processability, more excellent biocompatibility, which are promising for them to be used in electronic devices and drug delivery systems etc.. In particular, it will be an extremely valuable practice if we can prepare multi-shelled microspheres of conductive polymers (CPs) since they are a kind of organic material with unique electrical properties, controllable electrochemical and physicochemical properties.<sup>13</sup>

The synthesis of hollow spheres with multiple organic shells is essentially based on a layer-by-layer templating technique.<sup>14</sup> However LBL assembly is time-consuming and tedious when many layers are required. According to Wang and co-worker's report, hollow templating method can be a straightforward way to prepare multi-shelled polymers.<sup>15</sup> However, this method can be very difficult, since it require the shell possess transverse channel

allowing the precursor to reach the inner surface and an effective force to ensure the products coat on both outer and inner surface of the template. There are few successful examples attribute to the limited templates available, Yang et. al reported synthesis of functional polymer hollow spheres with double-shelled microspheres using hollow latex cages as templates,<sup>16</sup> unfortunately the complex how template and tedious after-processing which restrict its application. In a word, developing convenient and efficient methods to prepare multi-shelled functional organic materials is emergent needed.

Herein, we report for the first time on an ingenious and controllable one-step strategy for the synthesis of multi-shelled poly(3, 4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) hollow microspheres with tunable wall thickness under mild reaction condition by using Fe<sub>3</sub>O<sub>4</sub> hollow spheres as a sacrificial template. Taking advantage of the slow etching effect of acid dopant *p*-toluenesulfonic acid (*p*-TSA), monomer could penetrate into the inner surface of Fe<sub>3</sub>O<sub>4</sub> hollow template shell and the template was removed gradually via a programmed reaction temperature process. The formation mechanism of conductive polymer was also discussed in the article.

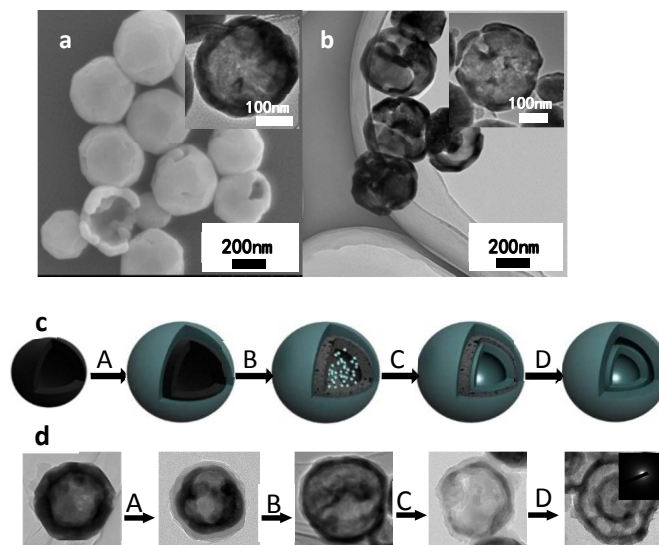


Fig. 1. a) SEM and TEM (inset) images of the  $\text{Fe}_3\text{O}_4$  hollow template; b) TEM images of the  $\text{Fe}_3\text{O}_4$  hollow template after etching by *p*-TSA for 6 h at 40 oC; c) Schematic illustration of the formation mechanism of double-shelled CP microspheres: A) CPs were coated on the surface of  $\text{Fe}_3\text{O}_4$  hollow shell; B) monomers entered the internal of the hollow  $\text{Fe}_3\text{O}_4$ ; C) CPs were coated on the inner surface of  $\text{Fe}_3\text{O}_4$  hollow shell; D)  $\text{Fe}_3\text{O}_4$  templates were dissolved completely and double-shelled CP microspheres were gained; d) TEM images of the product in each stage; insert image is the selected area electron diffraction (SAED) pattern of the inner shell.

In our previous report, it was proven that only by employing the  $\text{SO}_3^{2-}$  group in *p*-TSA molecules, CP could coated on the surface of the  $\text{Fe}_3\text{O}_4$  hollow microspheres to form a core-shell structure.<sup>17</sup> In this work, we discovered that *p*-TSA could dissolve the  $\text{Fe}_3\text{O}_4$  hollow template gradually with the increase of temperature. As shown in Fig. 1a the original surface of  $\text{Fe}_3\text{O}_4$  hollow template was compact and smooth, however, it became loose and porous, seem like the cell structures after etching by *p*-TSA for 6 h at 40 oC (Fig. 1b), which would result in the penetration of the 3, 4-ethylenedioxythiophene monomers into the cavity of the  $\text{Fe}_3\text{O}_4$  hollow micro-particles, so that allows a polymerization on the inner surface in addition to the outer surface of the template. Therefore at a certain time point when the templates were dissolved completely, double-shelled CP microspheres were successfully fabricated. During this process, *p*-TSA acid plays tri-functional roles: the bridge between monomer and  $\text{Fe}_3\text{O}_4$  hollow template, acid dopant<sup>14</sup> and the etchant of  $\text{Fe}_3\text{O}_4$  hollow template. Fig. 1c illustrates the synthesis of double-shelled CP hollow microspheres. TEM images in Fig. 1d show the products at different synthetic stages, which confirms the mechanism described in Fig. 1c. From the insert SAED pattern taken on the inner shell, no diffraction spot was observed, which indicated that the inner layer was composed of organic substance. In order to identify the components of reaction products, XRD and FTIR were characterized and plotted in Fig. 2 and Fig. S1, respectively.

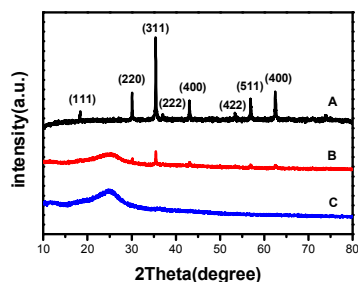


Fig. 2. Powder X-ray diffraction (XRD) of products for various reaction times at 40 oC: (A) 0 h; (B) 12 h; (C) 24 h.

Powder X-ray diffraction (XRD) confirmed that the template was composed of crystalline  $\text{Fe}_3\text{O}_4$  (Fig. 2A) (JCPDS card No. 19-0629). With the reaction time going on, the intensity of diffraction peaks reduced (Fig. 2B) and disappeared completely after 24h. Henceforth, two weak peaks at  $2\theta = 25.6^\circ$  and  $11.7^\circ$  appeared (Fig. 2C), assigned to PEDOT according to literature.<sup>18</sup> Besides, FTIR spectrum also confirmed the compositions of the products were PEDOT without any other phases presented (Fig. S1).<sup>19</sup>

From a broken microsphere, a spherical core inside the outer shell can be clearly seen (Fig. S2a, inset), EDS analysis of the as-synthesized core-shell microspheres gives strong signals from C, O, and S elements (Fig. S2b), which demonstrates the inner core and outer shell are homogeneous PEDOT.

The multiple shell formation process was studied in more detail by carrying out the reactions at different temperatures. Through a polymerization for 24 h, it was found in TEM images that PEDOT had tightly covered on the surface of  $\text{Fe}_3\text{O}_4$  template at 20 oC (Fig. 3a), whereas spaces appeared between polymer layer and the template when the sample was harvested at 30 oC. When reacting at

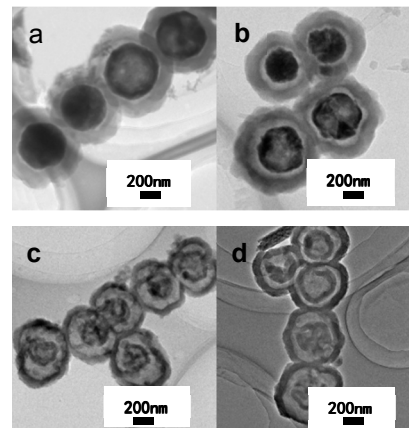


Fig. 3. TEM images of double-shelled PEDOT microspheres with different polymerization temperature: a) 20 oC for 24 h; b) 30 oC for 24 h; c) 40 oC for 24 h; d) 60 oC for 9 h.

40 oC, the inner  $\text{Fe}_3\text{O}_4$  template dissolved totally and second shell of PEDOT generated (Fig. 3c). Moreover, similar double-shelled PEDOT can also be obtained at an increased temperature (60 oC) but for shorter time (9 h) (Fig. 3d). Therefore, the acid dopant in the system could be efficiently utilized as an etchant to remove  $\text{Fe}_3\text{O}_4$  hollow template via a programmed reaction temperature process.

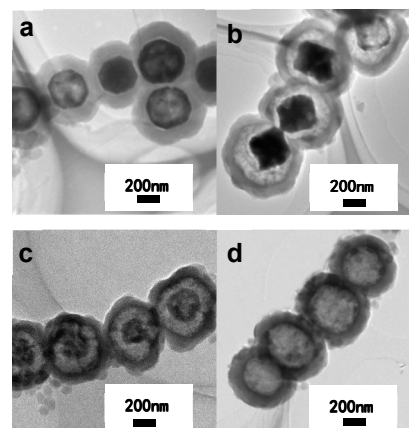


Fig. 4. TEM image of the obtained product microspheres prepared with different *p*-TSA concentration at 40 oC for 24 h: a) 0.05; b) 0.1; c) 0.2; d) 0.4 mol  $\text{L}^{-1}$ .

Furthermore, we explored the influence of *p*-TSA concentration on the formation of double-shelled PEDOT, due to the crucial role of *p*-TSA acid in the system. When the *p*-TSA concentration was 0.05 and 0.1 mol  $\text{L}^{-1}$ , the  $\text{Fe}_3\text{O}_4$  template couldn't be removed completely, so that the products were  $\text{Fe}_3\text{O}_4$ /PEDOT composites (Fig. 4a and 4b). With the increasing of *p*-TSA concentration, e.g. at 0.2 mol  $\text{L}^{-1}$ , the  $\text{Fe}_3\text{O}_4$  template was dissolved gradually, and double-shelled PEDOT with good morphology was obtained (Fig. 4c). Nevertheless, if the concentration of *p*-TSA acid reached to 0.4 mol  $\text{L}^{-1}$ , only hollow PEDOT micro particles could be gained (Fig. 4d).

Therefore the key factors for controlling the process are the dissolution rate ( $r_{\text{dis}}$ ) of  $\text{Fe}_3\text{O}_4$  and the polymerization rate of CP ( $r_p$ ). When  $r_{\text{dis}}$  is rapider than  $r_p$ , only single-shelled CP microspheres can be formed. In contrast, double-shelled CPs are acquired when the  $r_p$  is greater than  $r_{\text{dis}}$ , since monomers have enough time to enter the internal of  $\text{Fe}_3\text{O}_4$  hollow template and polymerize at the interior surface. As a comparison, we conducted a series of tests by adding different amount of etchant, i.e. HCl solutions, to the reaction system



in the room temperature rather than increasing the temperature. As shown in Fig. S3, core-shell  $\text{Fe}_3\text{O}_4$ -PEDOT composites and hollow PEDOT microspheres were mainly obtained. Even though, a few double-shelled PEDOT microspheres were observed, but with very slight inner shells. In addition, many redundant PEDOT solid particles appeared in the system, which indicated the use of additional acid etching could not control the formation of double-shelled PEDOT microspheres effectively. In our research, the slow etching effect of *p*-TSA can be better controlled with temperature, double-shelled PEDOT microspheres were prepared by one-step strategy efficiently and environmentally friendly, rather than adding any strong inorganic acids.

We further tested the conductivity of the double-shelled PEDOT (sample Fig. 4c) which was about  $1 \text{ S cm}^{-1}$ , much higher than that of hollow PEDOT microspheres reported in literature ( $8 \times 10^{-2} \text{ S cm}^{-1}$ ).<sup>20</sup> Likewise, the shell thickness and the conductivity of the double-shelled PEDOT could be adjusted through tuning the (EDOT)/( $\text{Fe}_3\text{O}_4$ ) ratio. It is found that the conductivities of double-shelled PEDOT increase with the (EDOT)/( $\text{Fe}_3\text{O}_4$ ) ratio increasing (Fig. S4 and Table S1).

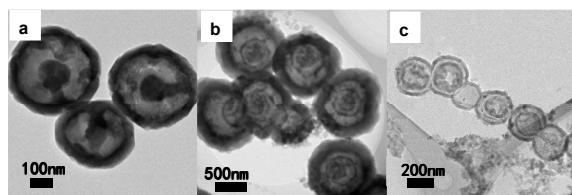


Fig. 5. TEM image of a) yolk-shell structured  $\text{Fe}_3\text{O}_4$  hollow template; b) triple-shelled PEDOT microspheres; c) double-shelled PPy microspheres.

This method is also available for the synthesis of triple-shelled PEDOT when yolk-shell structured  $\text{Fe}_3\text{O}_4$  hollow template is used, as it allows the monomers to polymerize on both the exterior and interior surfaces of the shell, besides it will also form a polymer shell on the surface of the inner solid particle (Fig. 5a and 5b). What's more double-shelled PPy could also be successfully fabricated by this sacrificial templating method<sup>21</sup> (Fig. 5c and Fig. S5). All these results suggest that this facile method has good universality and diversity of applications.

Multi-shelled microspheres made from conductive polymers can display enhanced electrical, electro-optical and electro-chemical properties. In this work we demonstrate the microwave absorption ability of the double-shelled PEDOT microspheres. The relative complex permeability ( $\mu_r$ ) and permittivity ( $\epsilon_r$ ) were measured and the reflection losses (RL) were calculated in the frequency range of 8-18 GHz at 20% volume fraction according to the transmit line theory (detailed calculation Equation S1 and S2, synthesis procedure for different morphology of PEDOT (Fig. S6) are presented in the Supporting Information).

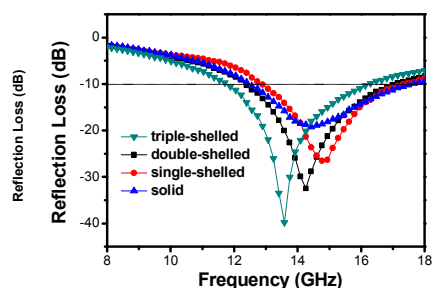
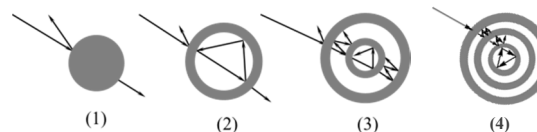


Fig. 6. Reflection losses for different morphology of PEDOT microspheres in the frequency range of 8-18 GHz at 20% volume fraction with a thickness of 2 mm.

It can be seen in Fig. 6 that with the increase of shell numbers, the microwave absorption properties of PEDOT microspheres enhanced obviously. The maximum RL value of the triple-shelled and double-shelled PEDOT is 39.7 and 32.4 dB respectively with a thickness of 2 mm, which is higher than that of PEDOT solid particles (19.2 dB) and single-shelled PEDOT (26.5 dB). Actually, the multi-shelled PEDOT shows better performance than the solid particles and single-shelled PEDOT within a thickness interval of 2-4 mm in the frequency range of 2-18 GHz at 20% volume fraction (Fig. S7).



Scheme 1. A microwave pathway illustration of 1) PEDOT solid structure; 2) PEDOT hollow structures; 3) double-shelled PEDOT hollow structures; 4) triple-shelled PEDOT hollow structures.

The excellent microwave absorption performance of the double-shelled PEDOT microspheres is attributed to the existing interfacial polarization between multiple core/shell/shell gradient interfaces, which are extremely favourable for electromagnetic attenuation.<sup>22</sup> Moreover, the relatively large specific surface area of the PEDOT hollow microspheres (57.5, 48.4, and  $20.2 \text{ m}^2 \text{ g}^{-1}$  for single-shell, double-shell, triple-shell hollow microspheres respectively; Fig. S8) than that of the solid PEDOT microspheres ( $5.4 \text{ m}^2 \text{ g}^{-1}$ ) and high void space in these multiple shell microspheres can provide more active sites for reflection and scattering of electromagnetic wave. In this way, electromagnetic waves can be effectively interrupted (Scheme 1). All these results suggested that the multi-shelled PEDOT microspheres were attractive candidates as high efficient microwave absorber with light weight, thin thickness, and strong absorption characteristics. Furthermore, making use of the large specific surface area and outstanding electrical properties, the hierarchical PEDOT multi-shelled hollow spheres may be used in other fields such as carrier, sensor and drug delivery.

In summary, we developed an ingenious and controllable one strategy to synthesis multi-shelled CP microspheres by using  $\text{Fe}_3\text{O}_4$  hollow microsphere as sacrificial template. The selection of *p*-TSA as etchant is the key factor that realizes the synthesis. The number and thickness of shells could be designed by adjusting the morphology of  $\text{Fe}_3\text{O}_4$  template, the concentration of *p*-TSA, reaction temperature and the monomer-to- $\text{Fe}_3\text{O}_4$  ratio. Moreover, these double-shelled PEDOT displays superb microwave absorbing performance, attributed to its large specific surface areas and outstanding electrical properties. Besides, the multi-shelled microspheres may also have excellent performances when using as carriers or sensors etc.. The strategy used herein may have enormous potential to the preparation of various multi-shelled hollow organic materials with multi-functions for multipurpose applications.

## Notes and references

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