Synthesis of Poly(3,4-ethylenedioxythiophene) Hollow Spheres in CTAB/DBS — Mixed Surfactant Solutions

*Jing Sui, Lijuan Zhang, Jadranka Travas-Sejdic, Paul A. Kilmartin**

Summary: Hollow microspheres of PEDOT (poly(3,4-ethylenedioxythiophene) ranging from 0.5 to 10 μm have been synthesized by chemically oxidative polymerization of EDOT(3,4-ethylenedioxythiophene) using ammonium persulfate in a catanionic surfactant solution obtained by mixing cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS). The effect of the molar ratio of CTAB to SDBS on the morphology of the PEDOT oxidation products has been investigated using SEM and TEM and by an analysis of the structural properties using UV-visible, FTIR and Raman spectroscopies, elemental analysis and conductivity measurements. The electro-catalytic activity of PEDOT hollow microspheres for the oxidation of ascorbic acid was investigated by cyclic voltammetry in a pH 6 citrate/phosphate buffer solution and compared to the activity of granular PEDOT particles formed in the absence of the catanionic surfactant.

Keywords: ascorbic acid; conducting polymers; hollow sphere; PEDOT; vesicles

Introduction

Over the past two decades, conducting polymers have received considerable attention as a new class of functional materials owing to their unique chemical and physical properties.[1] Recently, micro or nano scaled spheres of conducting polymers have attracted special attention because of their hollow structures, low effective density and high surface area[2–4] which make them promising materials for application in drug delivery,[5] biosensors,[6] catalysis[7] and encapsulation.[8]

Poly (3,4-ethylenedioxythiophene) (PEDOT) is a member of a family of thiophene-based conducting polymers that has attracted much attention because of their high conductivity, low band gap and excellent environmental stability.[9–11] However, compared with other conducting polymers such as polyaniline,[12,13] less research have been undertaken on the preparation and application of nano/micro-structured PEDOT, especially hollow spherical forms. There are only a limited number of reports about hollow spherical PEDOT prepared by chemical oxidation. Mumtaz et al. prepared PEDOT hollow spheres with diameters from 100 to 500 nm by dispersion polymerization in alcoholic media.[14] Wun et al.[15] synthesized PEDOT hollow spheres (1.7 to 4.6 μm in diameter) using injected bubbles as templates. Luo et.al[16] reported that PEDOT hollow spheres could be obtained by chemically depositing PEDOT on polystyrene beads, followed by the removal of polystyrene beads through solvent etching.

Mixtures of anionic and cationic surfactants are known to form rich microstructures such as spherical and rod-like micelles, vesicles, and lamellar phases in aqueous solution.[17] Among these microstructures, vesicles can be potentially applied to template-growth of materials with a hollow spherical morphology.[18]

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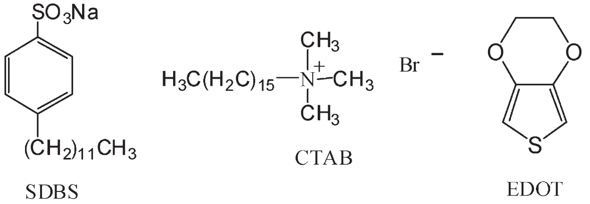

Scheme 1.
Molecular structures of the reactants.

Hollow spheres of CdSe,[19] silica[20] and polystyrene[21] prepared from catanionic surfactant mixtures have been reported. However, no previous work has been devoted to the use of surfactant mixtures as structure-directing agents to synthesize conducting polymer micro hollow spheres. In this article, we report the synthesis of PEDOT hollow microspheres ranging from 0.5 to 10 μm in size using a mixed solution of cetyltrimethylammounium bromide (CTAB) and sodium deodecylbenzenesulfonate (SDBS). PEDOT hollow microspheres showed more effective electrocatalytic activity for ascorbic acid (AA) oxidation compared with granular PEDOT particles.

Materials and Methods

Materials

3,4-ethylenedioxythiophene, ammonium persulfate (APS), cetylytrimethylammonium bromide (CTAB), sodium dodecyl bezenesulfonate (SDBS) and ascorbic acid (AA) were obtained from Aldrich Chem. Co. EDOT was distilled under reduced pressure and stored in the dark under nitrogen. The citrate/phosphate aqueous buffer at pH 6.0 was prepared by mixing 36.85 mL of 0.1 M citric acid and 63.15 mL of 0.2 M Na_2HPO4.

Synthesis of PEDOT Hollow Microspheres

In a typical synthesis, the mixed surfactant solution was first prepared by mixing a stock solution of CTAB (30 mM) and SDBS (30 mM) at a volume ratio of 3:7. Then 0.1 mL of 3,4-ethylenedioxythiophene was added into 10 mL of mixed surfactant solution and magnetically stirred for 1 h to disperse the EDOT. 0.228 g of ammonium persulfate (APS) was dissolved in 5 mL of mixed surfactant solution and this APS solution was added to the previously prepared EDOT – mixed surfactant solution all at once. The polymerization reaction was carried out at room temperature under static conditions for 96 h during which the precipitation of black–green products was observed. The obtained product was filtered and the precipitate was washed with water, methanol and acetone several times to remove the residual surfactants. The final product was dried in vacuum at room temperature for 24 h. A granular form of PEDOT was formed using a similar procedure, except without the addition of the mixed surfactants.

SEM and TEM Characterization

The morphologies of the products were investigated using a Philips XL30S field emission scanning electron microscope (SEM) and JEOL TEM-2010 transmission electron microscopy (TEM). Samples for SEM were mounted on aluminium studs using adhesive graphite tape and sputter-coated with platinum before analysis. Samples for TEM measurements were dispersed on micro grids copper coated on a carbon support film.

Structural Characterization

Infrared spectra were measured in the range 400–4000 cm^{-1} on PEDOT pellets made with KBr at a Perkin Elmer 1600 FTIR spectrophotometer, taking 20 scans at a resolution of 4 cm^{-1}. The Raman spectra of PEDOT samples were recorded using a Renishaw Raman spectrometer with 785 nm (red) laser excitation. The samples were examined under ambient conditions without any prior treatment. The UV-Vis spectra of the PEDOT products in DMSO were recorded in the range of 300-900 nm using a Shimadzu Pharmaspec UV-1700. Elemental analyses were carried out at the University of Otago, Dunedin, New Zealand. The room temperature conductivity of compressed pellets was measured using a standard four-probe method at a Jandel Model RM2 instrument.

Preparation of PEDOT Hollow Microspheres and PEDOT Granular Particles Modified Glassy Carbon Electrodes

The glassy carbon electrodes (GCE, 3 mm in diameter) were polished with a 0.05 μm alumina slurry followed by rinsing with distilled water and drying at room temperature. PEDOT hollow microspheres and granular particles were dispersed in distilled water to form a 5.0 mg/mL solution and ultrasonically treated for 5 min. The dispersed solution (20 μL) was dropped onto the pre-treated GCE surface and allowed to dry under ambient conditions.

Electro-Catalytic Activity for the Oxidation of Ascorbic Acid

The electro-catalytic activity of PEDOT for the oxidation of ascorbic acid was investigated by cyclic voltammetry using a CHI610 (CH Instruments) electrochemical workstation in a citrate /phosphate buffer solution (pH 6). Each sample was first dispersed in ethanol and the dispersion was dropped onto a (BioAnalytical Systems) 3 mm diameter glassy carbon electrode to form a film which was allowed to dry at room temperature. Ascorbic acid additions to the buffer solutions were made immediately prior to use. The solutions were purged with N_2 for approximately 10 min. Following this, N_2 was allowed to flow over the solution to prevent O_2 from re-entering the cell for the remainder of the experiment, which was undertaken at room temperature. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}, using an Ag/AgCl (+207 mV vs. SHE) reference electrode and a Pt wire counter electrode.

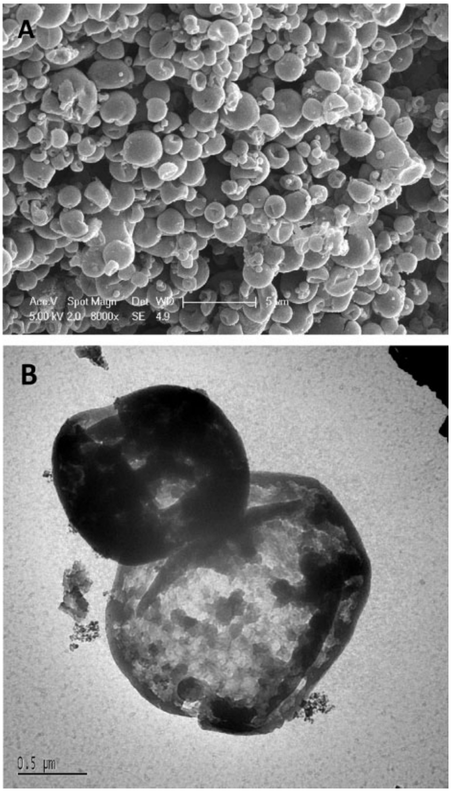

Figure 1.
SEM (A) and TEM (B) images of PEDOT hollow microspheres in the mixed surfactant solution with a molar ratio of CTAB to SDBS of 3:7.

Results and Discussion

Figure 1A shows an SEM image of PEDOT products prepared in a 30 mM mixed surfactant solution when the molar ratio of CTAB to SDBS was 3:7. The products clearly showed a cracked spherical morphology, and the size of these cracked spheres ranged from 0.5 to 3 μm measured from the SEM images. Figure 1B presents TEM images of the same products. The sharp contrast between the dark edges and the pale centres of the microspheres in the TEM images further confirmed that the

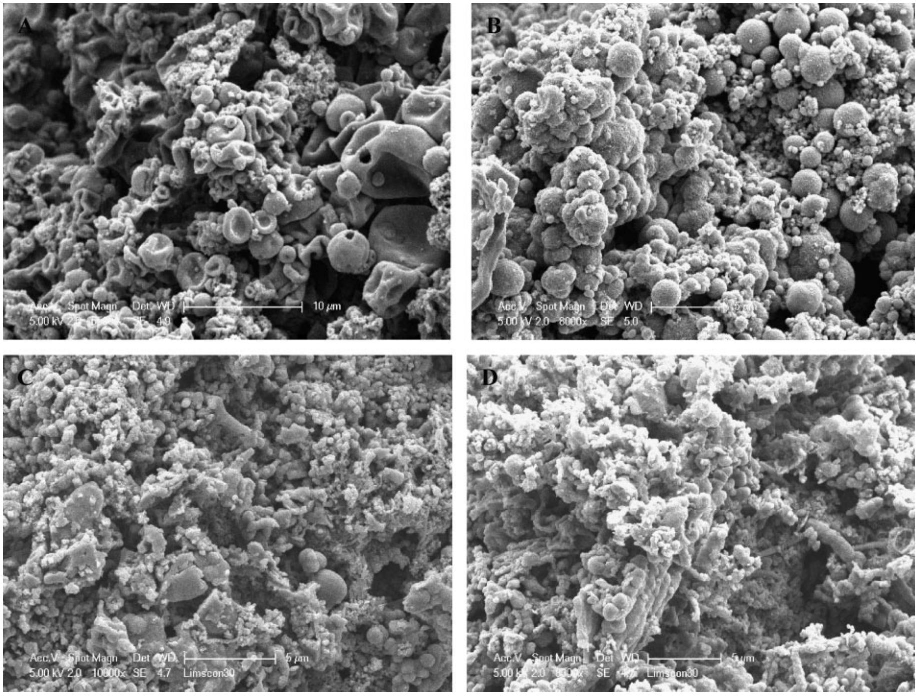

Figure 2.
SEM images of PEDOT prepared in the mixed surfactant solution with different molar ratios of CTAB to SDBS: (A) 2:8; (B) 4:6; (C) 7:3; (D) 8:2.

products were hollow inside. The thickness of the walls of the PEDOT hollow spheres was estimated to be around 60 nm according to measurements from TEM.

PEDOT samples were prepared using different molar ratios of CTAB to SDBS, and the SEM images of the products are given in Figure 2. As seen in Figure 2A, PEDOT hollow spheres ranging from 0.5 to 10 μm in size were obtained when the molar ratio of CTAB to SDBS was 2:8. The 3:7 ratio of CTAB to SDBS seemed to be better for the production of PEDOT hollow spheres with small diameters (Figure 1A). However, a further increase in the molar ratio of CTAB to SDBS did not lead to the preferential formation of PEDOT hollow spheres. Rather, when the molar ratio was 4:6, spherical PEDOT particles were obtained as seen in Figure 2B, which were shown by TEM to be solid in nature (results not shown here). Moreover, the products obtained in CTAB-rich solutions showed several different morphologies including granular particles, rods and spherical particles (Figure 2C and Figure 2D). By contrast, when a surfactant-free reaction solution was used (containing just EDOT and APS), typical granular PEDOT was obtained.

The formation of PEDOT hollow microspheres is suggested to follow the vesicle-template mechanism.[18] As reported previously, when the total concentration of surfactants is 30 mM and the molar ratio of cationic surfactant to anionic surfactant is 3:7, vesicles form spontaneously from the mixture of CTAB and SDBS.[22–23] Therefore, it is reasonable to expect that vesicles could be formed in our reaction system. On the other hand, the hydrophobic EDOT monomer could be solubilised in the hydrophobic region of the vesicle bilayers and cause the original surfactant vesicles to swell.[21] Since the APS oxidant is hydrophilic, the initial polymerization most probably takes place at the interface of water and the vesicle bilayer which results in a hollow structure. The removal of vesicle templates in the washing process may cause the cracked hollow spherical morphology that was observed. The formation of vesicles is commonly influenced by the ratio of anionic surfactant to cationic surfactant.[22]

The effect of the molar ratio of CTAB to SDBS on the formation of PEDOT hollow spheres might be attributed to a number of possibilities. Vesicles are generally formed in a mixture of cationic and anionic surfactants, but the size and structure of the vesicles is influenced by the surfactants employed and their relative ratios.[22] Secondly, catanionic vesicles are metastable and changes in solution conditions such as pH,[24] temperature[25] and salinity,[26] could cause a transformation of the vesicles into other surfactant aggregates. In a typical polymerization of PEDOT, ammonium persulfate has been used as the oxidant and the measured pH value of the system decreases from around 7 to 1.3 due to reduction of the oxidant and release of protons. As a result, the polymerization of PEDOT is likely to affect the stability of the vesicle system to some extent. Synergetic effects of formation and stability of vesicles under reaction conditions contribute to different formation possibilities with PEDOT hollow spheres under different molar ratios of CTAB to SDBS.

A typical UV–visible spectrum of the as-prepared PEDOT hollow spheres dissolved in dimethyl sulfoxide (DMSO) is shown in Figure 3A. The broad absorption centred at 500 nm is attributed to the π-π* transition of PEDOT.[27] The other broad absorption feature in the 700 to 900 nm range can be related to the charge-carrier band of PEDOT, further indicating that the hollow spheres are chemically the same structure as regular PEDOT in the doped state.[28]

An FTIR spectrum of the as-prepared hollow spheres is given in Figure 3B. The vibrations at 1330 and 1522 cm^{-1} are due to C−C and C=C stretching of the quinoidal structure of the thiophene ring.[29] The vibrations at 1204, 1145 and 1086 cm^{-1} originate from C−O−C bond stretching in the ethylenedioxy (alkylenedioxy) group.[30] The C−S bond stretching in the thiophene ring is also seen at 974, 841, and 687 cm^{-1}.[31] The small peaks ranging from 2800 to 3000 cm^{-1}, which are assigned to aliphatic C−H stretching modes coming from the long alkyl tail of dodecyl bezenesulfonate.[32] The appearance of these peaks indicated that dodecyl bezenesulfonate (DBS) is incorporated into the polymer chain as a dopant anion. Figure 3C

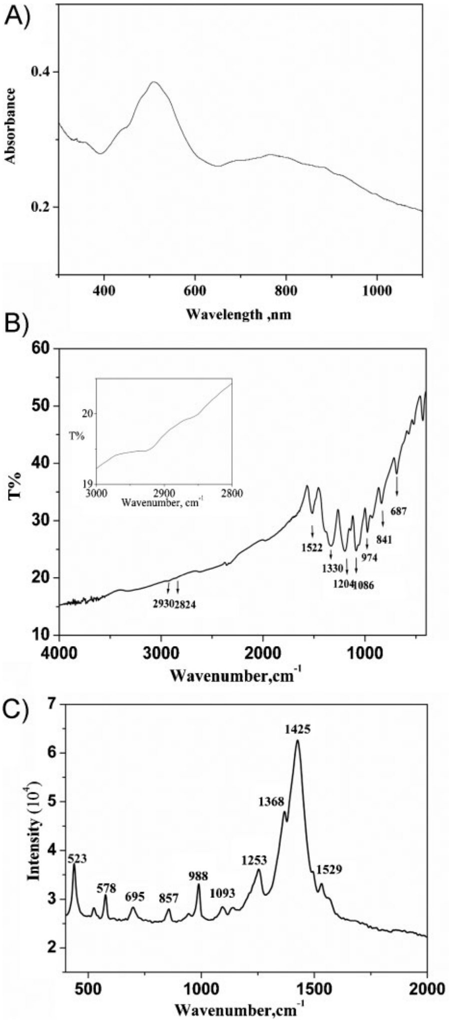

Figure 3.
(A) UV-vis; (B) FT-IR; and (C) Raman spectra of PEDOT hollow microspheres.

shows a Raman spectrum of the PEDOT hollow spheres examined with an excitation wavelength of 785 nm, and the result is in good agreement with previously reported spectra for PEDOT. The shoulder band at 1529 cm^{-1} is associated with the $C_\alpha{=}C_\beta$ antisymmetric stretching vibration, whereas the most intense band at 1425 cm^{-1} is assigned to the symmetric stretching mode of the aromatic $C_\alpha{=}C_\beta$ bond.[33] The 1368 and 1253 cm^{-1} bands are attributed to the stretching modes of single $C_\alpha{-}C_{\alpha,}$ bonds and the $C_\alpha{-}C_{\alpha,}$ inter-ring bonds, respectively.[34] The bands at 988 and 578 cm^{-1} are attributed to the oxyethylene ring deformation, while the band at 695 cm^{-1} is related to the symmetric C-S-C deformation.[31]

Elemental analyses were performed to examine the doping of the PEDOT hollow spheres. Considering the anions available to act as dopants, B^- and dodecyl bezenesulfonate coexisted in the mixed surfactant solutions, while HSO_4^- and SO_4^- were produced from the APS oxidant during the polymerization. All of these anions can potentially be incorporated into the polymer chain as dopants. Elemental analyses of the PEDOT hollow spheres are given in Table 1. As can be clearly seen, the as-prepared PEDOT hollow microspheres mainly consisted of C, H, S and O. The absence of the element Br showed that Br^- was not incorporated into the polymer to a measurable extent as dopant during polymerization. The higher content of oxygen in the PEDOT microspheres, and at a similar mass percentage and O/C ratio as the granular PEDOT particles doped with (bi)sulfate, points to the present of HSO_4^- and SO_4^- as major dopants in the PEDOT microspheres. At the same time, it can be noted that the molar ratio of sulfur to carbon in the PEDOT hollow microspheres is lower than that in granular PEDOT form, while the mass percentage of hydrogen is higher, both of which are consistent with the presence of some DBS as an additional dopant (relatively richer in carbon relative to sulfur), as observed in FTIR spectrum above.

The room temperature conductivity of the samples was measured using the standard four-probe method. The measured conductivity of a pellet of PEDOT microspheres was 12.2 ± 2.5 S cm^{-1}. This value is similar to results previously reported for chemically synthesised PEDOT granular particles.[35]

It has been reported that PEDOT is a good material to lower the potential for ascorbic acid oxidation.[36] On the other hand, our previous research has shown that an electrode modified by micro/nanostructures of conducting polymers such as polyaniline exhibit a more effective electro-catalytic activity for the oxidation of ascorbic acid.[31] Here, the electro-catalytic activity of PEDOT hollow microspheres for ascorbic acid oxidation was investigated using cyclic voltammetry at a scan rate of 50 mV s^{-1} in a pH 6 citrate/phosphate buffer and compared to the response obtained with same amount of PEDOT granular particles.

It is seen clearly that both PEDOT microspheres (Figure 4A) and granular PEDOT particles (Figure 4B) acted as effective redox mediators for ascorbic acid oxidation, and the oxidation peak current increased linearly with the concentration of ascorbic acid in the range of 0.1 to 3 mM;

Table 1.
Comparison of elemental compositions in PEDOT microspheres, granular particles, neutral PEDOT and dodecyl benzenesulfonate.

	C (mass %)	H (mass %)	S (mass %)	O (mass%)	S/C (molar)	O/C (molar)
PEDOT microspheres	45.1	3.53	19.42	31.95[a]	0.161	0.53
granular PEDOT particles	44.05	3.14	20.76	32.05[a]	0.177	0.54
Neutral (dedoped) PEDOT	51.4	2.9	22.8	22.9	0.167	0.33
DBS	66.46	8.92	9.85	14.77	0.056	0.167

[a] calculated by difference from the C,H and S values.

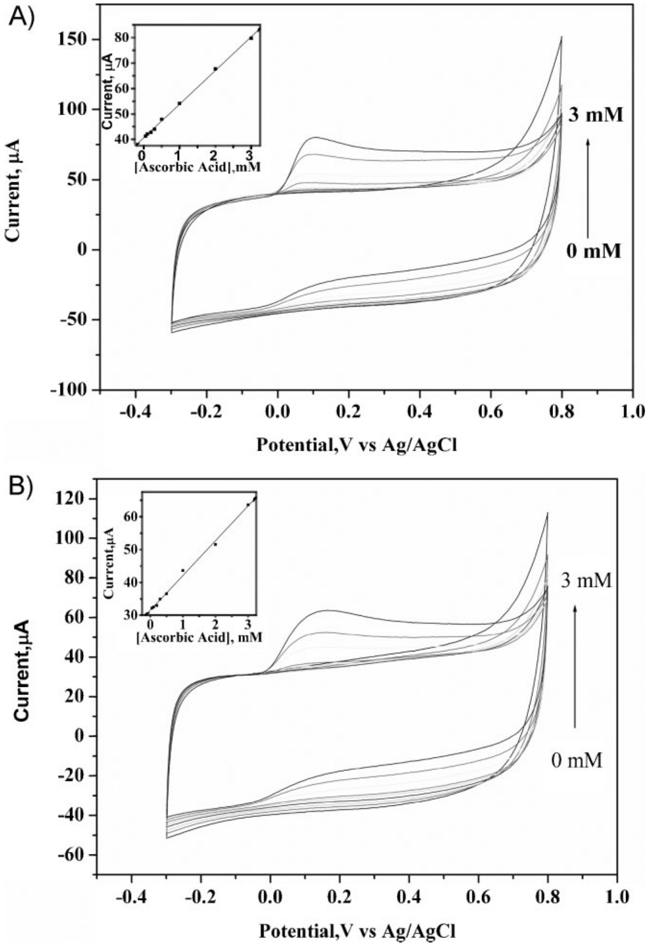

Figure 4.

Cyclic voltammograms recorded at a scan rate of 50 mVs^{-1} of PEDOT hollow microspheres (A), and granular PEDOT particles (B), cast on a glassy carbon electrode in the presence of ascorbic acid at concentrations of 0, 0.1, 0.2, 0.5, 1, 2 and 3 mM, in a pH 6 citrate/phosphate buffer solution. Insets: plot of anodic current versus ascorbic acid concentration at 97 mV for PEDOT hollow microspheres and at 130 mV for the PEDOT granular particles.

the correlation coefficients were 0.999 and 0.996 respectively for PEDOT microspheres and PEDOT granular cast film electrodes (see Figure insets). At the same time, it can be noted that the anodic peak potential for ascorbic acid oxidation was lower (at + 97 mV) for the PEDOT microspheres compared to the PEDOT granular particles (at +130 mV), while the peak current increased from 27 to 37 μA for 3 mM ascorbic acid (beyond the background current for PEDOT internal redox processes) with the PEDOT microspheres compared to the PEDOT granular film. This result showed that the cast film electrode made using PEDOT hollow microspheres showed a more effective

Conclusion

PEDOT hollow microspheres ranging from 0.5 to 10 μm were chemically synthesized in mixed surfactant solutions of CTAB and SDBS following a vesicle-template mechanism. The formation and the size of the PEDOT microspheres were influenced by the molar ratio of CTAB to SDBS. Structural characterizations showed that these hollow microspheres are typical of chemically synthesized PEDOT, and that the anionic surfactant DBS is incorporated into the polymer chain as a dopant. In addition, PEDOT hollow spheres exhibited a more effective electro-catalytic activity for the oxidation of ascorbic acid than granular PEDOT particles, as investigated by cyclic voltammetry.

The novel approach to forming hollow spheres obtained with this method may provide a new pathway for the fabrication of conducting polymer microspheres. However, it is noted that the PEDOT microspheres obtained showed a wide distribution in size. Therefore, efforts should be devoted to the size control in future work.

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