Facile Synthesis of Aqueous-dispersible Nano-PEDOT:PSS-co-MA Core/Shell Colloids Through Spray Emulsion Polymerization

Yu-Kai Han,* Jenq-Nan Yih, Mei-Ying Chang, Wen-Yao Huang, Ko-Shan Ho, Tar-Hwa Hsieh, Jhih-Gong Lou

This paper describes a novel spray emulsion polymerization technique for the preparation of aqueous-dispersible nanoscale core/shell poly(3,4-ethylenedioxythiophene) (n-PEDOT) colloids doped with poly[(4-styrenesulfonic acid)-co-(maleic acid)] (PSS-co-MA). Scanning electron microscopy and transmission electron microscopy images revealed that these n-PEDOT:PSS-co-MA colloids possessed sharp core/shell morphologies. X-ray diffraction and Raman spectroscopy measurements revealed semi-crystalline morphologies and quinoid-dominated structures for these n-PEDOT:PSS-co-MA colloids. The conductivities of n-PEDOT and n-PEDOT:PSS-co-MA pellets were ca. 3.2 and 0.29 S cm⁻¹, respectively, suggesting that PSS-co-MA acted as a shell that blocked the hopping of charges from the n-PEDOT core to neighboring latexes. The work functions of pristine n-PEDOT and n-PEDOT:PSS-co-MA, measured using photoelectron spectroscopy, were ca. 4.7 and 5.05 eV, respectively; thus, they are close to that of indium tin oxide. The PSS-co-MA used in this study featured two different types of interactive functional groups, which acted as oxidative sites, dopants, and core/shell stabilizers during polymerization.

Introduction

The preparation of nanostructured conducting polymer materials—including nanoellipsoids, nanorods, and nanotubes—has become an attractive field of research because, relative to their bulk counterparts, these nanostructures have high surface areas and exhibit different chemical and physical properties; as a result, they have applications in chemical sensors,[9] organic light emitting diodes,[4,5] organic photovoltaics,[6–9] organic thin film transistors,[10–12] electrochromic displays,[13] and plastic memories.[14]

Organic solar cells are green devices that benefit from the use of the amorphous microgel poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonic acid (PEDOT:PSS) as a hole transporting layer for charge hopping to the anode; the ionization potential of PEDOT:PSS is close to the work function of indium tin oxide (ITO), whereas its electron affinity (ca. 2.2 eV) is sufficiently low to block electrons.[15] In some cases, however, charge transport is limited by inefficient hopping along the poorly formed conduction pathways of PEDOT:PSS. Thus, routes that enhance charge...
transport are desirable to improve the performance of such photovoltaic cells. Nano-PEDOT (n-PEDOT) materials offer direct pathways for charge transport.\textsuperscript{[16–18]} They can be obtained through chemical synthesis using a hexane/water reverse micro-emulsion system featuring sodium bis(2-ethylhexyl) sulfosuccinate cylindrical micelles as the template and FeCl\textsubscript{3} as the oxidant.\textsuperscript{[19]} The as-synthesized n-PEDOTs are readily dispersed in common organic solvents to form films when cast on a variety of substrates, but they do not disperse well in aqueous media. In particular, little research has been performed previously on the development of aqueous-dispersible p-type PEDOT colloids.

In this paper, we report a facile and environmental friendly approach toward the fabrication of n-PEDOT core/shell spheres doped with poly[(4-styrenesulfonic acid)-co-(maleic acid)] (PSS-co-MA) polyanions, which serve as active sites for the polymerization of 3,4-ethylenedioxythiophene (EDOT) and as soft templates for assembly of the n-PEDOT:PSS-co-MA core/shell aqueous-dispersible nanoparticles. This one-step spray emulsion polymerization (SEP) process (Scheme 1) might be expandable to allow the preparation of other ordered nanostructures of conductive polymers through appropriate variations of the monomer, surfactant, dopant, and solvent. The SEP that we adapted combines two features: (i) an airbrush (spray gun) that disintegrates the monomer solution into microdroplets under a constant air-flow pressure and (ii) a dual-surfactant system with different functionalities to stabilize the core/shell morphology, manipulate the particle size distribution, and prevent the micelles’ aggregation, collision, and coalescence, which would result in the formation of ellipsoid- or nanorod-dominated morphologies of the conjugated polymers.\textsuperscript{[20,21]}

This SEP technique allows the formation of stable dispersions of n-PEDOT:PSS-co-MA colloids in aqueous media, without exposing n-PEDOT to other treatment conditions; it also has a soft effect on the conductivity and work function properties of n-PEDOT. In addition, the resulting n-PEDOT:PSS-co-MA materials exhibited a conductivity of ca. 0.295 cm\textsuperscript{-1}, much higher than those of commercial PEDOT:PSS materials (e.g., Al 4083; ca. 10\textsuperscript{-5} S cm\textsuperscript{-1}), and a work function of ca. 5.05, making them potentially good hole transporting materials for application in organic electronic devices.

**Experimental Part**

Three n-PEDOT materials were prepared in this study: ellipsoids and nano-colloids formed with and without PSS-co-MA. The difference between n-PEDOT formed with and without PSS-co-MA was the presence or absence of PSS-co-MA mixed with FeCl\textsubscript{3} in the aqueous solution. For brevity, a description is given here only of the synthesis of the n-PEDOT:PSS-co-MA colloids.

**3,4-Ethylenedioxythiophene (EDOT, Aldrich), n-dodecylbenzenesulfonic acid (DBSA, Tokyo Kasei Kogyo), FeCl\textsubscript{3} (Showa), PSS (M\textsubscript{w} ca. 75 000; Aldrich), and PSS-co-MA sodium salt (4-styrenesulfonic acid/MA mole ratio = 3:1; average M\textsubscript{w} ca. 20 000; Aldrich) were used without further purification.**

**n-PEDOT:PSS-co-MA Colloids**

A solution of DBSA (4.5 g, 0.013 mol) and EDOT (0.25 mL, 0.0017 mol) in hexane (15 mL) was stirred for 60 min and then loaded into the spraying chamber of the airbrush. A solution of deionized water (40 mL) containing PSS-co-MA (2%, w/v) and FeCl\textsubscript{3} (6.5 g, 0.035 mol) was stirred for 60 min. SEP was performed using an Airbrush AFC-300 spray gun featuring a nozzle possessing a 0.3-mm-diameter orifice. The nozzle was dipped 1 cm under the water surface. The droplet ejection rate was set to 10 mL min\textsuperscript{-1}; the compressed spray air flow (N\textsubscript{2}) was set to 5 psi. The polymerization occurred within a few seconds, causing the color of the solution to change from yellowish to dark-green. After gentle magnetic stirring for 3 h, a rotary evaporator was used to evaporate the solvents and the residue was washed in a Soxhlet apparatus with hexane as the extraction solvent to remove unreacted DBSA, FeCl\textsubscript{3}, and EDOT. The black precipitate from the Soxhlet apparatus was suction-filtered, washed with a copious amount of methanol, dried at 60°C for 24 h, and then stored in a vial under N\textsubscript{2} until required for further experiments.

Field emission scanning electron microscopy (FE-SEM) images were recorded for water- or hexane-diluted dispersions dried on cover glasses using a Hitachi FE-2000 apparatus. A four-probe (LUTRO MO-2001) apparatus was used for bulk conductivity measurements; the PEDOT powder was dried under vacuum and ground with a pestle in a mortar; the ground powder was then pelleted to a diameter of 13 mm and a thickness of 1.0 mm under high pressure. Wide-angle X-ray diffraction (XRD) patterns were recorded using a PANalytical instrument and Ni-filtered (40 kV, 40 mA) Cu Ka radiation. Raman spectra were recorded.
using a 532-nm diode solid state pumping laser (DSSP) over the scanning range from 400 to 2,000 cm$^{-1}$. Samples for FE-SEM (HR-TEM; Hitachi FE-2000) were prepared from acetone dispersion and dropped on carbonic-coated copper grids.

**Results and Discussion**

Scheme 2 presents the chemical structures of the compounds used in this study. The polyanion PSS-co-MA features two different interactive functional groups, suggesting that it would act not only as a soft template stabilizer and surfactant but also as a dopant when incorporated in shells around n-PEDOT cores; in addition, the n-PEDOT:PSS-co-MA colloids prepared using the SEP approach would, in essence, be aqueous-soluble n-PEDOT nanomaterials.

Scheme 3 displays images of n-PEDOT and n-PEDOT:PSS-co-MA dispersed in toluene (S1) and water (S2), respectively. The n-PEDOT was prepared using the SEP method through ejection of an EDOT/DBSA/hexane mixture into an aqueous medium containing only the oxidant FeCl$_3$ (i.e., without adding PSS-co-MA); in contrast, the n-PEDOT:PSS-co-MA was formed in an aqueous medium containing both the oxidant FeCl$_3$ and PSS-co-MA. Precipitates were formed in toluene when the n-PEDOT concentration was greater than ca. 2.5 wt.-%, presumably because van der Waals attractive forces dominated between the n-PEDOT chains, thereby decreasing their compatibility with the solvent molecules. The n-PEDOT:PSS-co-MA was dispersed well in the aqueous medium at concentrations up to ca. 4.5 wt.-%. PSS-co-MA acted as a soft template to stabilize the core/shell morphology through noncovalent interactions between the styrenesulfonic acid-co-MA functionality and the thiophene rings. Our findings clearly indicate that SEP can be used to synthesize aqueous-dispersible core/shell nanomaterials of well-distributed sizes when using PSS-co-MA as a polyanionic stabilizer. This improved solubility presumably resulted from electrostatic repulsive forces between colloidal particles and from hydrogen bonding interactions between the particles and water, making the core/shell clusters more dispersible in water.$^{[22,23]}$ Thus, the stabilizer, PSS-co-MA, played a key role in this novel SEP technique, enhancing the water-solubility of n-PEDOT.

For a comparative study, we prepared three types of nano-PEDOTs using three different methods: ellipsoidal PEDOT (e-PEDOT) through oxidative reverse emulsion polymerization with FeCl$_3$, n-PEDOT through SEP in the absence of the stabilizer PSS-co-MA, and n-PEDOT:PSS-co-MA through SEP in the presence of the stabilizer PSS-co-MA. We determined their morphologies using SEM. Surprisingly, the ellipsoidal (Figure 1a), nanosphere-like (Figure 1b), and nano-core/shell (Figure 1c) structures were well defined and clearly distinguishable. We attribute the different morphologies of e-PEDOT and n-PEDOT to the effect of micelle formation prior to polymerization. The e-PEDOT morphology was dependent on the surfactant-to-monomer molar ratio (i.e., the critical micelle concentration), whereas the n-PEDOT morphology was dependent on the disintegration of the microdroplets emitted from the spray gun and on the presence or absence of the stabilizer.

In the inset to Figure 1(c), we observe that the shell of the nanoparticle (NP) is slightly brighter than its dark inner core, confirming the core/shell structures of the n-PEDOT:PSS-co-MA particles, with n-PEDOT cores embedded within PSS-co-MA shells.

The morphologies and sizes of the sphere-like n-PEDOT NPs within its mixture of nanorods and sphere-like shapes
in Figure 1(b) were less homogeneous than those of the n-PEDOT:PSS-co-MA colloids in Figure 1(c). We attribute this difference to the effect of PSS-co-MA stabilizing the micelles when polymerization occurred at the micelle-to-water interface; in the absence of the stabilizer, some of the micelles coagulated to form larger rod-like micelle clusters, resulting in a mixture of NP shapes when using the SEP technique. The e-PEDOT and n-PEDOT NPs were slightly soluble only in organic solvents, whereas the n-PEDOT:PSS-co-MA NPs were soluble in water, indicating that PSS-co-MA did indeed play a determining role in the formation of water-soluble colloids. According to our SEM analyses, Scheme 3 presents one possible mechanism for the formation of the water-soluble core/shell spheres. PSS-co-MA acted as a soft template to stabilize the core/shell morphology through chemical interactions between the styrenesulfonic acid-co-MA functionalities and the thiophene rings. Our findings clearly indicate that SEP can be used to synthesize aqueous-dispersible core/shell nanomaterials with well-distributed sizes when using PSS-co-MA as a polyanionic stabilizer.  

The XRD patterns (Figure 2) of the n-PEDOT and n-PEDOT:PSS-co-MA NPs featured similar signals at scattering angles (2θ) of 6.5° (d = 13.9 Å), 12.8° (d = 7.0 Å), and 19.4° (d = 4.5 Å), which are indexed to the highly ordered semicrystalline pseudo-orthorhombic interchain packing structure, and at 25.9° (d = 3.4 Å), attributed to the interchain planar ring-stacking distance. The intensities of the signals for the (100) and (200) diffraction planes of n-PEDOT:PSS-co-MA were greater than those of n-PEDOT, indicating that n-PEDOT and PSS-co-MA formed well-defined core/shell structures with superior interchain overlapping. We suspect that the core/shell structure resulted from the PSS-co-MA polymer chains encircling the n-PEDOT cores, stabilized through doping interactions, to form n-PEDOT:PSS-co-MA spherical or sphere-like NPs (Scheme 3). The main reason why the n-PEDOT:PSS-co-MA colloids were soluble in water was because the hydrophilic tails of the undoped MA and styrenesulfonic acid functional groups interacted favorably with water. Therefore, PSS-co-MA can be considered as a “surfactant” that interacts with hydrophobic n-PEDOT to present hydrophilic acid groups on its surface, thereby resulting in stable dispersions of n-PEDOT:PSS-co-MA NPs in aqueous media.  

The work function is the minimum energy required to remove an electron from the surface of a material; it is strongly affected by the morphology and/or surface reactions (e.g., oxidation) of a surface. Measuring the work function after chemical manipulation can provide valuable information regarding the structure of a given surface. Table 1 lists the work functions and conductivities of n-PEDOT, amorphous PEDOT:PSS (AI 4083), and n-PEDOT:PSS-co-MA.
PSS-co-MA. The work functions of the materials increased from ca. 4.7 eV for undoped n-PEDOT to ca. 5.10 and 5.05 eV for PEDOT doped with PSS and n-PEDOT:PSS-co-MA, respectively. These changes resulted from the increased electric dipole strengths at the surfaces of the complex materials after doping; i.e., the polyanionic dopants disturbed the charge distribution near the surfaces of the complexes and affected their dipoles and charge redistributions, resulting in decreased conductivity. These results indicate that the oxidation behavior of the crystallized n-PEDOT — namely, the ability of electrons to escape to the vacuum level— was limited when it was not doped with either of the polyanionic compounds.[26]

Previous reports have indicated that higher DBSA doping levels increase the conductivity of PEDOT NPs relative to that of undoped particles.[27,28] The conductivities of our n-PEDOT and n-PEDOT:PSS-co-MA were 3.2 and 0.29 V cm$^{-1}$, respectively. The structure of each n-PEDOT:PSS-co-MA NP consisted of an insulating PSS-co-MA layer wrapped around an n-PEDOT core, stabilized through strong chemical interactions; this structure increased the interface dipole strength and the hole-injection barrier, thereby decreasing the conductivity relative to that of the undoped n-PEDOT. Thus, although the n-PEDOT:PSS-co-MA NPs featured a higher level of doping than the n-PEDOT NPs, the outer shell of PSS-co-MA acted as an insulating layer that blocked the hopping of electrons from one n-PEDOT core particle to another, thereby decreasing the conductivity. Our results suggest that, in these aqueous PEDOT:dopant systems, the conductivity depends not only on the doping level but also the morphology of the core/shell complexes. We suspect that the work function and conductivity of n-PEDOT:dopant species might be tunable when using dopants featuring different donating functional groups. Furthermore, the PEDOT-to-dopant molar ratio should also affect the hopping behavior of electrons; therefore, it should also affect the conductivity of the PEDOT:dopant complexes.[29]

Raman spectroscopy is one of the most useful tools for studying the doping of conjugated polymers.[30,31] We used it to confirm the presence of doping phenomena during the formation of n-PEDOT:PSS-co-MA latexes. Figure 3 compares the Raman spectra of n-PEDOT, n-PEDOT:PSS-co-MA, and the commercial amorphous PEDOT:PSS (AI 4083). We attribute the principle Raman bands at 1 267, 1 367, 1 433, 1 449, and 1 512 cm$^{-1}$ to C$_a$¼C$_a$ inter-ring stretching, C$_b$–C$_b$ stretching, symmetrical C$_a$¼C$_b$ stretching, oxidized symmetrical C$_a$¼C$_b$ stretching, and asymmetrical C$_a$¼C$_b$ stretching, respectively.[31,32] The intensity of the signal at 1 267 cm$^{-1}$ was greater for the PEDOT:PSS and n-PEDOT:PSS-co-MA complexes, indicating that the oxidative dopants PSS and PSS-co-MA cause the PEDOT polymer backbone to adopt predominantly the quinoid structure. The intensity of the C$_b$–C$_b$ stretching band at 1 367 cm$^{-1}$ decreased when the dopants PSS-co-MA and PSS were anchored as outer shells on the n-PEDOT cores and on the amorphous PEDOT chains, suggesting limited C$_b$–C$_b$ stretching and favored stabilization of the quinoid structure. The most important shift was that of the symmetrical C$_a$¼C$_b$ stretching band, which moved from 1 433 to 1 449 cm$^{-1}$, indicating that this vibration was sensitive to oxidizing (doping) and reducing (de-doping) behavior. We attribute this shift to higher wavenumber to decreased conjugation length of the neutral polymer backbone after further oxidation (doping). At low doping levels, the C$_a$¼C$_b$ stretching band was dominated by the neutral benzoid structure and, therefore,
it appeared closer to 1,433 cm\(^{-1}\); it shifted to 1,449 cm\(^{-1}\) when at higher doping levels. Thus, a transformation of the resonance structure of the n-PEDOT thiophene backbone occurred after doping with either PSS-co-MA or PSS. The intensities of the signals for the \(\text{C}_6=\text{C}_7\) asymmetric band at 1,512 cm\(^{-1}\) for both amorphous PEDOT:PSS and n-PEDOT: PSS-co-MA were lower than that of n-PEDOT, indicating that the doped structures featured predominantly the in-plane symmetric resonance-conjugated backbone.\(^{[32]}\)

**Conclusion**

We have developed a facile route, using SEP, for the synthesis of aqueous-dispersible n-PEDOT colloids doped with PSS-co-MA. SEM and TEM imaging revealed the presence of n-PEDOT cores embedded within PSS-co-MA shells, indicating that PSS-co-MA played a determining role during the formation of the stable n-PEDOT dispersions. XRD patterns indicated that the n-PEDOT:PSS-co-MA colloids featured highly ordered, semi-crystalline, pseudo-orthorhombic, interchain packing structures. The conductivity of n-PEDOT was greater than that of n-PEDOT:PSS-co-MA in pellet form, suggesting that PSS-co-MA acted as a shell that blocked charges from hopping to neighboring latexes, thereby lowering the conductivity. Moreover, the main changes in the Raman spectra were those for the signals of the \(\text{C}_6=\text{C}_7\) stretching bands, which were sensitive to the presence of doping. The higher level of doping in the n-PEDOT:PSS-co-MA NPs, relative to that in the n-PEDOT NPs, caused the band at 1,433 cm\(^{-1}\) to shift to 1,449 cm\(^{-1}\), indicating that the quinoid structure of PEDOT predominated in the presence of dopant. The morphologies of these NPs could be varied by changing the concentration and nated in the presence of dopant. The morphologies of these NPs could be varied by changing the concentration and molecular weight of the PSS-co-MA stabilizer. Because of the nature of the PSS-co-MA shells, the n-PEDOT:PSS-co-MA NPs were very stable over various lengths of time and exhibited interesting conductive properties related to the NP size; such studies are currently under investigation and the results will be published in a forthcoming paper.

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**Keywords:** colloids; emulsion polymerization; PEDOT; Raman spectroscopy

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