

Secondary Dopants Modified PEDOT-Sulfonated Poly(imide)s for High-Temperature Range Application

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ABSTRACT: Poly(3,4-ethylenedioxythiophene) (PEDOT) was polymerized using sulfonated poly(amic acid)s templates (SPAA1 and SPAA2) by batch operation. The new method was invented to enhance conductivities (ca. 100 - to 2000-fold) and with less reaction time from previous work (7 days vs. 3 days). Moreover, to increase the conductivity, many dopants were introduced as secondary doping compared with DMF, D-sorbitol, and surfynol that were previously used. After annealing at 180°C for 10 min, PEDOT-SPAA1 and PEDOT-SPAA2 doped with benzo-1,4-dioxan and quinoxaline showed the increase in conductivity by higher percentage than any other systems, especially doped with D-sorbitol and surfynol. These showed the promising tendency to develop the annealing activated superior conductivity materials after further modifying the conducting film forming processes. However, PEDOT-SPAA2 doped with benzo-1,4-dioxan, imidazole and quinoxaline via annealed at 180°C for 10 min were found to be more conductive than doped with DMF, but still lower conductive than doped with D-sorbitol and surfynol. In terms of particle size, the stable aqueous dispersions of conducting polymers prepared were comparable to polystyrene sulfonate template. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3840–3845, 2013

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INTRODUCTION

Poly(styrene sulfonic acid) (PSSA) is the traditional template for synthesis of viable aqueous dispersions of conducting polymers, such as PEDOT-PSS, PANi-PSS, and PPy-PSS, which have achieved popularity for applications in electrochromic displays,¹ organic light emitting diodes (OLEDs),² organic photovoltaic devices (OPVs),³ and transparent electrode,³ because of their advantageous properties (high conductivity, good film formation, and excellent transparency in the doped state). However, the temperature threshold for these materials is low, less than 200°C before conductivity decreases, which limits its usage in high-temperature processing especially when cooperated with metal oxide. For certain high-temperature processes (incorporated with metal oxide) and applications (high-heat areas such as deserts); an improvement for different template is needed. Moreover, in an application for organic electronic as transparent electrode, the sulfonate acid groups can cause high acidity which is detrimental to the lifetime of organic electronic component. An improvement to reduce acidity by destroying sulfo-

nate group at above 180°C while maintaining high conductivity is crucially needed.

Because of the acidic nature of sulfuric acid derivatized conducting polymer templates, it may be necessary to cleave the acid groups during annealing to make more stable devices. According to our previous work in Ref. 4, we have synthesized PEDOT with new template sulfonated polyimide (PEDOT-SPI) and their results showed more conductivity and thermal stabilities at high temperature than that commercial PEDOT-PSS, but using magnetic stirrer. Our previous work in Ref. 5, we have studied the conductivity and thermal stabilities of three conducting polymers (PEDOT, PANi, and PPy), which used two different templates (SPI1 and SPI2), but with limited dopants. Therefore, we used sulfonated poly(amic acid)s (SPAA) to template polymerize PEDOT, PANi, and PPy.^{4,5} Because of their excellent thermal stability,⁶ chemical resistance⁷ and ability to be sulfonated for ease of solubility in organic solvents.^{8,9} The resulting aqueous dispersions, when cast as films, showed the increase in thermal stability (up to 300°C with no losses in

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conductivity). However, these principles took long reaction time and their conductivities were still lower than expected, so the new method was applied (using mechanical stirring) to reduce reaction time with enhancing more conductivity of those conducting polymers. Moreover, we have investigated more secondary doping with five new dopants (benzo-1,4-dioxan, imidazole, quinoline, methyl viologen, and quinoxaline) compared with common dopants (DMF, D-sorbitol, and surfynol) that used in our previous work.^{4,5} The need for the new method (using mechanical stirring) to reduce reaction time with enhancing more conductivity of those conducting polymers together with doping investigation by more new dopants were the main theme of this work.

Herein, the high conductivities conducting polymers (PEDOT-PSS, PEDOT-SPAA1, and PEDOT-SPAA2) were synthesized by using sulfonated poly(amic acid) templates for the polymerization (SPAA1 and SPAA2). The colloidal dispersions obtained were comparable to PSSA template in terms of particle size and conductivity. The new dopants and annealing at high temperature have also been investigated to study the effect of conductivity responses of PEDOT/SPI systems.

EXPERIMENTAL

Materials

4,4'-Diaminodiphenyl ether (4,4'-ODA), 4,4'-oxydiphthalic anhydride (O-DPDA), triethylamine (Et₃N), *m*-cresol, fuming sulfuric acid (SO₃, 20%), poly(styrene sulfonic acid) (18 wt % in water), iron (III) *p*-toluene sulfonate hexahydrate, 3,4-ethylene dioxithiophene (EDOT), lithium trifluoromethanesulfonate, *N,N*-dimethylformamide (DMF), benzo-1,4-dioxan, methyl viologen and quinoxaline were purchased from Sigma-Aldrich. EDOT was distilled before use. 4,4'-Hexafluoroisopropylidene oxydiphthalic anhydride (6FDA) was purchased from TCI America. Concentrated sulfuric acid (95%), sodium hydroxide (NaOH), hydrochloric acid (HCl), and acetone were purchased from Fisher Scientific and were used as received. Surfynol[®] 2502 surfactant was purchased from Air Products. Ion-exchange resin DOWEX 50WX8 50–100 mesh, D-sorbitol, quinoline, and imidazole were purchased from Acros Organics. Dialysis tubes [molecular weight cut off (MWCO) = 3.5–5 kDa] were purchased from Spectrum Laboratories. Sodium poly(styrene sulfonate) and glass beads (50–100 μm) were purchased from Polysciences.

Preparation of Monomers and Sulfonated Poly(amic acid)s

Synthesis of 4,4'-Diaminodiphenyl ether-2,2'-disulfonic acid (4,4'-ODADS). To a 100-mL three-necked flask with a stirring device, 5.00 g (25.0 mmol) of 4,4'-diaminodiphenyl ether (4,4'-ODA) was added. The flask was cooled in an ice bath, and then 5 mL of concentrated (95%) sulfuric acid was slowly added while stirring. After 4,4'-ODA was completely dissolved, 18 mL of fuming (SO₃ 30%) sulfuric acid was slowly added to the flask. The reaction mixture was stirred at 0°C for 2 h and then slowly heated to 80°C and kept at this temperature for additional 3 h. After cooling to room temperature, the slurry solution mixture was carefully poured onto 40 g of crushed ice. The resulting white precipitate was filtered off and then re-dissolved in a sodium hydroxide solution. The basic solution was filtered, and the filtrate was acidified with concentrated hydrochloric

acid. The solid was filtered off, washed with water and methanol successively, and dried at 80°C in vacuum oven overnight⁹ (78.24% yield).

Synthesis of Sulfonated Poly(amic acid)s (SPAA1 and SPAA2). To a 100-mL three-necked flask with N₂ inlet and outlet, 3.5 g (9.71 mmol) of 4,4'-ODADS, 50 mL of *m*-cresol, and 1.96 g (19.42 mmol) of triethylamine were added. After 4,4'-ODADS was completely dissolved, 3.01 g (9.71 mmol) of O-DPDA for SPAA1 or 4.32 g (9.71 mmol) of 6FDA for SPAA2 were added and then stirred at room temperature for 3 days. When the reaction was complete, the reaction mixture was decanted into acetone (200 mL), filtered, washed with acetone (25 mL, two times), and dried at 50°C in a vacuum oven overnight⁹ (82.89% yield for SPAA1 and 77.56% yield for SPAA2).

Purification

The sulfonated poly(amic acid)s were purified via dialysis tube. SPAA1 and SPAA2 dissolved in water were loaded inside the dialysis tube and soaked in de-ionized water for 24 h, by changing the de-ionized water twice (two times at 12 h each).

Ion Exchange

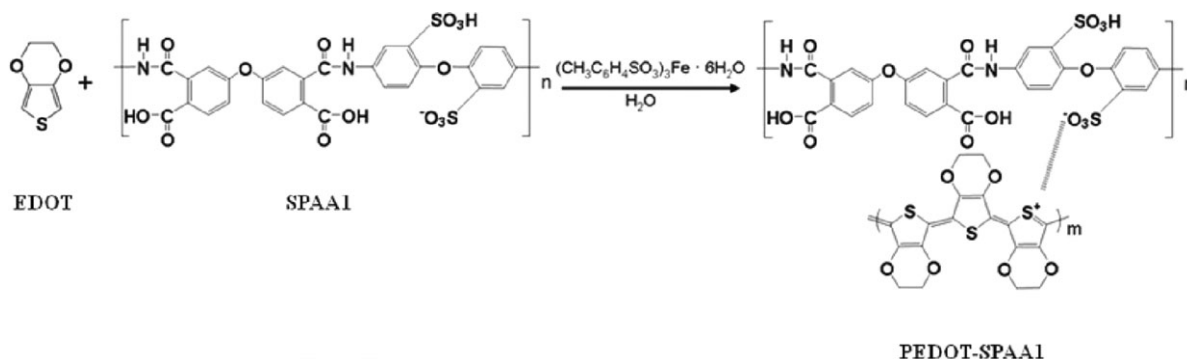
The purified SPAA1 and SPAA2 in salt form were changed to SPAA1 and SPAA2 in acid form with an ion exchange resin of strong acid type DOWEX 50WX8 (cation exchange resin) before polymerization with EDOT. The SPAA1 and SPAA2 in salt form were stirred in de-ionized water with the ion exchange resin for 3 h to convert them into the free acid form (SO₃H). They were centrifuged and filtered in a crucible filter and then dried at 50°C in vacuum oven overnight.⁵ Molecular weight and molecular weight distributions of SPAA1 and SPAA2 were $M_{n1} = 43,457$, $M_{w1} = 72,124$, $PDI_1 = 1.89$ and $M_{n2} = 39,987$, $M_{w2} = 68,322$, $PDI_2 = 2.67$.

Template Polymerization of EDOT and Poly(styrenesulfonic acid) (PEDOT-PSS)

To a 1000-mL LDPE bottle, 319.5 mg (2.25 mmol) of EDOT, and 4356 mg of 18 wt % PSSA aqueous solution were mixed. To this suspension, 1626 mg (2.4 mmol) of iron (III) *p*-toluene sulfonate hexahydrate was added. The total mass of all the reactants was adjusted to 150 g by adding an appropriate amount of de-ionized water. The reaction mixtures were added glass beads 10 g and stirred at 4000 rpm (using mechanical stirrer) for 3 days at room temperature leading to a dark blue dispersion. The solutions were purified according to literature procedure.¹⁰

Template Polymerization of EDOT and Sulfonated Poly(amic acid) (PEDOT-SPAA1 and PEDOT-SPAA2)

To a 1000-mL LDPE bottle, 319.5 mg (2.25 mmol) of EDOT, and 3015.0 mg (4.5 mmol) of SPAA1 or 3458.7 mg (4.5 mmol) of SPAA2 were added. To this suspension, 1626 mg (2.4 mmol) of iron (III) *p*-toluene sulfonate hexahydrate was added for both polymerizations as shown in Scheme 1. The total mass of all the reactants was adjusted to 150 g by adding appropriate amount of de-ionized water. To reaction mixtures, glass beads 10 g were added. The reaction was stirred vigorously at 4000 rpm (using mechanical stirrer) for 3 days for both of PEDOT-SPAA1 and PEDOT-SPAA2 at room temperature leading to a



Scheme 1. Synthesis PEDOT-SPAA1.

dark blue dispersion. The solutions were purified according to literature procedure.⁴

Preparation of Conducting Polymer Films

Both pristine films and doped films were prepared by drop casting onto glass slides at room temperature. The films were annealed at 180°C for 10 or 90 min, and 300°C for 10 min to improve conductivities by thermal treatment. Each film from each material was evaluated for conductivity at room temperature after annealing.⁵ To investigate the secondary doping, all of the films were also prepared with 0.1 wt % benzo-1,4-dioxan, 5 wt % imidazole, 0.1 wt % quinoline, 5 wt % methyl viologen,

0.1 wt % quinoxaline, 0.1 wt % DMF, 5 wt % of D-sorbitol, and 0.1 wt % surfynol[®] 2502.

Measurements

Fourier transform infrared spectroscopy (FTIR) was performed using a MAGNA-IR560. Spectra were taken on ground powder in a KBr matrix with a scanning range of 500–4000 cm⁻¹, 64 scans at a resolution of 4 cm⁻¹. Nuclear magnetic resonance (NMR) ¹H-NMR spectra were recorded on a Bruker DMX-500 NMR Spectrometer. Gel permeation chromatography (GPC) was done using a millipore model 150-C GPC system; DMAC was used as the mobile phase. The results were calibrated by

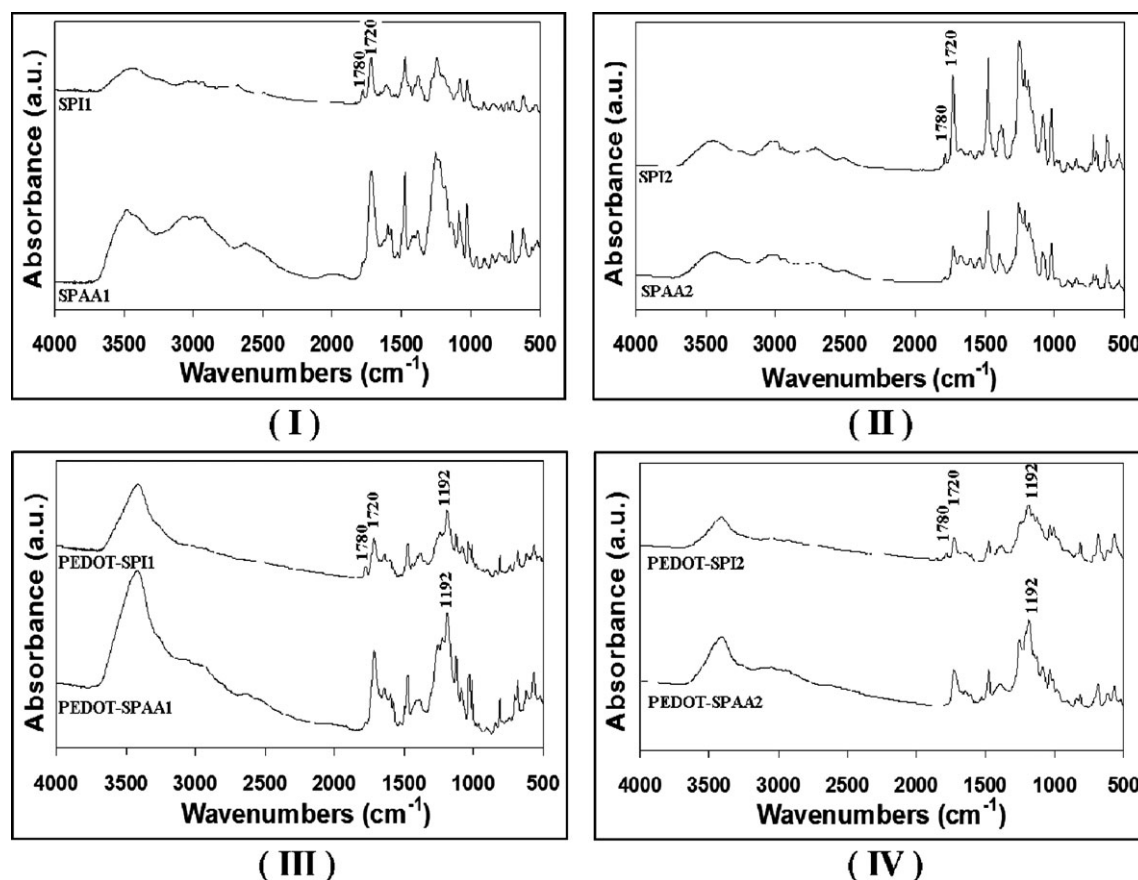


Figure 1. (I) FTIR spectrum of SPAA1 and SPI1, (II) SPAA2 and SPI2, (III) PEDOT-SPAA1 and PEDOT-SPI1, (IV) PEDOT-SPAA2 and PEDOT-SPI2.

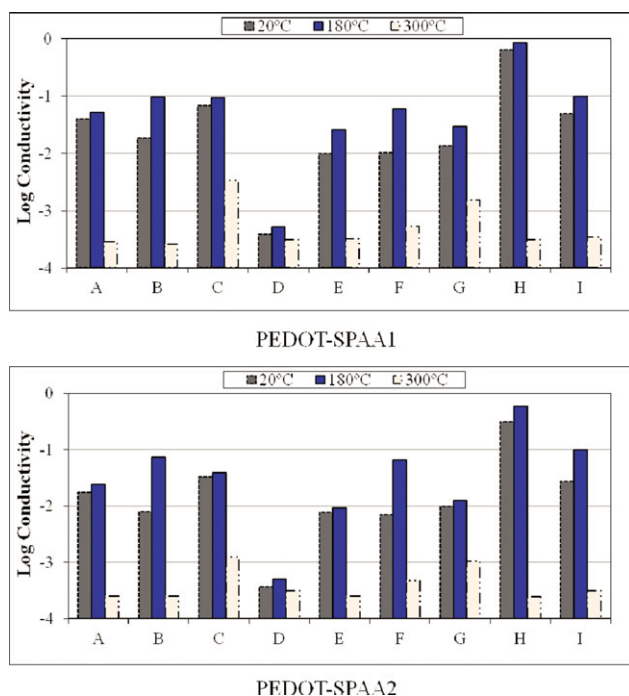


Figure 2. Conductivities of each system at 20, 180, and 300°C. (A: Undoped conducting polymers; B: doped with benzo-1,4-dioxan (0.1 wt %), C: doped with imidazole (5 wt %); D: doped with quinoline (0.1 wt %); E: doped with methyl viologen (5 wt %); F: doped with quinoxaline (0.1 wt %); G: doped with DMF (0.1 wt %); H: doped with D-sorbitol (5 wt %); I: doped with surfynol (0.1 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

standards of poly(methyl methacrylate). Conductivities were measured using a four-line collinear array utilizing a Keithley Instruments 224 constant current source and a 2700 Multimeter. The polymer was coated on the glass substrate, having four gold-coated leads on the surface across the entire width of the polymer and 0.25-cm apart from each other. The current was applied across the outer leads and voltage was measured across the inner leads.

Table I. Comparison Conductivities of Conducting Polymers Before and After Annealing at 180°C, 10 min

Sample	PEDOT-SPAA1			PEDOT-SPAA2		
	Conductivities (S/cm)			Conductivities (S/cm)		
	At RT	After 180°C	Increasing (%)	At RT	After 180°C	Increasing (%)
A	3.82×10^{-2}	5.11×10^{-2}	33.77	1.72×10^{-2}	2.37×10^{-2}	37.79
B	1.80×10^{-2}	9.51×10^{-2}	428.33	7.64×10^{-3}	7.09×10^{-2}	828.01
C	6.72×10^{-2}	9.30×10^{-2}	38.39	3.19×10^{-2}	3.84×10^{-2}	20.38
D	3.80×10^{-4}	5.05×10^{-4}	32.89	3.60×10^{-4}	4.83×10^{-4}	34.17
E	9.63×10^{-3}	2.50×10^{-2}	167.09	7.40×10^{-3}	9.12×10^{-3}	23.24
F	9.91×10^{-3}	5.79×10^{-2}	484.26	6.98×10^{-3}	6.43×10^{-2}	821.20
G	1.32×10^{-2}	2.84×10^{-2}	115.15	9.51×10^{-3}	1.24×10^{-2}	30.39
H	6.26×10^{-1}	8.30×10^{-1}	32.59	3.06×10^{-1}	5.85×10^{-1}	91.18
I	4.85×10^{-2}	9.80×10^{-1}	102.06	3.99×10^{-2}	9.71×10^{-2}	143.36

RESULTS AND DISCUSSION

Diamine Monomer and Sulfonated Poly(amic acid) Templates

Diamine monomer, 4,4'-Diaminodiphenyl ether-2,2'-disulfonic acid (4,4'-ODADS) was synthesized by direct sulfonation of the 4,4'-diaminodiphenyl ether (4,4'-ODA) with fuming sulfuric acid that used as a sulfonating agent. The monomer structure was confirmed by FTIR and $^1\text{H-NMR}$. The FTIR spectrum shows absorptions at (a) 1031.8 and (b) 1088.3 cm^{-1} assigned to the sulfonic acid group, and (c) 3481.7 cm^{-1} assigned to NH_2 of the diamine. The sulfonation primarily occurred at the meta position as shown in $^1\text{H-NMR}$ spectrum and showed the same results as previous works.^{4,5,9} (details in Supporting Information).

The structures of the poly(amic acid)s were confirmed with FTIR (Figure 1). The broad absorption band at 3476.9 cm^{-1} was assigned to the absorbed water in the sample (the sulfonic acid groups are highly hydrophilic). The peak at 1663.3 cm^{-1} indicated the absorption bands of the carbonyl group (C=O) and the peak at ca. 2500–3500 cm^{-1} indicated the absorption bands of the carboxylic acid (COOH). The sulfonic acid groups (SO_3H) appeared at 1029.0 cm^{-1} , which confirmed the formation of the prepared sulfonated poly(amic acid)s. After annealing at 180°C for short curing time (10 min), the polyamic acid was changed to polyimide with the strong absorption band around 1720 cm^{-1} assigned to the symmetric imide C=O stretching, and also the peak at 1780 cm^{-1} indicated the asymmetric imide C=O stretching. The appearance of imide characteristic peaks while characteristic peaks of amic acid was disappeared, confirmed the complete imidization of the sulfonated poly(imide)s (SPI).⁵ The peak at 1192 cm^{-1} indicated stretching in the ethylenedioxy group in the structure in which the differential peak existed, both SPI and SPAA. The other peaks at 1515, 1473, 1388, and 1311 cm^{-1} indicate the C=C and C-C bonds in thiophene.⁴

Conductivity

Conductivities from the new method (mechanical stirrer) were higher than that the old method (magnetic stirrer),^{4,5} ca. 100 - to 2000-fold (see Supporting Information). This is attributed to the highly shear-force exerted by mechanical stirrer while

stirring during polymerization. The observed aqueous dispersion of conducting polymers showed the particles size in nano-scale (Figure 3). The new method can not only increase the batch size but also reduce the reaction time from 7 days to 3 days to obtain dark blue colored solution.

The conductivities of PEDOT-PSS were decreased after annealed at 180°C or at 300°C, resulted in less thermally stable than PEDOT-SPAA1 and PEDOT-SPAA2 (see Supporting Information). However, undoped PEDOT-SPAA1 and PEDOT-SPAA2 showed the lower conductivity than that PEDOT-PSS, which drove the needs to use the secondary doping technique to enhance the conductivity. The effects from new dopants (benzo-1,4-dioxan, imidazole, quinoline, methyl viologen, and quinoxaline) of PEDOT-SPAA1 and PEDOT-SPAA2 are investigated and compared with the common dopants (DMF, D-sorbitol, and surfynol) at room temperature, 180°C and 300°C, respectively (Figure 2). The results in doping with imidazole were showed more conductive than undoped PEDOT-SPAA1 and PEDOT-SPAA2, and still higher than doped with DMF and surfynol at room temperature. Moreover, the further increased in conductivity of 20–30% when annealing at 180°C, 10 min (Table I) were observed with imidazole doping system. Although the conductivities of the systems doping with benzo-1,4-dioxan and quinoxaline were lower than undoped PEDOT-SPAA1 and PEDOT-SPAA2 at room temperature, surprisingly their conductivities were enhanced 428–828% after annealed at 180°C for 10 min. After heat treatment, the chain alignment within the films would be changed due to the differences in rigidity of the poly(amic acid), before heated, and the poly(imide), after heated, leading to the modified morphologies, which caused the enhancement in the observed conductivities.⁵ On the other hand, doping with quinoline and methyl viologen showed the decrease in conductivity due to the accumulated particles of PEDOT-SPAA1 and PEDOT-SPAA2 in aqueous solution after doping, indicated the poor alignment of structure when cast as films on glass template. The conductivity results from using the first template (SPAA1) were higher than that using the SPAA2. However, after heat treatment at 300°C, 10 min, the conductivities of PEDOT-SPAA1 and PEDOT-SPAA2 systems were decreased due to decomposition of the structure of the conducting polymers at higher temperature.

Particle Size Distribution Analysis and Morphology

The particle size of the colloidal dispersions PEDOT-PSS and PEDOT-SPAA1 and PEDOT-SPAA2 were investigated by TEM, as shown in Figure 3. TEM images of the samples clearly indicate that the materials have uniform solid nanoparticles network and their diameters of PEDOT-PSS(a), PEDOT-SPAA1(b) and PEDOT-SPAA2(c) samples were about 54, 45, and 78 nm, respectively.

CONCLUSIONS

The new method (mechanical stirring) to synthesis PEDOT with sulfonated poly(amic acid) template was undertaken and caused less reaction time and more conductivity than our earlier systems (magnetic stirring). The conductivities of PEDOT-SPAA1 could be further enhanced by using the secondary dopants and

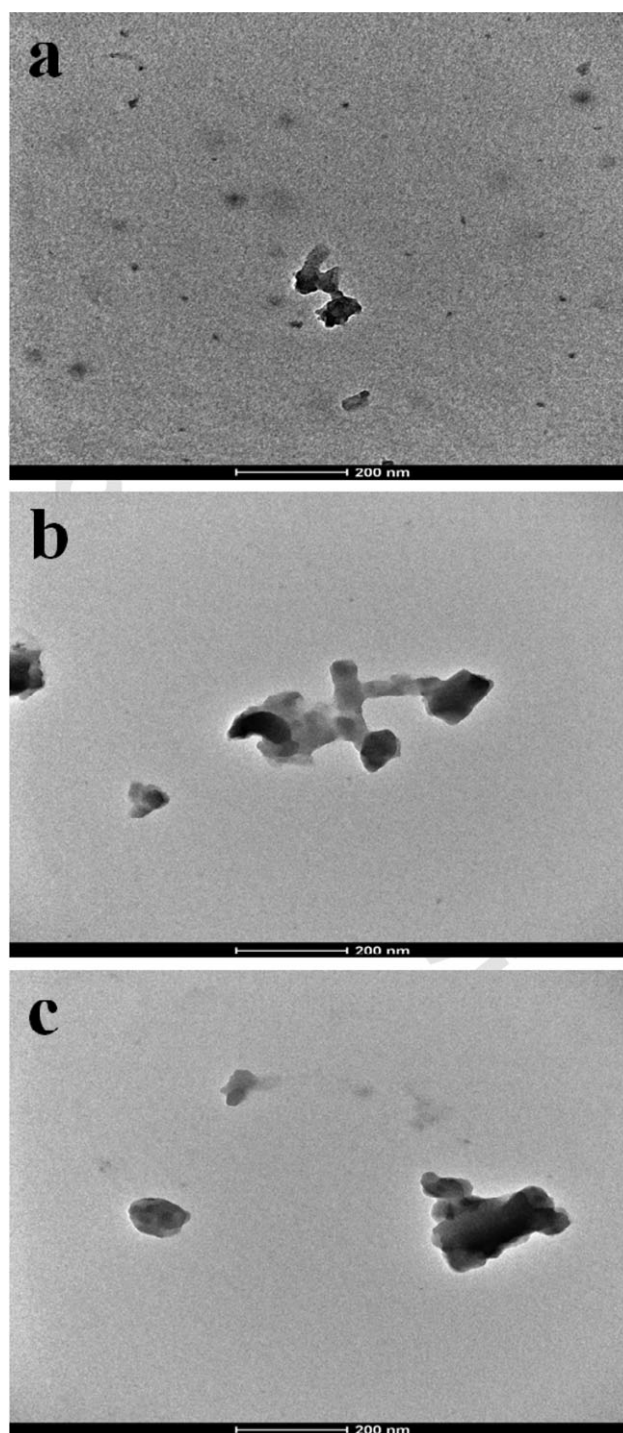


Figure 3. TEM images of PEDOT-PSS (a), PEDOT-SPAA1 (b), and PEDOT-SPAA2 (c).

heat treatment. After heat treatment, the structures of PEDOT-SPAA1 were changed to PEDOT-SPIs and their conductivities were increased as the same time. Benzo-1,4-dioxan, imidazole and quinoxaline were investigated as the new dopants and could be used as well as surfynol to improve the conductivity (better than DMF dopant). However, the condition of secondary doping with new dopants could be further improved in term of concentration and annealing time to enhance the maximum

conductivity. Finally, the high-thermal stability and highly conductivity PEDOT-SPI have successfully been synthesized to apply for higher application temperature or higher processing temperature without detrimental to the conductivity.

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REFERENCES

1. Tang, Z.; Donohoe, S. T.; Robinson, J. M.; Chiarelli, P. A.; Wang, H. L. *Polymer* **2005**, *46*, 9043.
2. Huh, D. H.; Chae, M.; Bae, W. J.; Jo, W. H.; Lee, T. W. *Polymer* **2007**, *48*, 7236.
3. Tarkuc, S.; Sahin, E.; Toppare, L.; Colak, D.; Chianga, I.; Yagci, Y. *Polymer* **2006**, *47*, 2001.
4. Somboonsub, B.; Invernale, M. A.; Thongyai, S.; Prasertthdam, P.; Scola, D. A.; Sotzing, G. A. *Polymer* **2010**, *51*, 1231.
5. Somboonsub, B.; Srisuwan, S.; Invernale, M. A.; Thongyai, S.; Prasertthdam, P.; Scola, D. A.; Sotzing, G. A. *Polymer* **2010**, *51*, 4472.
6. Suzuki, T.; Yamada, Y.; Tsujita, Y. *Polymer* **2004**, *45*, 7167.
7. Tsai, M. H.; Whang, W. T. *Polymer* **2001**, *42*, 4197.
8. Faure, S.; Cornet, N.; Gebel, G.; Mercier, R.; Pineri, M.; Sillion, B. In Proceedings of the International Symposium on New Materials for Fuel Cell and Modern Battery Systems, II, Montreal, **1997**, p 818.
9. Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* **2002**, *35*, 9022.
10. Bayer, A. G. Eur. Pat. 3,39,340 (**1988**).