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Enhancement in electrical conductive property of polypyrrole-coated cotton fabrics using cationic surfactant

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ABSTRACT: Recently, great efforts have been made to gain highly conductive fabrics for smart textiles and flexible electromagnetic shielding materials. Different from the conventional chemical synthesis method, fibrillar polypyrrole was synthesized on the cotton fabrics via a simple chemical polymerization process with micelles of cationic surfactant (cetyltrimethylammonium bromide, CTAB) as soft template. The modified cotton fabric exhibited excellent electrical conductivity and electromagnetic interference shielding effectiveness due to the formation of fibrillar polypyrrole on the fiber surface. Electrical conductivity of fabric surface were studied by four-probe resistivity system. The highly conductive fabric with surface conductivity of 5.8 S cm^{-1} could be obtained by changing cationic surfactant concentration. The electromagnetic interference shielding effectiveness (EMI SE) of the modified fabrics was evaluated by the vector network analyzer instrument. Compared with the sample without using surfactant, the EMI SE value of PPy-coated cotton fabrics increased by 28% after using 0.03 M CTAB as soft template. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43601.

KEYWORDS: coatings; composites; conducting polymers; fibers; textiles

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INTRODUCTION

Wearable conductive materials are of great importance for the development of emerging smart textiles, which have potential application in medical monitor and therapeutics,[1,2] military garment devices and wearable displays.[3,4] On the principles of flexibility and stretchability, many substrates, such as carbon fiber,[5] textiles,[6] polymer,[7] and metal foils,[8] have been researched as wearable electronic devices. Cotton fabric, as one of the most widely used textiles, performs several advantages over other platforms in the development of flexible electrodes, such as wearing comfort, light weight, high porosity, large surface area, and good reactivity.

To improve the conductivity of cotton fabric, many attempts were made to incorporate conductive polymers [e.g., polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh), and polyindole (PIn)] into cotton fibers.[9–11] Through this approach, conventional cotton fabric were endowed with various functional properties, such as antistatic electricity,[12] electromagnetic shielding,[13] microwave absorbing,[14] flexible power storage,[15] chemical sensors,[16] and corrosion resistance.[17] Among these conductive polymers, PPy (Figure 1) is considered as the most promising candidate for conducting layer due to its low cost, high electrical conductivity, and remarkable environmental stability.[18–21] For example, a flexible polypyrrole-coated fabric counter electrode was prepared by Xu *et al.* for application in dye-sensitized solar cells.[22] The research group of Wallace *et al.* designed stretchable polypyrrole/fabric electrodes for supercapacitor.[23]

Generally, the preparation methods for conductive polymers include chemical oxidative polymerization[24–26] and electrochemical polymerization.[27] Particularly, the comparatively simple chemical method can allow more homogenous mixing of the components and easily control the morphology of conductive polymer depositions. However, because of the low accessible degrees of doping agent and mass transport limitations within dense polymeric layers, the fabrics coated with the granulated conductive polymers by chemical oxidative polymerization exhibited relatively lower surface conductivity. The fibrillar materials with porous structure show better performance in micromolecule permeability than granulated polymers.[28–31] Therefore, recently some research groups have introduced soft template into the chemical polymerization to improve the morphology of conductive polymers.[32]

Soft template synthesis is one of the most effective ways to generate polymeric layers with diverse morphology owing to its

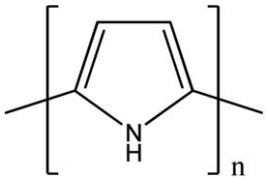

Figure 1. Structure of polypyrrole (PPy).

unique structure tailoring effect during the polymerization.[33] Soft templates are often long-range order, self-assembled structure from certain surfactants. They provide well-defined spaces or channels to build tube-, ribbon-, thread- and fiber-like polymer morphology with micrometer or nanometer size.[34–37] These soft template surfactants are easy to remove after polymerization and the microstructure of resulting polymers can be maintained. To our knowledge, there are few literatures reported about cationic surfactant with long molecular chain in the preparation of PPy-coated textiles. Herein, we prepared PPy-coated fabrics via chemical polymerization using cationic surfactant (CTAB) as soft template. The evolution of morphology, elemental composition, electrical conductivities, electromagnetic interference shielding effectiveness, and thermal property of the resulting textiles were investigated in detail.

EXPERIMENTAL

Materials

Bleached plain cotton fabrics were commercially available. Pyrrole monomer (Py) was of AR grade and purchased from Aladdin Chemical Reagent Co, China, and was distilled under reduced pressure before use. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), cetyltrimethylammonium bromide (CTAB) were of AR grade and purchased from Sinopharm Chemical Regent. Hydrochloric acid (HCl) and ethyl alcohol (CH_3CH_2OH) were of AR grade and purchased from Chongqing Chuandong Chemical (group). These chemicals were used without further purification and all the solutions were prepared with distilled water.

Preparation of PPy-Coated Cotton Fabric

To remove impurities and auxiliaries attached on the cotton fabric samples, they were treated with 0.5% Na_2CO_3 for 30 min followed by rinsing with deionized water till neural pH and drying at 80 °C. The polymerization process includes four main steps: worm-like micelles formation,[38] solubilization of pyrrole, polymerization reaction of pyrrole, removal of surfactants as shown in Figure 2. First, cationic surfactants (CTAB) self-assembly form worm-like micellar aggregates in hydrochloric acid solution. Second, the hydrophobic organic pyrrole monomers added into solution are preferentially solubilized into the core of the micelles. Third, in the presence of an oxidizing agent, the monomers in the micelle run polymerization reaction to form fibrillar polymer. After the polymerization, surfactants as soft template were removed by washing repeatedly to expose the polymeric layer on the fabric surface.

In a typical procedure, the cotton fabric samples were immersed in 100 mL of aqueous solution containing 0.03M Py, 1M HCl and quantitative amount of CTAB (concentration of CTAB used in this reaction system was from 0.005M to 0.03M, over the ranges of micelle aggregations) for 30 min. Then, 100 mL of 0.5M $FeCl_3{\cdot}6H_2O$ aqueous solution was dropwise added into the reaction solution slowly under stirring. Deposition of pyrrole (Py) on fabrics was carried out by *in situ* chemical oxidative polymerization in icewater bath for 2 h. After polymerization, the resulting fabrics were then washed with deionized water several times, dried at room temperature. In this way, a series of conductive cotton fabrics were obtained.

Characterization of PPy-Coated Cotton Fabric

The viscosity of the reaction mixture solution was determined by NDJ-79 type rotating viscometer. The scanning electron microscopy (SEM) images of fabric samples were taken by an FEI Quanta-250 scanning electronic microscope to study the surface morphology of pure cotton and PPy-coated cotton fabrics. The sample surfaces were sputtered with gold to get good electrical contact and avoid charging before observations. The surface elemental composition of samples was examined by using energy dispersive spectroscopy (EDS, AMETEK Energy Disperse Spectroscopy). The conductivity of the fabrics was measured by a four-probe resistivity system (RTS-9, 4 probes Tech., China) with copper electrodes. FTIR spectra of PPy powder samples were recorded with ALPHA German Brooke Fourier Infrared Spectrometer. The wavenumber of FTIR spectrophotometer ranged from 2000 to 500 cm^{-1} for 16 scans with a resolution of 4 cm^{-1}. Thermal stability of PPy-coated cotton

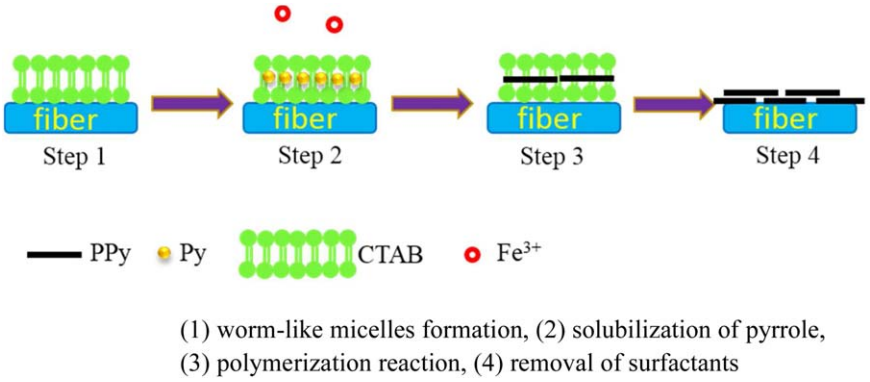

Figure 2. Steps of pyrrole polymerization process in CTAB micelle solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

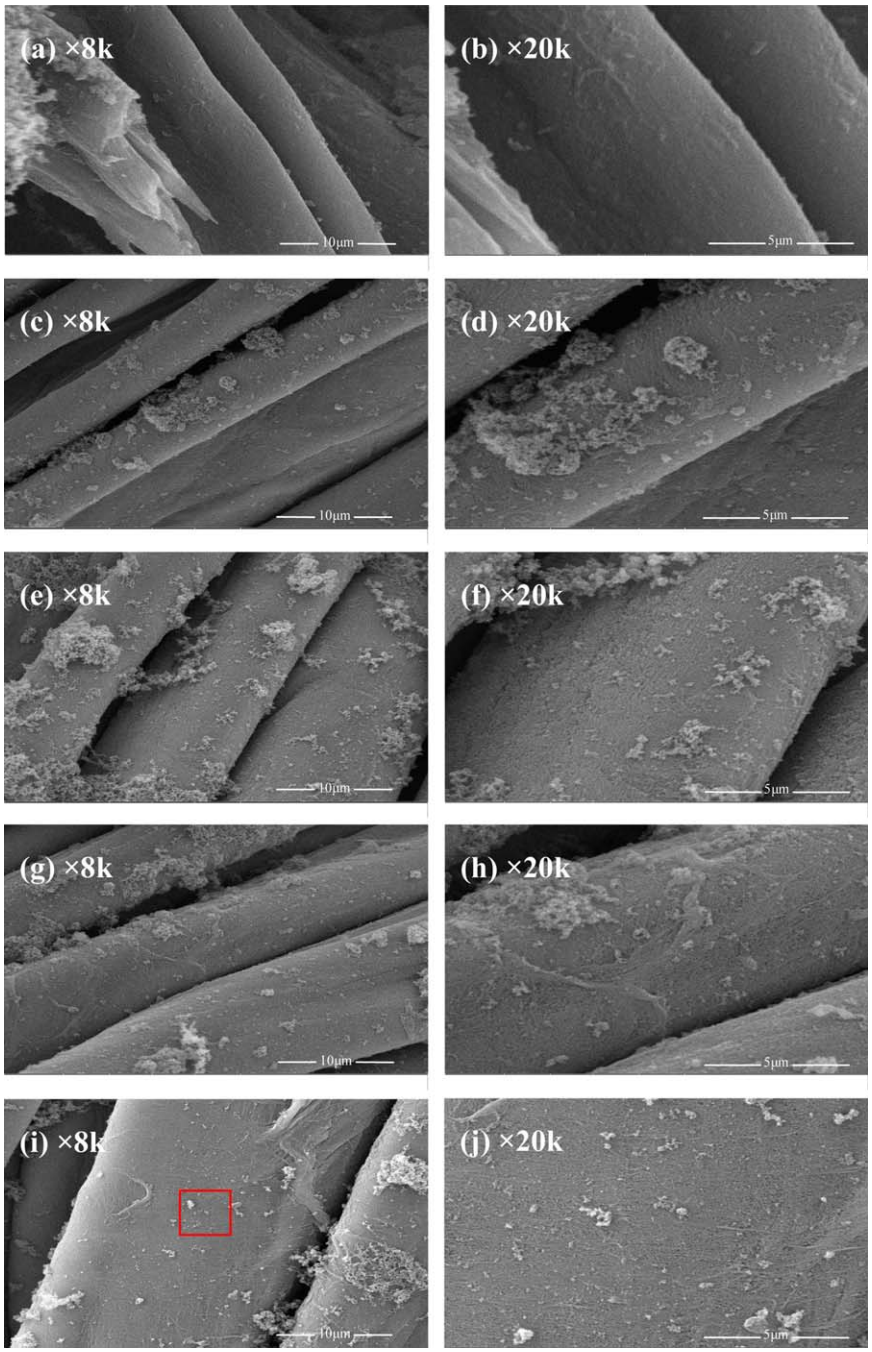

Figure 3. Scanning electron microscopy (SEM) images of PPy-coated cotton fabrics with different concentrations of CTAB and 1M HCl: (a,b) no surfactant, (c,d) 0.005 M CTAB, (e,f) 0.01M CTAB, (g,h) 0.02M CTAB, (i,j) 0.03M CTAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fabrics was performed by thermogravimetric analysis (TGA) on TG 209F3 Thermogravimetric Analyzer from NETZSCH. The samples were heated from 40 to 700 °C at a heating rate of 20 °C min^{-1}, under nitrogen flow rate of 60 mL min^{-1}. The electromagnetic interference shielding effectiveness (EMI SE) of the composite fabrics was measured by the vector network analyzer instrument (FY800). This method used a flanged circular coaxial transmission line holder. The EMI SE values of composites were obtained by subtracting the background value. The frequency of EMI SE measurement was set from 300 KHz to 3000 MHz in this investigation.

RESULTS AND DISCUSSION

Surface Morphology

The surface morphology of the PPy-coated cotton fabrics with different concentrations of CTAB were observed by SEM shown in Figure 3. The surface of the PPy-coated fabric without using CTAB was very smooth and clean. In contrast, the PPy-coated

Table I. Viscosity of the Mixture Solutions Containing CTAB

Concentration of CTAB (M)	Viscosity (mPa s)	
	No HCl	1 M HCl
0	1.7	1.8
0.005	2.3	2.4
0.01	2.3	3.6
0.02	2.4	4.9
0.03	2.5	8.6

fabrics using soft template synthesis method presented relatively coarse surface covered by fine fibrillar conductive polymers. The micelle of cationic surfactant played a key role in the formation of fibrillar structure polypyrrole due to the interaction between surfactants and hydrochloric acid in the reaction systems.[39] Chloride ions could effectively reduce the electrostatic repulsion between the micellar molecules. As a result, micelle volume increased in the solution. With the increasing CTAB concentration, the worm-like micelles formed gradually which could be proved by the increasing viscosity of mixture aqueous solution of CTAB and HCl[40] (Table I). In the solution of 1.0M HCl, viscosity of mixture solutions increased by nearly four times, from 1.8 to 8.6 mPa s while concentration of CTAB increased from 0 to 0.03M. However, the viscosity of the solutions without hydrochloric acid showed no significant change. The dramatic increase of solution viscosity indicated the evolution of micellar aggregation which was favorable to build fibrillar conductive polypyrrole.

Thermal Stability

Thermal gravimetric analysis curves of untreated cotton fabrics and PPy-coated cotton fabrics are shown in Figure 4. Generally, the cellulose fiber is degraded by three stages. The first weight loss stage in the temperature range up to 290 °C is mainly due to the removal of absorbed water from the samples. The second weight loss stage of cotton fabrics between 290 and 380 °C is related to the breakage of glucosidic bond and ether bond. The last stage above 380 °C is attributed to the combustion of carbon skeleton.[41] In comparison, a lower weight loss temperature is observed for PPy-coated cotton fabrics than that of untreated fabric due to doping acid accelerating decomposition of the composites. Interestingly, there was not obvious thermal transition temperature for PPy-coated cotton fabrics, while the thermal decomposition temperature of untreated cotton is ~380 °C. At 700 °C, the finally residues for PPy-coated cotton fabrics prepared without CTAB and with 0.03M CTAB were about 30 and 40%, respectively, whereas that of the untreated cotton fabric was only 2%. The excess residue available in the treated fabrics is attributed to the presence of polypyrrole.

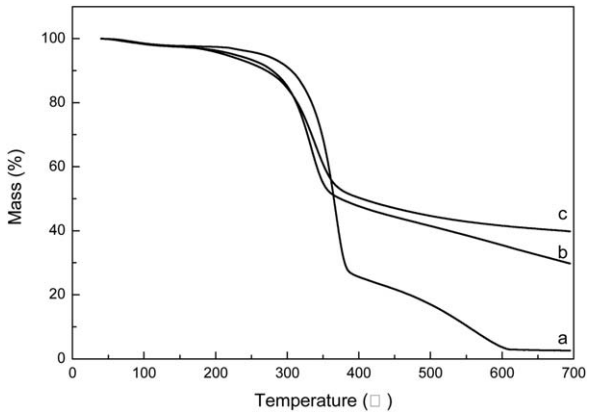

Figure 4. TG analysis of cotton fabrics: (a) untreated cotton, (b) PPy-coated cotton fabrics without using surfactant, (c) PPy-coated cotton fabrics using 0.03 M CTAB.

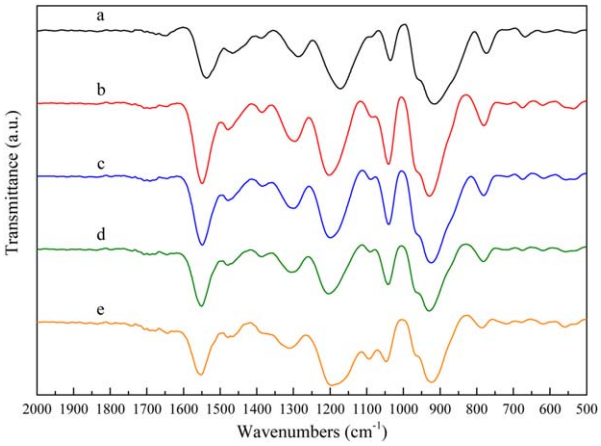

Figure 5. FTIR spectra of PPy with different concentrations of CTAB and 1M HCl: (a) no surfactant, (b) 0.005M CTAB, (c) 0.01M CTAB, (d) 0.02M CTAB, (e) 0.03M CTAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR Spectra

Figure 5 presents the FTIR spectra of fibrillar polypyrrole prepared with diverse concentrations of CTAB and reveals that their characteristic peaks are almost the same. The bands at about 1550 and 1470 cm^{-1} are assigned to the C—C and C—N stretching vibration of pyrrole rings.[42] The band at 1300 cm^{-1} is attributed to the C—H and C—N inplane deformation. The bands at about 1200 and 920 cm^{-1} correspond to the stretching

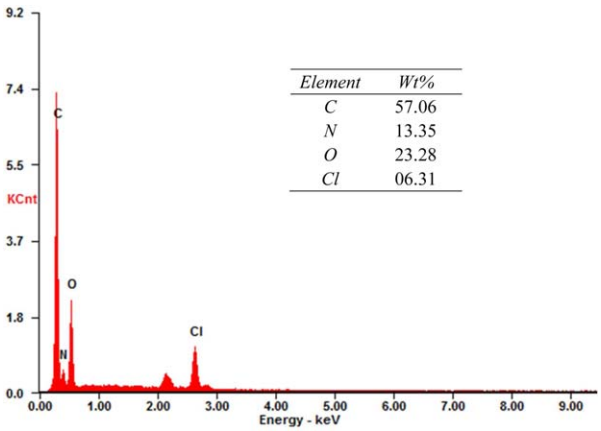

Figure 6. EDS of PPy-coated cotton fabrics prepared with 0.03 M CTAB and 1 M HCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

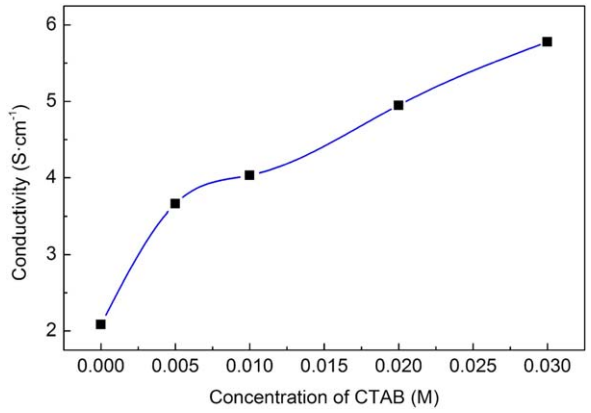

Figure 7. Surface conductivity of PPy-coated fabrics prepared with different concentrations of CTAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibration of pyrrole ring doped by HCl. The peak at about 1040 cm^{-1} is assigned to the N—H inplane deformation vibration. The band of NH^+ group which is formed in the polypyrrole chain by protonation is situated at 1090 cm^{-1} and appears enhanced in relatively higher concentrations of CTAB.[43]

EDS Spectrum

The chemical composition of the fibrillar polypyrrole coated cotton fabric is further ascertained by the EDS shown in Figure 6. Results indicate that PPy-coated cotton fabric prepared with CTAB and HCl is mainly composed of four elements including carbon, nitrogen, oxygen, and chlorine. The mass ratio of nitrogen to carbon is 23.40%, lower than that of pure polypyrrole, furtherly suggesting that polypyrrole was certainly deposited on the surface of cotton fibers. In addition, the presence of chlorine confirms the doping of hydrochloric acid into polypyrrole coating.

Electrical Conductivity of PPy-Coated Cotton Fabrics

Electrical conductivity of the fibrillar polypyrrole coated cotton fabrics synthesized using CTAB as soft template and $FeCl_3$ as an oxidizing agent was measured with the standard Van Der Pauw direct current four-probe method, and the results are shown in Figure 7. After coated with fibrillar polypyrrole, the surface of modified cotton fabrics shows typical metallic behavior. The conductivity value increased rapidly from 2.0 to 5.8 S cm^{-1} at 25 °C when the concentration of CTAB increased from 0 to 0.03M. It could be speculated that the concentration of CTAB was the significant influence factor of electrical conductivity, because CTAB microstructure under CTAB/HCl mixture solution could be favorable to fibrillar polypyrrole growth. In addition, the fibrillar structure of the polypyrrole prepared with CTAB should facilitate doping ions transport and maximizing the electroactive area.

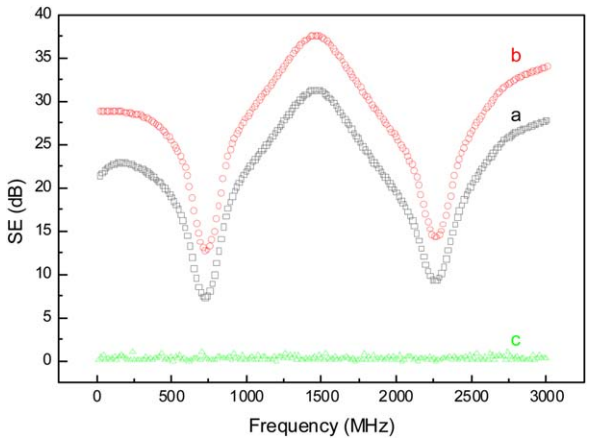

Figure 8. EMI SE of the samples: (a) PPy-coated cotton fabrics without surfactant, (b) PPy-coated cotton fabrics using 0.03 M CTAB, and (c) untreated fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electromagnetic Interference Shielding Effectiveness

The electromagnetic interference shielding effectiveness of the treated fabrics was shown in Figure 8. As expected, the EMI SE value of the untreated cotton fabric is zero and almost all of the incident microwaves are transmitted within 300 KHz–3000 MHz. The PPy-coated fabrics without surfactant have a great capability of shielding electromagnetic waves owing to the intrinsic electrical conductivity of doped polypyrrole. Compared with the sample without surfactant, the EMI SE value of PPy-coated cotton fabrics increased by 28% after using 0.03M CTAB as soft template. This advanced shielding property may be ascribed to better conductivity and fibrillar coarse surface structure, which improve reflection and absorption towards electromagnetic waves.

CONCLUSIONS

Fibrillar PPy-coated cotton fabrics were successfully prepared via chemical polymerization method using CTAB as soft templates. The role of CTAB micelle in altering the morphological structure and electrical conductivity of polypyrrole coating was studied through indepth characterizations. Due to the formation of fibrillar conductive network, conductivity of PPy-coated cotton fabric prepared by soft template synthesis method was significantly enhanced. Furthermore, benefiting from the excellent surface conductivity the modified cotton fabric exhibited higher electromagnetic interference shielding effectiveness. Soft-template assisted chemical polymerization method offer a novel route to prepare the high conductive cotton fabrics and will provide more high performance flexible electronic components for development of smart textile.

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