Electronic Supplementary Information (ESI) Materials for Journal of Materials Chemitry C

A strategy to improve thermoelectric performance of conducting polymer nanostructure

Jian Zhao,[#a] Dongxing Tan[#a,b] and Guangming Chen*[b]

[a] *Key Laboratory of Rubber-Plastics, Ministry of Education, Qingdao University of Science and Technology, Qingdao 266042 P. R. China*

[b] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.*

E-mail: chengm@iccas.ac.cn (G. Chen).

*Corresponding author.

Experimental

Reagents and materials

The monomer of 3,4-ethylenedioxythiophene (EDOT) was purchased from Sinopharm Chemical Reagent Co. Ltd, with a purity of higher than 99.0%. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 96%) was bought from Alfa Aesar. Anhydrous sodium sulfate (Na_2SO_3), methyl alcohol, n-hexane and sulfuric acid (H_2SO_4) were purchased from Beijing Chemical Corporation. Iron (Ⅲ) chloride ($FeCl_3$) and sodium dodecyl sulfate (SDS) were bought from Aladdin Industrial Corporation and Sigma Aldrich, respectively.

Synthesis of PEDOT nanorods

The PEDOT nanorods were synthesized by chemical oxidation polymerization in an aqueous surfactant solution or a reverse micro-emulsion.

A typical preparation by the aqueous surfactant solution containing H_2O, $FeCl_3$, SDS and methyl alcohol is briefly described in the following. First, 0.209 g SDS was dissolved in a mixture of methyl alcohol (10 mL) and water (70 mL), and stirred for 1 h. Subsequently, 0.9732 g $FeCl_3$ was added. After being stirred for 3 h, 200 μL of EDOT monomer was added into the above aqueous surfactant solution, with continuous stirring. The polymerization reaction proceeded for 8 h at 50℃. The colour of the solution changed from yellow to green and finally to dark blue. Finally, the product was washed with deionized water and ethanol, and dried at 60 ^oC for 24 h.

The reverse cylindrical micelle phase was prepared using H_2O, $FeCl_3$, and AOT in hexane, where the schematic preparation is shown in Fig. S1. First, 3.02 g AOT was dissolved in 20 mL hexane, and 0.54 mL (7 M) $FeCl_3$ aqueous solution was progressively titrated into the AOT/hexane system. After being stirred for 4 h at 50 ^oC, 100 μL EDOT monomer was added into the mixed

reverse cylindrical micelle phase. The polymerization reaction lasted for 8 h at 20 ^{o}C. Finally, the product was washed with deionized water and ethanol, and dried at 60 ^{o}C for 24 h.

H_2SO_4 treatment of PEDOT nanorods

A certain amount of PEDOT nanorods was dispersed into 20 mL of sulfuric acid aqueous solution at different concentration (0.5 M, 1.0 M, 1.5 M or 2.0 M), and endured an ultrasonic treatment for 30 min. Then, the product was moved to a separation funnel, and washed with ethanol and deionized water for several times. Finally, the product was washed with deionized water and ethanol, and dried under vacuum at 60 ^{o}C for 24 h.

Na_2SO_3 treatment of PEDOT nanorods

A certain amount of PEDOT nanorods treated by 1.5 mol L^{-1} sulfuric acid was dispersed into 20 mL 1.0 wt% Na_2SO_3 aqueous solution, and undergone ultrasonic treatment for a certain period of time (5 s, 10 s, 30 s or 60 s). Then, the product was moved to a separation funnel, and washed with ethanol and deionized water for several times. Finally, the product was rinsed with deionized water and ethanol, and dried under vacuum at 60 ^{o}C for 24 h.

Morphological and structural characterizations

The morphology of the PEDOT nanorods was observed using a HITACHI S-4800 field-emission scanning electron microscopy. The UV–Vis-NIR absorption spectra were taken with a UV-2600 spectrometer within the wavelength range between 300 and 1300 cm^{-1}. The XPS analysis was carried out with a multipurpose X-ray photoemission spectroscope (Thermo Scientific ESCALAB 250Xi). The Raman spectra was collected by a Raman spectrometer (Renishaw in Via plus) using a laser diode at an excitation wavelength of 514

nm, ranging from 900 to 1800 cm^{-1}. Powder XRD measurements were conducted on a Rigaku D/max 2400 diffractometer with Cu Kα radiation (λ= 0.15418 nm) at a scanning rate of 2^{o} min^{-1}.

Measurements of Thermoelectric Performance

The pellets of PEDOT nanorods used for thermoelectric measurements (electrical conductivity and Seebeck coefficient) were obtained by cold pressing the powder samples at 15 MPa. The electrical conductivities and the Seebeck coefficients at room temperature were measured by a commercial instrument, Thermoelectric Parameter Test System (Namicro-F3), made by JiaYiTong Company. During the measurements, a quasi-steady-state mode was applied. For the Seebeck coefficient measurement, the temperature gradient along the length of the sample (one end of the sample was heated) was determined through two thermocouples. The slope of the linear relationship between the thermoelectric voltage (ΔV) and the temperature difference (ΔT = 10 K) was then used to calculated the Seebeck coefficient ($S = -\Delta V/\Delta T$).

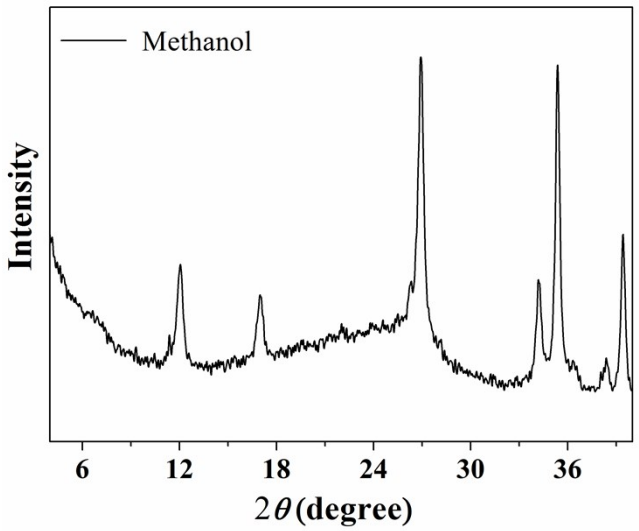

Figure S1 XRD pattern of the pristine PEDOT nanorods prepared by aqueous phase

polymerization.

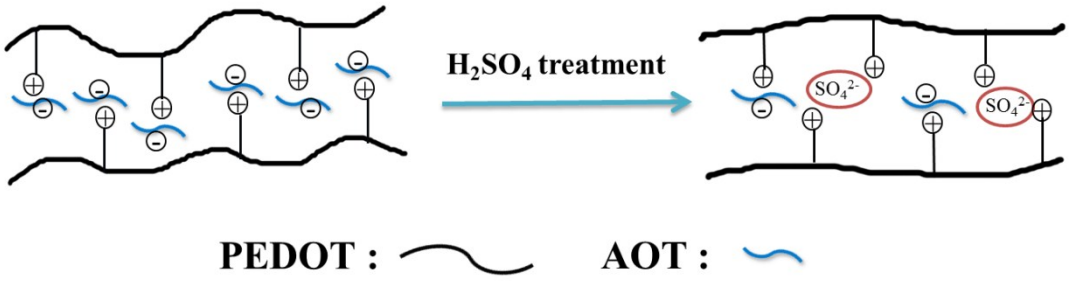

Figure S2 Schematic structure of the transition of the PEDOT after the acid post-treatment process by H_2SO_4.