



Capacitive behavior and material characteristics of congo red doped poly (3,4-ethylene dioxythiophene)

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ABSTRACT

Congo red doped poly(3,4-ethylene dioxythiophene) with loose granular morphology and some clear channels was synthesized by chemical oxidative polymerization using congo red as dopant and surfactant, and the formation mechanism of its morphology was confirmed by means of fourier transform infrared spectrum, X-ray diffraction, UV–Vis absorption spectrum and scanning electron microscope. The influences of feeding molar ratio of congo red to ethylene dioxythiophene on its electrochemical properties were discussed by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The results showed that the maximum specific capacitance of congo red doped poly(3,4-ethylene dioxythiophene) could reach 206 F/g when the feeding molar ratio of congo red to ethylene dioxythiophene was 0.08:1, which was 58% higher than that of poly(3,4-ethylene dioxythiophene). The improved specific capacitance of congo red doped poly(3,4-ethylene dioxythiophene) could be due to its special molecular structure and loose granular morphology with some clear channels.

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1. Introduction

Poly (3,4-ethylene dioxythiophene) (PEDOT) has been widely used in antistatic coating, electroluminescent device, printed circuit board, solid electrolytic capacitor, supercapacitor, and so on [1–3], because of its high electrical conductivity, significant photoelectric conversion efficiency, good chemical and thermal stabilities. As an electrode material for supercapacitor, PEDOT had the linear π -conjugated molecular structure with fewer structural defects, narrower band gap and more stable oxidation state than the conventional π -conjugated polymer such as polyaniline (PANI), polypyrrole (PPy) and poly (phenylene vinylene) (PPV) [4–9]. Therefore, PEDOT exhibited great chemical and electrochemical stabilities in air, water vapor or aqueous solution [10], which were incomparable to conventional π -conjugated polymers and were beneficial to the widespread application of PEDOT as electrode material for supercapacitor [11]. However, the theoretical specific capacitance of PEDOT was about 210 F/g due to its relatively higher molar mass and lower doping level, which was much lower than that of PPy with the similar molecular structure (about 620 F/g) [12,13]. In fact, PEDOT tended to aggregate during the synthesizing

process, which decreased the surface area for participating redox reaction and resulted in the reduction of specific capacitance [14].

In order to improve the specific capacitance of PEDOT, many efforts have been made. For example, PEDOT was combined with carbon materials, metal oxides and other π -conjugated polymers [15,16]. Lota et al. [17] prepared the PEDOT/CNTs composites by chemical or electrochemical polymerization of EDOT directly on the carbon nanotubes (CNTs) and the results showed that the value of specific capacitance for PEDOT/CNTs composite was in the range of 60–160 F/g and such composite exhibited a good cycling performance with a high stability in acidic, alkaline and organic electrolytic solutions. Huang et al. [18] electrochemically loaded hydrous RuO_2 particles into PEDOT doped poly (styrene sulfonic acid) (PEDOT-PSS) matrix with a porous structure to fabricate the PEDOT-PSS- $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ composite. It was observed that the specific capacitance of composite increased with the loaded amount of hydrous RuO_2 particles in PEDOT-PSS, and the maximum specific capacitance of 653 F/g was achieved. Xu et al. [19] prepared PEDOT/PPy composite with horn-like structure by electrochemical polymerization of EDOT on the surface of PPy and the results showed that the specific capacitance of composite was up to more than 200 F/g, which was much higher than that of either PEDOT or PPy due to the synergic effect of PEDOT and PPy.

Azo dyes were organic compounds bearing the functional group $\text{R}-\text{N}=\text{N}-\text{R}'$, where R and R' were usually aryl. Dai et al. [20]

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synthesized PPy, PANI microtubules and PEDOT microtubular fragments using one-dimensional methyl orange fibrils as soft templates. It was found that the conductivities of tubules at room temperature were 1.4 , 4×10^{-2} and 6×10^{-2} S/cm for PPy, PANI and PEDOT, respectively. Wang et al. [21] synthesized the acid blue AS doped polypyrrole (PPy/AS) nanomaterials with different morphologies via chemical oxidative polymerization of pyrrole in the presence of acid blue AS as dopant and surfactant. The results showed that the morphology of PPy/AS nanomaterials changed from nanoparticles to clusters of nanofibers and nanoparticles, then nanorods with the increase of feeding molar ratio of AS to pyrrole. The PPy/AS nanomaterials with the morphology of the clusters of nanofibers and nanoparticles showed the highest electrical conductivity of 20 S/cm and the largest specific capacitance of 427 F/g. Our research group have synthesized PANI with coral-like nanostructure via chemical oxidative polymerization in the presence of sunset yellow (SY) as dopant and surfactant [22]. The results showed that in comparison with the microsized bulky structure of PANI undoped with SY, the coral-like nanostructure of PANI doped with SY (PANI/SY) was observed and the diameter of coral branch decreased from 180 nm to 100 nm with the increase of feeding molar ratio of SY to aniline. Coral-like PANI/SY showed the large specific capacitance of 467 F/g and good electrochemical stability when the feeding molar ratio of SY to aniline was 0.035:1, owing to its special coral-like nanostructure and high conductivity of 15.0 S/cm.

Although there were some reports on the effects of azo dyes on the electrochemical performances of PANI and PPy [23–25], the effect of large azo dye containing the azo unit and sulfonate anion as dopant on the molecular structure, morphology and electrochemical performance of PEDOT was not investigated in detail so far. In this paper, cargon red (CR) with an azo unit and two sulfonate anions as shown in Fig. 1 was used as dopant for the synthesis of CR/PEDOT for the first time. Here, CR was not only used as a dopant but also played the role of surfactant. It could enhanced the solubility of both EDOT and PEDOT oligomer in the water during the process of polymerization and be helpful in the formation of loose granular morphology with some clear channels, which were favourable to the increase of π -conjugated degree and surface area of CR/PEDOT for participating redox reaction, thus it was conducive to increasing the specific capacitance of PEDOT. In addition, CR could provide the pseudocapacitance because of its π -conjugated molecular skeleton after PEDOT was doped with CR, which also contributed to the increase of specific capacitance of PEDOT.

2. Experimental

2.1. Materials

3,4-ethylene dioxithiophene (EDOT) of 99.7% purity was obtained from Sigma-Aldrich Chemical Reagent Co., Ltd. CR of 98% purity was purchased from Aladdin reagent Co., Ltd. (Shanghai, China) without further purification. Hydrochloric acid (HCl), ferric chloride (FeCl_3), methanol, carbon black, polyvinylidenedifluoride

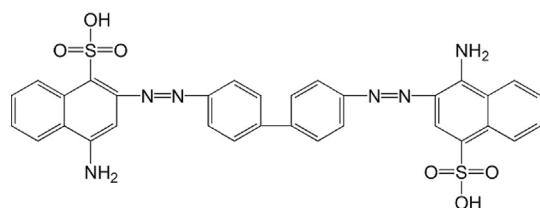


Fig. 1. Molecular structure of congo red.

(PVDF) and N-methylpyrrolidone (NMP) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Deionized (DI) water was used throughout the experiment.

2.2. Synthesis of CR/PEDOT

CR/PEDOT was synthesized by chemical oxidative polymerization and the feeding molar ratio of CR to EDOT prior to polymerization was varied as 0.02:1, 0.04:1, 0.06:1 and 0.08:1 in view of the solubility of CR in water and the rate and yield of polymerization of EDOT [26]. A certain amount of CR was added to 10 mL DI water and stirred for 5 min. 2 mmol EDOT was added to the above solution and the mixture was sonicated for 30 min. 10 mL aqueous solution containing 6 mmol FeCl_3 and 0.5 mL HCl was added drop by drop to the above mixture within 1 h and the mixture continued to be stirred at room temperature for 24 h. The dark blue CR/PEDOT sample was settled by methanol and washed repeatedly with methanol and DI water to remove the residual chemical agents and oligomers until the filtrate was colorless, and then dried under vacuum at 60 °C for 24 h. For comparison, PEDOT without CR was synthesized under the same reaction conditions. For the convenience of discussion, the resulting CR/PEDOT samples were designated as CP-1, CP-2, CP-3 and CP-4 with the increase of feeding molar ratio of CR to EDOT.

2.3. Measurements

Fourier transform infrared (FT-IR) spectrum and UV–Vis absorption spectrum were recorded by Nicolet 5700 fourier transform infrared spectrometer and Hitachi U-2001 UV–Visible spectrometer, respectively. X-ray diffraction (XRD) measurements were conducted on X'Pert Pro MPD at a rate of 5°/min from 5° to 40°. Scanning electron microscope (SEM) analysis was taken using a Zeiss SUPRA 55 scanning electron microscopy at an accelerating voltage of 3 kV. All the electrochemical experiments were carried out in a three-electrode system with a working electrode, a platinum counter electrode and a standard calomel reference electrode (SCE). For the preparation of working electrode, the active material (PEDOT or CR/PEDOT), carbon black and PVDF were mixed in a mass ratio of 80:15:5 and dispersed in NMP to form uniform slurry. Then the slurry was coated onto the stainless steel (SS) substrate (1 cm × 1 cm) and dried in an oven at 60 °C for 24 h. Finally, the working electrode was obtained by subjecting the SS substrate after coating to a pressure of 10 MPa. The mass loading of material on the SS substrate was obtained by measuring the weight difference before and after coating using a microbalance, eighty percent of which was the weight of active material. The weight of active material loaded on the SS substrate was about 3 mg and the thickness of working electrode was about 0.5 mm. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed on a CHI660E electrochemical workstation in a 1 mol/L H_2SO_4 aqueous solution. The potential range for CV and GCD tests was -0.2 V to 0.8 V. EIS test was carried out in the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 5 mV.

The specific capacitances (C) was calculated from the GCD curves according to the following equations [27].

$$C = I\Delta t/m\Delta V \quad (1)$$

where I, Δt , ΔV and m were the constant current, the discharge time, the total potential deviation and the weight of active material, respectively.

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