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# Hexavalent chromium synthesized polyaniline nanostructures: Magnetoresistance and electrochemical energy storage behaviors

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## ABSTRACT

In this work, the oxidant Cr(VI) dose was observed to have influenced the polyaniline (PANI) nanostructures as well as the crystallization structure. The temperature dependent resistivity study revealed a quasi 3-dimensional variable range hopping (VRH) electrical conduction mechanism. The permittivity was found to be affected by the PANI nanostructures. The observed positive MR at room temperature in the synthesized PANI samples was analyzed by the wave-function shrinkage model. The electrochemical energy storage was investigated using the cyclic voltammetry (CV) and galvanostatic charge–discharge measurements. The highest gravimetric capacitance of 298.5 F $g^{-1}$ was obtained in the prepared PANI sample using 3 mmol $K_2Cr_2O_7$ derived from the CV at a scan rate of 5 mV $s^{-1}$ and the maximum value of gravimetric capacitance of 330.2 F $g^{-1}$ was achieved in the galvanostatic charge–discharge measurements at a current density of 0.5 A $g^{-1}$. After applying an external magnetic field, the capacitance decreased due to the observed positive magnetoresistance phenomenon. The cyclic stability studies revealed that the synthesized PANI samples exhibited good durability and retained around 80% of the capacitance even after 1000 charge–discharge galvanostatic cycles.

## 1. Introduction

Recently, owing to the climate change and the depletion of fossil fuels, such as oil, coal and natural gas, the design of new energy storage systems is imperatively required [1–3]. Electrochemical capacitors (ECs) have been extensively studied as the new generation of energy storage systems [4] due to the high energy and power density as well as long cycle life [5,6], which can be used in the electric vehicles and portable electronic device [7,8]. Generally, there are two types of ECs depending on the charge storage mechanisms as well as the active electrode materials [9]. One is called electrical double-layer capacitors (EDLCs), which has the high power density (power per unit volume) with long cycling life and is predominately due to the double-layer charging effects [10] arising from the electrolyte ion adsorption [11]. However, this kind of capacitor (commonly used materials are activated carbon materials with large specific surface area) has the low energy density (energy per unit volume, typically 5–10 Wh $kg^{-1}$), which limits its applications. Another one is called pseudocapacitors or supercapacitors, which is based on the Faradaic process. Pseudocapacitance is an interfacial phenomenon, which is related to the specific surface area of the electroactive materials and achieved by the charge transfer through the surface Faradaic (redox) reaction [12]. And the pseudocapacitors have higher specific capacitance than EDLCs [13].

Conducting polymers have been considered as the promising pseudocapacitor electrode materials due to their low cost, easy synthesis process, flexibility and high capacitance [14]. The commonly studied conducting polymers include polythiophenes (PTs), polypyrrole (PPy), poly(DNTD) [15,16], and polyaniline (PANI) [17,18]. Among these conducting polymers, PANI is the most investigated for supercapacitor application because of its high conductivity, good environmental stability, versatile redox behavior and high pseudocapacitance [19,20]. The specific capacitances of PANI-based electrode materials are strongly dependent on the fabrication method [21]. Generally, PANI is synthesized by chemical or electrochemical oxidation polymerization of aniline monomers

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followed by the head to tail formation mechanism [22]. The commonly and widely used oxidant for PANI in the chemical polymerization method is ammonium persulfate (APS) [23,24]. The oxidants such as ferric chloride ($FeCl_3$) [25], hydrogen peroxide ($H_2O_2$) [26], perchloric acid ($HClO_4$) [13], vanadic acid [27], manganese dioxide ($MnO_2$) [28,29], tetrachloroaurate ($AuCl_4^-$) [30] and hexavalent chromium (Cr(VI)) have been reported to prepare PANI as well [31]. Cr(VI) is a strong oxidant in the acidic solution due to its high redox potential (1.33 V) and can be reduced to the stable Cr(III) species [32]. Though the Cr(VI) has served as an oxidant in preparing multi-walled carbon nanotubes (MWNTs) nanocomposites [31], the Cr(VI) dose effect on the polymerization of aniline and properties including permittivity and magnetoresistance of synthesized PANI has not been reported yet together with the electrochemical capacitive properties and energy storage behavior.

In this work, different PANI nanostructures were prepared by using different doses of Cr(VI) in Cr(VI) aqueous solution. The chemical structure and crystallinity as well as the morphology of PANI synthesized by different doses of Cr(VI) were studied using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The frequency dependent permittivity, temperature dependent resistivity and magnetic field dependent resistivity (MR) were also studied. The electrochemical performances of the synthesized PANIs for the energy storage device applications were studied using cyclic voltammetry (CV), galvanostatic charge–discharge measurements and electrochemical impedance spectroscopy (EIS) techniques. An equivalent circuit was also proposed to disclose the nature of the capacitive behavior. The effects of oxidant doses and the magnetic field on the electrochemical energy storage as well as the stability were also investigated systematically.

## 2. Experimental

### 2.1. Materials

Aniline ($C_6H_7N$) and *p*-toluene sulfonic acid (PTSA, $C_7H_8O_3S$) were purchased from Sigma Aldrich. Potassium dichromate ($K_2Cr_2O_7$) was purchased from Alfa Aesar Company. Carbon Conductive Tabs with a diameter of 6 mm, PELCO Tabs™, were provided by Ted Pella, Inc. Carbon paper – 2050-A 10 cm × 10 cm was obtained from Fuel Cell Store. All the chemicals were used as-received without any further treatment.

### 2.2. Synthesis of PANI by different doses of Cr(VI)

The PANI was synthesized by different doses of Cr(VI). Specifically, the PTSA (15 mmol) and $K_2Cr_2O_7$ (0.75, 3, 4.5 or 9 mmol) were added into 100 mL deionized water in an ice-water bath for half an hour mechanical stirring (SCILOGEX OS20-Pro LCD Digital Overhead Stirrer, 300 rpm) combined with sonication (Branson 8510). Then the aniline solution (18 mmol in 25 mL deionized water) was mixed with the above solution and mechanically stirred and sonicated continuously for additional 1 h in an ice-water bath for further polymerization. The final product was vacuum filtered and washed with deionized water. The precipitant was further washed and doped with 1 mol $L^{-1}$ PTSA. The final powders were dried at 60 °C in an oven overnight. The samples synthesized from different $K_2Cr_2O_7$ doses were named PANI-0.75, PANI-3, PANI-4.5 and PANI-9, respectively.

### 2.3. Preparation of PANI electrode

About 1 mg PANI samples synthesized by different doses of Cr(VI) were weighed using microbalance (UMX2 ultra-microbalance, METTLER TOLEDO company) and pressed uniformly onto a PELCO Tabs™ carbon conductive tape with a diameter of 6 mm on a carbon paper substrate. Each sample was weighed for five times within a deviation of ±3% to obtain the average value.

### 2.4. Characterizations

The morphology of the synthesized PANI was observed in the JEOL JSM-6510LV SEM after coated with carbon. The FT-IR spectrometer coupled with an ATR accessory (Bruker Inc., Vector 22) was used to characterize the chemical structure of the synthesized PANI in the range of 4000–500 $cm^{-1}$ at a resolution of 4 $cm^{-1}$. X-Ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 Discover diffractometer with GADDS (General Area Detector Diffraction System) operating with a Cu-K$\alpha$ radiation source filtered with a graphite monochromator ($\lambda = 1.5406$ Å). Data were collected in a range of 5–30°. Permittivity was investigated by an LCR meter (Agilent, E4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of $20–2 \times 10^6$ Hz at room temperature. The synthesized different PANI samples were pressed in a form of disc pellet with a diameter of 25 mm by applying a pressure of 50 MPa in a hydraulic presser and the average thickness was about 6 mm. The same sample for LCR measurement was also used to measure the resistivity ($\rho$) by a standard four-probe method from 100 to 290 K. The temperature dependent resistivity was used to determine the electrical conduction mechanism in the PANI-0.75 and PANI-3 samples. Magnetoresistance was carried out using a standard four-probe technique by a 9-T Physical Properties Measurement System (PPMS) by Quantum Design at room temperature. The four probes were 0.002 inch diameter platinum wires, which were attached by silver paste to the sample. And the magnetic field was applied perpendicular to the current. The UV–vis spectra were performed on a Jasco V-670 spectrophotometer. The sample was dissolved in the N-methyl-2-pyrrolidone (NMP) solution (1 mg of PANI samples diluted in 10 mL of NMP).

The electrochemical behaviors were evaluated using cyclic voltammetry (CV), galvanostatic charge–discharge measurements, and electrochemical impedance spectroscopy (EIS) techniques on an electrochemical working station VersaSTAT 4 potentiostat (Princeton Applied Research). A typical electrochemical cell consisting of a reference electrode (saturated calomel electrode (SCE)), a working electrode, and a counter electrode (a platinum (Pt) wire) was employed. The CV was scanned from −0.2 to 0.8 V *vs* SCE at a series of scan rates in 1.0 mol $L^{-1}$ $H_2SO_4$ electrolyte aqueous solution. EIS was carried out in the frequency range from 100,000 to 0.01 Hz at amplitude of 5 mV referring to the open circuit potential. The endurance of the composites was also assessed using galvanostatic charge–discharge measurements at a current density of 8 A $g^{-1}$ for 1000 cycles. The whole electrochemical cell was fixed between two magnetic poles of an electromagnet (EM4-HVA H-Yoke, Lake Shore Cryotronics, Inc., USA) to test the electrochemical property of the materials in a magnetic field [33]. The magnetic field flux density was controlled through tuning the magnitude of the current, which was measured to be 305.0 G (or Oe) by a Gauss/Tesla meter (7010 Gauss/Tesla meter, Sypris).

## 3. Results and discussion

### 3.1. Morphology, FT-IR, X-ray diffraction, UV–vis spectra

Fig. 1 shows the SEM images of the PANI-0.75, PANI-3, PANI-4.5 and PANI-9 samples. Different morphologies are observed for the PANI nanostructures fabricated by different doses of Cr(VI). The particle size of PANI increases with increasing Cr(VI) doses and the PANI becomes more ordered with increasing Cr(VI) dose.