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Transition metal doped poly(aniline-*co*-pyrrole)/multi-walled carbon nanotubes nanocomposite for high performance supercapacitor electrode materials

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ABSTRACT

In this present communication, copolymer of polyaniline (PANI) and polypyrrole (PPy) that is poly (aniline-*co*-pyrrole) [poly(An-*co*-Py)], copper chloride ($CuCl_2$) doped poly(aniline-*co*-pyrrole) [poly (An-*co*-Py) Cu], and $CuCl_2$ doped poly(aniline-*co*-pyrrole)/multi walled carbon nanotubes (MWCNTs) [poly(An-*co*-Py) Cu CNT] nanocomposite have been prepared by a simple and inexpensive *in-situ* chemical oxidative polymerization method, using ammonium persulfate (APS) as oxidant and hydrochloric acid (HCl) as dopant and investigated as high performance supercapacitor electrode materials. The possible interaction between $CuCl_2$ with copolymers and MWCNTs was investigated by Fourier transform infrared spectroscopy (FTIR) and UV–visible spectroscopy analysis. The morphological characteristic of all the electrode materials were analyzed by Field emission scanning electron microscopy (FESEM) and Transmission electron microscopy (TEM) study. The electrochemical characterizations of all the electrode materials were carried out by three electrode probe method where, standard calomel electrode and platinum were used as reference and counter electrodes, respectively. Among all the electrode materials, poly(An-*co*-Py) Cu CNT nanocomposite achieved highest specific capacitance value of 383 F/g at 0.5 A/g scan rate. The nanocomposite showed better electrical conductivity at room temperature and also attained nonlinear current–voltage characteristic. Based on the superior electrochemical as well as other properties the as prepared nanocomposite can be used for high performance supercapacitor electrode materials.

1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted great attention over the past few years due to their high energy densities than conventional capacitors. Further, these are also capable to provide superior power densities and long cycle life than secondary batteries. For that reason, supercapacitors have been used as an efficient component in various applications like portable electronic devices, electric vehicles, automobiles, etc. [1,2]. Based on charge–discharge mechanism, supercapacitors can be classified into two categories. The first one is called electric-double later capacitors (EDLC), which is mainly based on carbon materials with high surface area such as carbon, carbon nanotubes and graphene, and utilizes the capacitance occurring from charge separation at the electrode/electrolyte interface. The second one is known as pseudo-capacitors, which is mainly constructed from conducting polymers and transition-metal oxides and utilizes the pseudo-capacitance arising from the fast, reversible redox reactions arising from the electrode surface. Conducting polymers are one of the most widely investigated polymers for several applications like sensor, light-emitting diodes, batteries, electrochemical supercapacitors, etc. [3–6]. Among all the conducting polymers, polyaniline (PANI) and polypyrrole (PPy) are considered as the most important materials for portable device applications, due to their easy synthesis, low cost, high electrical conductivity, favorable physiochemical properties and environmental stability [7,8]. As these two conducting polymers individually showed enormous application potential for the construction of various devices, a combination of two can display superior potential for device applications.

Several scientific reports are available on the synthesis of copolymer based on PANI and PPy via different synthetic techniques and the researchers are investigated their various properties such as morphological, thermal, and electrochemical. Zhang et al. prepared the composite of PANI and PPy by two-step electrochemical polymerization method and investigated their

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electrochemical performance [9]. Xu et al. investigated the morphological and electrochemical reactivity of poly(aniline-*co*-pyrrole), prepared by chemical oxidative copolymerization methods [10]. Mavundla et al. reported the morphological evolution, optical and structural properties of poly(aniline-*co*-pyrrole), synthesized by chemical oxidative copolymerization process [11]. Qin et al. prepared poly(aniline-*co*-pyrrole) by chemical oxidative polymerization methods using cetylmethyl ammonium chloride (CTAC) as template and investigated their electrochemical performances [12]. Palaniappan et al. synthesized poly(aniline-*co*-pyrrole) by inverted emulsion polymerization technique and checked their electrochemical properties [13]. Zhu et al. reported hallow poly(aniline-*co*-pyrrole)-Fe_3O_4 composite synthesized by oxidative polymerization method and investigated their microwave absorption behavior [14]. More recently, Javadian et al. synthesized PANI/PPy copolymer by *in-situ* chemical polymerization technique and investigated its capacity for the removal of Co(II) from aqueous solutions [15]. Bhaumik et al. prepared PANI-PPy nanofibers via *in-situ* chemical polymerization method and examined their adsorption efficiency towards Congo red [16]. Nawaz et al. synthesized multilayered PANI/PPy/MWCNTs nanocomposite via layer-by-layer oxidative polymerization and checked their morphological and thermal properties [17]. Li et al. synthesized sodium molybdate doped PANI-PPy copolymer on stainless still by cyclic voltammetry and studied their corrosion prevention properties [18]. Deng et al. prepared PPy-PANI/TiO_2 nanocomposite by *in-situ* oxidative polymerization technique and investigated the morphology, structure, optical and photoelectrochemical properties [19]. Dubal et al. synthesized PANI-PPy nanocomposite by simplest oxidative chemical polymerization method and studied their electrochemical properties [20].

There are numerous researches going on carbon nanotubes (CNTs) in the fields of chemistry, physics, materials science and engineering. Due to their excellent mechanical characteristics, nanometer size, good electrical conductivity, and extremely accessible surface area, CNTs can be used for the preparation of the multifunctional composites with outstanding mechanical and electronic properties [21]. The incorporation of both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) into the polymeric composites enhances the electrochemical properties. The increment of electrochemical properties mainly resulted due to several superior properties of SWCNTs and MWCNTs like small size, high conductivity, high stability and high surface area [22–24]. It was reported that the doping of conducting polymers by transition metal ions like Cu^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{3+} (works as redox active materials) improves the capacitance and thus enhances the energy density [25–27].

In one of our previous study we have synthesized $CuCl_2$ doped PANI/MWCNTs nanocomposite for supercapacitor electrode [28]. In another study we have studied the electrochemical properties of $CuCl_2$ doped PPy/MWCNTs nanocomposite [29]. More interestingly in this present study we want to know how $CuCl_2$, MWCNTs both and the copolymer of PANI and PPy effects on the electrochemical properties. Herein, we have synthesized the copolymer of PANI and PPy i.e., poly(An-*co*-Py), poly(An-*co*-Py) Cu, and poly(An-*co*-Py) Cu CNT nanocomposite via *in-situ* chemical oxidative polymerization techniques using APS as oxidant in HCl medium. The molar ratio of PANI and PPy monomer was 2:1. The capacitive behaviors of the polymeric composites were characterized by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) analysis. Their morphological characteristics, electrical conductivity and chemical interactions of the doped polymeric composites were also investigated.

2. Experimental

2.1. Materials used

The monomers aniline and pyrrole used in this study were supplied by Merck, Germany. APS [$(NH_4)_2S_2O_8$], HCl, $CuCl_2$, H_2SO_4, HNO_3 and Dimethylformamide (DMF) used in this study were also supplied by Merck, Germany. MWCNTs (MWCNTs-1000) were obtained from Iljini nanotechnology, Korea. These MWCNTs are having the diameter of 10–20 nm, length 20 μm and aspect ratios of ~1000. Cetyltrimethylammonium bromide (CTAB) was purchased from Loba Chemie Pvt. Ltd. (Mumbai, India).

2.2. Acid modification of MWCNTs

To remove the impurities, MWCNTs were modified by mixed acid treatment. At first, 500 mg of MWCNTs were mixed with mixed acid solutions containing 3 mol/L of conc. H_2SO_4 and 1 mol/L of conc. HNO_3 (H_2SO_4:HNO_3 = 3:1). The MWCNTs were mixed with the acid solution at ratio of 1:100 and the whole solution was stirred at 60 °C for 24 h. After that, the total mixture was washed with distilled water until the pH of the solution becomes neutral. Then, the entire solution was centrifuged for 20 min at 3000 rpm and separate out the product. Lastly, it was dried at 100 °C for 24 h to yield the carboxylic acid-functionalized MWCNTs.

2.3. Doping on poly(aniline-co-pyrrole)

The poly(An-*co*-Py) Cu was synthesized by *in-situ* oxidative polymerization techniques using $(NH_4)_2S_2O_8$ as oxidant in 1.5 M HCl medium. The monomers, aniline and pyrrole were mixed at a ratio 2:1. At first, the monomers aniline (0.67 ml) and pyrrole (0.33 ml) were dissolved in 1.5 M, 70 ml HCl solution in a 200 ml beaker. After that, $CuCl_2$ solution was added drop wise to the above solution. In another beaker, 2 g of APS was dissolved in 20 ml deionized water. This APS solution was then added drop by drop to the doped monomer solution. The entire solution was then stirred at constant speed for 5 h at room temperature. After completion of polymerization process, the whole solution was filtered, washed with deionized water and ethanol several times, and dried at 70 °C for 12 h. The pure poly(An-*co*-Py) was also synthesized by the same procedure without the addition of $CuCl_2$.

2.4. Synthesis of nanocomposite

For the synthesis of nanocomposite, a typical *in-situ* oxidative polymerization technique was employed. Initially, 1.24 g of CTAB and 60 mg of MWCNTs were added in 150 ml of 1.5 M HCl solution and sonicated for 30 min at room temperature. In another beaker, 0.67 ml of aniline and 0.33 ml of pyrrole were dissolved in 1.5 M HCl (60 ml) solution. Into this solution, $CuCl_2$ solution was added drop wise and stirred for 15 min. After that, $CuCl_2$ doped monomers solution was added in the well dispersed suspension of MWCNTs solution. Subsequently, 60 ml of deionized water containing 2 g of APS was then added drop by drop to the above solution and stirred at constant speed for 5 h at room temperature. After complete polymerization process, the entire solution was kept at 1–5 °C for 12 h. Then, the resultant precipitate was filtered and washed with deionized water and ethanol several times and dried at 70 °C for 12 h to get the poly(An-*co*-Py) Cu CNT nanocomposite. The schematic representation of the synthesis method of the nanocomposite is illustrated in Fig. 1.

3. Characterization

3.1. FTIR analysis

To understand the interactions of Cu^{2+} with the copolymer chains and also with the MWCNTs, the electrode materials were characterized by FTIR spectroscopy. FTIR analysis was performed using NEXUS 870 FT-IR (Thermo Nicolet) instrument in the range from 400 to 4000 cm^{-1}. The samples were made by mixing of potassium bromide (KBr) and the electrode materials in weight ratio of 10:1 and pelletized to make the disk and the disks were analyzed for getting the spectrum.

3.2. UV–visible spectroscopy

The UV–visible spectra of all the electrode materials were taken by using Perkin Elmer, Lambda 750 spectrophotometer. The UV–visible spectra were recorded within the 200–800 nm wave length regions.