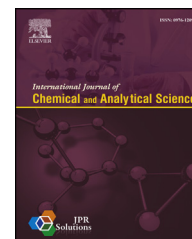


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Original Article

Enhanced electrocapacitive performance of graphene oxide polypyrrole nanocomposites

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ABSTRACT

Aim: Graphene oxide/polypyrrole nanocomposites (PNCs) with enhanced electrocapacitive performance were prepared through a cationic surfactant assisted dilute solution polymerization of pyrrole in presence of GO at various concentrations (% w/w) ranging 10.0–40.0 and ferric chloride as oxidant.

Methods: PNCs has been characterized through Fourier transformed infrared spectra, X-ray diffraction, scanning electron microscopy and simultaneous thermogravimetric-differential scanning calorimetry. Electrochemical capacitance (C_s , F/g) of electrodes fabricated from PNCs over 316 stainless steel in presence of sulphonated polysulphone as binder has been investigated in KOH solution (1.0 M) with reference to Ag/AgCl at scan rate (V/s) ranging 0.2–0.001.

Results: PNCs with 20.0% w/w of GO have shown highest C_s of 1073.64 as compared to 92.33 for pure PPy at a scan rate of 0.001 V/s. PNCs rendered a low electrocapacitive decrease during the first 500 cycles at scan rate of 0.1 V/s indicating their appreciable electrochemical performance for fabrication of supercapacitor electrodes.

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1. Introduction

Polymer nanocomposites derived through various combinations of conducting polymers with carbon based nanofillers has recently been considered as a viable alternative for development of portable electronics, automobiles and related high power energy-storage systems. For best possible conservation and storage of electrochemical energy, there has been growing demand of PNCs bearing high specific capacitance (C_s), reduced over potential at high charge-discharge rates and high cycling

stability over long cycle-life.^{1–5} In this context, PNCs based on graphene,^{6–11} reduced graphene oxide (GO)^{12,13} and PPy grafted graphene onto GO^{14–20} due to their ease of preparation, low cost, outstanding electrical, electrochemical, charge-balancing properties, large surface area²¹ has extensively been used as filler for polypyrrole (PPy) due to their remarkable electrical conductivity and pseudo capacitance for development of electrochemical energy storage systems.^{12–19,21} Literature overview reveals that irrespective to the method of preparation and electrochemical measurements, the C_s of electrodes derived

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from PNCs in presence of GO (% w/w) ranging 5 to 80 has contributed their specific capacitance (C_s , F/g) ranging 181 to 633.

The present investigation reports a simplified approach of preparation of graphene oxide/polypyrrole nanocomposites (PNCs) bearing improved electrocapacitive performance and cyclic stability through cetyltrimethylammonium bromide (CTAB) assisted dilute solution polymerization of PPy in presence of GO at concentration (% w/w) ranging 10 to 40 and ferric chloride as oxidant. The sulphonated polysulphone (SPS) binded electrodes of PNCs with 20.0% w/w of GO over 316 stainless steel display relatively higher C_s of 1073.64 at a scan rate of 0.001 V/s with low electrocapacitive decrease during the first 500 cycles at scan rate of 0.1 V/s in KOH solution (1.0 M) with reference to Ag/AgCl.^{14–20}

2. Experimental

2.1. Starting materials

Commercially available Pyrrole (>99%), polysulfone (Mw; 16×10^3), CTAB, (>99%), chlorosulfonic acid (>99%) were purchased from Sigma Aldrich. Other chemicals and solvents were obtained from sd. Fine Chemicals India. SPS was synthesized through sulfonation of polysulfone with chlorosulfonic acid.²² GO was prepared according to modified Hummers method based on oxidation of graphite powder (average particle size 500 μm , 5 mg) with sulfuric acid (120 mL, $d = 1.84$ g/cc) over ten minutes at -5°C followed by treating the contents with potassium permanganate (15 g) over 30 min. The contents were diluted with de-ionized water (200 mL) at $35 \pm 1^\circ\text{C}$, further oxidized with hydrogen peroxide (30%, 50 ml) and re-diluted with warm de-ionized water (450 mL). The slurry was treated with hydrochloric acid (5%, 50 mL) where GO in the form of grey–black solid was separated. The separated solid was washed with de-ionized water till free from salt impurities and dried at $45 \pm 1^\circ\text{C}$ over 48 h.

2.2. Synthesis of PNCs

The synthesis of PNCs has been conducted in a thermostatically controlled glass reactor assembly comprising three necked flask equipped with mechanical stirrer thermometer and a dropping funnel charged with solution of FeCl_3 (30 mL, 1.85×10^{-2} mol/dL). A suspension of pyrrole (0.28 M, 30 mL) in de-ionized water stabilized with (CTAB, 1.145 g) along with requisite concentration of GO was placed in the flask. The polymerization was initiated through addition of solution of FeCl_3 at the rate of 1 mL/min to the contents under mechanical stirring at the rate of 600 rpm over 24 h at $30 \pm 1^\circ\text{C}$. The PNCs were isolated in yield (%) ranging 85–95 through centrifugation at 6000 rpm over 10 min, followed by filtration, washing with de-ionized water and drying at $50 \pm 1^\circ\text{C}/400$ mm Hg over 8 h. PPy was also synthesized in yield (%) 80 under the identical reaction conditions.

2.3. Preparation of working electrodes

The commercially available 316-SS was cut into 1 cm^2 area and finished with an emery paper (mesh size 320,600). It was then de-greased with acetone and subjected to surface

oxidation at $50 \pm 1^\circ\text{C}$ over 1 h. A composition of PPy or respective PNCs (65 mg) along with graphite (10 mg) and SPS (5 g/dL) in N-Methyl-2- pyrrolidone was sonicated over 15 min. The sonicate (50 μL) was applied over SS substrate and contents were allowed to stand at room temperature for 2 h, followed by drying at $100^\circ\text{C}/400$ mm Hg for 48 h. This has afforded working electrodes with mass thickness of electro-active materials by 5 ± 1 mg over 316-SS substrate.

3. Characterization

FTIR spectra were recorded on Thermo Nicolet FTIR Spectrophotometer in KBr. XRD spectra of powdered samples were recorded at room temperature over Rigaku-Geigerflex X-Ray Diffractometer using $\text{Cu-K}\alpha$ radiation. SEM of the gold coated specimen derived from GO, PPy and respective PNCs were recorded over JEOL (JSM-6610 LV) with beam voltage 5 KV at 5.0 KX, 2 μm . TG were recorded over TGA-50H with sample weight ranging from 2.16 to 6.64 mg under N_2 at the rate of 30 mL/min from $\sim 20^\circ\text{C}$ to 600°C . DSC thermograms were scan over DSC-60 at a flow rate of 30 mL/min from $\sim 25^\circ\text{C}$ to 275°C . Cyclic voltammograms were recorded over IVIUM Potentiostat-Galvanostat Netherlands BV at current compliance 10 mA, voltage ranging -0.1 to -0.6 V, scan rate (V/s) of 0.001–0.20 using three electrode cell assembly equipped with reference to Ag/AgCl, Pt foil (1 cm^2) as counter electrodes and working electrode in KOH solution (1.0 M). C_s of materials was calculated from the voltammetric charges by the CV curve, according to relation: $C_s = qa + |qc|/2m\Delta V$, Where qa and qc are the voltammetric charges on anodic and cathodic scans in the capacitive potential region (ΔV) and m being the mass of active material.^{1–3}

4. Results and discussion

CTAB assisted dilute solution polymerization of pyrrole in presence of exceptionally high concentration of GO (% w/w) ranging 10–40 and ferric chloride oxidant has afforded as series of PNCs with yield (% w/w) ranging 85 to 95. The identical reaction conditions have afforded polypyrrole with yield 80. Fig. 1 shows the comparative FTIR spectra of graphite, GO, PPy and a representative PNCs synthesized at 20% w/w concentration of GO. Graphite revealed characteristic wave number (cm^{-1}) at 3447.28 ($\nu_{\text{O-H}}$) and 1628.79 ($\delta_{\text{O-H}}$) which attributes to the presence of absorbed moisture (Fig. 1a). GO indicates characteristic absorptions at ~ 3333 cm^{-1} ($\nu_{\text{O-H}}$), 1723 (ν_{COOH}), 1613 (remaining sp^2 character), 1378 (ν_{COC}), 1221.20 (C–O for oxirane) and 1033 (ν_{COH}) (Fig. 1b). PPy shows characteristic absorptions corresponding to 1500 ($\nu_{\text{C=C}}$) and 1475 ($\nu_{\text{C-N}}$) for symmetric ring stretching. The broad wave number centered at 1300 corresponds to in-plane deformation of C–H and C–N. The peaks near 1190 and 922 represent the doping state of PPy with Fe^{3+} and the peak at 1050 attributes to N–H deformation. Wave numbers appeared at 901 and ~ 3450 are attributed to C–H out of plane deformation and $\nu_{\text{N-H}}$ (Fig. 1c). Fig. 1d shows FTIR spectrum of the PNCs derived from PPy and 40% GO. Comparing to FTIR spectra of individual GO and PPy, all peaks have also appeared in the PNCs which implies that PPy chains have been integrated with GO to form the PNCs. It is worth

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