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Full Length Article

Supercapacitor application of nickel phthalocyanine nanofibres and its composite with reduced graphene oxide

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ABSTRACT

The combination of double layer capacitor and pseudocapacitor materials are the next generation composites for energy storage. Nitrogen enriched species like metal phthalocyanines with metal redox centres may be combined with electrical double layer capacitive carbon materials for improved charge storage. We have explored electrochemical capacitance applications of nickel phthalocyanine (NiPc) nanofibres and its composite with reduced graphene oxide (rGO) synthesized through simple chemical routes. The composite material exhibits a superior specific capacitance, 223.28 Fg^{-1} at 1 Ag^{-1}, four fold higher than the individual components and also good stability over continuous cycling for 1000 cycles. The synergistic effect of NiPc and rGO with excellent physical interface offers less charge transfer resistance and better charge storage capacity.

1. Introduction

Metal phthalocyanines (MPcs) constitute a fascinating class of organic semiconductors whose chemical structure is composed of four isoindole units bearing active nitrogen sites bonded to accommodate the metal ion in their central cavity. They possess 18 π electrons delocalized around the macrocycle that facilitate charge transport and self-assembly through π-π stacking. Their versatile optical and electrical properties enable them to be useful candidates for solar cells, gas sensors, field effect transistors, electrocatalysis, etc. [1,2]. MPcs are thermally and chemically very stable and hence, can be used in adverse environment like high temperatures, acidic or basic conditions. However, the conductivity of divalent MPcs like NiPc, CuPc falls in the range of 10^{-12} Scm^{-1} [3] and hence, efforts have been made towards achieving improved activity by combining them with conducting carbon materials like carbon nanotubes, reduced graphene oxide (rGO) and porous carbon structures for varied applications [4,5].

Recent reports have shown that MPcs are also excellent candidates for charge storage applications. Electrochemical capacitors are of two types, electrical double layer capacitors (EDLC) and pseudocapacitors. The EDLC systems are the ones that store charges at the electrode and electrolyte interface, while the pseudocapacitors are the materials that possess charges as a virtue of their redox properties, referred as faradaic process. The combination of EDLC and pseudocapacitors can provide an overwhelming performance in terms of higher specific capacitance and good cycling stability. There is enormous interest to explore transition metal complexes as potential electrode systems for supercapacitor applications. Among them, nickel complexes have become popular due to the predicted large theoretical specific capacitance (2573 Fg^{-1}), well-defined redox behaviour and environmental benignity [6]. Ruan et al. elaborately reviewed nanostructured nickel based materials utilized for superior specific capacitance ranging from 300 to 1100 Fg^{-1} depending on the specimen structure and preparation approach [7]. Phthalocyanine complexes are exciting for investigation because they also possess nitrogen active sites along with metal centres capable of redox reactions. For combination with EDLC materials, rGO is one of the promising solutions since they possess large surface area with oxygen functional groups for anchoring other materials and a basal plane of conductive carbon network providing π-π interactions. They can be prepared in bulk amounts through simple chemical routes and thus form a cheap alternative to other expensive carbon materials. The applications of rGO composites cover a broad area in the field of energy, photovoltaics, bio-imaging, etc. [8–10]. It also has fast electrolyte transfer channels, which are vastly desirable for high power applications.

The commercially obtained MPcs are mostly macroscopic needle-like crystals with poor solubility in most of the solvents. Since the electrochemical properties are strongly interface driven, it is important to have a control over the structure and morphology of the electrode material. It will be interesting to tailor the mor-

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phology of MPcs forming nanostructures that may lead to better performance. In addition, the poor solubility of MPc powder makes them less viable for solution processable electrode modifications and for most such purposes, substituted MPcs are employed. Substituted metal phthalocyanines with amino, nitro and carboxyl groups are mostly investigated for electrochemical energy storage studies [11–14]. In this work, we have prepared nanofibres of NiPc (NiPc NF) and the NiPc NF-rGO composite materials via simple chemical routes. They can be dispersed well in polar solvents for slurry preparation to coat on electrodes. Furthermore, NiPc nanofibres can readily associate with other π conjugated systems like graphene, or carbon nanotubes via π-π interactions, van der Waals forces, coordinate bonding, etc. [15]. These structures form stable composites that can be exploited for various applications. The resulting materials are characterized by different techniques to study their optical, structural and electrochemical properties. It is seen that integration of NiPc NF and rGO in the composite material could synergistically improve the charge storage property in comparison to the individual counterparts.

2. Experimental section

2.1. Chemicals

Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) Merck, 97%, phthalonitrile ($C_6H_4(CN)_2$) TCI, >99%, ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) Merck, 83%, ethylene glycol ($C_2H_6O_2$) Alfa Aesar, >99% were purchased and used without further purification.

2.2. Preparation of NiPc NF- rGO composite

Phthalonitrile (0.9×10^{-3} mol) and nickel chloride (0.225×10^{-3} mol) in 1:4 mole ratio were homogeneously mixed in presence of ammonium heptamolybdate (5 mg). The mixture was suspended in ethylene glycol (15 mL) and sonicated to obtain a uniform suspension. The resulting solution was heated to 100 °C for 8 h. The deep blue coloured solution obtained was purified by centrifugation using ethanol and purified NiPc NF can be stored as an ethanolic dispersion or a powder obtained by filtration and drying at 60 °C for a few hours.

Graphene oxide was prepared by modified Hummer's method [16]. 100 mg of GO dispersed in *N-N*-Dimethylformamide (DMF) was sonicated to obtain a uniform dispersion and separately, 20 mg of NiPc nanofibres was suspended in trifluoroacetic acid (TFA) resulting in a homogeneous solution. These solutions were combined and heated to 100 °C in a hydrothermal vessel for about 24 h. After cooling down, the solution was filtered and the product was washed with ethanol followed by drying at 60 °C for a few hours.

2.3. Characterization of materials

The materials obtained from the above syntheses were characterized by different techniques for their optical and structural properties. The optical absorption of the ethanol dispersions of samples was recorded using Perkin-Elmer Lambda 750 spectrophotometer. The morphology of the synthesized materials was studied using field emission scanning electron microscopy (FESEM) TESCAN MIRA3 LM equipment. The crystal structure of the synthesised nanomaterials was studied using Rigaku Smartlab X-ray diffractometer (XRD) equipped with Cu Kα radiation. Raman spectra of the samples were collected using Horiba XploRA PLUS spectrophotometer with a 50X objective and 532 nm laser source. ESCA + Oxford Instruments was used for X-ray photoelectron spectroscopy (XPS) measurements to study the chemical nature of composite material employing 1486.7 eV incident energy. Brunauer-Emmett-Teller (BET) analysis was carried out to find out the specific surface areas of different nanomaterials using Quantachrome Autosorb 1C instrument. The samples were degassed at 100 °C for 12 h and the measurements were performed at liquid nitrogen temperature of 77 K. The N_2 used for the studies was 99.99% pure. The specific surface area was calculated from BET theory using Quantachrome ASiQwin software.

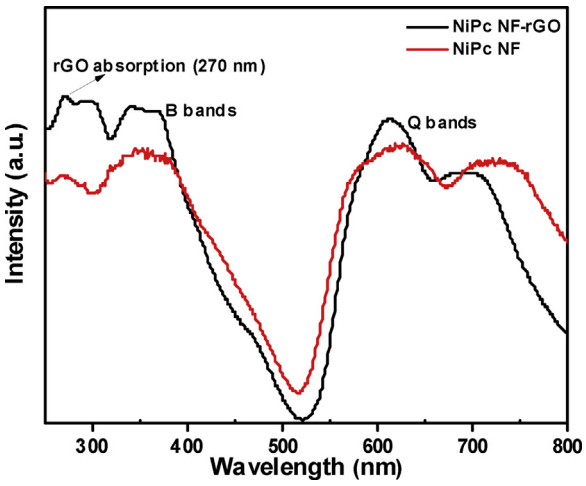

Fig. 1. UV–vis absorption spectra of ethanol dispersion of NiPc NF and NiPc NF-rGO composite.

2.4. Electrochemical measurements

The electrochemical measurements of differently modified electrodes were performed using CH Instrument 660E. Electrochemical performance of NiPc nanofibres and its composite with rGO was studied employing cyclic voltammetry (CV), chronopotentiometry charge-discharge and electrochemical impedance in an electrochemical workstation with a typical three-electrode configuration. A standard Ag/AgCl was used as a reference electrode and a platinum wire as the counter electrode in an aqueous acidic electrolyte solution. Pencil graphite rods (PGE) of 0.7 mm diameter were used as working electrodes. The use of pencil graphite as an electrode is cost-effective, disposable and eco-friendly. PGE electrodes were thoroughly cleaned by immersing them in a dilute solution of nitric acid for 30 min, followed by rinsing in milli-Q water. A plastic micro tip was used to serve as a support through which the PGE was inserted exposing 2 mm of the electrode. A copper wire was wound around the graphite rod which establishes the electrical connection. DMF slurry of NiPc NF and NiPc NF-rGO composite and other samples like commercial NiPc powder and rGO obtained by hydrazine hydrate reduction were prepared by drop casting on the PGEs and left to dry overnight in a vacuum desiccator. The dried electrodes were weighed (the weight of the active material ~ 40 μg) before performing electrochemical studies. All the measurements were performed in 1 M H_2SO_4 solution as an electrolyte in the potential range of −0.2 to 0.5 V.

3. Results and discussions

The synthesized NiPc NF and NiPc NF-rGO composite in the powder form were dispersed in ethanol for optical characterization. Fig. 1 shows the UV–vis spectrum of the dispersions. The spectrum of NiPc NF shows the characteristic absorption peaks, B bands at 275 nm and 350 nm and the Q bands appearing as a doublet at 625 and 750 nm. These electronic transitions between the molecular orbitals originate from HOMO and LUMO assigned to π-π* transition states. In the case of the composite, the B and Q bands are accompanied by an additional peak around 270 nm. This corre-

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