



Research paper

Fabrication of nanoclay based graphene/polypyrrole nanocomposite: An efficient ternary electrode material for high performance supercapacitor



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ABSTRACT

Nanoclay based ternary graphene/polypyrrole (PPy) nanocomposite were synthesized by both in-situ and ex-situ chemical oxidative polymerization approach. The surface morphology analysis by scanning electron microscope and field emission microscope revealed both nanoclay and graphene was coated with PPy. Electrochemical performances of all nanocomposites were analyzed with cyclic voltammetry, potentiostatic charging–discharging and electrochemical impedance spectroscopy. The in-situ nanocomposite showed relatively higher specific capacitance (347 F/g) as compared to ex-situ nanocomposite, at a scan rate of 10 mV/s in 1 M KCl as an electrolyte. The variation of specific capacitance with sequential addition of nanoclay was explored. These features collectively demonstrated the potential and attractive application of the as synthesized nanocomposite for energy storage.

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1. Introduction

Energy storage is a growing concerns of 21st century and emerged as a key technological challenge. Because of the intrinsically high efficiency of electrochemical energy conversion and its compatibility with power generation, there is a growing interest in the development of low-cost, high-power electrochemical energy-storage devices (Lee et al., 2012). As a new kind of energy-storage device, supercapacitors (SCs), also known as the ultracapacitor, have received increasing attention due to their high power density, fast charging–discharging process including average rate, excellent cycling stability and safety (Yu et al., 2013). SCs can store energy at the electrode-electrolyte interface through electric double layer capacitance (EDLC) and the other way of energy storage involves the redox reactions occurring in the electrode material, these are known as pseudocapacitor (Ghosh et al., 2013). It is widely used in electronics, bioenergetics and uninterrupted power supply devices. These EDLCs are comprised of high surface area carbon materials such as activated carbon, carbon nanotube, graphene etc. On the other hand the pseudocapacitor comprises of the metal–metal oxides, conducting polymers, spinel compounds etc. (Ghosh et al., 2013). The surface area and the morphology of the electrode material plays an important role in the energy storage and hence nanostructured electrode materials played an effective role in such energy storage application due to their high surface area and high porosity. Thus, composites of nanomaterial

have become an important area of research in view of value addition to the unique properties of the material for SC application.

The integration of nanoscale building blocks into a macroscale level has been recognized as one of the most effective strategies for the practical application of the nanomaterial. In this respect combination of polymer and carbon- nanomaterial nanocomposite have been widely studied. Graphene, a 2D material with zero band gap, with patterned hexagonal rings have emerged as a bulging candidate for SC application. With its unique properties like high surface area, exceptionally high conductivity, thermal and environmental stability in addition to its high stretchability and flexibility (Lee et al., 2012). In recent times, it has gained momentum in the long run of energy storage. Former studies have shown that various supramolecular interactions including hydrogen bonding, electrostatic interaction and pi–pi interaction have made graphene based 3D nanostructures electrically conductive, mechanically strong and thermally stable (Zhang et al., 2013).

In comparison to the carbon materials, pseudocapacitive materials, which uses faradic redox reactions for the charge storage, exhibit higher energy density and have attracted huge attention as electrode materials. Structural properties and charge transfer are the two vital factors determining the electrochemical performance of the nanocomposite which can be used as the pseudocapacitive material (Zhou et al., 2013). For instance to further boost up the pseudocapacitive performance, carbon materials were coupled with metal oxide as metal oxide can be uniformly immobilized onto the carbon based electrode due to their easy penetration in the bulk material (Zhou et al., 2013). However the cost of metal oxides restricts their use as good pseudocapacitive material, their direct use is limited due to their low abundance, high cost raw

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material, poor rate capability and toxic nature. On the other hand, conducting polymers (which conducts electricity due to π electron conjugation in the polymer chain) due to ease of synthesis and easy processability have wide range of application in electronics and energy-storage devices. Coupled with carbon materials, they can store charges via faradic charge transfer which often results in three-dimensional charge storage mechanism. Among various pseudocapacitive materials, PPy is one of the prominent conducting polymer opted as enhanced electrode material with its significant advantages such as high specific capacitance, good conductivity, outstanding mechanical property and biocompatibility (Yu et al., 2013). Recent reports have shown that design and synthesis of the nanostructured PPy based electrodes with rational architectures can remarkably improve the electrochemical performance of the electrode material. Some of the studies showed multilayer nanoarchitecture of graphene nanosheets and PPy nanowires nanocomposite which exhibited a maximum specific capacitance of 165 F/g synthesized by electropolymerization (Biswas and Drzal, 2010). It is reported that graphene/PPy based nanocomposites synthesized by in-situ chemical oxidative polymerization shows an exceptionally high specific capacitance of 318.6 F/g at the scan rate of 2 mV/s (Xu et al., 2011). To further enhance the capacitive behavior and the electrochemical activity of the SC electrode material, efforts have been devoted in the modification and fabrication with different nanostructured material in the present study.

In this paper, we focus on the novel synthesis of in-situ and ex-situ ternary nanocomposite with distinct architecture. Nanoclay which are organically modified layered silicates are promising in polymer nanocomposite as a reinforcement phase (Das et al., 2008) and as catalyst. In this work we are presenting nanoclay as a dopant for SC application. The role of nanoclay was explored as a dopant to facilitate charge storage and better electrolyte access. We have also studied the effect of nanoclay on energy storage of PPy and graphene/PPy based nanocomposite.

2. Experimental section

2.1. Materials

Nanoclay (cloisite 30B) used in this study is an organically modified montmorillonite purchased from southern clay products (now BYK Additives), USA. Cloisite 30B is a clay organically treated by methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (MT2EtOH) with a concentration of 90 meq/100 g clay. Graphite powder was obtained from S.D. fine chemicals Limited, Mumbai (India) (99.9% particle size and 100 μ m). Nitric acid was obtained from RFCL limited, New Delhi (India). Pyrrole (extra pure 99%) and sulphuric acid (98% pure) was supplied by Merck specialist private limited, Mumbai, India. Ammonium per sulfate (APS) was obtained from CDH private limited, New Delhi (India). All the chemicals were used as received, without any further purification.

2.2. Graphene oxide synthesis

Graphene oxide (GO) was synthesized from Graphite powder (100 μ m) by modified Hummer's method (Xu et al., 2010). Graphite powder (1.5 g) and NaNO_3 (1.5 g) were added separately in 69 ml concentrated H_2SO_4 (98% w/w) in 1000 ml flat bottom flask at low temperature. This solution was stirred vigorously followed by another slow addition of KMnO_4 (9 g). The whole reaction mixture was stirred vigorously at room temperature for 1 h. This results in gradual change of color from dark black to thick and dusty green with the progression of time. Approximately, 33.33 ml of distilled water was added and consequently temperature was increased to 90 °C for 30 min. This was further diluted with 300 ml distilled water followed by careful addition of 10 ml 30% H_2O_2 in dark. The color of resulted mixture consequently turned to light yellow. The obtained product was filtered and washed several times with distilled water until pH reaches around 6. It was dispersed in water methanol (1:5) ratio with three repeated centrifugation steps

at 12,000 rpm for 30 min. The final product was treated with desired amount of ethanol and dried under vacuum oven at 60 °C.

2.3. Reduction of GO to reduced graphene oxide

Graphene was synthesized by reducing GO using hydrazine hydrate (Stankovich et al., 2007). The as synthesized GO (1.5 g) was added to 750 ml distilled water. The mixture was sonicated in ultrasonic bath for 30 min for complete dispersion. Hydrazine hydrate (19 ml) was added slowly to the dispersed GO solution and reaction was carried out at 95 °C for 1 h. The whole reaction mixture was cooled down at room temperature followed by filtering, washing and drying under vacuum for 24 h at 60 °C to get reduced graphene oxide (here after denoted as graphene).

2.4. Synthesis of nanoclay based graphene/PPy nanocomposite

The in-situ graphene/nanoclay/PPy nanocomposite (GNP), was synthesized by mixing graphene (50 mg) and nanoclay (25 mg) under constant stirring with the help of magnetic stirrer. This was then well sonicated for 30 min. While under stirring pyrrole was added drop-wise to mixture containing graphene and nanoclay. The polymerization was initiated by drop-wise addition of ammonium persulphate (APS) (2.5 g dissolved in 50 ml distilled water). This solution was stirred for 4 h in an ice bath for the progression of polymerization. The prepared hybrid nanocomposite was filtered and washed several times with distilled water. The obtained nanocomposite was then dried under vacuum at 45 °C. The ex-situ graphene/PPy/nanoclay nanocomposite (GPN) was synthesized by following similar procedure as that of GNP using equal quantity of graphene (50 mg), pyrrole (1 ml) and APS (2.5 g in 50 ml distilled water). Only nanoclay (25 mg) was added separately after the completion of polymerization. Sample codes along with their compositions are given in Table 1. A schematic diagram of the nanocomposite synthesis and the distribution of graphene and nanoclay is shown in Fig. 1.

3. Characterization

Raman analysis was carried out with SEKI STR 500 Raman system with a 488 nm laser incident light. The FTIR spectra of nanoclay coated graphene/PPy based nanocomposite material were recorded within the wavelength range of 400 to 4000 cm^{-1} using Perkin Elmer RXI. Pellets were prepared by mixing small amount of as prepared sample with spectroscopic grade of KBr in the ratio of (10:1) for IR analysis. The microstructure and surface morphology of prepared hybrid nanocomposite were analyzed by using scanning electron microscope (SEM) (HITACHI S-3400N), field emission scanning electron microscope (FESEM) Supra 55 (Carl Zeiss, Germany) transmission electron microscopy (TEM, CM 12 PHILIPS) were used with the applied voltage of 5 kV and 120 kV, respectively.

3.1. Electrochemical measurement

To reveal its electrochemical property cyclic voltammetry (CV), potentiostatic charging–discharging (CD) and electrochemical impedance spectroscopy (EIS) were conducted on electrochemical workstation CHI 760D. The conventional three electrode system was employed for

Table 1
Sample codes and composition of nanocomposites.

Different composition of graphene (G) and nanoclay (N) for the fabrication of nanocomposite						
Sample	In-situ		Ex-situ		Pyrrole (ml)	APS (g/50 ml)
	G (mg)	N (mg)	G (mg)	N (mg)		
GP	50	–	–	–	1	2.5
GNP	50	25	–	–	1	2.5
GPN	–	–	50	25	1	2.5

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