



Enzymatic synthesis of polyaniline/multi-walled carbon nanotube composite with core shell structure and its electrochemical characterization for supercapacitor application



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ABSTRACT

A new method involving laccase-mediator system has been developed for environmentally friendly synthesis of polyaniline/multi-walled carbon nanotubes (PANI/MWCNT) composite. Fungal laccase, potassium octocyanomolibdate(4+) and atmospheric oxygen served as catalyst, redox-mediator and terminal oxidant, respectively. The structure, morphology and electrical conductivity of composites with different PANI content were investigated. The energy storage of enzymatically obtained composite consists of an electrical double layer capacitance as well as pseudocapacitance of conducting polymer. The obtained PANI/MWCNT composite with PANI content *ca.* 49 wt.% had high specific capacitance and cycle stability during doping/dedoping. The specific capacitance of this composite measured by cyclic voltammetry technique with potential scan rate of 5 mV/s was *ca.* 440 F/g. The specific capacitance of the composite decreased by less than 7% of its maximum value after 1000 scan cycles between -0.1 and 0.7 V. Supercapacitor (SC) shell was made from flexible adhesive tape (regular Scotch tape) and current collector was formed after its separation from the surface of graphite foil. The ethanol dispersion of PANI/MWCNT composite was deposited on the current collector surface. The gel polymer electrolyte (polyvinyl alcohol in 1 M phosphoric acid) was employed as both electrolyte medium and separator. The energy and power densities under an operating window of 0.7 V were *ca.* 7.03 Wh/kg and 5.2 kW/kg, respectively.

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1. Introduction

In recent years great attention has been paid to the development of new energy storage systems based on flexible supercapacitors and batteries. Supercapacitors (SC), also called electrochemical capacitors have not only high power density, high cyclic stability and high discharge rate, comparable to dielectric capacitors, but also high energy density comparable to that of the batteries. [1–3].

Supercapacitors are divided into two groups according to their charge storage mechanism. The first group includes devices with electrical double layer in which capacitive effect occurs on the electrode/electrolyte interface. The electrodes of such supercapacitors are usually made of different carbon materials, such as activated carbons, carbon nanotubes, carbon fibers and graphene [4–12]. Specific capacitance of these devices increases

with the extension of specific surface area of the material due to its porosity. However, reducing the pore size leads to the problem of their filling with electrolyte. The energy density of electrochemical double layer supercapacitors can reach 4–5 Wh/kg [13,14].

The second group consists of so-called pseudocapacitors which capacitance is caused by Faradaic reaction at the electrode/electrolyte interface in addition to the double layer capacitance. Transitional metal oxides and conducting polymers are usually used as materials for these SC [15–21]. Metal oxides have high specific capacitance but their usage is limited because of high specific weight and high toxicity. Conducting polymers possess high specific capacitance but have poor cyclic stability during charge/discharge process. Besides this, drastic change of polymer conductivity during doping/dedoping leads to a significant alteration of the electrode resistance.

Carbon nanotubes are promising materials for SC electrodes because of their high conductivity, mechanical strength and low specific weight. However, CNTs have rather low specific capacitance of 5–40 F/g [22].

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The combination of Faradaic redox reaction (pseudocapacitive effect of conducting polymers) and capacitance of carbon material allows increasing specific capacitance and stability of SC electrodes.

Polyaniline is one of the promising conducting polymers for SC development due to its stability, rather simple production method and low cost of monomer. A common method used for the synthesis of PANI is chemical or electrochemical polymerization of monomer.

The chemical oxidation of aniline by equivalent or excess amount of strong oxidants, such as ammonium persulfate, iron(III) salts, dichromate or permanganate salts, is rather simple way to obtain composites based on PANI and carbon materials. However, reduction products of these compounds must be utilized that requires extra costs. Moreover, chemical synthesis of polyaniline needs to be conducted in high acidic medium to obtain conducting polyaniline with “head-to-tail” structure [23–26]. Electrochemical method of aniline polymerization is not technological enough for SC electrodes construction because of electrode geometrical size limitation.

The usage of biocatalysts such as high redox-potential fungal laccases for obtaining of PANI/CNT composites is an alternative to traditional methods of polymer synthesis [27]. Enzymatic catalysis allows conducting process of oxidative aniline polymerization at environmentally friendly and rather mild conditions (aqueous slightly acidic solutions and room temperature) without toxic byproducts formation such as benzidine. Atmospheric oxygen being reduced to water serves as an oxidant in laccase-catalysed aniline polymerization reaction [28]. However, the aniline polymerization rate with laccase alone is relatively low because of aniline high oxidation potential. Laccase redox mediators can accelerate polymerization reaction of monomer and make it possible to obtain PANI with different molecular weight and solubility [29]. Thus, biocatalytic approach meets the requirements of “green” chemistry [30,31].

The usage of composites based on carbon nanotubes and conducting polymers for SC electrodes formation were extensively studied [32–40]. In all these works chemical or electrochemical polymerization of monomer was used to obtain conductive PANI. Meng et al. [34,36] reported the production of the SC electrodes made of CNT bucky-paper and chemically synthesized PANI. The SWCNT films used as template to electrodeposit PANI were directly prepared by a floating chemical deposition method [37]. Described in these papers PANI deposition methods on preformed CNT films are the conventional techniques.

The specific capacitances of PANI/CNT composites prepared by chemical methods were described in following papers [41–44] and their values were 163–485 F/g. The energy density and power density of SC based on chemically synthesized PANI/MWCNT composite with gel electrolyte separator were 7.1 Wh/kg and 2189 W/kg [36] or 0.5 Wh/kg and 0.3 kW/kg [41].

The aim of the present work was the development of environmentally benign enzymatic synthesis of PANI/MWCNT composite with core shell structure and high specific capacitance, the research of its electrochemical properties, and, finally the fabrication of flexible SC prototype using obtained composite. The electrochemical performance of the supercapacitor was also investigated.

2. Experimental

2.1. Materials

Aniline (Labtech, Russia) was distilled under reduced pressure before using. Potassium octocyanomolybdate (4+), poly(vinyl alcohol) (hydrolyzed 99+%, Mw 89,000–98,000), H₃PO₄ (Aldrich), Na₂HPO₄, citric acid anhydrous (Riedel-de Haen, Germany) were

used without further purification. Flexible graphite foil (thickness 0.2 mm) was purchased from (Unichimtek, Russia). Multi-walled carbon nanotubes “Taunit M” (NanoTechCentre Ltd, Tambov, Russia) were used after treatment with hot 70% nitric acid (fMWCNT). Fungal laccase from *Trametes hirsuta* (Wulfen) Pilát CF-28 was purified to homogeneity as described previously [45]. The specific activity of the enzyme was ca. 200 U/mg of protein using catechol as a chromogenic substrate.

2.2. Preparation of PANI/fMWCNT composite

PANI/fMWCNT composite was obtained by *in situ* enzymatic aniline polymerization. Atmospheric oxygen served as terminal oxidant. Fungal laccase catalyzed aniline polymerization in the presence of potassium octocyanomolybdate (4+) as redox mediator. The reaction of aniline polymerization was carried out under conditions described early [29].

2.3. Preparation of flexible electrodes for supercapacitor

Supercapacitor electrodes were made by forming graphite current collector on adhesive tape (Scotch) followed by alcohol dispersion of PANI/fMWCNT composite deposition. Gel polymer electrolyte (10 wt.% PVA + 1 M H₃PO₄) was sandwiched between the electrodes for fabrication of thin flexible supercapacitor.

2.4. Characterization

Cyclic voltammetry and galvanostatic charging/discharging measurements of PANI/fMWCNT composites and supercapacitor device were performed using potentiostat/galvanostat (Metrohm Autolab, Holland) and BAS CV-50W voltammeryic analyzer (Bio-analytical System, USA). The electrochemical cell with commercial Ag/AgCl electrode (Bioanalytical System, USA) as the reference electrode and platinum sheet as counter electrode was used for an electrochemical investigation. Electrochemical measurements of PANI/fMWCNT composite were carried out with electrodes immersed in 1 M H₂SO₄ aqueous electrolyte. The morphology of PANI/fMWCNT composites was characterized by scanning electron microscopy (SEM, Supra 40 VP, Carl Zeiss) and by transmission electron microscopy (TEM, LEO 912 AB OMEGA, Carl Zeiss). FTIR spectra were recorded using KBr pellets on a FTIR spectrometer (IRPrestige Fourier, Shimadzu, Japan). Four-point conductivity measurements were carried out with Loresta GP (Mitsubishi, Japan).

The weight for specific capacitance calculation (F/g) was determined based on the whole mass of the electroactive material (PANI/fMWCNT) composite. The specific capacitance (C_s) of the composites was calculated from both the cyclic voltammetric and galvanostatic measurements. In the case of non-rectangular shape, the CV curves were integrated for specific capacitance calculation.

The formula $C_s = \frac{\int IdE}{v\Delta Em}$ was used, where ΔE is the potential range, v is the potential scan rate, m is the mass of electroactive material. For galvanostatic measurements formula $C = it/\Delta Vm$ was applied (t is the discharge time; ΔV is the voltage drop upon discharging; m is the mass of electroactive material).

3. Results and discussion

3.1. Enzymatic synthesis of PANI/fMWCNT composite.

A commercial MWCNTs generated *via* chemical vapour deposition process are hydrophobic material. Therefore, it is impossible to obtain their stable dispersion in polar solvents. This is one of the reasons, why *in situ* deposition of PANI on the surface of as-received carbon nanotubes doesn't lead to the formation of

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