Colloids and Surfaces A: Physicochem. Eng. Aspects 446 (2014) 15–22

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

New colloidal route for electrostatic assembly of oxide nanoparticle – carbon nanotube composites

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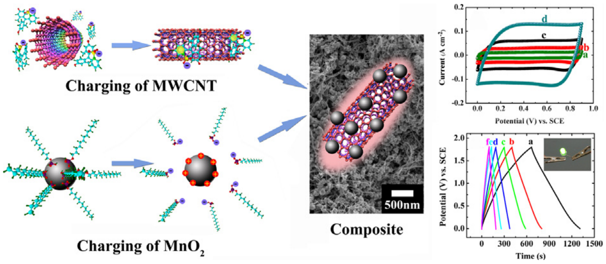
HIGHLIGHTS

- New colloidal approach was proposed for the fabrication of composites.
- Metal oxide particles were positively charged and dispersed using phosphate ester.
- Carbon nanotubes were negatively charged and dispersed using organic dye.
- MnO_2–carbon nanotubes composites were obtained by heterocoagulation.
- Composites are promising materials for electrochemical supercapacitors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 November 2013
Received in revised form 15 January 2014
Accepted 16 January 2014
Available online 26 January 2014

Keywords:
Manganese dioxide
Nanoparticles
Carbon nanotubes
Dispersion
Supercapacitor
Composite

ABSTRACT

A conceptually new colloidal method for the fabrication of metal oxide–multiwalled carbon nanotube (MWCNT) composites is proposed. The approach is based on the use of phosphate ester (PE) for the dispersion of oxide nanoparticles and *m*-cresolsulfonphthalein (CS) dye for the dispersion of MWCNT. PE imparts a positive charge to the particles in ethanol. The adsorption of anionic CS on MWCNT allows the formation of stable suspensions of negatively charged MWCNT in ethanol. The adsorption of CS on MWCNT is confirmed by Fourier transform infrared and UV–vis spectroscopy. The heterocoagulation of positively charged oxide nanoparticles and negatively charged MWCNT allows the fabrication of advanced nanocomposites with improved dispersion of individual components. The proof of principle is demonstrated by the fabrication of MnO_2–MWCNT composite electrodes for electrochemical supercapacitors, which exhibited significant improvement in capacitance at high charge–discharge rates, reduced electrical resistance and good cycling stability. The hybrid cells, containing composite MnO_2–MWCNT electrodes, show promising electrochemical performance.

1. Introduction

Carbon nanotube (CNT)–metal oxide nanocomposites are currently under development for electrochemical [1], photovoltaic [2], biomedical [3] and electronic applications [4]. Colloidal methods are of special interest for the fabrication of nanocomposites with advanced microstructure and properties. One of the major challenges in the fabrication of CNT–metal oxide nanocomposites by colloidal methods is the dispersion of CNT. Numerous investigations were focused on the development of methods for CNT dispersion in various solvents. Many attempts have been made to disperse CNT by their oxidation in strong acids [5–7]. The treatment in hot acids [5–7] resulted in the formation of carboxylic and other oxygen-containing groups on the CNT surface. These acidic groups electrostatically stabilized CNT in the suspensions. The dispersion of CNT can also be achieved by covalent functionalization methods [8]. It is important to note that the oxidation and

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http://dx.doi.org/10.1016/j.colsurfa.2014.01.032

functionalization strategies introduce defects and reduce the electronic conductivity and mechanical properties of CNT. Moreover, the acidic treatment is known to cut long CNT into smaller fragments with lower aspect ratio [9]. Therefore, for applications based on conductive and mechanical properties of CNT, such treatment must be avoided. Another strategy was based on the use of polyelectrolytes, which adsorbed on CNT and provided their electrosteric stabilization. However, the adsorption of polyelectrolytes can result in the formation of CNT bundles [8].

Especially interesting are the investigations of anionic and cationic surfactants for CNT dispersion. Anionic sodium dodecyl sulfate and cationic hexadecyltrimethylammonium bromide[10,11] are promising surfactants for the fabrication of stable aqueous suspensions of CNT. It should be noted that adsorbed long chain surfactants create insulating layers on the CNT surface and reduce electrical conductivity of the composites. The analysis of the literature indicates that relatively high concentrations of surfactants are necessary for CNT dispersion [12–15]. It was found [14,15] that the formation of the surfactant micelles promoted depletion-induced aggregation of CNT. Another approach is based on the use of charged organic dyes [16–18], which adsorbed on the CNT surface and provided electrosteric stabilization. The adsorption of dyes on CNT surface was attributed to π–π interactions [19,20]. The adsorption of dyes on the CNT surface is of critical importance for the dispersion. It should be noted that this mechanism cannot be used for the dispersion of oxide nanoparticles. However, the success in the fabrication of metal oxide–CNT nanocomposites requires efficient dispersion of both individual components.

The efficient dispersion of CNT and metal oxide nanoparticles in nanocomposites is of special interest for application in electrodes of electrochemical supercapacitors. The interest in MnO_2–CNT electrodes is attributed to high specific capacitance [21–23] of MnO_2. However, the electronic conductivity of MnO_2 is low. The addition of CNT allows improved electronic conductivity of the composites [24,25]. It is important to note that the CNT content in the composites must be minimized due to low specific capacitance of CNT and relatively high cost of this material. Moreover, the agglomeration of CNT and MnO_2 nanoparticles in the composites must be avoided. Therefore, the efficient dispersion of MnO_2 and CNT is necessary for the development of advanced MnO_2–CNT supercapacitors.

The goal of this investigation was the development of a new strategy for the fabrication of metal oxide–multiwalled carbon nanotubes (MWCNT) composites. The approach is based on the dispersion of oxide nanoparticles using phosphate ester and dispersion of MWCNT using an organic dye. The method allowed the formation of positively charged oxide nanoparticles and negatively charged MWCNT. The electrostatic heterocoagulation resulted in the fabrication of composites with uniform distribution of MWCNT and oxide particles. The results presented below indicated that this method can be used for the fabrication of advanced MnO_2–MWCNT electrodes for electrochemical supercapacitors with enhanced electrochemical performance. Moreover, it was found that this method can be used for the fabrication of other nanocomposites.

2. Experimental procedures

2.1. Materials

Poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB, average $M_w = 50{,}000–80{,}000$), *m*-cresolsulfonphthalein sodium salt (CS) and $KMnO_4$ were purchased from Aldrich company. Manganese dioxide nanoparticles with an average particle size of 30 nm and an oxidation state of Mn of 3.6 were prepared by the reduction of aqueous $KMnO_4$ solutions using the method described in a previous investigation [26]. Multiwalled carbon nanotubes (MWCNT) were purchased from Bayer company. Phosphate ester (Emphos PS 21-A, PE) was purchased from Richard E. Mistler company. Ni foams with a porosity of 95% were supplied by Vale company.

2.2. Fabrication of suspensions and electrophoretic deposition experiments

Ethanol was used as a solvent for the fabrication of $10\,g\,L^{-1}$ suspensions of oxide nanoparticles and $1\,g\,L^{-1}$ suspensions of MWCNT. PE and CS were added to the suspensions of oxide particles and MWCNT. The concentration of PE and CS in the suspensions was varied in the range of $0–1\,g\,L^{-1}$. The suspensions were ultrasonically agitated during 30 min before the sedimentation tests.

The limitations of the zeta potential concept for the analysis of electrokinetic properties of nanoparticles, containing adsorbed organic molecules, were described in the literature [27–29]. Therefore, the charging mechanism and electrokinetic behavior of the particles were investigated by deposition yield measurements in electrophoretic deposition (EPD) experiments. Moreover, the use of EPD provided a possibility of investigation of dispersant adsorption by analysis of particles, removed from the substrate after deposition. The EPD cells contained a stainless steel or Pt working electrode and a Pt counter electrode. The distance between the electrodes was 15 mm. The cell voltage was varied in the range of 20–100 V. Deposition yield was studied for the deposits formed on stainless steel substrates. A minimum of three samples were prepared in each deposition experiment. All the deposits were obtained using fresh suspensions. The deposition yield measurements were repeatable, and the error was less than 5%.

2.3. Characterization techniques

The deposits were removed from Pt working electrodes after drying in air for 72 h for Fourier transform infrared spectroscopy (FTIR) and UV–vis studies. FTIR investigations were performed using Bio-Rad FTS-40 instrument. The UV–vis spectra were obtained using Cary-50 UV–vis spectrophotometer. Electron microscopy studies were performed using a JEOL JSM-7000F scanning electron microscope (SEM).

2.4. Fabrication of electrodes and cells

The MnO_2 suspensions, containing PE dispersant, and MWCNT suspensions, containing CS dispersant, were mixed and the obtained precipitates were washed with ethanol. For comparison, MnO_2 and MWCNT were mixed without dispersing agents and obtained precipitate was washed by the same method. The mixtures were used for the fabrication of slurries in ethanol, containing MnO_2 and MWCNT with total concentration of $10\,g\,L^{-1}$ and $0.2\,g\,L^{-1}$ of PVB binder. The slurries were used for the impregnation of Ni foam current collectors. The impregnated current collectors were dried in air and then pressed to 30% of original thickness. The mass of the impregnated material was $40\,mg\,cm^{-2}$ (based on projected area). The fabrication of activated carbon electrodes is described in the supporting information. Composite MnO_2–MWCNT electrodes and activated carbon electrodes (described in supporting information), separated by a porous polyethylene membrane (mean pore size 0.4 μm, Vale, Canada) were combined for the fabrication of coin cells (CR2032 type, MTI corporation, USA), which were sealed using a hydraulic crimping machine (MSK-110, MTI Corporation, USA).

2.5. Electrochemical characterization

Electrochemical studies were performed using a potentiostat (PARSTAT 2273, Princeton Applied Research). Surface area of the