Synthesis and characterization of (polypyrrole/carbon) nanotubes/metal oxide composites for application as supercapacitors

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ABSTRACT

The production of nanostructured organic materials represents an interesting and promising area of investigation if considered the increasing demand for eco-friendly techniques which require good levels of high power density and energy density. In this work we have explored the synthesis of hybrid composites based on interaction of carbon nanotubes, polypyrrole nanofibers and metal oxide nanoparticles. Electrical characterization of resulting powder indicates that improvement in the conductivity is verified with mutual inclusion of carbon nanotubes and metal oxide particles, as a result of synergistic interaction of electrical double layer capacitance (EDLC) and pseudocapacitance of components. Electrochemical properties of material indicate that superior specific energy density is result of strong interaction between nanotubes and homogeneous distribution of metal oxide nanoparticles on surface of synthesized nanotubes.

Keywords: supercapacitors, polypyrrole, titanium dioxide, carbon nanotubes, impedance.

1 INTRODUCTION

Conducting polymers have received significant attention in the literature due to their superior chemical properties, environmental stability, high conductivity, high flexibility, good biocompatibility *in vivo* and superior electrochemical response. In spite of extensive literature about transport mechanisms and optimization of electrical conductivity of doped conducting polymers, the relation involving influence of morphology on transport mechanisms remains an emerging topic if considered novel applications such as amperometric sensors, supercapacitors, photothermal cancer therapy and DNA sensors [1-4].

The synthesis of nanostructured polymeric templates introduces typical advantages of nanomaterials, including high surface-volume ratio, fast electron transfer and reduction in the path for electron transport. Diverse morphologies and related new applications of conducting polymers have been reported in the literature: I. Das et al. report the synthesis of dendrimers of polypyrrole prepared from electropolymerization in the presence of different surfactants [5]; K. Wang et al. describe applications of supercapacitors based on aligned nanowire arrays [4]; Q. Wang et al. make use of polypyrrole nanoparticles in cancer therapy [1].

In this direction, the development of polypyrrole nanofibers represents an interesting and promising method of synthesis in which high surface area is obtained as a result of production of material with low mass density and improved electrical response, due to the reduced path for electron transfer. The synthesis of polymeric nanofibers is typically based on chemical oxidation of pyrrole on the surface of tubular templates of methyl orange. The incorporation of additives such as carbon nanotubes contributes with the synthesis of core-shell tubular structures of carbon/ polypyrrole tubes.

The association of high conductivity of carbon nanotubes and EDLC behavior induced by dispersed carbon derivatives on polymeric nanostructures contributes with both mechanisms: improvement in the electron transport and reinforcement in the secondary mechanism of charge storage at interface.

In previous work, we have synthesized binary and ternary composites of polypyrrole, carbon nanotubes and metal oxide particles [6,7]. The results indicate that synergistic interaction is established during polymerization and superior electrical properties result from insertion of metal oxide and carbon derivatives on supporting polymeric matrix.

In this work, we have explored the influence of morphology of polypyrrole on the electrical response of matrix, composed by hollow nanotubes of polypyrrole and core-shell structures of single walled carbon nanotubes/ polypyrrole tubes decorated with titanium dioxide nanoparticles.

An important aspect to be reported from these composites is relative to the resulting power density and energy density. The association of electrical double layer capacitance of single walled carbon nanotubes and pseudocapacitance of polypyrrole/ titanium dioxide nanoparticles induces Faradaic and non-Faradaic processes and additional charge storage processes, which result in the production of promising materials for application as electrode of supercapacitors [8].

2 MATERIALS AND METHODS

Single walled carbon nanotubes (Aldrich), methyl orange (Vetec), titanium dioxide (Aldrich) and ferric chloride (Vetec) were used as received. Pyrrole was distilled before the use and stored at dark condition.

Galvanostatic charge-discharge technique was explored for calculation of energy density and power density (Ragone plot) and electrochemical measurements were performed in a Potentiostat/ Galvanostat Metrohm Autolab AUT302N.

Specific energy density was calculated from relation $E_{SP}=\Delta Eit/m$ and power density using the relation $P_{SP}=\Delta Ei/m$, where $\Delta E=(E_{max}+E_{min})/2$, with E_{max} is defined as the potential of beginning of discharge and E_{min} is the potential at end of discharge procedure; I is the current established during discharge; t is the time of discharge and m is the total mass of powder used in the device.

Electrodes, disposed symmetrically between two parallel plates of sample holder Solartron 12962, were prewetted in an electrolyte (KCl – 1M) and separated by a porous membrane (Celgard). Impedance measurements were performed using an impedance analyzer Solartron 1260+ dielectric interface solartron 1296. For impedance measurements, single pellet of dry powder is disposed between two parallel plates and characterized in the range of frequency from 1Hz to 1 MHz with AC excitation of 10 mV and no external DC voltage. SEM images from a scanning electron microscopy (SEM Vega 3XMU) were analyzed in order to identify the morphology and relative distribution of nanotubes and metal oxide nanoparticles.

2.1 Preparation of samples

Polypyrrole nanotubes and ternary composites of core/shell of single walled carbon nanotubes/ polypyrrole decorated with titanium dioxide were prepared according the procedure established by X. Yang et al [9]. For preparation of samples, 0.1 g of methyl orange is dispersed in 60 mL of Millipore water and maintained under continuous stirring until complete dispersion of dye. Titanium dioxide (2.4 mg) and single walled carbon nanotubes (2.4 mg) are dispersed in aqueous solution and sonicated during 10 minutes for complete solubilization of additives. 0.21 mL of pyrrole is dispersed into solution (maintained in an ice bath) and a reaction is established during 24 hours. The resulting powder is washed in abundance with a mixture of ethanol and water (for elimination of residual methyl orange) and dried in an oven (60^0C). 100 mg of powder is separated for preparation of pellets and applied as electrodes of supercapacitors.

3 RESULTS

The synthesis of core-shell structures of carbon nanotubes/ polypyrrole results in the production of material with high level of porosity, low mass density and homogeneous distribution of nanotubes, as shown in the Fig. 1.

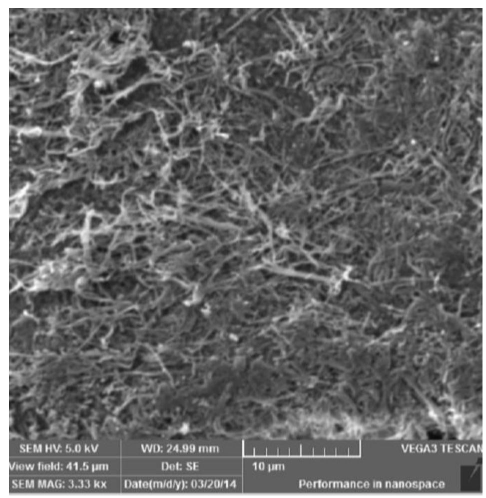

Figure 1 – SEM image of core-shell composite of carbon nanotube/ polypyrrole.

The inclusion of titanium dioxide nanoparticles during chemical oxidation of pyrrole induces the dispersion of small aggregates of semiconductor along the structure of fibers, as shown in the images of Fig. 2a and 2b (absence/ presence of TiO_2), respectively.

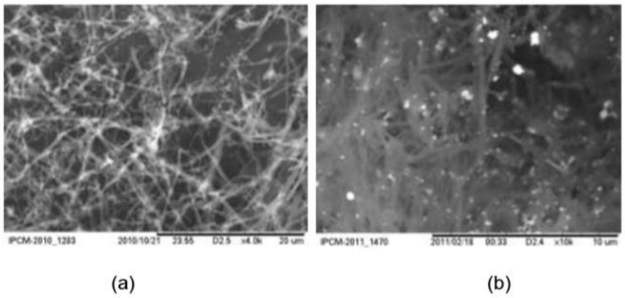

Figure 2 – SEM of polypyrrole nanotubes (a) and decorated polypyrrole nanotubes with titanium dioxide nanoparticles (b).

The strong interaction of components in the core-shell structures results in the improvement of electrical response of devices. As shown in the Fig. 3, the diameter of characteristic semicircle in the RX diagram is reduced with incorporation of SWCNT and SWCNT+TiO_2 nanoparticles. In spite of relative low conductivity of titanium dioxide particles, their incorporation in the surface of nanotubes contributes with development of powder with superior electrical properties. From these results, it is possible to verify that mutual incorporation of additives results in the lower level of charge transfer resistance which characterizes superior electrical properties of resulting powder.

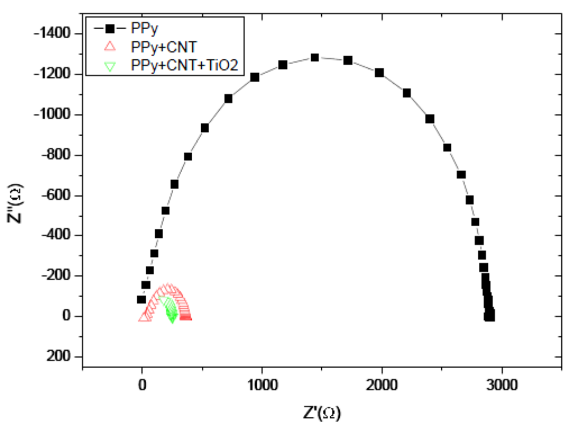

Figure 3 – Nyquist plot of polypyrrole, polypyrrole/carbon nanotube and polypyrrole/carbon nanotube/ titanium dioxide composite.

Progressive reduction in the level of impedance from incorporation of carbon nanotubes can be attributed to the reinforcement in the electrical transport induced by structures of conducting nanotubes, which is facilitated by reduction in the free path for electron and ionic transport along the complex net established by crosslinking of carbon nanotubes and polymeric nanostructures.

The plot of specific energy versus specific power density (defined as Ragone plot) represents an interesting schematic representation of degree of efficiency of resulting device applied in the process of energy storage.

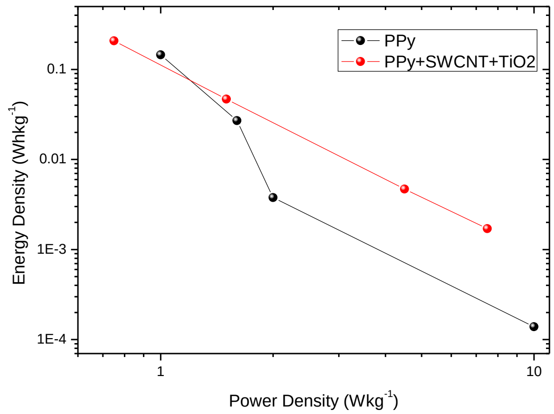

Figure 4 – Ragone plot of the PPy and PPy+MWCNT +TiO_2 composites.

As we can see in the Fig. 4, as expected, the energy density varies inversely with power density. The most important aspect to be reported is related with the comparison between response of supercapacitors of neat polypyrrole and ternary composite of polypyrrole+single walled carbon nanotube+ titanium dioxide nanoparticles. As we can see, in a wide range of power density, the resulting energy density of devices with incorporation of additives reveals superior electrochemical performance, in an indication that improvement in the electrical response (measured from electrical impedance spectroscopy) is accomplished by additional mechanisms for charge storage, as a result of incorporation of pseudocapacitance of titanium dioxide nanoparticles and electrical double layer capacitance of carbon nanotubes.

4 CONCLUSION

Superior electrical and electrochemical properties of core-shell SWCNT/PPy nanotubes decorated with titanium dioxide nanoparticles indicate that optimization in the morphology of conducting polymers and convenient association with EDLC and pesudocapacitance effects represents an interesting procedure to be applied for production of more efficient supercapacitors. Particularly, the development of polymeric tubular structures can be considered a low cost and promising procedure for production of superior electrodes for applications in supercapacitors.

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