



## Polypyrrole/lanthanum strontium manganite oxide nanocomposites: Elaboration and characterization

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### ABSTRACT

The synthesis of organic–inorganic hybrid polypyrrole (PPy)–lanthanum strontium manganite oxide  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSMO) nanocomposites via chemical oxidative polymerization of pyrrole in presence of LSMO nanoparticles using ferric chloride as oxidant and sodium p-toluene sulfonate as efficient dopant is investigated. The morphology of polypyrrole and its nanocomposites was examined by scanning electron microscopy which have shown that the presence of LSMO nanoparticles strongly affects the particle size of the nanocomposites. The specific interactions between the conducting polymer and the inorganic nanoparticles is highlighted by FTIR characterizations. Transmission electron microscopy and X-ray diffraction measurements of the nanocomposites confirm a core–shell structure with LSMO coated by polypyrrole macromolecular chains. Electrochemical properties of nanocomposites were investigated by cyclic voltammetry measurements in 2 M KOH. In such a media, polypyrrole nanocomposite electrode with 30 wt% LSMO nanoparticles has shown specific capacitance of  $530 \text{ F g}^{-1}$  which is significantly higher than pristine polypyrrole i.e.,  $246 \text{ F g}^{-1}$ . These charge storage differences between the pristine polypyrrole and polypyrrole/LSMO nanocomposite has been attributed to the morphology of the nanocomposite in which the particle sizes, the specific surface area, and pore size distribution have been modified with the incorporation of nanoparticles in the polypyrrole matrix.

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### 1. Introduction

The advance in the field of materials science has taken a new way since the arrival of the nanocomposites. Novel properties of nanocomposites can be derived from the successful combination of the characteristics of parent constituents into a single material. These materials are combinations of one or more inorganic nanoparticles with a polymer so that unique properties of the former can be taken together with the existing qualities of the latter. Many investigations [1] regarding the development of the incorporation techniques of the nanoparticles into the polymeric matrices have been published. In most cases [1], such combinations require blending or mixing of the components, taking the polymer in solution or in melt form. Resulting nanocomposites have found successful applications in versatile fields namely fuel cells [2], flexible displays [3], sensor [4], Lithium ion batteries [5], supercapacitors [6] etc.

Among conducting polymers, polypyrrole (PPy) has attracted considerable interest [7–9] mainly because of its reasonable thermal and chemical stability in air, utilization as electronic conductors and catalysts in electronic devices, application in electrochromic devices, optical switching devices, sensors, batteries, supercapacitors etc. [10]. To improve the properties of PPy by nanostructuring of the conducting polymer, many methods were developed. For example, Debiemme-Chouvy prepared oriented polypyrrole nanowire with a diameter in the range of 40–120 nm, in which no template was introduced [11]. Lee and co-workers [12] investigated the electrochemical properties of electrospun polyacrylonitrile/multi-walled carbon nanotubes coated with PPy, in which PPy was immobilized by in situ chemical polymerization, with an intention to enhance the specific capacitance of the nanocomposite. Sharma et al. [13] have synthesized manganese dioxide ( $\text{MnO}_2$ ) embedded PPy nanocomposites, aiming to develop novel supercapacitor materials, in which  $\text{MnO}_2$ /PPy was electrosynthesized by a galvanostatic method. Zang et al. [14] synthesized well-aligned cone-shaped nanostructure of PPy/ $\text{RuO}_2$  and studied its electrochemical supercapacitor (ES) properties. Previously, our group reported on the synthesis and electrochemical

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characterization of nanohybrid PPy/iron oxide materials for electrochemical storage applications. The incorporation of nanoparticles inside the PPy notably increases the charge storage capability in comparison to the pristine conducting polymer. These charge storage modifications have been attributed to the morphology of the composite in which the particle sizes and the specific surface area are modified by the incorporation of nanoparticles [16,17].

In conducting polymer based nanocomposites, the nanoparticles generally provide the system a kind of processability (colloidal stability or mechanical strength), although the specific properties of the latter are also utilized in some respects. Depending on the nature of the association between inorganic and organic components, nanocomposites are classified into two categories: one in which the inorganic particle is embedded into an organic matrix and the other where organic polymer is confined into inorganic template. However, in each case the composite formation demands some entrapment or encapsulation rather than simple blending or mixing. This paper focuses on the former class of nanocomposite, introduced here as the “inorganic particle-in-organic polymer matrix” system which bridges the inorganic nanoparticles with the ones of the macromolecules. In most cases, researchers used carbon materials, transition metal oxides like  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{RuO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  to improve the supercapacitor properties of the PPy materials [18]. In the present work, we use  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSMO) nanoparticle as a core and coated with PPy shell to form PPy/LSMO nanocomposites. Substituted Lanthanum manganites with the general formula  $\text{A}_{1-x}\text{B}_x\text{MnO}_3$  ( $\text{A}=\text{La}$ ,  $\text{B}=\text{Ca}$ ,  $\text{Sr}$ ) have attracted a lot of attention due to their exceptional electric and magnetic properties [19,20]. Generally, manganite based materials are commonly used in the fabrication of solid oxide fuel cells (SOFCs) as the cathode material, because it displays good electrical conductivity, electrocatalytic activity toward oxygen reduction reaction (ORR) [21], and high thermal and chemical stability between  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  [22]. LSMO has also been used as a spin-polarised anode in polymer light-emitting diodes [23]. Some other studies report on a large enhancement in magnetoresistance in the LSMO layers by incorporating a  $\pi$ -conjugated semiconducting polymer layer in between them [24]. LSMO have been studied as a “dopant” in “classical” composites polymer/LSMO [25,26] or in association with carbon nanotubes [27]. Other electronic conjugated materials/LSMO nanocomposites such as sexithienyl/manganite [28], polyphenylene sulfide/manganite [29] polyparaphenylene vinylene/manganite [30] or polyaniline/manganite [31] has been also reported.

In this study, we have elaborate nanocomposites of PPy/LSMO by chemical oxidative polymerization and studied their specific interactions. Nanocomposite's morphology and surface area were investigated by SEM, TEM and BET measurements and correlated with its electrochemical properties. The molecular structure and crystallinity of the nanocomposites were studied by the FTIR and XRD measurements respectively. In addition, cyclic voltammetry was carried out to explore their electrochemical and pseudocapactive properties.

## 2. Experimental

### 2.1. Materials

Pyrrrole (Sigma–Aldrich) was distilled under reduced pressure before use. Ferric chloride ( $\text{FeCl}_3$ ) (Sigma–Aldrich) as an oxidant and sodium p-toluene sulfonate (PTS) (Sigma–Aldrich) as a dopant were used as received. All other chemical reagents were of high purity grade and used without further purification.

### 2.2. Synthesis

PPy was prepared by chemical polymerization of 1 g of pyrrole (Py) using 2.5 equiv. of  $\text{FeCl}_3$  (6.05 g) with the addition of 5.8 g of sodium p-toluene sulfonate (PTS) as dopant anion (corresponding to a molar ratio  $\text{PTS}/\text{Py}=2$ ) in distilled water at  $5^\circ\text{C}$  for 8 h. The black powder obtained was filtered, washed in water, and vacuum dried at  $50^\circ\text{C}$  during 24 h. LSMO was synthesized by previously reported procedure [32]. The compound LSMO was synthesized from stoichiometric amounts of  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$ , and  $\text{Mn}(\text{NO}_3)_2$  by an organic gel-assisted citrate process in order to obtain homogeneously mixed reagents and ultra fine powders. All the required cations in the appropriate ratios were dissolved into a nitrate solution and chelated by adding triammonium citrate solution. A polyacrylamide network was formed in situ by the organic monomers consisting of acrylamide and N,N' methylenebis-acrylamide which were co-polymerized by heating at about  $100^\circ\text{C}$ . The gel was placed in furnace at  $500^\circ\text{C}$  for 5 h to give an intermediate black–brown powder of LSMO nanoparticle. LSMO was ground by ball milling in 2-propanol for 24 h. Then 2-propanol was removed by evaporation and fine powder of LSMO nanoparticle was obtained. The LSMO powder was ball milled with water for 24 h before used in the polymerization. PPy/LSMO nanocomposites were prepared by chemical polymerization of Py into the suspension solution of LSMO, as described for PPy. In an experiment, 0.700 g of Py (1 equiv; 10.4 mmol) was added to the suspension solution containing 0.300 g of LSMO under constant stirring. Then, an aqueous solution of 4.22 g of  $\text{FeCl}_3$  (2.5 equiv. of  $\text{FeCl}_3/\text{Py}$ ), 4.04 g of PTS (2 equiv. of  $\text{PTS}/\text{Py}$ ) was added dropwise, with continuous stirring at  $5^\circ\text{C}$  for 15 min and the stirring was continued for 8 h. After the reaction time, black colored PPy/LSMO nanocomposite which was synthesized from 70 wt% Py and 30 wt% LSMO was formed and labeled as P70M30. The PxMy means x wt% polypyrrole and y wt% LSMO. The obtained PPy/LSMO nanocomposite was filtrated, washed in water, and dried at  $50^\circ\text{C}$  under vacuum for 24 h. Using the same procedure, and keeping the concentration of pyrrole constant, the amount of LSMO was varied (10%, 20%, 30%, 40%, 50%, 70% and 90%) and the nanocomposite was synthesized. The mass of P90M10, P80M20, P70M30, P60M40, P50M50, P30M70 and P10M90 was found to be 1.184 g, 1.123 g, 1.141 g, 0.944 g, 0.894 g, 0.770 g, 0.510 g, and 0.811 g respectively.

### 2.3. Characterization

For SEM experiment, powder samples were dispersed on carbon adhesive mounted on standard Al holders. Samples were metallized with a thin (4–5 nm) Platinum coating, using a GATAN Precision Etching and Coating System (PECS®). Image acquisition was performed on a Zeiss ULTRA Plus Field Emission SEM. For TEM experiment, nanoparticles were dispersed in distilled water. A drop of the suspension was then deposited on a thin carbon film supported by a 3 mm TEM copper grid before drying. TEM observations were performed on a JEOL JEM-1230 (120 kV accelerating voltage). X-ray diffraction (XRD) patterns of PPy and nanocomposites were recorded using a diffractometer Bruker D8 with  $\text{Cu K}\alpha$  radiation of wavelength  $1.54 \text{ \AA}$ . The diffraction patterns were recorded in  $2\theta$  range of  $10\text{--}110^\circ$  with a step size of 0.02. The specific surface and pores distribution were obtained from BET method (Brunauer, Emmett, Teller) using ASAP 2010 analyzer by nitrogen adsorption at 77 K. Fourier Transform Infra-Red (FTIR) measurements were performed with a Bruker Tensor 27 ( $400\text{--}4000 \text{ cm}^{-1}$ ) with a resolution of  $\pm 2 \text{ cm}^{-1}$ . Biologic versatile multipotentiostat was used for electrochemical measurement. The electrochemical tests were performed on composite polymer electrodes. The working electrode was prepared by mixing first: 70 wt% active material

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