Graphene/polyaniline nanocomposites thin films totally chemically synthesized for supercapacitor application

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Introduction

Supercapacitors are energy storage devices which have been extensively studied due to the high power and energy density, fast charge-discharge process and high stability over several charge-discharge cycles.[1] Among the several materials used for supercapacitor, graphene and polyaniline composites are the most prominent materials since it is possible to join in the same material the electrochemical double-layer capacitance (EDLC) from 2D material and the fast pseudocapacitive behavior of the conducting polymer.[2] Many approaches have been done to synthesize graphene/polyaniline composites, but in all of them it is necessary previous steps to prepare the graphene sheets for further synthesize the composite. Herein, we demonstrate the chemical synthesis of both graphene (from benzene) and polyaniline (from aniline) simultaneously and in one pot-reaction. The new composites are synthesized and assembled as thin films using the interfacial system.

Results

The composites were synthesized from the addition of anhydrous $FeCl_3$ to the benzene/aniline/H_2SO_4 (1 mol L^{-1}) mixture under magnetic stirring. After three hours, a thin film was observed assembled on the interface of the liquids. The composites were removed directly from the interface over several types of substrates for further characterization. Different composites were synthesized varying aniline ratio (2, 10, 20 and 100 μL) and a neat graphene sample was also prepared. The materials were characterized by TEM, UV-vis and Raman spectroscopy, cyclic voltammetry and charge/discharge measurements. From the TEM image of neat graphene in Figure 1 (a) it is possible to detect the presence of interconnected and randomly assembled graphene sheets. This morphology is expected for neat graphene film since this one was removed directly from the interface. Figure 1 (b) shows the presence of some graphene sheets surrounded by polyaniline fibers. The presence of polyaniline in the emeraldine salt form with secondary doping profile was detected through the UV-Vis spectroscopy, while the Raman spectroscopy indicated that presence of polaronic structure was dependent of aniline ratio.

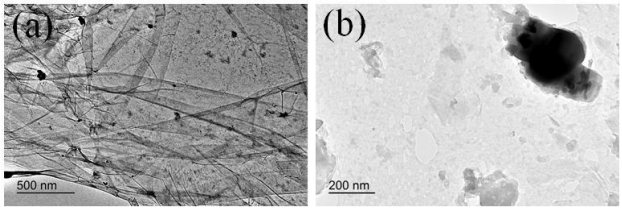

Figure 1 – TEM images for chemically synthesized graphene (a); graphene/polyaniline composite (b).

The cyclic voltammetry curves presented the characteristics peaks of the polyaniline around 0,2V and 0,81V, corresponding to the conversion between the leucoemeraldine to emeraldine and emeraldine to pernigraniline forms of the polyaniline.
The charge-discharge measurements showed an increase in the charge-release time with the increase of the amount of polymer in the composite, but the best result volumetric specific capacitance (C*v*) was achieved by the composite with 20 μL of aniline, with C*v* value of 267.2 $F.cm^{-3}$, indicating the good graphene/polyaniline ratio for this composite.

Conclusions

Chemically synthesized graphene/polyaniline composites were prepared using the interfacial method to assemble the materials as thin films. The composites presented good capacitive results. This is the first time that composites of graphene and polyaniline were synthesized from a graphene bottom-up approach.

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[1] S. Xiong, Y. Shi, J. Chu, M. Gong, B. Wu, X. Wang, Electrochim. Acta **2014**, 127, 139
[2] X. Liu, P. Shang, Y. Zhang, X. Wang, Z. Fan, B. Wang, Y. Zheng, J. Mater. Chem. A **2014**, 2, 15273