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Synthesis and Characterization of Conducting Polyaniline doped with $H_3PMo_{12}O_{40}$ and its Application as Counter-Electrode in Dye-sensitized Solar Cells

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Abstract - This work describes the synthesis and characterization of Polyaniline (PANI) doped with phosphomolybdic acid ($H_3PMo_{12}O_{40}$), named PANI-$H_3PMo_{12}O_{40}$. The infrared spectra displayed characteristic peaks for both materials and the thermogravimetric analysis (TGA) indicated a slightly higher stability for PANI-$H_3PMo_{12}O_{40}$ than dedoped PANI. The conductivity measurements provided values close to 0.1 S cm^{-1}. This material was also applied as counter-electrodes in Dye-sensitized solar cells (DSCs) exhibiting promising responses for future application in solar energy conversion.

Among the most technologically promising conducting polymers, polyaniline lends itself a wide range of applications, especially in view of its good environmental stability, low cost and adequate conductivity. Among many variables, the type of the synthesis and doping material employed will determine such properties and thus direct the applications [1].

In this work, the synthesis of conducting PANI by chemical polymerization in presence of one Keggin-type heteropolyacid ($H_3PMo_{12}O_{40}$), which served as doping material, is described. The synthesis was initially performed from a mixture of 10.6 mmol of aniline and 3.0 mmol of $H_3PMo_{12}O_{40}$ in 30 mL of acetonitrile followed by the slow addition of 3 mL of aqueous solution of ammonium persulphate (3.0 mmol mL^{-1}). The polymerization was carried out under ambient temperature during 24 hours providing, after filtration, a solid conducting PANI doped with $H_3PMo_{12}O_{40}$.

The infrared spectra showed peaks within the region 1100-1600 cm^{-1}, assigned to C-C an C-N stretching vibrations, evidencing the formation of the PANI. The peaks in the region 800-1100 cm^{-1} suggest the incorporation of the $H_3PMo_{12}O_{40}$ into the polymer's matrix. Conductivity measurements carried out by the standard four-probe method provided values close to 0.1 S cm^{-1}, which is much higher than the conductivity for dedoped PANI, an insulating material. The thermogravimetric analysis (TGA) indicated a remarkable difference of thermal behavior between PANI-$H_3PMo_{12}O_{40}$ compared to dedoped PANI (Figure 1) - the former is slightly more stable due to the presence of $H_3PMo_{12}O_{40}$, which is a highly stable inorganic material. The morphology of the material has been investigated by scanning electron microscopy (SEM). As can be seen in Figure 2 (a) and (b), the dedoped PANI consists of large agglomerates with smoothened aspect, while the PANI- $H_3PMo_{12}O_{40}$ displays a roughness morphology, which may be assigned to the modification of the polymer's matrix by the heteropolyacid.

The application of PANI-$H_3PMo_{12}O_{40}$ composite materials as the counter-electrodes in dye-sensitized solar cells (DSCs) provided promising photoelectrochemical properties, as may be seen in Figure 3. Despite the poor fill factor (FF) values, arising mainly from the high series resistance, relatively high photocurrent densities (up to 4 mA cm^{-2}) could be achieved by using Pani-$H_3PMo_{12}O_{40}$ as the catalytic layer for the counter-electrode in the DSCs. The optimization of the catalytic layer based on the composite material studied herein is expected to improve the FF and efficiency (η) values by increasing the surface area of the counter-electrode. Such optimization studies are underway in our laboratory.

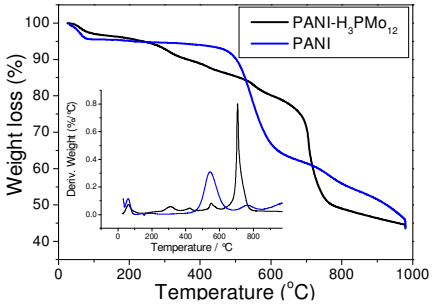

Figure 1. Thermogravimetric curves of PANI-$H_3PMo_{12}O_{40}$ and dedoped PANI.

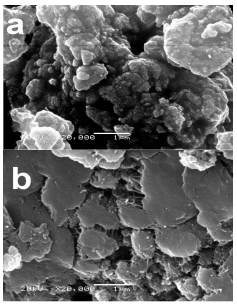

Figure 2. SEM images of PANI-$H_3PMo_{12}O_{40}$ (a) and dedoped PANI (b).

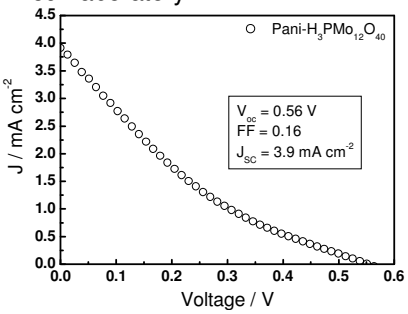

Figure 3. *J-V* curves of the dye-sensitized solar cells based on the PANI- $H_3PMo_{12}O_{40}$ as the counter-electrode.

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[1] *Conjugated polymers – Theory, Synthesis and Characterization,* edited by T. A. Skotheim and J. R. Reynolds, ***2007***, CRC Press, Boca Raton, Flórida.