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Nanocomposite hybrid material based on carbon nanofibers and polyoxometalates

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We prepared nanocomposite hybrid materials based on previously oxidized carbon nanofibers (fCNFs) and polyoxometalates (POM). We analyzed fCNFs by XRD and TEM where we observed the presence of carbon nanocoils, and the removal of amorphous carbon and thin fibers. The nanocomposite hybrid sample (fCNFs-POM) microstructure was observed by SEM, and EDX analyses revealed the presence of Cs, P, Mo, and O that form the POM, and C from fCNFs. In addition, FTIR spectra confirmed the intact presence of both components that conform the hybrid, where their interaction was not evident, but we presume a chemisorption of POM onto fCNFs through carbonyl groups. Finally, solid-state symmetric supercapacitor cells were assembled, showing higher capacitance values (120mF/g) for the cell with hybrid electrodes, revealing the pseudocapacitive contribution of POM aside from the double layer of CNFs.

Keywords: Polyoxometalates; carbon nanofibers; hybrid materials; supercapacitors; energy storage.

Sintetizamos y caracterizamos materiales híbridos nanocompositos a base de nanofibras de carbón previamente oxidadas (fCNFs) y polioxometalatos (POM). Las fCNF se analizaron por TEM y XRD donde detectamos la presencia de nanoespirales de carbono y la eliminación de carbono amorfo y de las fibras mas delgadas. La microestructura del material híbrido nanocomposito (fCNFs-POM) se observó por SEM, y los análisis de EDX mostraron la presencia de Cs, P, Mo, y O del POM y C de fCNFs. Además, los espectros de FTIR confirmaron la presencia de ambos componentes del híbrido, donde su interacción no ha sido clarificada pero intuimos la quimisorción del POM a las fCNFs mediante grupos carbonilos. Finalmente, ensamblamos celdas simétricas supercapacitivas de estado sólido, donde la celda con electrodos híbridos mostró una capacitancia mucho mayor de 120 mF/g, mostrando tanto la contribución pseudocapacitiva del POM como la doble capa de las nanofibras de carbono.

Descriptores: Polioxometalatos; nanofibras de carbono; materiales híbridos; supercapacitores; almacenamiento de energía.

PACS: 81.05.UW; 84.60.-1; 82.47.Uv

1. Introduction

Nanocomposite hybrid materials represent an excellent approach to disperse two different compounds at a molecular level with complementary properties, and put them to work for a specific application [1]. The main idea when developing hybrid materials is to take advantage of the best properties of each component, trying to decrease or eliminate their drawbacks, getting synergic effects, and obtaining new materials with new properties

Phosphomolybdic compounds with Keggin structure are known within the group of polyoxometalates (POMs), which are metal oxide clusters formed by a central tetrahedral PO_4 surrounded by 12 edge-sharing metal-oxygen MoO_6 . This phosphomolybdate polyanion can be balanced either by protons or by other cations, and can undergo reversible multi-electron reduction processes both electrochemically and photochemically. [2]. Nevertheless, the large solubility of POMs in typical solvents has caused them to be ignored as active compounds for solid-state applications, since they need to be anchored to a solid framework. Thus, POM has been anchored to conducting polymer networks and used as electrodes for lithium rechargeable batteries and supercapacitors [2-5]. In spite of the solubility problem, POMs molecules are well known and have been used in catalysis [6-7], photocatalysis [8-9], luminescence applications [10-12], and nu-

clear waste remediation [13]. Polyoxometalates with Keggin and Dawson structures have also been used to disperse carbon nanoparticles through a strong chemisorption of POM onto carbon surface [14-16]. This interaction involves functional groups created on the surface of carbon and their concentration will have a strong relation with the amount of POM particles adsorbed.

The objective of our work was to synthesize nanocomposite hybrid materials based on oxidize CNFs and POM, in order to have both components disperse at a molecular level as shown in Fig. 1. The increased dispersion of POM on the oxidized CNFs (fCNFs) surface will impact both, the nanofibers tendency to agglomerate creating higher surface area, and the large solubility of POM enhancing the effective interface required. Also, we will evaluate the pseudocapacitive contribution of POM in the supercapacitor cells.

2. Experimental

2.1. Reagents

We used HNO_3 (69%) from Productos Químicos Monterrey to oxidize the surface of CNFs. Cesium phosphomolybdate salt ($\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$) was synthesized from phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, $\text{PM}=1825.25_{+aq}$, 99.917%), cesium chloride (CsCl , 99.9%), and triton 100X from Sigma-

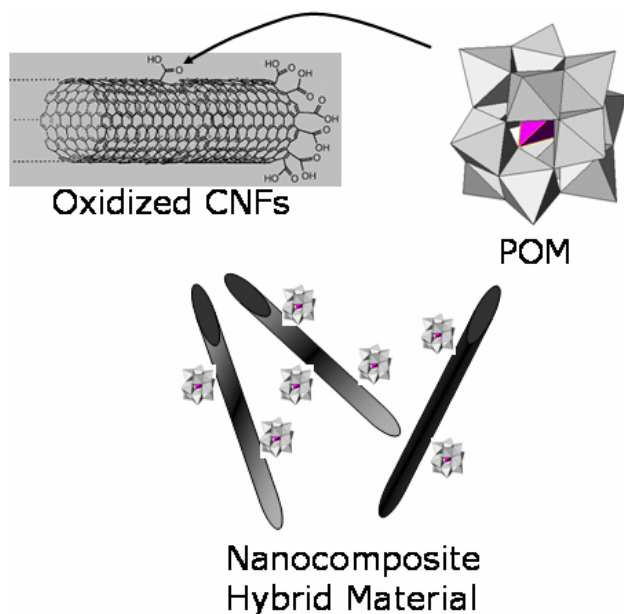


FIGURE 1. Schematic representation of oxidized carbon nanofibers (left), POM (right), and the nanocomposite hybrid material (bottom).

Aldrich. This salt was used in combination with functionalized CNFs in NN-Dimethyl Formamide (99%) from SIGMA-ALDRICH in order to obtain the nanocomposite hybrid. Finally, for the supercapacitive cell assembly we used plastic electrodes made of polyvinyl acetate (PVA), dibutyl phthalate (DBP), and acetone all from Sigma-Aldrich; and a Nafion 117 membrane impregnated with H_2SO_4 from Aldrich as electrolyte.

2.2. Synthesis

CNFs were functionalized in order to oxidize the surface and create carbonyl groups by means of a reflux procedure with a 2.5M HNO_3 dissolution during 7 hours [14]. Functionalized CNFs were left standing for 17 hrs in the acidic dissolution, filtered-off, washed with deionized water, and dried at 100°C for 2 hours. On the other hand, $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ (POM) was synthesized using a solid-state method described in the literature [14], where the formation of metastable microcells made of triton100-X and crystal water from POM precursor, provided the reaction fields for a rapidly formation of the salt. The exact procedure for the synthesis of this salt and characterization is explained elsewhere [17]. Finally, for the synthesis of fCNF-POM nanocomposite hybrid material a specific amount of functionalized CNFs (fCNFs) was mixed with 50%w of POM salt, following the next procedure: 0.05 g of fCNFs were sonicated in 30ml DMF (dimethyl formamide) for 20 minutes in an ultrasound bath, we added 0.05g of POM and sonicated again for another 20 minutes obtaining a suspension that was vacuum-filtered using a Millipore filter, washed with the solvent and subsequently dried at 100°C for 1 hr.

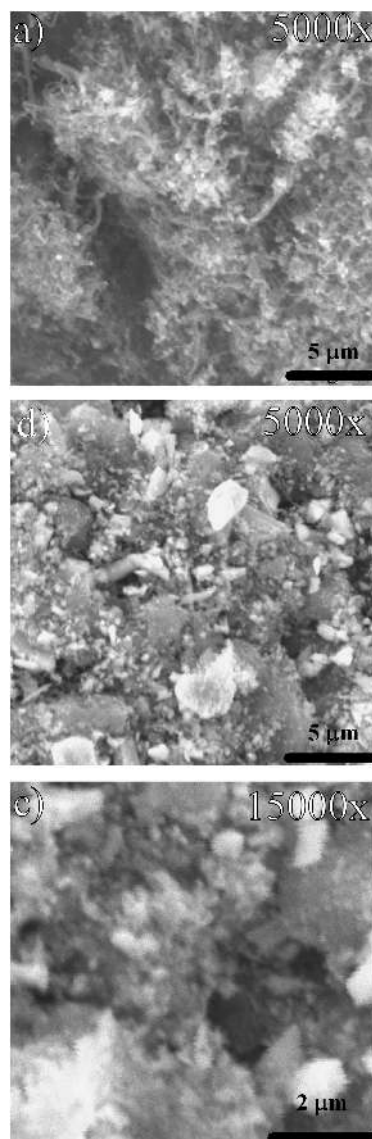


FIGURE 2. SEM images of CNFs at 5000x (a) and CNFs-POM nanocomposite hybrid at 5000x (b) and 15000x (c).

2.3. Plastic electrodes

Plastic electrodes were fabricated in order to evaluate our different materials in solid-state symmetric supercapacitor cells, using polyvinyl acetate (PVA) as binding agent, and dibutyl acetate as dispersant. These plastic or film electrodes were made by suspending in acetone 0.05gr of our active materials (CNFs or fCNFs-POM) with 1 drop of DBP and a certain percentage of PVA (60%w was used for CNFs, and 25%w for the hybrid material). This suspension was thoroughly mixed by magnetic stirring for 12 hours to yield a homogeneous paste. The paste was tape cast onto a glass surface letting the acetone evaporate to obtain a self-standing plastic film, which was cut in circles of 0.8 mm of diameter to obtain the plastic electrodes.

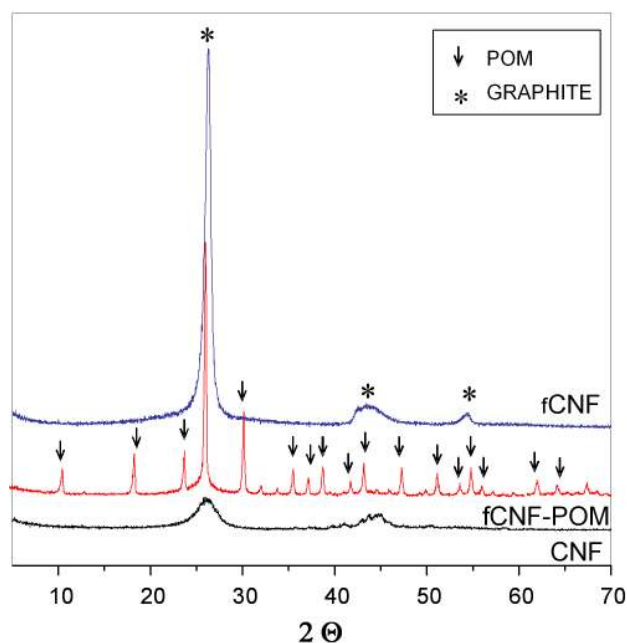


FIGURE 3. Powder XRD patterns of CNFs, fCNFs, and CNFs-POM nanocomposite hybrid, where (*) indicates graphite pattern and the arrows POM pattern.

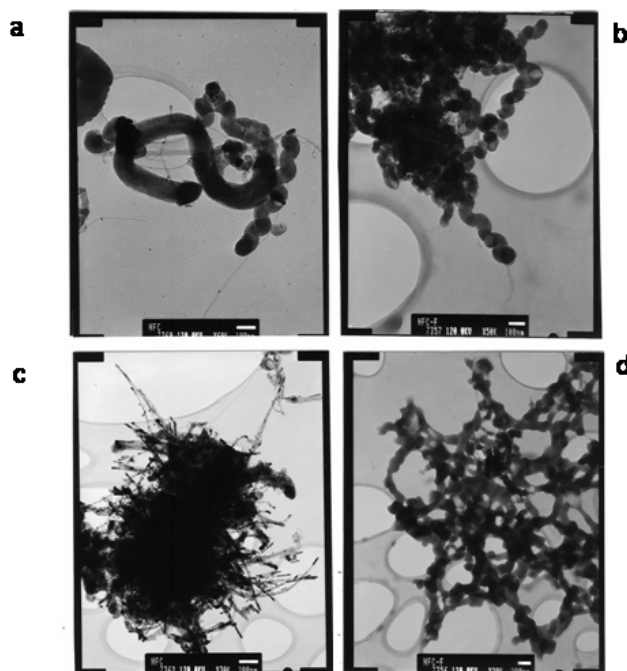


FIGURE 4. TEM images of fCNFs (a), (b), and (d), and CNFs (c).

2.4. Characterization

XRD studies were carried out in a Rigaku Ultima +D system with Cu-K α radiation ($\lambda=1.54$ Å). FTIR analyses were carried out using a Bruker spectrophotometer model Equinox 55 with the samples diluted in KBr pellets, to detect the presence of carbonyl groups on fCNFs and the vibrational modes of POM. Scanning electron microscopy (SEM) studies were

performed in a JEOL JSM-5400LV microscope to detect microstructure differences. Transmission Electron Microscopy (TEM) analyses were performed using a JEOL JEM-1200EX electron microscope operated at 200 kV, and the samples prepared by gravimetric methods. Supercapacitive cells were assembled with 2 identical plastic electrodes in Swagelok cells, using an activated Nafion membrane [18] as electrolyte. The electrochemical characterizations of symmetric supercapacitor cells were carried out in a Solartron potentiostat model SI 1287, using a galvanostatic cyclic technique in order to study 500 successive charge-discharge cycles. The capacitance values were calculated by

$$C = (It)/V \quad (1)$$

where I is the current density applied, t the discharge time of the supercapacitor cell, and V the voltage window used for cycling the cell (1.9V).

3. Results

We characterized CNFs-POM nanocomposite hybrid material by using different techniques as SEM, TEM, FTIR, and XRD. In Fig. 2 we show SEM images at different magnifications of CNFs (a) and of the CNFs-POM nanocomposite hybrid (b and c). Figure 2a clearly shows the nanofibers microstructure used for the formation of the hybrid, and in Fig. 2b the nanocomposite hybrid microstructure at the same magnification (5000x). Small particles were detected on the hybrid sample (Fig. 2b) that seemed to agglomerate forming bigger particles with an undefined shape. We did not detect the nanofibers microstructure in the hybrid sample, not even at greater magnifications (15000x, Fig. 2c), suggesting the integration of both components in a single phase. EDX and a mapping technique showed the homogeneous presence of C from the fCNF, and O, P, Mo, Cs from POM in the nanocomposite hybrid.

Figure 3 shows powder XRD patterns of CNFs, fCNFs, and CNFs-POM nanocomposite hybrid. CNFs pattern revealed wide diffraction peaks characteristic of graphite. When these fibers were oxidized (fCNFs) the diffraction pattern profile changed to narrower diffraction peaks, indicating the elimination of amorphous carbon. On the other hand, diffraction pattern of CNFs-POM nanocomposite hybrid showed characteristic peaks of POM [17] marked with arrows, as well as of graphite.

In Fig. 4 we show TEM images where we observed agglomeration of CNFs (Fig. 4c) that when oxidized, amorphous carbon was not detected nor the smaller fibers (Figs. 4b and d) detected on Fig. 4c. In addition, the oxidizing method revealed the presence of what is known as *nanocoils* [19](Figs. 4a and b). On the other hand, in some nanocomposite hybrid TEM images (not shown here) dark spots on the surface of carbon nanofibers were hardly revealed, which could indicate the presence of POM. Nevertheless, more TEM studies are necessary to assign these spots to POM.

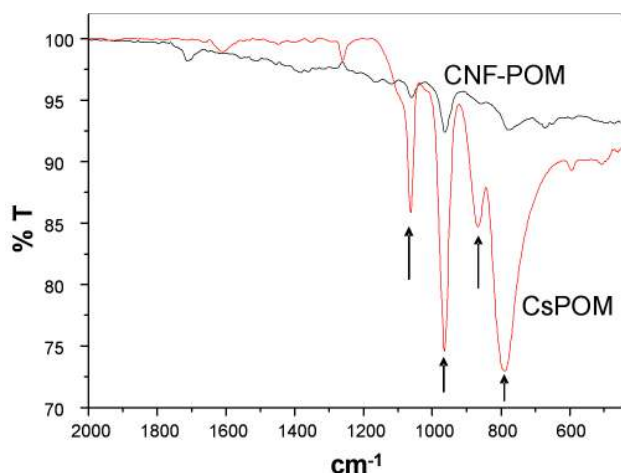


FIGURE 5. FTIR spectra of POM and CNFs-POM nanocomposite hybrid, where the arrows mark the vibrational modes of the Keggin unit of POM.

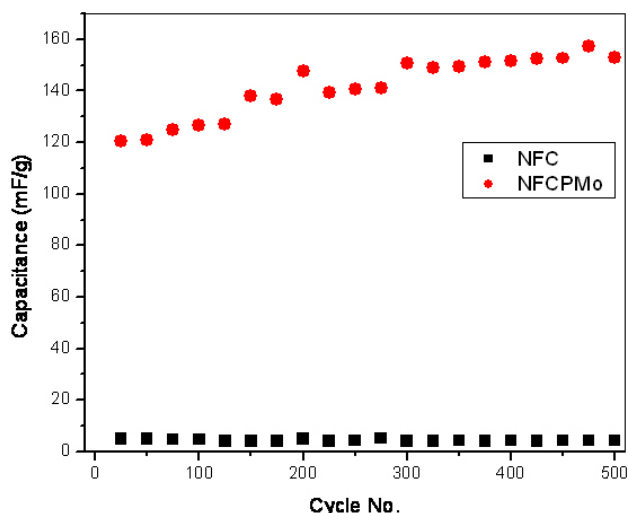
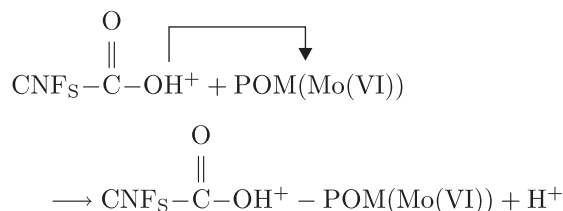


FIGURE 6. Successive 500 charge-discharge cycles of symmetric supercapacitor cells using an activated Nafion 117 membrane as electrolyte, a $I = 25$ mA/g, and a voltage window of 1.9V (from 0.9V to 1V). Our materials were used as plastic electrodes as indicated in the experimental section.

We carried out FTIR analyses of the nanocomposite hybrid (Fig. 5) and POM in KBr pellets, where we detected and compared the characteristic vibrational modes of POM [2]. The nanocomposite hybrid spectrum showed these vibrational modes at 1060 cm^{-1} for P-O, a slight shift to higher energies of Mo=O to 962 cm^{-1} , and a shift to lower energies of Mo-O bonding to 859 cm^{-1} and 780 cm^{-1} . These bonds (Mo-O and Mo=O) are localized at the perimeter of the Keggin unit [2], suggesting that these shifts can be related with the interaction of POM with its surroundings. This interaction of POM can be attributed to their chemisorption onto carbon nanofibers or nanocoils. In addition, we detected a peak at 1700 cm^{-1} indicative of carbonyl groups from fCNFs (oxidized fibers), which can be the interaction point with POM as previously suggested [17]. A probable schematic reaction mechanism could be the following:



We carried out the electrochemical characterization of these materials in 2-electrode symmetric supercapacitor cells, using our materials as plastic electrodes (experimental section) and Nafion 117 membrane activated with acid as the electrolyte. In Fig. 6 we show 500 successive charge-discharge cycles of our cells, where we observed higher capacitance values of 120 mF/g for the cell assembled with nanocomposite hybrid material as electrodes, which increase up to 160mF/g with cycling. This increment can be related with the rearrangement of the electrodes during cycling, due to an increase of the electro-active surface area [2]. On the other hand, comparing this cell with the cell assembled with CNFs electrodes, it was clear that the higher capacitance values are due to the contribution of POM with its pseudocapacitance property (redox activity) [2,17]. This work is based on preliminary results and more experimentation and analyses are underway to clarify more issues regarding this type of materials and their application as electrodes in supercapacitor cells.

4. Conclusions

Characterization techniques (SEM, TEM, XRD, and FTIR) confirmed the presence of both components in the nanocomposite hybrid material. TEM images showed the removal of amorphous carbon and thin fibers when CNFs were oxidized, revealing also the presence of carbon nanocoils, in good agreement with XRD patterns. SEM analyses revealed the microstructural homogeneity of the nanocomposite hybrid material and the presence of C, O, P, Mo, and Cs. FTIR spectra confirmed the presence of both components of the hybrid material, and suggested some sort of interaction of POM with the fCNFs through carbonyl groups (Fig. 1). Electrochemical experiments in symmetric supercapacitor cells showed the pseudocapacitive contribution of POM in the hybrid electrodes. From our characterization techniques it is clear the presence of both components in the hybrid, nevertheless, more studies will need to be carry out in order to understand their interaction.

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