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Functionalized Carbon–Silicates from Caramel–Sepiolite Nanocomposites**

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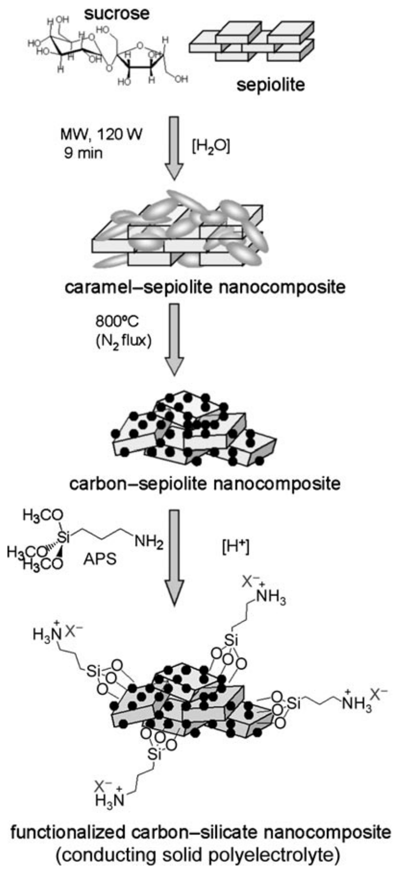
The nanochemistry of multifunctional materials represents a rich and innovative area of research based on the design and synthesis of nanostructured solids that involves the assembly of diverse functional entities.[1] An excellent example is given by organic–inorganic hybrid compounds, versatile, flexible, and easily functionalized compounds that lead to different advanced applications.[2] Nanocomposites, particularly polymer–clay nanocomposites, are a representative group of hybrid materials as functionalities can be introduced at both the organic moiety and the inorganic component.[3] Carbon–clay nanocomposites are nanostructured porous materials that conduct electricity and are synthesized by the graphitization of organic compounds assembled on the clay surface. In these materials, the inorganic counterpart commonly is a layered solid such as layered double hydroxides (LDHs) and silicates (e.g., montmorillonite), which is used to prepare templated carbon materials.[4,5] Olefins and polyacrylonitrile preassembled on sepiolite also afford silicate–carbon solids.[6,7]

We reported recently the preparation of conducting porous nanocomposites from the graphitization of caramel–montmorillonite intercalation compounds.[8] On the basis of this approach, we intended to introduce additional functionality onto conducting carbon–silicate nanostructured compounds derived from sepiolite. Functionality has been introduced by grafting silanes onto sepiolite to act as a template for the formation of conducting carbon. Herein we report the synthesis of novel hybrid compounds that are simultaneously electrical conductors and able to recognize ions.

Sepiolite is a microfibrous magnesium silicate, $Si_{12}O_{30}Mg_8(OH,F)_4(H_2O)_4\cdot 8H_2O$, with an ability to adsorb large quantities of water and polar organic molecules, owing to its large specific surface area (ca. 300 m^2g^{-1}), which is related to the presence of pores of different sizes (micro- and nanopores) that allow the inclusion of molecular and polymeric species.[9] Interestingly, the surface of sepiolite is covered with free silanol groups (SiOH), which can be functionalized with organic groups after treatment with organosilanes.[10,11]

When a mixture of sepiolite and sucrose (1:2 w/w; 1 g) is mixed with water (2.5 mL) and heated with microwave (MW) radiation by using a focused furnace (monomode; 120 W applied power) over various periods (typically 9 min), the sucrose is caramelized onto the mineral surface and forms homogeneous nanocomposite materials (Scheme 1). Further heating (1 h, 800 °C) of these caramel–sepiolite compounds, previously equilibrated in an atmosphere of H_2SO_4 (96 % concentration) for 6 days, was carried out under an oxygen-free atmosphere (N_2 flux). The acidity conferred to the caramel nanocomposites favors the formation of conducting carbon, as reported previously.[5]

X-ray diffraction (XRD) patterns of the starting sucrose–sepiolite mixtures show characteristic diffraction peaks of both crystalline components. After 10 minutes of heating, the reflections corresponding to sucrose have almost completely



Scheme 1. Preparation of functional and conducting APS–carbon–sepiolite nanocomposites.

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disappeared, thus indicating the nearly complete conversion of sucrose into caramel. Features typical of amorphous caramel, as well as reflections assigned to anhydrous sepiolite appear in the diffractograms of samples heated to 700 °C. Under these conditions, the caramel is transformed into an amorphous carbonaceous material and the sepiolite into an anhydrous and partially magnesium-dehydroxylated silicate.[12]

The carbon content deduced from elemental analyses of caramel–sepiolite nanocomposites is approximately 30 %; as this content is approximately 45 % in conventional caramel and taking into account the starting sepiolite/sucrose mixture is 1:2 (w/w), we deduce that weight loss during the caramelization process is approximately 37 %. In fact, aldehydes, furans, carbon dioxide, and other volatile compounds are eliminated during conventional caramelization.[13] The loss of these volatile compounds is confirmed by endothermic peaks obtained in differential thermal analyses (DTA) and the associated curves from thermogravimetric analysis, which show a weight loss of approximately 40 % between 25 and 250 °C. However, the carbon content in the caramel–sepiolite nanocomposites is almost unchanged after graphitization, which takes place at higher temperatures. After thermal treatment, ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR spectroscopy signals characteristic of caramel formed on the sepiolite surface disappear and are replaced by a large signal centered at 130 ppm, which is assigned to graphene units in the carbonaceous nanocomposite. This assignment is in agreement with those for carbonaceous materials derived from caramel–montmorillonite nanocomposites.[8]

The Brunauer–Emmett–Teller (BET) specific surface area of the starting sepiolite (ca. 340 m^2g^{-1}) considerably decreases during caramelization (0.6 m^2g^{-1}), which suggests that the polycondensate fills completely the diverse pores on the surface of the sepiolite. It is noteworthy that the graphitized compounds show a significant increase in the surface area and reach values of 240 m^2g^{-1}, which is in agreement with the formation of nanosized carbon particles as detected by transmission electron microscopy (TEM; see below).

Thermal transformation of the insulating caramel–sepiolite nanocomposites (ca. 10^{-4} $S\,cm^{-1}$) into electrically conducting carbon–sepiolite compounds (ca. 10^{-1} $S\,cm^{-1}$) was monitored by in situ electrochemical impedance spectroscopy (EIS; Figure 1). Interestingly, after the sample was cooled to room temperature, the conductivity was approximately 10^{-2} $S\,cm^{-1}$. This electrical behavior, together with the relatively high specific surface area of these carbon–clay nanocomposites, makes them suitable for use as electrode materials.

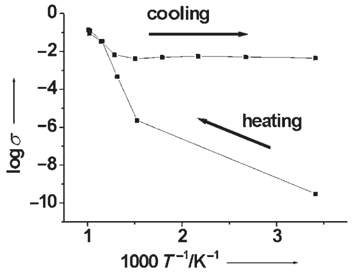
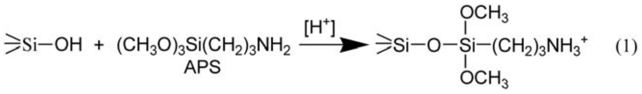


Figure 1. Electrical conductivity (σ / $S\,cm^{-1}$) of the caramel–sepiolite nanocomposite (deduced from in situ EIS measurements) as a function of temperature during the graphitization process under an N_2 flux.

Carbon–sepiolite nanocomposites treated over 15 h at 65 °C with (3-aminopropyl)trimethoxysilane (APS) in acidic media (HCl/isopropyl alcohol) give the corresponding ammonium propylsilyl derivatives [Eq. (1)]. The amount of grafted silylpropyl ammonium species is around 30 mmol per 100 g, as deduced from the nitrogen content (0.42 %). The carbon content increases from 29.1 % in the carbon–sepiolite nanocomposite to 35.0 % in the modified carbon–silicate nanocomposite. At first glance, the increase in the carbon content of the modified nanocomposite could be ascribed to the incorporation of the grafted groups. However, it must also be considered that the mass of the silicatelike component has decreased during grafting. In fact the acidic medium leaches Mg^{2+} ions from the sepiolite structure, thus increasing the available silanol groups, which facilitates further grafting of the aminopropyl species [Eq. (2)].[10] From energy-dispersive X-ray (EDX) semiquantitative analyses of the grafted solids, we deduce that approximately 60 % of the magnesium is extracted.



$$\geqslant Si{-}OH + \underset{APS}{(CH_3O)_3Si(CH_2)_3NH_2} \xrightarrow{[H^+]} \geqslant Si{-}O{-}\overset{OCH_3}{\underset{OCH_3}{Si}}{-}(CH_2)_3NH_3^+ \quad (1)$$

$$\geqslant Si{-}O{-}Mg{-}O{-}Si\leqslant \xrightarrow{[H^+]} 2 \geqslant Si{-}OH + Mg^{2+} \quad (2)$$

TEM images of the nanocomposites (Figure 2) can be interpreted as superstructural arrangements resulting from the assembly of transversally broken residual sepiolite microfibers with pseudospherical carbon nanoparticles cemented by the polysiloxane network. Heating sepiolite above 500 °C induces folding to give anhydrous sepiolite, which still preserves its surface silanol groups.[14] This heating, together with the loss of Mg^{2+} ions, results in the sepiolite microfibers breaking transversally,[10,15] as seen by TEM.

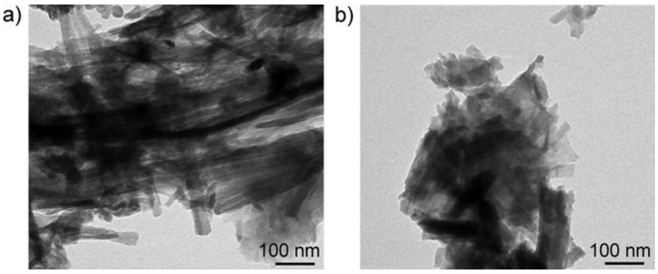


Figure 2. TEM images of a) carbon–sepiolite and b) APS–carbon–sepiolite nanocomposites.

The grafting of positively charged groups that can act as anion-exchange sites covalently bonded to a silicic substrate, which is intimately associated with conducting carbon, is the key to obtaining a sensing material useful for the recognition of negatively charged ions in solution. The APS–carbon–sepiolite compound can be used for the preparation of carbon-paste electrodes (CPEs) that simultaneously offer electrical transduction and sensing. The novelty relies on the fact that the incorporation of additional carbon is not required to assure the electrical conductivity necessary for the building of CPEs. Potentiometric response (Figure 3) towards NO_3^- and Cl^- ions of a CPE sensor based on this type of material is linear in the 10^{-4}–10^{-1} M range: plots of potential (E/mV) versus log of the ion concentration (C_x/M) give slopes of −52.1 (NO_3^-) and −48.0 mV decade^{-1} (Cl^-). These values are close to the values predicted by the Nernst equation for monovalent anions, which indicates excellent recognition of these ions. It is noteworthy that the ions are discriminated based on their effective ionic diameter, which is attributed tentatively to the nanoporosity inherent to the nanocomposites. Thus, NO_3^- and Cl^- ions, with effective diameters of 0.3 nm, are well detected, whereas ClO_4^- and SO_4^{2-} ions, with higher effective diameters, show a positive slope in the linear range of response: +18.3 and +17.4 mV decade^{-1} for SO_4^{2-} and ClO_4^-, respectively (Figure 3).

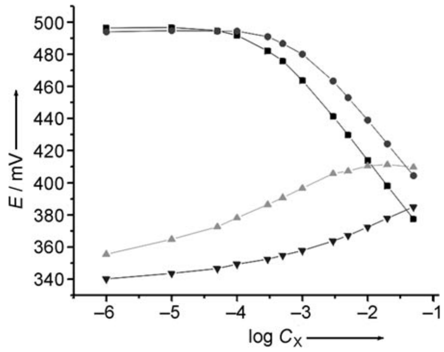


Figure 3. Potentiometric response of a CPE based on APS–carbon–sepiolite nanocomposites for various ions: NO_3^- (■), Cl^- (●), SO_4^{2-} (▲), ClO_4^- (▼).

When electrodes are prepared from APS-grafted sepiolite with graphite added to ensure electrical conductivity (i.e., a conventional CPE), there is a significantly different potentiometric response with respect to that of the APS–carbon–sepiolite with a strong deviation from the expected value of the slope (−29.8 and −31.6 mV decade^{-1} for Cl^- and NO_3^-, respectively). Thus, it is evident that the carbon generated in situ plays a significant role in the selectivity of the ion recognition offered by this type of electrochemical sensor.

In conclusion, the procedure presented herein opens a way to diverse multifunctional materials based on functionalized conducting clay nanocomposites. For example, the nanocomposites may be functionalized with thiosilanes to recognize heavy metal ions. Alternatively, sulfonate groups may be anchored to prepare mixed proton–electron conductors useful as electrocatalysts. All of these solids are especially attractive as they are low-cost and eco-friendly materials.

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[1] G. A. Ozin, A. C. Arsenault, *Nanochemistry*, RSC Publishing, Cambridge, **2005**.

[2] a) E. Ruiz-Hitzky in *Functional Hybrid Materials* (Eds.: P. Gómez-Romero, C. Sánchez), Wiley-VCH, Weinheim, **2004**, chap. 2, pp. 15–49; b) C. Sanchez, B. Julián, P. Belleville, M. Popall, *J. Mater.* **2005**, *15*, 3559–3592; c) E. Ruiz-Hitzky, *Chem. Rec.* **2003**, *3*, 88–100; d) "Polymer- and biopolymer-layered solid nanocomposites: organic–inorganic assembling in two-dimensional hybrid systems": E. Ruiz-Hitzky, P. Aranda, M. Darder in *Bottom-Up Nanofabrication: Supramolecules, Self-Assemblies, and Organized Film* (Eds.: K. Ariga), American Scientific Publishers, **2006**, in press.

[3] a) T. J. Pinnavaia, G. W. Beall, *Polymer–Clay Nanocomposites*, Wiley, Chichester, **2000**; b) K. A. Carrado, *Appl. Clay Sci.* **2000**, *17*, 1–23; c) M. Alexandre, P. Dubois, *Mater. Sci. Eng. Rep.* **2000**, *28*, 1–63; d) E. Ruiz-Hitzky, A. Van Meerbeeck in *Clay mineral and organoclay–polymer nanocomposites, Handbook of Clay Science* (Eds.: F. Bergaya, B. K. G. Theng, G. Lagaly), Elsevier, Dordrecht, **2006**, chap. 10.3, pp. 583–621; e) "Clay-Based Polymer Nanocomposites": P. Aranda in *Clay Minerals Society Workshop Lectures Series*, *Vol. 14* (Eds.: K. A. Carrado, F. Bergaya), The Clay Minerals Society, Chantilly (Virginia, EEUU), chap. 6, in press; f) P. Aranda, M. Darder, R. Fernández-Saavedra, M. López-Blanco, E. Ruiz-Hitzky, *Thin Solid Films* **2006**, *495*, 104–112.

[4] a) L. Duclaux, E. Frackowiak, T. Gibinski, R. Benoit, F. Beguin, *Mol. Cryst. Liq. Cryst.* **2000**, *340*, 449–454; b) F. Leroux, E. Raymundo-Piñero, J. M. Nedelec, F. Beguin, *J. Mater. Chem.* **2006**, *16*, 2074–2081; c) T. Kyotani, N. Sonobe, A. Tomita, *Nature* **1988**, *331*, 331–333.

[5] A. Bakandritsos, T. Steriotis, D. Petridis, *Chem. Mater.* **2004**, *16*, 1551–1559.

[6] G. Sandí, K. A. Carrado, R. E. Winans, C. S. Johnson, R. Csencsitsc, *J. Electrochem. Soc.* **1999**, *146*, 3644–3648.

[7] R. Fernández-Saavedra, P. Aranda, E. Ruiz-Hitzky, *Adv. Funct. Mater.* **2004**, *14*, 77–82.

[8] M. Darder, E. Ruiz-Hitzky, *J. Mater. Chem.* **2005**, *35*, 3913–3918.

[9] E. Ruiz-Hitzky, *J. Mater. Chem.* **2001**, *11*, 86–91.

[10] E. Ruiz-Hitzky, J. J. Fripiat, *Bull. Soc. Chim. Fr.* **1976**, 1341–1348.

[11] a) E. Ruiz-Hitzky, J. J. Fripiat, *Clays Clay Miner.* **1976**, *24*, 25–30; b) E. Ruiz-Hitzky, P. Aranda, J. M. Serratosa in *Handbook of Layered Materials* (Eds.: S. M. Auerbach, K. A. Carrado, P. K. Dutta), Marcel Dekker, New York, **2004**, chap. 3, pp. 91–154.

[12] J. L. Ahlrichs, J. C. Serna, J. M. Serratosa, *Clays Clay Miner.* **1975**, *23*, 119–124.

[13] R. L. Whistler, J. R. Daniel in *Food Chemistry* (Ed.: M. Dekker), O. R. Fennema, New York, **1985**, chap. 3, pp. 69–137.

[14] T. Fernández-Alvarez in *Proc. Reunión Hispano-Belga de Minerales de la Arcilla* (Ed.: J. M. Serratosa), CSIC, Madrid, **1970**, pp. 202–209.

[15] a) T. Fernández-Alvarez in *Proc. Clay Conf.* (Ed.: J. M. Serratosa), CSIC, Madrid, **1972**, pp. 571–588; b) E. Ruiz-Hitzky, PhD thesis, Université Catholique de Louvain, **1970**.