



Interplay of carbon–silica sources on the formation of hierarchical porous composite materials for biological applications such as lipase immobilization



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ABSTRACT

The porous inorganic materials, with hierarchical structures, find application in many processes where the chemical stability and pore connectivity are key points, such as separation, adsorption and catalysis. Here, we synthesized carbon–silica composite materials, which combine hydrolytic stability of the carbon with the surface chemical reactivity of silica in aqueous media. The polycondensation of carbonaceous and siliceous species from sucrose, Triton X-100 surfactant and tetraethylortosilicate during the hydrothermal synthesis led to the formation of hydrochar composite materials. The subsequent carbonization process of these composite hydrochars gave carbon–silica hierarchical porous materials. The study of the micellar reaction system and the characterization of the derivative materials (carbon–silica composite, carbon and silica) were carried out. The results indicate that synthesis conditions allowed the formation of a silica network interpenetrated with a carbon one, which is produced from the incorporated organic matter. The control of the acidity of the reaction medium and hydrothermal conditions modulated the reaction yield and porous characteristics of the materials. The composite nature in conjunction with the hierarchical porosity increases the interest of these materials for future biological applications, such as lipase immobilization.

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1. Introduction

The carbon–silica composite materials are intermediate products during the synthesis of mesoporous silica and carbon, templated by surfactants and porous silica molds, respectively, but the interest of many papers concerns only with the final materials [1–4].

The benefit of combining the chemical and mechanical properties of each counterpart is one of the reasons for devoting attention on the synthesis of these composite materials. They can be obtained by different routes, for example, avoiding the step of elimination of one of these counterparts. The silica–surfactant interactions and their self-assembly lead to the formation of silica networks with surfactant trapped in their cavities [5]. Even the first objective can be to eliminate the surfactant for having free pores, a treatment with sulfuric acid and posterior carbonization creating a composite material. This was put in contact with fluorhydric acid for eliminating silica and producing mesoporous carbon [6,7]. In another approach for producing mesoporous carbon, the co-assembly of Pluronic P123 surfactant and silica species from tetraethylortosilicate (TEOS) in the presence of sucrose is achieved during the first steps of synthesis. In this case, the formed silica network

acted as a porogen and protected the structure against the collapse during the subsequent thermal treatments for the formation of the carbon network [8]. The presence of sucrose, which is a cheap and available carbon source, in the reaction medium increases the reaction yield. The sucrose has been also reported as a carbon source through nanocasting pathway by using mesoporous silica as a solid mold for the formation of ordered mesoporous carbon [9]. The effective prepolymerization of sucrose allows one to create a stable carbon network that does not collapse after silica elimination [10]. Even the emphasis in all of the precedent reports has been put in one of the two components of the system [11,12], these routes are simple, fast and cost-effective for producing composite materials. Their hydrophobic–hydrophilic properties can be modulated for being used as support for biocatalysts. For example, immobilization of lipase in nanocarbon-in-silica composite materials improved the catalytic behavior and stability of the resultant biocatalysts [13–15]. The immobilization of the lipase was chosen as an application example of carbon–silica composite materials because it is strongly adsorbed in hydrophobic support, suffering an interfacial activation [16–18]. However, high hydrophobicity of the support implies dispersion problems during the immobilization of enzymes, which is made from aqueous solution. Therefore, the combination of hydrophobicity and hydrophilicity in the same material could be a great advantage.

The goal of this article is to obtain hierarchical porous composite materials that combine the benefits of silica and carbon. The synthesis

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route from acidic reaction mixture of sucrose, Triton X-100 surfactant and TEOS is simple and cheap. The control in the prepolymerization degree of both siliceous and carbonaceous networks during the hydrothermal synthesis allows modulating the characteristics of the materials. Some insights about the mechanism formation of them are given through different characterization techniques. These materials are good candidates for enzyme immobilization like lipase from aqueous medium.

2. Materials and methods

2.1. Materials

The analytical grade reagents were used without further modifications: Triton X-100 (Sigma), commercial sucrose, sulfuric acid (98% H₂SO₄, Mallinckrodt), hydrochloride acid (35% HCl, Sigma), tetraethylortosilicate (TEOS, Merck), and fluorhydric acid (40% HF, Sigma-Aldrich).

2.2. Synthesis and characterization of carbonaceous–siliceous composite materials

The reaction mixture was prepared by dissolving 0.015 mol H₂SO₄ and 0.003 mol sucrose in a 0.066 M Triton X-100 solution (in 2 M HCl). The 0.017 mol TEOS were added and the final mixture was magnetically stirred for 30 min. The clear solution was heated under the conditions shown in Table 1. The obtained hydrochar (Sx-H) was carbonized in inert atmosphere (60 mL min⁻¹ nitrogen), at 900 °C or 600 °C. A portion of the carbon–silica composite material (Sx-CS) was put in contact with 40% HF for dissolving the silica and obtaining a pure carbon (Sx-C) and another portion was submitted to calcination at 500 °C for 3 h at 10 °C min⁻¹ for obtaining the silica (Sx-S).

2.3. Characterization

Dynamic Light Scattering (DLS): The hydrodynamic diameter for the species present in the reaction systems before and after heating was determined from the DLS measures (Horiba Scientific LB-550 instrument, LB-550-3.57 version software) by using the Stokes–Einstein equation [19].

Infrared spectroscopy (FTIR): The chemical groups on the hydrochar, carbon–silica composite, carbon and silica materials were determined from Infrared spectra (500 cm⁻¹ to 4000 cm⁻¹) taken in a PerkinElmer Spectrum One instrument, in transmittance mode (KBr pellets, 32 scans).

Thermal analysis (TGA): The thermogravimetric profile of composite hydrochar materials was obtained in air and nitrogen, at 10 °C min⁻¹, from 25 °C to 600 °C, in a TA instrument TGA Q500 V6.7 Build 203 (TA Instruments Universal Analysis 2000 Version 4.2E (4.2.038) software). The carbon content was calculated from the difference between the residual mass in these two atmospheres above 600 °C.

Table 1
Reactions systems for synthesis of different kind of materials (S3* is a reaction mixture prepared without HCl).

System	Hydrothermal conditions (sealed system)	Drying conditions (solvent elimination in open system)	Carbonization temperature
S1	60 °C (72 h), 110 °C (24 h)	110 °C (6 h), 160 °C (6 h)	900 °C
S4	60 °C (24 h), 110 °C (24 h)	110 °C (6 h), 160 °C (6 h)	900 °C
S2	110 °C (24 h)	110 °C (6 h), 160 °C (11 h)	900 °C
S3*	110 °C (24 h)	110 °C (6 h), 160 °C (11 h)	900 °C
SB	100 °C (24 h)	100 °C (6 h), 160 °C (6 h)	600 °C
SF	100 °C (3 h)	100 °C (6 h), 160 °C (6 h)	600 °C
SH	160 °C (3 h)	100 °C (6 h), 160 °C (6 h)	600 °C
SD	180 °C (3 h)	100 °C (6 h), 160 °C (6 h)	600 °C

Porosity: The nitrogen adsorption–desorption isotherms were measured for the materials, activated under vacuum at 250 °C for 12 h, in a Micromeritics ASAP 2020 instrument at 77 K. The porous parameters were calculated from different known models by using software of the instrument (Micromeritics Data Master V 4.03): microporous, mesoporous and total area (t-plot, BJH and BET models, respectively); microporous, mesoporous and total pore volume and size (Horvath–Kawazoe, BJH and BET models, respectively).

Scanning Electron Microscopy (SEM): The materials were covered with Au, at high vacuum and analyzed in a JEOL JSM-6490LV SEM instrument. The SEM images and electron diffraction spectra (EDS) were obtained.

Transmission Electron Microscopy (TEM): The materials were covered with Au, at high vacuum and analyzed in a FEI instrument, TECNAI 20 Twin - angio 200 Kv model. The TEM images were obtained.

Zeta potential: It was measured in a Horiba Zeta Potential instrument, for samples dispersed in water at pH 7.0 (25 mM potassium phosphate) and 25 °C.

Water dispersibility and potential application as support for enzyme immobilization: A 1.00 g of S4-CS composite material (carbonized at 600 °C) was dispersed in aqueous buffer solution (25 mM potassium phosphate), at pH 7.0 and 25 °C. After that, 10 mg of lipase QL from *Alcaligenes* sp. was offered to this support (110 IU g⁻¹ support) and the immobilization occurs by interfacial adsorption [16–18] in the porous and external surface of the composite materials after 1 h of contact. The protein loading efficiency was calculated as the ratio of loaded to offered protein. Bradford method was used for quantifying the protein [20]. The expressed activity of the loaded (immobilized) lipase (IU g⁻¹ support) for the hydrolysis of 0.4 mM pNPB at 25 °C and pH 7.0, was determined by UV–Vis spectroscopy at 348 nm [18]. One international unit of lipase QL activity (IU) was defined as the amount of enzyme that hydrolyzes 1 μmol of pNPB per minute under these conditions. The immobilization efficiency in terms of activity was calculated as the ratio of expressed and offered activity per gram of support.

3. Results and discussion

The synthesis of the carbon–silica composite materials was carried out by steps: hydrothermal synthesis at low and high temperature, elimination of the solvent in an open system and carbonization of the obtained hydrochar (Table 1). The elimination of the silica or carbon, through well-established procedures, led to carbonaceous and siliceous materials, respectively. The micellar reaction mixture, the composite materials and their respective carbonaceous and siliceous counterparts were characterized in function of the hydrothermal synthesis conditions.

3.1. Study of the micellar reaction mixture

The micellar system was evaluated by DLS. The main hydrodynamic diameter of the Triton X-100 micelles in aqueous acidic solution (2 M HCl) is 13 nm. The addition of sucrose and sulfuric acid displaces this diameter toward minor values but the polydispersity is increased. These results are due to the dehydrating effect of the sulfuric acid, which favors the decreases of size and at the same time, the cross linking of PEG chains of the Triton X-100. The presence of unhydrolyzed TEOS, which is located in the micellar core due to its hydrophobic character, increases the average micelle hydrodynamic diameter (Fig. 1a).

A bimodal hydrodynamic size distribution is observed in the reaction system after its heating at 60 °C for 24 h, probably due to the presence of micelles and nanoparticles. These are formed in the reaction system from polycondensation and aggregation of carbon and silica species (Fig. 1b). Only the DLS signal for the big species remains if the heating is continued at 100 °C for 24 h (S4 system, Fig. 1b). This indicates the incorporation of the micelles into hydrochar nanoparticles.

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