Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 133 (2014) 619–625

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Infrared and Raman spectroscopic characterization of some organic substituted hybrid silicas

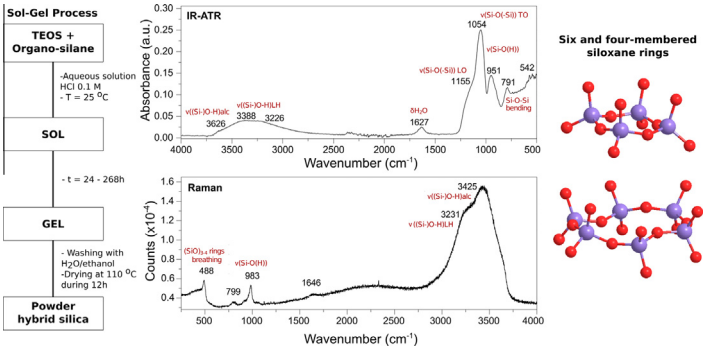
Larissa B. Capeletti [a], Ione M. Baibich [a], Ian S. Butler [b], João H.Z. dos Santos [a,*]

[a] Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre, Brazil
[b] Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal H3A 2K6, Canada

HIGHLIGHTS

- Hybrid silica studied by infrared and Raman spectroscopies.
- Raman can efficiently describe the different organic groups.
- Infrared was useful to evaluate the silica network and Si—O bond related bands.
- Four and six-membered siloxane rings formation were also outlined.
- Infrared and Raman techniques were complementary for hybrid silica characterization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2014
Received in revised form 16 May 2014
Accepted 28 May 2014
Available online 7 June 2014

Keywords:
Hybrid silica
Organosilanes
Sol–gel process
Infrared and Raman spectroscopy

ABSTRACT

Nine hybrid silicas bearing the organic substituent groups methyl, octyl, octadecyl, vinyl, phenyl, mercaptopropyl, isocyanatopropyl, chloropropyl and glycidoxypropyl were synthesized by an acid-catalyzed, hydrolytic sol–gel process. The resulting solid materials were characterized by their absorbance and attenuated total reflection (ATR) IR and Raman spectra. The latter technique proved to be particularly useful in the identification of the organic moieties in the hybrid silicas. The effect of the presence of the organic groups on the silica networks was also investigated – there were increases observed in both the Si—O—Si bond angles and bond lengths. Moreover, deconvolution of the IR-active antisymmetric Si—O—Si stretching bands permitted detection of the four- and six-membered siloxane rings present in the silicas. There proved to be a greater number of four-membered rings on the surfaces of the particles. Both IR and Raman spectroscopy proved to be invaluable in the characterization of these hybrid materials.

Introduction

The term "hybrid material" is broadly used in a variety of different contexts. According to Yamada et al. [1], a hybrid material consists of a mixture of two or more materials with new properties that result from the formation of new electronic orbitals between each material, such as a covalent bond. In this sense, a mixed oxide produced by the combination of different metal precursors in a sol–gel process represents an example of a hybrid material [2] A similar definition has been advanced by Makisima [3] in which a hybrid material is considered to be a mixture of two or more materials, at the sub-micron level, with newly formed chemical bonds. Gómez-Romero and Sanchez defined hybrid materials as organic–inorganic materials or inorganic-biomaterials [4]. Their definition requires an atomic or nanometer level mixture of materials, but not necessarily the formation of new electronic orbitals or chemical bonds. In this case, the encapsulation of catalysts [5],

* Corresponding author. Tel.: +55 5133087238.
E-mail address: jhzds@iq.ufrgs.br (J.H.Z. dos Santos).

http://dx.doi.org/10.1016/j.saa.2014.05.072
1386-1425/

cocatalysts [6], pH indicators [7] or drugs [8] represent examples of hybrid materials. More pragmatic definitions consider hybrid materials as "a combination of two or more materials in a predetermined geometry and scale, optimally serving a specific engineering purpose" [9] or "as an intentional combination of two or more materials, complementing each other to have super-functions or new functions which component materials did not possess [10]". A critical review of the terms in vogue to describe hybrid materials has been published [11]. In the present manuscript, the expression hybrid materials, or more precisely hybrid silicas, refers to silicas that have been chemically modified with organic substituent groups.

Hybrid silicas have been the subject of numerous investigations in the literature. Recent examples of such materials embrace their use as super-hydrophilic coatings [11], scaffolds for bone tissue engineering [12], scratch-resistant hybrid coatings [13], thermo/pH-sensitive drug carriers [14] or coatings for the corrosion protection of carbon steel [15]. In previous studies, we have reported the synthesis of silicas containing encapsulated indicators, prepared by different sol–gel routes [7,16]. As an extension of this research we have investigated the encapsulation of such molecules in hybrid silicas containing different organic substituent groups. The aim of such modifications is to evaluate the effect of the introduction of organic moieties on the performance of the materials with changes in pH. It is worth emphasizing that the introduction of organic groups may provide alternative if not better compatibility of such materials with other matrices, such as polymers. The characterization of the networks themselves and of the presence of the organic groups within the inorganic domains of these materials plays an important role in their properties. Infrared and Raman spectroscopy are known to be powerful techniques for identifying the local environment and structure of hybrid silicas and hybrid materials.[17–19]. In the present paper, we have focused on the structural characterization of several hybrid silicas that were later employed to prepare colorimetric based sensors. These materials were investigated by absorbance and ATR-IR and Raman spectroscopy, the results of which measurements may well serve to guide in the development of new sensor materials with improved or differentiated performance.

Materials and methods

Materials

Tetraethoxysilane (C_0) (TEOS, Merck, 98%), methiltriethoxysilane (C_1) (Sigma Aldrich, X%), octyltriethoxysilane (C_8) (Dow Corning, X%), octadecyltrimethoxysilane (C_{18}) (Sigma Aldrich, 90%), vinyltrimethoxysilane (Vy) (Dow Corning, 98%), phenyltrimethoxysilane (Ph) (Dow Corning, 97%), mercaptopropyltrimethoxysilane (SHp) (Sigma Aldrich 98%), isocyanatepropyltriethoxysilane (NCOp) (Sigma Aldrich, 97%), chloropropyltrimethoxysilane (Clp) (Wacker silicones, 98%) and glycidoxypropyltrimethoxysilane (Gp) (Sigma Aldrich 98%) were used as received. Hydrochloric acid (Nuclear, 38%) was employed as the catalyst in 0.2 M aqueous solution.

Hybrid silica synthesis by sol–gel method

In a typical preparation by the acid hydrolytic sol–gel route, 12 mL of a mixture of TEOS and the organosilane in the molar ratio 5:1 was employed. To this mixture 6 mL of a 0.2 M HCl aqueous solution were added while stirring magnetically. After gelification (from 3 to 168 h depending on the organosilane), the monoliths were milled, washed with a mixture of water/ethanol 1:1 (v/v) and dried over a period of 24 h at 110 °C.

Attenuated total reflectance infrared spectroscopy (ATR-IR)

The ATR-IR spectra were recorded at room temperature on a Bruker spectrometer (Alpha T model) in the absorbance mode. The spectra were measured over the range of 4000–400 cm^{-1} (38 scans, 4 cm^{-1} resolution).

Fourier transform IR spectroscopy (ATR-IR)

The IR spectra of the sensor materials and the silica were also obtained using a Varian 640-IR instrument in the absorbance mode by coadding 32 scans at 4 cm^{-1} resolution. The spectra were measured in the 4000–400 cm^{-1} range. The samples were pressed into tablets of approximately 1 mm in thickness and 5 mm in diameter. A dilution of approximately 10% was prepared in dried KBr. Band deconvolution was performed using Gaussian curves in the 1350–1000 cm^{-1} region.

Raman spectroscopy

Measurements were performed at room temperature using an inVia Renishaw Raman spectrometer equipped with NIR diode laser (514.5 nm), a CCD detector, a 1200 lines/mm diffraction grating and edge filter. The samples were mounted on a manual stage of a Leica microscope and the laser beam was focused onto the samples through a 20× long-working distance objective. The spectra were recorded using a laser power at about 15 mW and a slit width of 50 μm. Several scans were collected in order to improve the signal-to-noise ratio. The acquisition time was varied from sample-to-sample in the range of 10–20 s. The Raman spectrometer was calibrated prior to the measurements using a Si wafer placed under the microscope and by performing the automatic offset correction. The data acquisition and analyses were accomplished using the proprietary WiRE™ software. The peak positions are estimated to be accurate to at least ±1 cm^{-1}.

Response time tests

Response time tests were performed for pH indicator Alizarin red encapsulated within the hybrid silicas. Samples were prepared according to the same protocol employed for the synthesis of hybrid silicas (Section 'Hybrid silica synthesis by sol–gel method'). The tests were carried out using a NH_3 gas atmosphere in a closed glass system consisting of two vessels connected by a Rotaflow® valve. In a typical test, a given mass of sensor was placed in contact with the gas generated by a standard volume of NH4OH concentrated solution (29% w/v) at room temperature, as described in a previous study [16] The response time was measured between the time of opening the valve to the time when the color change could be observed with the eye.

Results and discussion

ATR-IR and Raman spectra

The nine hybrid silicas were analyzed by IR and Raman spectroscopy and the spectra observed are discussed below. For comparative reasons, a silica sample prepared in the absence of any organosilane (SG-C_0), i.e., obtained solely from TEOS, was also analyzed. Fig. 1 shows the IR and Raman spectra for SG-C_0. This sample was used as the control sample to evaluate the silica bands and its network vibrations.

From the SG-C_0 IR spectrum, it was possible to identify all the main bands of silica. The high wavenumber region (3600–3000 cm^{-1}) exhibits bands due to the stretching modes ν(O—H)