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Silica and silica organically modified nanoparticles: Water dynamics in complex systems

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ABSTRACT

Four silica-based porous nanosystems were synthesized with different organic substitutes and the molecular dynamics of water in these constrained environment was investigated. The nanosystems were silica and three organic modified silica nanoparticles (NP) with diameters in the range 80–300 nm with different porous dimensions, surface areas, and surface properties (e.g. hydrophilicity/hydrophobicity). Molecular dynamics was studied by pulsed field gradient NMR and by proton spin-lattice relaxation in a broad range of Larmor frequencies. A coherent analysis of the diffusion coefficients and spin-lattice relaxation data is presented taking into account a relaxation model associated to water molecular dynamics in close contact with NP surfaces. From our results it was possible to access the details of the water molecular movements in the nanosystems and to single out two water populations presenting distinct molecular dynamics. Characteristic distances for water rotations mediated by translational diffusion were estimated in consistency with the NP's dimensions and pores sizes obtained by TEM and BET experimental techniques. This knowledge has both fundamental and practical relevance since these NP have applications in nanomedicine, not only in therapy but also in diagnostic procedures and more recently in theranostic.

1. Introduction

Due to their large surface area microporous and mesoporous solids have a huge range of applications like in catalysis and adsorption processes. In the form of nanoparticles these materials gain an additional interest since the large surface area/volume ratio is of extreme importance and carefully studied surface effects can be turned to achieve enhanced properties for particular applications. Microporous and mesoporous nanoparticles are also a very interesting media to study molecular dynamics of small molecules (e.g. water molecules) in complex and constrained environments. It is known that the local molecular organisation and dynamics of water molecules near interfaces or in porous is modified [1,2], as the ”bulk” water structure resulting from a balance between the hydrogen bonds' ordering and the thermal motions is seriously affected by the presence of solid interfaces in the nanoscale. The knowledge of water interaction with surfaces is important for a great variety of scientific domains like: electronics, biology, chemistry, environmental sciences. The molecular dynamics of water in mesoporous and microporous nanosystems is of particular importance, as they have a strong presence in biomedical applications [3]. Several parameters influence the water/surface organization, for instance the hydrophilicity/hydrophobicity of the solid surface. Different studies indicate that the modified layer of water due to the surface has a thickness around 10 Å [1].

Silica nanoparticles (SiO_2) are widely used in biomedical applications such as in drug delivery, cell tracking, gene transfection [4], and as coating of superparamagnetic nanoparticles used as contrast agents for Magnetic Resonance Imaging (MRI) [5]. Recently, it was reported that in vivo toxicity of (SiO_2) was mainly influenced by nanoparticles' porosity and surface characteristics [6].

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In this work, water dynamics in four silica and organic modified silica (ORMOSIL) nanoparticles will be investigated and the results will be compared with those obtained for bulk water studies [7].

2. Materials and methods

Tetraethylorthosilicate (TEOS) was purchased from Merck, 3-aminopropyltriethoxysilane (APTES), (3-Glycidoxypropyl)methyldiethoxysilane (GPTMS), aqueous ammonia solution (NH_4 OH, 28%) and aqueous sodium silicate solution ($Na_2O \cdot SiO_2$, 27 wt.% SiO_2) (SSS) were purchased from Sigma–Aldrich, and ethanol (CH_3CH_2OH, EtOH) were obtained from Panreac. In Fig. 1 are presented the chemical formulae of the TEOS, APTES and GPTMS precursors used for the sol–gel inorganic and hybrid silica nanoparticles.

2.1. Synthesis of sol–gel inorganic and hybrid silica NP

Inorganic and hybrid silica NP were grown following the LaMer method, a bottom-up base-catalyzed sol–gel approach. The most common bottom-up approach for silica/ORMOSIL nanoparticles is the reverse microemulsion process. However, besides having low yields reverse microemulsion process uses a large amount of potentially toxic surfactants and organic solvents, and demands extensive washing before any biological application, to avoid disruption or lyses of biomembranes by the surfactant molecules, rendering the process slow, expensive and not environmental-friendly. The sol–gel Stöber's method [8] arises as an eco-friendly alternative, where the hydrolysis and condensation of a mixture of alkoxysilanes takes place in mild basic aqueous medium, to create monodisperse, spherical, electrostatically-stabilized particles. Although parameters such as solvent, temperature, base concentration, and water to TEOS ratio can be adjusted to control the particles' size and dispersion, regular shape silica NP (<100 nm) are difficult to obtained.

The LaMer method, supported on the protocols by Arkhireeva et al. [9] and Buining et al. [10], allowed the synthesis of ORMOSIL NP (<100 nm), at room temperature, in less than 1 h. This was achieved by using aqueous sodium silicate solution (SSS) as a nucleating agent, and a combination of inorganic TEOS and hybrid silica precursors according to [11]. First, aqueous sodium silicate solution (SSS) (2.2 wt.% SiO_2) was ultrasonicated for 15 min. An aliquot of 300 μl was diluted with 25 ml of ethanol, under magnetic stirring (15 min). A mixture, of 13 ml of ethanol and 28 ml of ammonia solution, was then added to the suspension and stirred for an extra 5 min. Second, a 1500 ml mixture of the inorganic/hybrid silica precursors, with different TEOS:ORMOSIL ratios presented in Table 1, was added to the suspension, under stirring. The sol was then stirred for half an hour before centrifuge and washed with ethanol and bi-distilled water.

Aiming to prepare monodisperse ORMOSIL NP, the rate of addition of the precursors, reaction time, water, ammonia solution concentrations, were optimized.

Table 1
NP composition in molecular percentage.

NP	APTES	TEOS	GPTMS
APTES	10	90	–
GPTMS 9:1	–	90	10
GPTMS 5:5	–	50	50
TEOS	–	100	–

Four nanoparticles systems were prepared: TEOS, GPTMS 9:1, APTES, and GPTMS 5:5. In GPTMS 9:1 and APTES NP one in ten Si atoms are linked to organic groups. In GPTMS 5:5 one in two Si atoms are linked to the organic groups. Therefore, GPTMS 9:1 and APTES are slightly modified TEOS nanoparticles in comparison with the GPTMS 5:5 NP.

2.2. Transmission electron microscopy

Particles' morphology features, size (static diameter -TEMD) and size distribution were studied by transmission electron microscopy (TEM). TEM micrographs were obtained using a Hitachi H-8100, using an applied tension of 200 kV. To analyse the samples, a droplet of the suspension was deposited on the copper grid and dried at room temperature.

2.3. Porosimetry

N_2 adsorption/desorption isotherms of the four NP where obtained and exhibit a characteristic type IV isotherm as expected for a porous SiO_2 material. From these studies the porosity and pores diameters of the NP was obtained.

Each nitrogen adsorption isotherm was obtained at 77 K in a gas posimeter, model ASAP 2010, Micromeritics. The samples were degassed at 150 °C for at least 6 h.

The bulk density of the NP was obtained from Hg adsorption. The mercury intrusion and extrusion data was obtained in a mercury porosimeter, model Autopore IV 9500, Micromeritics.

2.4. NMR studies

The obtained NP where dried in a stove for several days. For each of the NP 30 mg was transferred to a 5 mm standard NMR tube and bi-distilled water was added just to cover the NP. The prepared samples where closed and left to stabilise for 24 h, before measuring.

2.4.1. PFG NMR

Water diffusion coefficients were measured in a 7 T Bruker Avance III NMR spectrometer with a pulsed gradient stimulated echo sequence [12], using 16 values of magnetic field gradient with a maximum value of 147 G/cm and a gradient pulse length of 1 μs. Each signal was averaged 8 times to allow for phase cycling compensation. The measurements were performed at 25 °C. Each

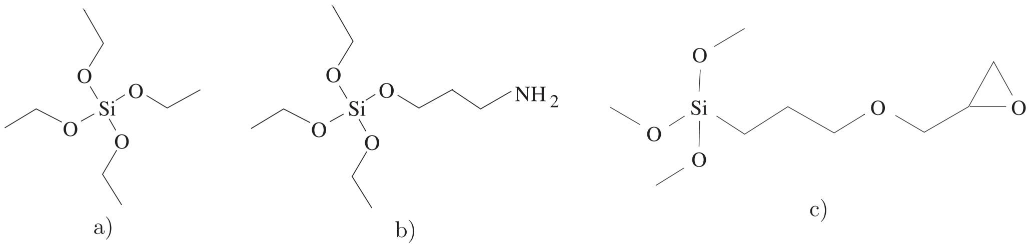

Fig. 1. Chemical formulae of the NP precursors: a) TEOS, b) APTES, c) GPTMS.