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Halloysite nanotube with fluorinated lumen: Non-foaming nanocontainer for storage and controlled release of oxygen in aqueous media

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ABSTRACT

Halloysite clay nanotubes were selectivity modified by adsorbing perfluoroalkylated anionic surfactants at the inner surface. The modified nanotubes formed kinetically stable dispersions due to the enhanced electrostatic repulsions exercised between the particles. We proved that the modified nanotubes can be used as non-foaming oxygen nanocontainers in aqueous media. The gas release from supersaturated dispersions can be controlled by external stimuli and system composition. In conclusion, we managed to put forward an easy strategy to develop smart materials from natural nanoclays, which can endow important applications like the storage and delivery of gas.

1. Introduction

Covalent or non-covalent nanoparticle modification is a well known strategy to design new target properties. Sustainable nanoparticles are represented by clays available with different shapes, sizes and surface chemical properties. Most common clay nanoparticles possess a nanolayered morphology, such as kaolin and montmorillonite. Notwithstanding, there are natural nanoclays with hollow tubular shape [1,2] of great scientific interest due to potential applications. Promising nanoclays as nanocontainers with controlled release properties are imogolite [1] and natural halloysite (HNT) [2]. Besides the interesting properties, imogolite presents a certain toxicity [3]. Halloysite mineral is well known [4] since 1946 but its application in smart sustainable materials has been proposed only a few years ago [2]. HNT is abundant, durable and biocompatible and, furthermore, it is cheap compared to synthetic nanomaterials with similar morphology. HNT is generated by rolling-up a kaolin sheet with a still unknown mechanism; its size ranges between 0.5 and 1 μm in length and between 15 and 100 nm in the inner diameters [2].

The different chemistry of the inner and the outer surfaces makes HNT a tremendous tool. Being that the external surface is composed of Si–O–Si groups and the internal surface of a gibbsite-like array of Al–OH groups, the aqueous acid–base equilibria confer negative and positive charges, at the outer and inner surfaces respectively, in a wide pH range [5,6]. Consequently, selective adsorption of ionic species may strategically control the charge. The hydrophobic modification of HNT lumen with anionic surfactant stabilized successfully nanotubes in water [7] as a consequence of canceling the positive charges at the surface due to the entrapment of the anionic molecule into the HNT lumen generating a large net negative charge. Nanotube applications have been proposed for controlled release in healing anticorrosion [8,9], water purification [10], polymer composites [11,12] and antimicrobial coatings [13]. The covalent modification of the inner surface generated HNT able to incorporate more ferrocene than pristine nanoclay [14]. To the light of the phase behaviors of HNT dispersion, those nanoparticles are considered strategic for fabrication of long-range ordered nano-objects [15]. Thus, development of tube-like materials with tunable properties is one of the most scientific challenges.

We report the modification of HNT lumen by incorporating perfluoroalkylated anionic surfactants. This was done with the intent at obtaining rather stable colloidal dispersions in water with enhanced oxygen solubilization ability. Fluorinates are well established for chemical and biological inertness, fire extinguishing and flame retardant materials [16]. Finally, fluorinated biocompatible surfactants have been proposed as oxygen carriers in biomedical applications [17].

2. Experimental section

2.1. Materials

Halloysite nanotubes (HNTs) and kaolin are Sigma products. Perfluorooctanoic acid (PFC8H), Perfluoroheptanoic acid (PFC7H)

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and Perfluoropentanoic acid (PFC5H) from Fluka were crystallized from carbon tetrachloride and dried at room temperature. Their sodium salts (NaPFC8, NaPFC7 and NaPFC5) were prepared by neutralization with an aqueous sodium hydroxide solution. The products were crystallized twice from an ice-cold solution and dried in a vacuum oven at 60 °C for at least 4 days before their use. The structure of the surfactants is given in Chart 8.

Water from reverse osmosis (Elga model Option 3) with a specific resistivity greater than 1 MΩ cm was used.

2.2. Preparation of surfactants functionalized HNTs

To aqueous surfactant solutions (0.1 mol kg^{-1}) 0.02 g cm^{-3} of HNTs was added. The obtained dispersions were magnetically stirred for ca. 1 day. Afterward, they were taken in a vacuum oven at 50 °C and at 100 mbar overnight. The solid was separated by centrifugation and rinsed several times with water until the surface tension of the supernatant was close to the value for pure water (ca. 72 mN m^{-1}). This ensures the absence of unbound surfactant. All of the solids dried at 80 °C were investigated by means of thermogravimetric analysis (TG) to estimate the surfactant loading into the HNT lumen.

2.3. Methods

ζ-potential and dynamic light scattering (DLS) measurements were carried out by means of a Zetasizer NANO-ZS (Malvern Instruments). The field-time autocorrelation functions were well described by a single decay, which provides the decay rate (Γ) of the diffusive mode. For the translational motion, the collective diffusion coefficient at a given concentration is $D_t = \Gamma/q^2$ where q is the scattering vector given by $4\pi n\lambda^{-1}\sin(\theta/2)$ being n the water refractive index, λ the wavelength (632.8 nm) and θ the scattering angle (173°).

The functionalized nanotubes were imaged by using a microscope ESEM FEI QUANTA 200F. The measurements were carried out in high vacuum mode (<6×10^{-4} Pa) for simultaneous secondary electron, the energy of the beam was 30 kV and the working distance was 10 mm. Before each experiment, the sample was coated with gold in argon by means of an Edwards Sputter Coater S150A to avoid charging under electron beam.

The thermogravimetric analyses were done by using a Q5000 IR apparatus (TA Instruments) under the nitrogen flow of 25 cm^3 - min^{-1} for the sample and 10 cm^3 min^{-1} for the balance at the heating rate of 10 °C min^{-1}. Temperature spanned from ambient to 900 °C. The surfactant:HNT ratio was determined from the residual mass by taking into account for the water content as reported in the literature [16,12].

The densities ($\pm 1 \times 10^{-6}$ g cm^{-3}) and speed of sound (±0.1 m s^{-1}) of the liquid dispersion were determined at 25.000 ± 0.001 °C by using a density and sound velocity meter (DSA 5000 M, Anton Paar).

The specific volume of pristine or modified HNTs (v_{sp}) was calculated as follows

$$v_{sp} = 1/d - 10^2(d - d_0)/(C_S \times d \times d_0) \quad (1)$$

where d and d_0 are the dispersion and water densities, respectively; C_S is the concentration of solid material into the dispersion in g/100 g of solvent. The isentropic compressibility coefficients of the dispersions (β) were obtained as $100/(u^2 \times d)$ being u the ultrasonic velocity of the dispersion. The specific isentropic compressibility (k_s) was calculated using the following equation.

$$k_s = v_{sp}\beta + 10^2(\beta - \beta_0)/(C_S \times d_0) \quad (2)$$

where β_0 is the isentropic compressibility coefficients of water and the other symbols have the same meaning as above.

The sedimentation volume of pristine and modified HNTs was determined by using tubes of borosilicate glass with an inner diameter of ca. 2.3 mm and length of ca. 125 mm. The tubes were filled with the dispersion and left to equilibrate in vertical position. Two phases were observed, an upper transparent phase and a lower milk-like phase. The transparent upper phase is water according to the density value. On this basis, the concentration of either HNTs or functionalized HNTs in the lower phase (C_{LP}) was determined as $C_{LP} = C_S/R_{LP:T}$, where C_S is the stoichiometric initial concentration of material in water, $R_{LP:T}$ is the V_{LP}/V_T ratio being V_T and V_{LP} the total and the lower phase volumes, respectively. The tubes were imaged and $R_{LP:T}$ was estimated from the height of the meniscus in the capillary by using an image analyzer software (ImageJ 1.43u).

The oxygen desaturation curves were obtained by using a HD22559.2 apparatus (Delta Ohm). Water, HNT and modified HNT aqueous dispersions (ca. 15 cm^3) were saturated with oxygen by bubbling the pure gas for ca. 1 h. The oxygen concentration was registered every 2 min. The experiments were carried out under static conditions and under magnetic stirring at 1250 rpm. The oxygen concentration was normalized for the solubility of the gas in water, $[O_2]_{sat}$, at the experimental conditions (25 °C and 1 atm).

3. Results and discussion

The alumina inner surface of the nanotube was selectively modified with perfluorinated anionic surfactants rendering the total charge of the nanotube significantly changed. The as prepared hybrid nanotubes exhibit an enhancement of stability in water and a core to successfully entrap oxygen in aqueous media.

3.1. Physico-chemical characterization of functionalized Halloysite nanotubes

The amount of surfactant adsorbed onto the HNT (Table 1) was estimated from the thermogravimetric analysis from the residual mass by taking into account for the water content as reported in the literature [16,12]. These values are far below the maximum loading ability of HNTs being that the hollow cavity represents ca. 10% of the nanoclay volume. By assuming an adsorbed surfactant monolayer and considering 760 m^2 g^{-1} for the occupied area of NaPFC8 at the alumina/water interface [19], one calculates the surfactant loading of 0.90 wt% that is in straightforward agreement with the experimental value (Table 1). These calculations cannot be extended to NaPFC7 and NaPFC5 because, to the best of our knowledge, no adsorption data at the alumina/water interface are available; nevertheless, it is expected a behavior rather comparable in terms of area per molecule if an extended chain configuration is considered [19]. From experimental loading data one can conclude that NaPFC7 and NaPFC5 did not fully cover the HNT lumen.

Table 1
Surfactant loading, diffusion coefficient and ζ-potential for HNT/surfactant hybrid materials[a].

	Surfactant loading	$D^\circ \times 10^{12}$	ζ-potential
HNT		1.5; 0.94[b]	−21; −19.6[b]
HNT/NaPFC5	0.29	1.2	−27
HNT/NaPFC7	0.62	1.0	−29
HNT/NaPFC8	0.86	0.90	−32

[a] Units are: surfactant loading, wt%; D°, m^2 s^{-1}; ζ, mV. Errors are: surfactant loading, 4%; D°, 5%; ζ, 4%.
[b] From Ref. [7].