Core–shell nano-architectures: The incorporation mechanism of hydrophobic nanoparticles into the aqueous core of a microemulsion

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A B S T R A C T

This work presents an in-depth investigation of the molecular interactions in the incorporation mechanism of colloidal hydrophobic-capped nanoparticles into the hydrophilic core of reverse microemulsions. [1]H Nuclear Magnetic Resonance (NMR) was employed to obtain molecular level details of the interaction between the nanoparticles capping amphiphiles and the microemulsion surfactants. The model system of choice involved oleic acid (OAC) and oleylamine (OAM) as capping molecules, while igepal-CO520 was the surfactant. The former were studied both in their "free" state and "ligated" one, i.e., bound to nanoparticles. The latter was investigated either in cyclohexane (micellar solution) or in water/cyclohexane microemulsions. The approach was extremely useful to gain a deeper understanding of the equilibria involved in this complex system (oleic acid capped-Bi_2S_3 in igepal/water/cyclohexane microemulsions). In difference to previously proposed mechanisms, the experimental data showed that the high affinity of the capping ligands for the reverse micelle interior was the driving force for the incorporation of the nanoparticles. A simple ligand-exchange mechanism could be ruled out. The collected information about the nanoparticle incorporation mechanism is extremely useful to develop new synthetic routes with an improved/tuned coating efficiency, in order to tailor the core–shell structure preparation.

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1. Introduction

Core–shell nano-architectures have attracted great interest for their high added value applications [1–9], since the formation of shells around colloidal nanoparticles yields composites with significantly different properties, when compared to those of their core (e.g., increased stability, adhesion, surface area, magnetic and optical properties). In the literature, several approaches are reported for shell fabrication, such as surface chemical reactions, precipitation of inorganic salts, reverse microemulsion formation, sol–gel and seed-mediated growth processes [3]. All these synthetic strategies have both advantages and drawbacks, each of them resulting in a different shell uniformity, thickness, and composition. Procedures that employ preformed nanoparticles and make use of reverse micelles as nano-reactors for shell growth are widely considered to be among the most efficient approaches to obtain a highly homogeneous coating, especially with silica [10–19].

In particular, the igepal/cyclohexane/water microemulsion is considered to be the most efficient technique. Both hydrophilic [18] and hydrophobic [13–15,17] nanoparticles can be coated, resulting in monodisperse core–shell nanostructures with tunable shell thickness. Recently, some of the authors have reported the synthesis of core/shell $CoFe_2O_4/SiO_2$ nanoparticles, based on the igepal/cyclohexane/water microemulsion, starting from both hydrophilic [20] and hydrophobic [21] nanoparticles. However, while on the one hand, a hydrophilic nanoparticle naturally tends to enter the aqueous core of the reverse microemulsion, on the other hand, a hydrophobic nanoparticle should be expected to have the tendency to disperse in the nonpolar solvent. Thus, the coating process, which takes place inside the microemulsion core, should be inhibited for the latter. Surprisingly, the coating process was found to be more efficient in the case of hydrophobic nanoparticles. Such an unexpected behavior aroused much interest in the scientific community, but only few authors proposed a theory, Selvan et al. [16] suggested the exchange of hydrophobic capping agents by igepal, Darbandi et al. [22] by tetraethyl orthosilicate

(TEOS), while Zhang and coworkers [14] proposed a mechanism involving the tail-to-tail intercalation of oleic acid (OAC) in the nanoparticles' capping layer with igepal CO520, and the subsequent interaction of the igepal's polar head groups with water to form an external water shell. In any case, direct evidence for the proposed mechanisms was not provided. Recently, Koole et al. [13] reported convincing experimental data from an in-depth time-resolved fluorescence spectroscopy investigation. They showed that both igepal and hydrolyzed TEOS do replace the original hydrophobic amine ligands of quantum dots, facilitating the successive transfer of the latter into the hydrophilic interior of the reverse microemulsion. They have also shown that, the stronger the ligand nanoparticle binding, the more hindered is the replacement by TEOS or igepal. However, this model only describes the mechanism from a phenomenological point of view, but no details are given about the molecular interactions involved.

The present work aims at elucidating the mechanism for incorporation of hydrophobic nanoparticles into the hydrophilic cores of reverse microemulsions, with the inter-molecular interactions involved between the capping ligands and the non-ionic surfactant igepal CO-520 being our focus. Liquid-state Nuclear Magnetic Resonance spectroscopy (NMR) has been the method of choice. First, a careful analysis was carried out on the interactions between free ligands (i.e., in the absence of nanoparticles) and either the igepal reverse micelles (in cyclohexane) or the corresponding liquor ammonia and water microemulsions. The collected information was fundamental when, following the same approach, OAC-capped Bi_2S_3 nanoparticles were used in the successive stage. Besides monitoring chemical shift and multiplicity variations for selected ^1H-NMR resonances, the $MnCl_2$ was also employed as a paramagnetic probe to estimate the insertion depth of the capping agents in the igepal micelles or in the microemulsions. The diamagnetic Bi_2S_3 has been the model-system of choice instead of the previously employed $CoFe_2O_4$, due to the ferrimagnetic properties of the latter, that results in extreme nmr line broadening, making the system difficult to investigate. The chosen nanoparticles are shown to be silica-coated to the same degree as the cobalt ferrite, thus representing a valuable model to get more general information about the aforementioned incorporation mechanism. The NMR approach was found to be capable of providing fundamental details about the complex equilibria involved in this kind of synthesis, being not only interesting for the specific system here investigated, but also as a more general route to compare different ligands and/or surfactants before undertaking the synthesis trials.

2. Materials and methods

2.1. Materials

Cyclohexane (CHX) was purchased from Panreac (Barcelona, Spain) at PA grade, while all the other chemicals were purchased from Sigma–Aldrich (St. Louis (MO), USA). In particular, polyoxyethylene (5) nonyl phenol ether, igepal-CO520 with an average M_n of 441 g/mol (hereinafter referred to simply as igepal), oleic acid (OAC; 90%), oleylamine (OAM; 70%), tetraethyl orthosilicate (TEOS; 98%), ammonia (NH_3 30% w/w), $MnCl_2$ (98%), and cyclohexane-d$_{12}$ (99.6 atm.% D) were employed.

2.2. Hydrophobic inorganic core, $CoFe_2O_4$ and Bi_2S_3 nanoparticles synthesis

OAC-OAM capped $CoFe_2O_4$ and OAC-capped Bi_2S_3 nanoparticles were prepared by following the procedures described in detail elsewhere [21,23,24].

2.3. Hydrophilic silica shell, core/shell $CoFe_2O_4/SiO_2$ and Bi_2S_3/SiO_2 nanoparticles synthesis

Silica coating of the hydrophobic nanoparticles was carried out as described in detail elsewhere [14,20,21]. Specifically, 0.56 mmol of the nonionic surfactant igepal was dispersed in 4 mL of CHX by sonication. Then, 300 μL of a CHX dispersion of hydrophobic nanoparticles (0.8 mg/mL for $CoFe_2O_4$ and 8 mg/mL for Bi_2S_3), previously sonicated for a few minutes, was added, and the mixture was vigorously stirred at room temperature for 15 min. TEOS (20 μL) was added, and the resulting mixture stirred for 30 min, prior to liquor ammonia (35 μL) addition. The reaction was allowed to proceed at room temperature for 24 h under stirring.

2.4. Transmission electron microscopy

The colloidal suspensions were dropped on carbon-coated copper grids and observed in Bright-Field mode with a TEM (JEOL 200CX), operating at 200 kV. Particle size distribution was calculated on about 200 nanoparticles. Different images, obtained in bright-field mode, were analyzed with Adobe Photoshop determining the diameters manually.

2.5. Nuclear Magnetic Resonance spectroscopy

Five different groups of NMR samples were prepared: (i) cyclohexane solutions, (ii) liquor ammonia microemulsions, (iii) water microemulsions, (iv) paramagnetic probe microemulsions, and (v) OAC-capped Bi_2S_3 nanoparticles dispersions.

Cyclohexane (90% non-deuterated + 10% perdeuterated for frequency-lock) was always employed as solvent, and all the solutions have been prepared at room temperature (∼298 K).

(i) First, starting from a concentrated stock solution of either igepal, or OAC, or OAM, differently diluted samples were prepared in the 0.2–140 mM range for critical micelle concentration (CMC) determination. Then, OAC (2 mM) and OAM (2 mM) were investigated separately, or as a 1, 1 mixture. In particular, they have been studied either in the absence or in the presence of igepal at two different concentrations, namely, 2 and 140 mM, i.e., well-below and well-above the CMC (26.1 ± 0.8 mM, see the Supplementary Information (SI)).

It is important to stress here that, due to the crowding of the low-frequency region of the NMR spectrum, other authors [25] have chosen the homolog igepal-CA520 for their experiments. Nevertheless, we decided to use the CO520, which is the surfactant typically employed in the aforementioned synthesis protocols [14,15,20–22].

(ii) The "ammonia microemulsions" were obtained by addition of liquor ammonia (2% v/v) to a 140 mM solution of igepal, i.e. the same proportion as in the syntheses published by some of the authors [20,21]. Then, proper amount of OAC, OAM or both were added, up to 2 mM.

(iii) The "water microemulsions" were obtained exactly as the ammonia ones, employing distilled water.

(iv) The "paramagnetic probe microemulsions" were prepared using a $MnCl_2$ water solution, either 0.3, or 3.0 or 30.0 mM.

(v) OAC-capped Bi_2S_3 nanoparticles were dissolved either in the absence or in the presence of igepal (140 mM) reverse micelles. OAC final concentration was ∼2 mM. Then, the corresponding water microemulsion was prepared, either in the absence or in the presence of $MnCl_2$ (3.0 mM).