

Core-shell Structured Composite Silica Micro- and Nanoparticles with Ability Release a Defined Quantity „on Demand“

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The aim of this work was the preparation of biocompatible micro- and nanoparticles with a hollow interior. The particles must be able to encapsulate and store a chemical payload for a certain time, followed by the release on demand of this payload. In our previous work [13] we have prepared silica microparticles with a hollow core and found that the diffusion across the mesoporous silica shell was strongly dependent on temperature. In this work, we used this dependence and attached iron oxide nanoparticles on the surface of the silica shell to create composite iron oxide/silica particles. The iron oxide nanoparticles were able to heat up in the presence of an alternating magnetic field. This property allowed us to use magnetic field as a tool for remote control of diffusion across the particle shell. To avoid spontaneous leakage of encapsulated payload in time, we have modified the surface of the composite microparticles with a layer of palm oil. Palm oil is a phase change material which is solid under 37 °C. We showed that the resultant composite particles are able to store a payload for several months and release a defined quantity on demand by the application of a magnetic field. The particles were characterised in shape, size, heating ability and their mass transport properties.

Keywords: Silica, Radiofrequency field, Controlled release, Encapsulation.

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1. INTRODUCTION

In recent years there has been an increasing interest in iron oxide/silica composites. Due to their special properties such as large surface area and low material density these microparticles are very attractive as catalysts [1], microwave absorption materials [2] or in drug delivery systems [3]. Major methods for the preparation of iron oxide/silica composite microparticles are: sol-gel process [4]; layer-by-layer techniques [5]; coprecipitation [6] and surface reaction [7].

Coating applied to the surface of materials can improve its properties as it allows control of the interaction of a material with its environment [8]. Nowadays, the application range of coatings extends much beyond the simple decoration and protection aspects, and functional coatings have become an enabling technology in a vast variety of different high-tech areas. Fields in which such high-tech coatings are applied range from computer chips and hard disk manufacturing [8] to the use of special coatings in biomedical and aviation applications [9].

In this work, we introduce a fabrication method of hollow composite iron oxide/silica particles. The size, morphology and stability of the composite particles was systematically investigated and the effect of iron oxide:silica ratio on their heating rate and the release kinetics of a model compound (vitamin B12) was determined.

2. EXPERIMENTAL

2.1 Materials

Tetraethyl orthosilicate (TEOS, 98%), n-octylamine (99%), oleic acid (65-88%), acetone (99%), ammonium

hydroxide solution (25%), iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, n-heptane and palm oil were purchased from Sigma-Aldrich. Nitric acid (p.a., 65%) and ethanol were purchased from Fluka. All chemicals were used as received. Deionized water (Aqual 25, 0.07 μ S/cm) was used for all reactions and treatment processes.

2.2 Synthesis of iron oxide nanoparticles

The iron oxide nanoparticles used for this work were prepared by the co-precipitation method [10] and stabilized with oleic acid to make them dispersible in non-aqueous media. In a typical synthesis, 0.25 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.125 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 40 ml of deionised water in a three-neck flask equipped with a reflux condenser and heated to 80°C. Then 0.2 ml of oleic acid dissolved in 5 ml of acetone were added. Iron oxide precipitation was induced by adding 5 ml of NH_4OH ; the mixture was stirred at 500 rpm for the next 10 min, followed by five additions of 0.2 ml of oleic acid at 5 minute intervals. The mixture was stirred for another 30 min and then cooled down to ambient temperature. Dry iron oxide nanoparticles dispersible in non-aqueous media were obtained by freeze-drying.

2.3 Synthesis of composite iron oxide/silica microparticles

The fabrication of the composite iron oxide/silica microparticles was made in two steps: i) formation of hollow-core mesoporous silica microparticles by a liquid templating method [11, 12], followed by ii) coating of the external silica surface by iron oxide nanoparticles

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prepared as described in Section 2.2. The overall synthesis procedure is shown schematically in Fig. 1. In a typical synthesis, 10 ml of TEOS (silica precursor) was added into 10 ml of octylamine and the mixture was stirred at 800 rpm for 3 min at room temperature to create a dispersion of octylamine droplets in TEOS. This was followed by a quick addition of water (100 ml) acidified by 0.2 ml of nitric acid to promote the hydroly-

sis and polycondensation of TEOS around the octylamine droplets. The molar ratio of TEOS:OA:H₂O:HNO₃ was 1:1.36:113:0.05. After 3 min of reaction, the resultant microparticles were collected by centrifugation (5 min, 6000 rpm), washed with acetone and dried in air. Finally, the particles were calcined at 600 °C for 9 h in air to fully remove the organic template.

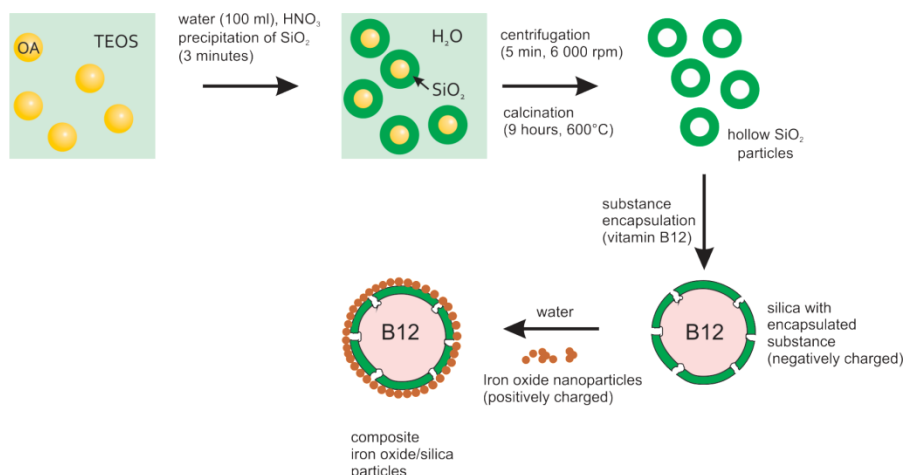


Fig. 1 – The scheme of preparation of composite iron oxide/silica particles

2.4 Particle characterisation

Scanning Electron Microscopy (SEM) images were taken on a Jeol JCM-5700 scanning electron microscope. The samples were sputter-coated with a 5 nm thin film of gold prior to imaging. Some particles were mechanically broken by using a mortar with a pestle in order to reveal their core-shell structure. The particle size distribution was evaluated by the laser diffraction particle size analyzer (Horiba Partica LA 950/V2). The temperature rise with time of prepared composite microparticles was measured by a 400 kHz, 2.5 kW generator of external alternating magnetic field (Power-Cube 32/400). The permeability of the composite iron oxide/silica shell was characterized indirectly by measuring the uptake/release kinetics using UV/VIS spectrophotometry (Specord 205 BU).

3. RESULTS

3.1 Size and morphology of prepared particles

The silica particles as well as the resultant compo-

site iron oxide/silica microparticles had a spherical shape (Fig. 2) with a relatively narrow size distribution (Fig. 4). The mean particle diameter was 26 μm for microparticles and 250 nm for nanoparticles. Five different composite particle samples with increasing iron oxide/silica ratio were prepared and further characterized (Table 1).

Table 1 – Sample codes and corresponding iron oxide/silica particle ratios used for the preparation of the composite microparticles.

Sample	Used mass ratio silica vs. iron oxide
1	1:0.0
2	1:0.1
3	1:0.2
4	1:0.4
5	1:0.8

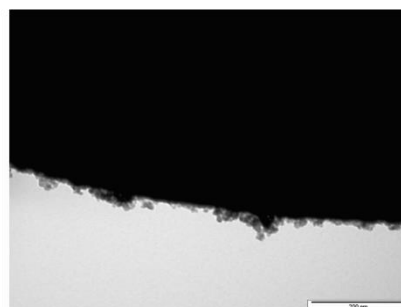
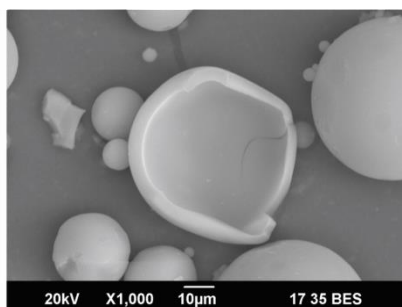
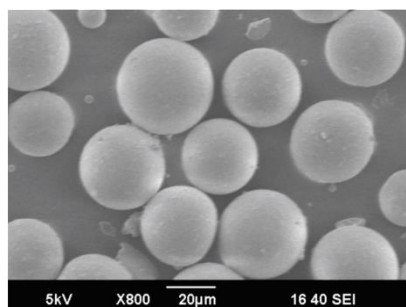


Fig. 2 – Composite silica microparticles, they core/shell structure and the detail from TEM microscopy on the surface of the composite shell.

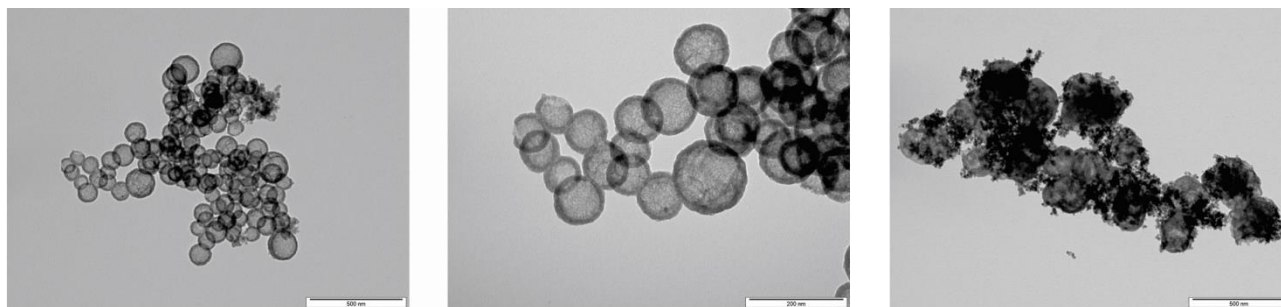


Fig. 3 – First two images are pure silica nanoparticles and the last one is composite iron oxide/silica nanoparticles.

3.2 Radiofrequency induced release

The composite particles loaded with the model compound (vitamin B12) can be stored in the dry state for several months without a loss of functionality. Once rehydrated, a step change in the release rate can be induced by the application of the RF magnetic field, which causes local heating of the microparticles. Figure 4 shows the time-dependence of the quantity released in the case of seven cycles consisting of 5 min of RF field ON, followed by 20 min of RF field OFF. While essentially no release was observed during the “cold” periods, a step change in the released quantity was achieved in each of the “hot” periods. The relative amount released during each step was gradually lower as the concentration difference between the particle core and the surrounding bulk decreases. The amount released in each step also depends on the composition of the particles, i.e. on the iron oxide:silica ratio, which determines the temperature achieved when the RF field is on. The higher the ratio and therefore the heating rate, the higher the amount released after a given number of steps. Thus, the quantity released can be controlled relatively accurately both by the initial particle composition and by the RF trigger sequence.

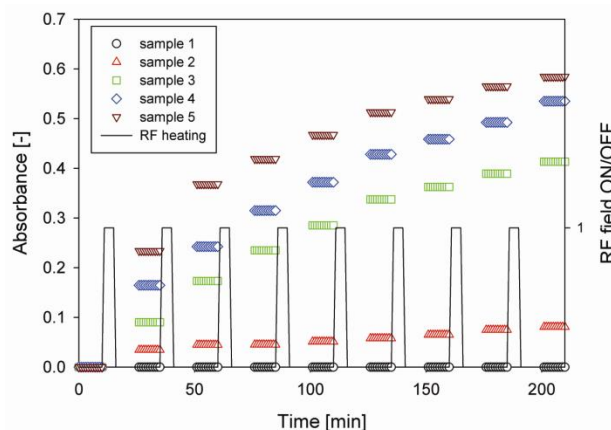


Fig. 4 – Radiofrequency induced release from composite iron oxide/silica microparticles.

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