

Controlled Stöber Growth of Tunable Silica Shells on Ligand-Stripped Hydrophobic Nanoparticles

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Abstract

The encapsulation of hydrophobic nanocrystals in silica is often limited by the need to optimize coating conditions for each core material and by difficulties in controlling shell thickness over a broad range. Here, we describe a ligand-stripping and semibatch Stöber strategy for coating selected hydrophobic nanoparticles with tunable silica shells. Native oleate ligands were removed using nitrosonium tetrafluoroborate (NOBF_4), enabling phase transfer into N,N-dimethylformamide (DMF) and subsequent silica growth in an ethanol/DMF mixture. By varying the initial ammonia concentration and the total tetraethyl orthosilicate (TEOS) volume, we obtained silica shells with thicknesses ranging from approximately 10 to more than 500 nm. Secondary silica nucleation remained below 4% under the conditions investigated. The approach was demonstrated using Fe_3O_4 nanoparticles and upconversion nanoparticles (UCNPs) with different morphologies and crystal phases. In phosphate-buffered saline, UCNPs coated with silica shells thicker than 400 nm retained more than 75% of their initial luminescence after 168 h, whereas thinner coatings provided less effective protection. These results demonstrate that ligand stripping can facilitate semibatch Stöber growth on the nanoparticle systems examined here and provide a practical route to silica coatings with adjustable thickness and aqueous stability.

Introduction

Hydrophobic nanocrystals synthesized in organic media—including quantum dots, plasmonic nanoparticles, magnetic nanoparticles, and upconversion nanophosphors—possess useful optical, electronic, and magnetic properties. However, their native oleate- or oleylamine-based ligands generally limit dispersion in aqueous and other polar media. This limitation can hinder their incorporation into composite materials, sensing platforms, and biological systems. [1–6] Silica encapsulation is a widely used strategy for improving the environmental compatibility of hydrophobic nanoparticles. A silica shell can increase colloidal stability in polar media and provide a silanol-rich outer surface that can be further functionalized with amines, carboxylates, azides, or other chemical groups. These functionalities enable subsequent bioconjugation, molecular recognition, or incorporation into hybrid materials. [7–12]

The thickness of the silica shell is an important design parameter because it determines both the dimensions and the functional properties of the resulting core–shell particles. Thin shells, typically a few nanometers thick, are advantageous when a small hydrodynamic diameter or short interparticle distance is required, for example in Förster resonance energy-transfer and plasmonic systems. In contrast, thicker shells can improve physical separation, limit the access of water and reactive ions to the nanoparticle core, and enable the preparation of larger core–shell and multilayer architectures. [13–15] Such structures may function as diffusion barriers, optical or magnetic spacers, or sacrificial templates for the preparation of hollow and multicomponent nanoparticles. [16–19]

The use of thick silica shells is therefore application dependent. Although large shells may be undesirable for applications requiring rapid biological transport or a small hydrodynamic diameter, they can be advantageous when chemical protection, extended aqueous stability, controlled interparticle

spacing, or structural transformation is the primary objective. In the present work, we focus on protection and diffusion control and use UCNP luminescence preservation in phosphate-buffered saline as a test of the protective effect of shell thickness. Large silica shells are therefore not proposed as universally optimal; rather, they are investigated here as protective and structurally functional layers. Despite these potential advantages, obtaining continuous and reproducible control over silica-shell thickness across a broad size range remains challenging.

Several strategies have been developed to incorporate hydrophobic nanoparticles, including UCNPs, into silica-containing structures. Reverse microemulsion methods are widely used for coating oleate-capped UCNPs and can produce uniform or mesoporous silica shells. [20–22] Ligand-exchange, one-pot, and mixed-component approaches have also been reported for the preparation of silica-coated UCNPs and magnetic–upconversion nanocomposites. [23,24] These studies demonstrate that silica coating of hydrophobic or partially hydrophobic nanoparticle systems is feasible. However, the coating process can be sensitive to the nanoparticle surface chemistry, solvent composition, surfactant concentration, and reaction conditions. Reverse microemulsion procedures generally rely on amphiphilic surfactants, such as IGEPAL CO-520, and may require optimization of the water-to-surfactant ratio and nanoparticle surface chemistry. Stepwise procedures combining reverse microemulsion with subsequent silica growth have extended the accessible shell thickness, but they still involve an initial surfactant-mediated coating stage. [20–24] The conventional Stöber process is scalable and can produce relatively thick silica layers, but it is often poorly suited to oleate-capped nanoparticles because these particles do not readily disperse in the polar alcohol–water–ammonia mixtures typically used for silica growth. Successful coating therefore generally requires a modified surface chemistry, a mixed-solvent system, a reverse microemulsion, or additional surfactants. [25–29] The main challenge is therefore not whether hydrophobic UCNPs can be coated with silica, but whether a relatively simple and surfactant-free procedure can provide reproducible shell growth over a broad thickness range across different nanoparticle systems. In this context, Lu and co-workers showed that residual lanthanide oleates can cause precipitation and coating failure during the reverse-microemulsion coating of hydrophobic NaLnF_4 nanoparticles, where Ln denotes a lanthanide element, particularly when substoichiometric F/Ln ratios are used. [12] These findings highlight the importance of controlling the nanoparticle surface before silica growth. An approach that separates nanoparticle surface chemistry from silica-growth kinetics could therefore simplify the coating process and improve its reproducibility.

Here, we investigate a ligand-stripping strategy for the controlled silica coating of selected hydrophobic nanoparticles. We used nitrosonium tetrafluoroborate (NOBF_4) to remove native oleate ligands and generate a BF_4^- -associated nanoparticle surface, enabling phase transfer from nonpolar solvents into DMF. [30] The ligand-stripped nanoparticles were subsequently coated using a modified semibatch Stöber process in an ethanol/DMF mixture. TEOS was added continuously using a syringe pump to limit the instantaneous precursor concentration and reduce the likelihood of homogeneous silica nucleation, thereby favoring growth on the nanoparticle seeds.

By varying the initial ammonia concentration and the TEOS volume, we obtained silica shells with thicknesses ranging from approximately 10 to more than 500 nm. We demonstrate the applicability of the method to Fe_3O_4 nanoparticles and UCNPs with different morphologies, including spheres, prisms, and plates, as well as different crystal phases. Under the conditions investigated, secondary silica nucleation remained below 4%, indicating that growth predominantly occurred on the nanoparticle seeds. We then examine the relationship between silica-shell thickness and UCNP stability during incubation in phosphate-buffered saline. Thick silica shells retained more than 75% of the initial UCNP luminescence after 168 h, whereas thinner coatings provided less effective protection. These results show that ligand stripping can facilitate semibatch Stöber growth on the nanoparticle systems examined here and provide a practical route to silica coatings with adjustable thickness and improved aqueous stability.

Materials and Methods

Materials

11 nm Fe_3O_4 nanoparticles solution in toluene at 5 mg/mL (Sigma-Aldrich 700312), Yttrium (III) chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99%), ytterbium (III) chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), erbium (III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%), ytterbium (III) oxide (Yb_2O_3 , 99.9%), yttrium (III) oxide (Y_2O_3 , 99.9%), erbium (III) oxide (Er_2O_3 , 99.9%), nitrosonium tetrafluoroborate (NOBF_4 , 95%), sodium trifluoroacetate (TFA, 98%), 1-octadecene (ODE, tech. grade 80%), oleic acid (OA, tech. grade 90%), oleylamine (OM, tech. grade 70%), sodium hydroxide (98%), ammonium fluoride (98%), methanol (99.9%), chloroform (CHCl_3 , 99.8%), N,N-dimethylformamide (DMF, 99%), and trifluoroacetic acid (TFA, 99%) were purchased from Sigma-Aldrich (Merck). Lithium trifluoroacetate anhydrous (LiTFA , 97%) was purchased by Thermo Scientific Chemicals. All other organic solvents were purchased from Labbox.

Methods

Synthesis of $\beta\text{-NaYF}_4\text{:Yb}^{3+}_{0.2}\text{Er}^{3+}_{0.02}$ UCNPs

The synthesis of $\beta\text{-NaYF}_4\text{:Yb}^{3+}_{0.2}\text{Er}^{3+}_{0.02}$ was carried out by the thermal coprecipitation method in organic media. [31] $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (236.63 mg, 0.78 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (77.47 mg, 0.20 mmol), and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (7.63 mg, 0.02 mmol) were dissolved in 1 mL of methanol (MeOH). This solution was then added to a 100 mL three-necked round-bottom flask containing 6 mL of OA and 15 mL of 1-ODE. The content of the flask was heated up to 140°C and connected to a vacuum pump to remove traces of water, methanol, and hydrochloric acid. Subsequently, the flask was allowed to cool down naturally to room temperature (RT). Next, a freshly prepared solution of 10 mL methanol containing 100 mg of NaOH (2.5 mmol) and 148.16 mg of NH_4F (4.0 mmol) was added under moderate stirring to the flask. The resulting mixture was stirred for 30 minutes at RT, then the mixture was heated up to 110°C for 20

minutes under a gentle vacuum to remove MeOH and H₂O traces. Afterward, the temperature was increased to 315°C at a rate of 20°C min⁻¹ and maintained for 1 hour. The reaction mixture was then cooled down to RT, and the resulting UCNPs were divided into four centrifuge tubes. Each tube received 4 mL of MeOH, which was shaken and allowed to separate. The MeOH was discarded, and this process was repeated twice. The product was then centrifuged at 3000x g for 10 minutes. After centrifugation, the supernatant was discarded, and the pellets were rinsed twice, without dispersing them, using 2 mL of ethanol each time.

Synthesis of LiYF₄:Yb³⁺_{0.2};Er³⁺_{0.02} UCNPs

The synthesis of the LiYF₄:Yb³⁺_{0.2};Er³⁺_{0.02} cores was realised via the thermal decomposition of the trifluoroacetate precursors LiTFA, Y(TFA)₃, Yb(TFA)₃, and Er(TFA)₃. [32] For a 0.5 mmol scale synthesis 60 mg of LiTFA (0.5 mmol), 167.5 mg of Y(TFA)₃ (0.39 mmol), 51.2 mg of Yb(TFA)₃ (0.1 mmol), and 5 mg of Er(TFA)₃ (0.01 mmol) were dissolved in a mixture of 15 mL of 1-ODE, 7 mL of OA and 7 mL of OM in a three-necked round bottom flask. Next, the solution was heated up to 130°C under vacuum using a Schlenk line for 25 minutes to remove any traces of water. The resulting solution must be transparent and without bubbles. Then, the mixture was heated up to 315°C at a rate of 20°C/min under an Ar atmosphere and stirred for 40 min before letting it cool down to RT. The obtained cores were collected and washed with ethanol, then centrifuged at 3000x g for 10 minutes, the supernatant discarded and the solid washed with a mixture of ethanol/n-hexane (4:1) and finally dispersed in 2 mL of n-hexane for further use. This final dispersion was completely transparent and colourless.

Removal of UCNPs' Capping Agent

The procedure for removing OA (capping agent) from the UCNPs' surface was standardised across all the different kinds of UCNPs utilised in this study. [30] Initially, 8 mL of DMF was added to a 25 mL round-bottom flask equipped with a magnetic stirring bar. Subsequently, 100 mg of UCNPs in n-hexane were ultrasonicated for 5 minutes and added on top of the DMF without stirring. Finally, 120 mg of NOBF₄ was introduced into the flask, and the two phases were mixed for 10 minutes under stirring. The confirmation of the removal of the majority of OA molecules from the UCNPs' surface was achieved by their phase transfer from n-hexane to DMF. The DMF solution was then divided into two Teflon centrifuge tubes, filled with CHCl₃, and centrifuged at 10000x g for 10 minutes. Subsequently, each pellet was redispersed in 1 mL of DMF, and the centrifuge tubes were supplemented with 7 mL of CHCl₃ before undergoing another centrifugation step at 10000x g for 10 minutes. This process was repeated twice more. Finally, the UCNPs were redispersed in 4 mL of DMF and stored.

Silica shell growth

The silica shells were grown using a modified semi-batch Stöber process. [25] The ligand-stripped UCNPs dispersion had a concentration of approximately 25 mg/mL. For a typical silica-coating experiment, 400 µL of this dispersion, corresponding to approximately 10 mg of UCNPs, was added to 8 mL of absolute

ethanol. Assuming spherical 40 nm particles and a NaYF_4 density of 4.2 g/cm^3 , this corresponds to approximately 6.2×10^{13} UCNPs in the reaction mixture, or approximately 8×10^{12} NPs/mL relative to the initial ethanol volume. Aqueous ammonia (29% NH_3) was then added to adjust the NH_3 concentration in the reaction medium, and a volume ratio of NH_3/TEOS was established equal to 2. For example, to obtain silica shells of approximately 45 nm thick, 0.5 mL of aqueous ammonia (0.90 M) was added before 0.25 mL of TEOS was introduced using a syringe pump at a constant rate of 0.02 mL/min. The scalability of the method was confirmed by maintaining this $V(\text{NH}_3)/V(\text{TEOS}) = 2$ ratio at higher volumes (e.g., 4:2 or 6:3 mL). After complete addition of TEOS, the mixture was stirred at 600 rpm for 24 h at room temperature. The resulting UCNPs@SiO_2 were isolated by centrifugation ($3000 \times g$ for 5 minutes), the supernatant was discarded and washed three times with absolute ethanol.

Morphological Characterization

TEM images were acquired by using a JEOL JEM 2100 working at 200 kV and coupled to a GATAN Orius SC1000 digital camera. Samples were prepared by depositing a 10 μL drop of the NPs- SiO_2 dispersion onto the carbon-coated copper grids and after 60 seconds the drop was blotted and dried at RT.

Optical Characterization

Upconversion photoluminescent spectra were collected using a BWTek spectrofluorometer. The 980 nm continuous-wave laser had an adjustable output power ranging from 0 to 3 W (MDL-H-980-3W) was transmitted through a 200 μm core fiber, which was coupled to a collimator lens. For each measurement, a cuvette containing the corresponding pure solvent was used as a blank under 980 nm laser excitation at the selected power density. To maximize signal collection and minimize internal filtering effects, luminescence was recorded in a reflection geometry (relative to the excitation beam). All measurements were performed with a laser power of 2W focused with a 10x objective, 10 s of integration time and 3 scans to average. All fluorescence experiments were repeated at least three times as independent measurements.

Nanoparticles concentration

The concentration of UCNPs (in NPs/mL) was estimated using a gravimetric method supported by thermogravimetric analysis (TGA, Mettler Toledo). The average particle diameter was obtained from TEM measurements of over 100 nanoparticles, and the particle volume was calculated assuming spherical geometry. Using the density of NaYF_4 (4.2 g/cm^3), the mass of a single nanoparticle was estimated. A known volume of the UCNPs dispersion was evaporated, and TGA was used to determine the dry inorganic mass, excluding surface ligands and residual solvents. The total number of particles was calculated by dividing the dry mass by the mass of a single UCNPs.

Results and discussion

NOBF₄-Mediated Ligand Exchange and Phase Transfer

The coating strategy is based on transferring hydrophobic, oleate-capped nanoparticles (NP–OA) into a surface-chemistry state compatible with Stöber silica growth. We used NOBF₄ to remove native oleate ligands and generate a BF₄[−]-associated surface that enabled phase transfer into DMF. This treatment enables phase transfer from nonpolar solvents, such as hexane or toluene, into polar DMF for several nanoparticle systems, including UCNPs, Fe₃O₄, and FePt. [30] To examine the applicability of this approach across different substrates, we selected UCNPs with different compositions, sizes, morphologies, and crystal phases, together with commercially sourced Fe₃O₄ nanoparticles (Fig. 1). The oxidative character of NOBF₄ should nevertheless be considered a limitation of the method, because it may be unsuitable for nanoparticles containing oxidation-sensitive components, such as sulfide-based quantum dots.

Fourier-transform infrared (FT-IR) spectroscopy of NOBF₄-treated UCNPs (β-NaYF₄:Yb³⁺,Er³⁺; 40 nm cores) showed the strong attenuation of the characteristic C–H stretching bands associated with surface-bound oleate ligands (Figure S1). This result is consistent with substantial removal of oleate during the NOBF₄ treatment. Previous studies have reported oleate-removal efficiencies of approximately 80–85% using related ligand-exchange procedures. [31,32–34] Following treatment, all tested nanoparticle systems formed clear and stable dispersions in DMF, enabling their subsequent use in silica-shell growth.

Control of Silica Shell Thickness

Once NPs were stably dispersed in DMF, we employed a modified Stöber protocol to grow the silica shell. To provide a consistent experimental framework, we fixed the nanoparticle concentration at 8×10¹² NPs/mL across all experiments, a seeding density aligned with established literature for controlled silica growth. [35,36]

Notably, our methodology allows for a wide range of shell thicknesses across different nanoparticle substrates. Shell dimensions can be tuned from tens to hundreds of nanometers by adjusting the TEOS precursor volume to account for the specific requirements of each seed type. For instance, encapsulation of small cubic Fe₃O₄ seeds (11 nm) with 0.1 mL of TEOS resulted in a uniform shell of approximately 27 nm (Fig. 2a). To achieve significantly thicker, homogeneous shells on larger tetragonal LiYF₄ and hexagonal β-NaYF₄ cores, where the total nanoparticle surface area in the reaction mixture is larger, the TEOS volume was increased to 1.0 mL (Fig. 2b–d). These results show that the protocol produced well-defined core–shell architectures for the Fe₃O₄ and UCNP substrates examined here, despite differences in core composition, size, morphology, and crystal phase.

Optimization of Growth Kinetics: The Role of Ammonia

The formation of silica shells is governed by the delicate balance of hydrolysis and condensation rates, which depend strongly on the catalytic environment. [37–40] To systematically evaluate the influence of the catalyst while maintaining a controlled supersaturation regime, we conducted a parametric study using 40 nm β -NaYF₄:Yb,Er UCNP as a model system. In all experiments, the nanoparticle concentration was standardized at 8×10^{12} NPs/mL in 8 mL of ethanol. To limit the instantaneous concentration of hydrolyzed silica species and reduce secondary nucleation, 0.25 mL of TEOS was introduced using a syringe pump at a constant rate of 20 μ L/min across all samples, following the optimized addition protocol established by Kembuan et al. [35] This semibatch approach is intended to limit the accumulation of hydrolyzed silica species and favor heterogeneous growth on the UCNP surfaces over homogeneous silica nucleation. The initial NH₃ concentration was varied by adjusting the volume of aqueous ammonia (2 %) from 0.25 mL to 1.0 mL, corresponding to a range of approximately 0.46 M to 1.70 M. As shown in Fig. 3, the ammonia concentration strongly influences the observed shell growth. At low ammonia concentration (0.46 M), the silica layer was thin (10 ± 1.2 nm) and poorly defined (Fig. 3a), indicating a low condensation rate. Increasing the concentration to 0.90 M significantly promoted the reaction kinetics, yielding uniform shells of 46 ± 3 nm (Fig. 3b). The growth reached a plateau at 128 ± 3 nm and 134 ± 4 nm for NH₃ concentrations of 1.31 M and 1.70 M, respectively (Fig. 3c, 3d). This trend (Fig. 3e) indicates that at higher concentrations, the system transitions away from a catalyst-limited regime. In this state, the growth rate is no longer primarily restricted by the catalytic strength of the medium and appears to be governed by the total amount of TEOS precursor. These results suggest that balancing the initial catalytic environment with the TEOS flux enables the preparation of uniform core–shell architectures with reproducible dimensions across the range of conditions examined.

To further explore the limits of the method, we investigated the effect of increasing the TEOS volume while keeping the concentration of 40 nm β -NaYF₄ seeds and the ammonia concentration at 0.90 M. As shown in Fig. 4, increasing the TEOS volume from 1 to 3 mL increased the silica-shell thickness from approximately 150 to 230 nm. The coating remained uniform at these higher TEOS loadings. Using 6 mL of TEOS, we obtained particles with a total diameter of approximately 1.1 μ m (Figure S2). Less than 4% of secondary silica particles were observed under these conditions. These results show that the ligand-exchanged nanoparticle interface remains compatible with silica growth during extended TEOS addition.

Chemical Protection and Luminescence Preservation

A major hurdle for the practical implementation of NaYF₄-based UCNP is their susceptibility to dissolution in aqueous environments. These NPs are ionic inorganic fluoride materials and can undergo surface degradation and ion leaching when dispersed in aqueous media, particularly under dilute conditions. [41–44] This structural disintegration leads to a dramatic loss of upconversion luminescence, limiting their use in sensors, displays, or any application involving humid or aqueous media. To mitigate this problem, Lahtinen and colleagues proposed the addition of fluoride ions to shift the solubility equilibrium, slowing down the disintegration of polymer-coated UCNP. [43] Alternatively, Kembuan and colleagues explored silica shells of varying thicknesses (7–21 nm) on NaYF₄:Yb,Er nanocrystals. [45] Their findings revealed that even shells of 21 nm were insufficient to completely

prevent ion leaching, likely because Stöber-grown silica is inherently porous, with pore sizes in the range of 1–3 nm. [46]

Our method allows for precise control of the silica shell thickness over a wide range (10–500 nm), offering a flexible platform to systematically study and enhance the chemical stability of UCNPs. To investigate how the shell thickness affects structural and optical integrity, we incubated UCNPs@SiO₂ with varying shell thicknesses in phosphate-buffered saline (PBS, pH 7.4) at a constant UCNP core concentration of 50 µg/mL. Phosphate ions are particularly aggressive because they react with free lanthanide ions (Y³⁺, Yb³⁺, Er³⁺) to form thermodynamically stable lanthanide phosphates, shifting the solubility equilibrium and driving complete UCNP dissolution. [42]

We assessed structural integrity by TEM after 48 hours of incubation in PBS (Figs. 5a–d). UCNPs with a thin 10 nm silica shell (Fig. 5a) were almost indistinguishable, with both the core and shell appearing degraded, indicating that such a thin layer fails to provide sufficient protection. Increasing the shell thickness to 45 nm (Fig. 5b) resulted in slightly more defined structures, but the shells exhibited noticeable holes and irregularities, and the UCNP cores remained compromised, as shown by their faint and blurred outlines. This intermediate thickness still does not offer robust protection. In contrast, UCNPs coated with a 120 nm silica shell (Fig. 5c) remained well-defined, with clearly visible and smooth core–shell structures, and no significant aggregation or morphological degradation was observed. Finally, UCNPs with a 200 nm shell (Fig. 5d) displayed a smooth and homogeneous silica layer, with the core remaining clearly distinguishable, identical in shape and contrast to the pre-incubation images. Under the conditions of this experiment, a shell thickness of approximately 120 nm was sufficient to preserve the overall core–shell morphology during 48 h of incubation in PBS.

To complement the morphological analysis, we monitored upconversion luminescence over 168 hours (Fig. 5g). The characteristic green emission of Er³⁺ (²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2}) was used as a sensitive optical probe to evaluate the protection afforded by the silica shells. Full emission spectra for all intermediate shell thicknesses (10, 45, 120, 200, 300, and 420 nm) are provided in Figures S3–S9. Representative spectra for samples with 10 nm and 420 nm shells are shown in Figs. 5e and 5f, respectively. For the 10 nm shell (Fig. 5e), the emission intensity dropped to ~ 50% of its initial value after 24 hours and nearly vanished after 48 hours, consistent with the structural degradation observed by TEM. In striking contrast, the 420 nm shell (Fig. 5f) showed no significant decrease in luminescence over 96 hours. The relatively stable emission observed for the 420 nm shell is consistent with enhanced protection of the UCNP core by the thick silica layer.

Figure 5g presents the normalized emission intensity over 168 hours for six different shell thicknesses (10, 45, 120, 200, 300, and 420 nm). Three distinct protective regimes are observed: (i) Thin shells (10–45 nm) exhibit a rapid intensity decline, with the 10 nm sample losing > 50% within 24 hours and the 45 nm sample showing a steady decrease to ~ 30% after 168 hours. The rapid luminescence decrease is consistent with insufficient protection against the access of water and phosphate-containing species to the core. (ii) Medium shells (120–200 nm) demonstrate a more balanced profile, with a moderate

decrease (retaining 40–60% after 168 hours). This thickness appears sufficient to shield the core from immediate quenching, indicating that these shell thicknesses provide intermediate protection over the observation period. (iii) Thick shells (300–420 nm) provide the most stable emission intensities, retaining > 75% of the initial luminescence even after 168 hours of continuous incubation in PBS. This preservation supports the interpretation that sufficiently thick silica shells reduce the access of aqueous species to the UCNP core and thereby slow core degradation.

Across the tested UCNP and Fe_3O_4 systems, the method enabled silica-shell thicknesses ranging from approximately 10 to more than 500 nm. This range allows the silica-layer thickness to be selected according to the intended function, from maintaining a relatively small separation between the nanoparticle core and its environment to providing enhanced protection against aqueous degradation. For the UCNPs, the luminescence measurements reveal a clear relationship between shell thickness and resistance to aqueous degradation. The results also demonstrate that the ligand-stripping/semibatch-growth approach can be applied to nanoparticle substrates with different compositions, morphologies, and crystal phases.

Conclusions

In summary, we have developed a strategy for the encapsulation of hydrophobic nanocrystals within silica shells with tunable thickness. The use of NOBF_4 as a ligand-stripping agent allows the transition from hydrophobic nanocrystals to a surface chemistry compatible with the Stöber process, enabling silica coating without the need for bulky surfactants.

The method provides control over shell thickness in the range of 10 nm to over 500 nm, with consistent shell dimensions across the conditions examined. The approach was tested on several core nanoparticles with different morphologies (nanospheres, nanoprisms, and nanoplates), crystal phases, and compositions. The results indicate that NOBF_4 treatment provides a sufficiently uniform surface for subsequent silica growth on the substrates examined here.

The silica shells also serve as a functional barrier. Thin shells are suitable when small hydrodynamic diameters are required, while thicker coatings (> 120 nm) offer improved chemical protection. In particular, shells thicker than 400 nm preserved more than 75% of the UCNP luminescence after 168 h of incubation in PBS, showing that thicker layers can reduce degradation in aqueous media.

The procedure described here offers a practical route to silica-coated nanoparticles with adjustable shell thickness and improved aqueous stability. The approach produced consistent coating outcomes under the conditions examined and does not require surfactants, which may simplify the preparation of core-shell particles for applications where thickness control is relevant.

The size tunability of the UCNP@SiO_2 particles could also be of interest for preparing sacrificial templates, for example in the fabrication of metal nanovoids with controlled dimensions.

Declarations

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Data Availability: The authors declare that the data supporting the findings of this study are available within the paper and its supplementary file. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request (email to: marclaur@ucm.es).

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Figures

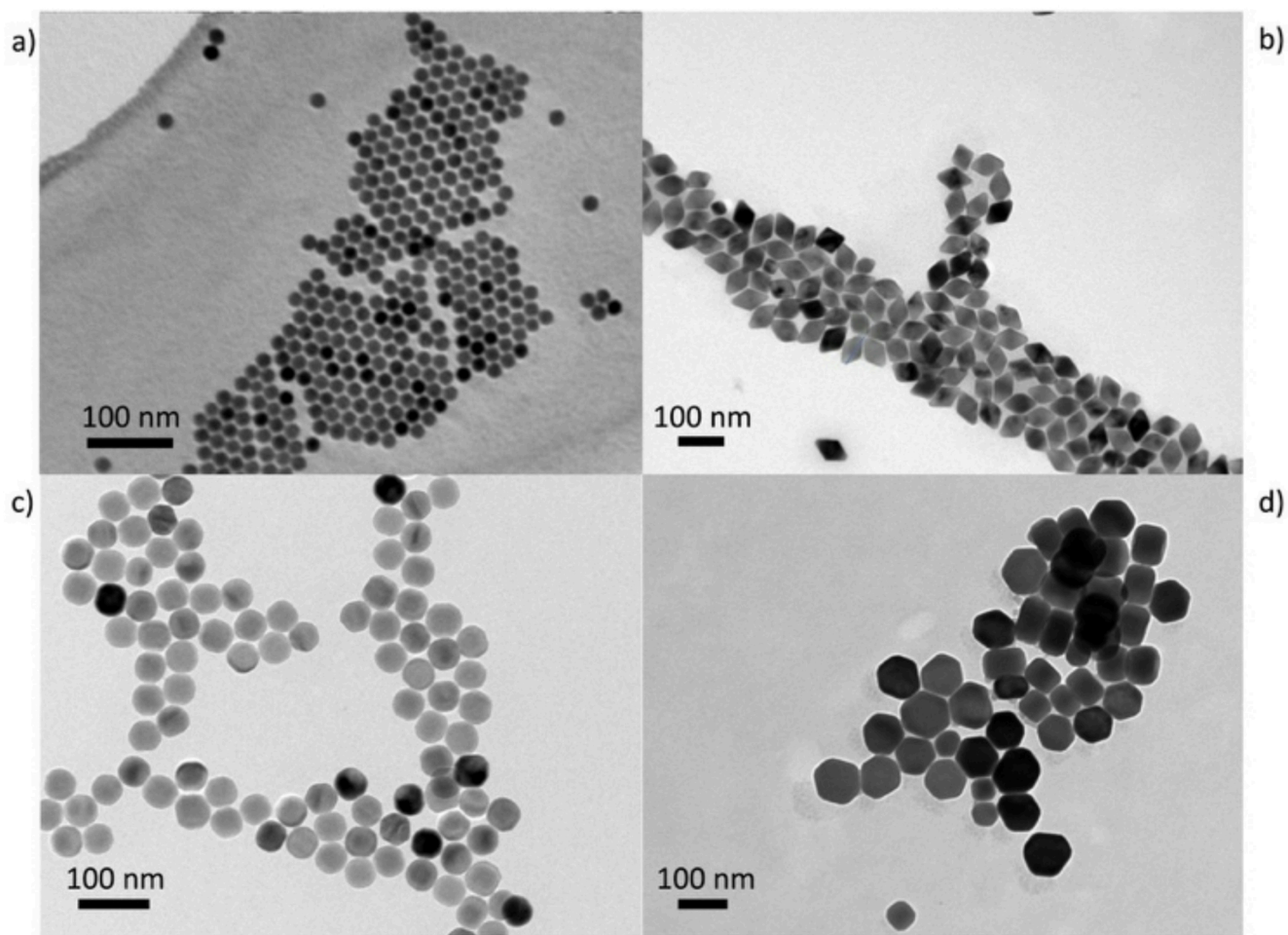


Figure 1

TEM images showing the nanoparticle substrates used in this work, including different morphologies and crystal phases: (a) cubic Fe_3O_4 , 11 ± 2 nm; (b) tetragonal $\text{LiYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$, 56 ± 3 nm; (c) hexagonal $\beta\text{-NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$, 40 ± 4 nm; and (d) hexagonal $\beta\text{-NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$, 120 ± 20 nm

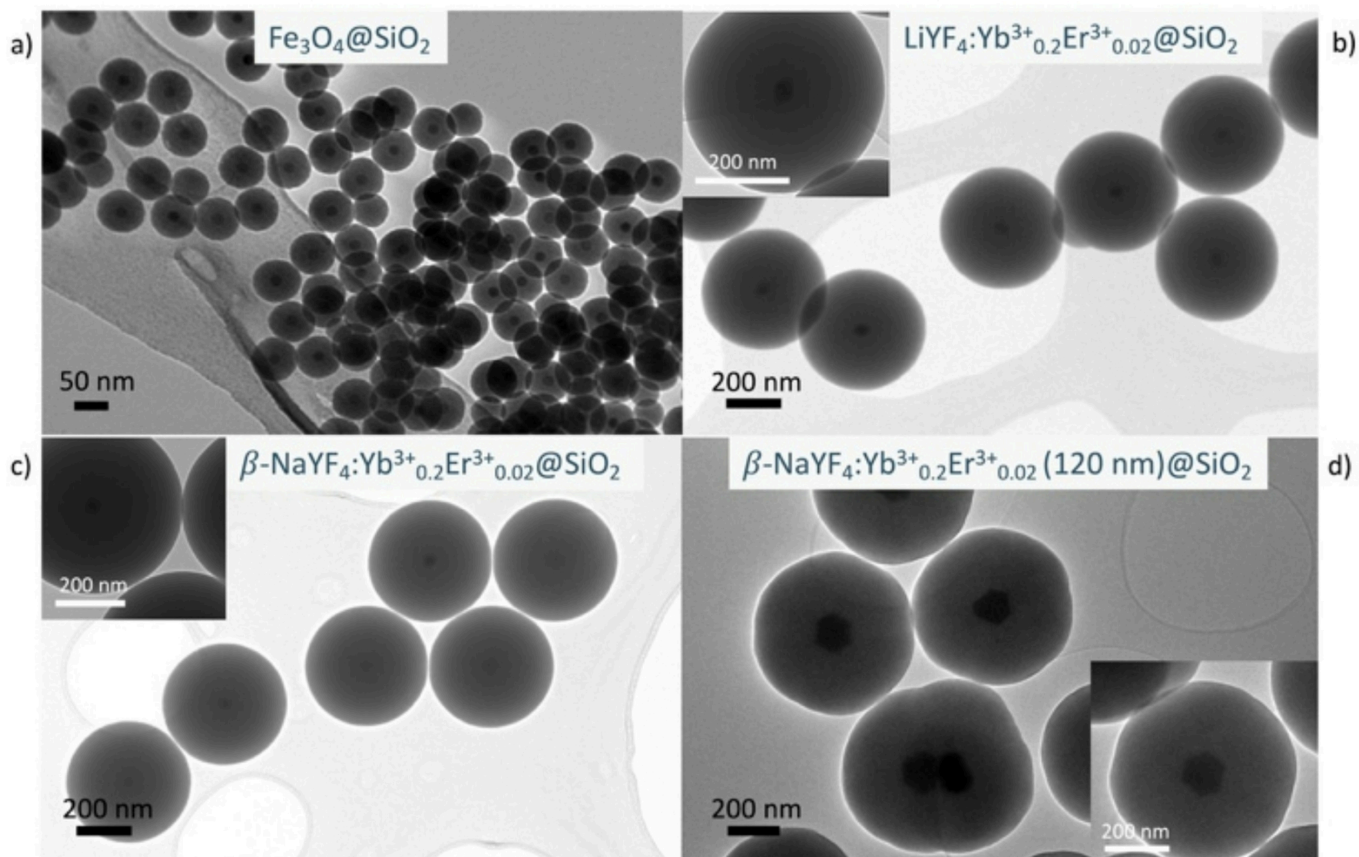


Figure 2

Versatility of the silica coating platform across diverse nanocrystal substrates. TEM images demonstrating uniform encapsulation of a) cubic Fe_3O_4 (11 nm cores, 27 nm shell), b) tetragonal $\text{LiYF}_4:\text{Yb},\text{Er}$ (56 nm cores, 190 nm shell), c) hexagonal $\beta\text{-NaYF}_4:\text{Yb},\text{Er}$ (40 nm cores) with 180 nm shell, and d) hexagonal $\beta\text{-NaYF}_4:\text{Yb},\text{Er}$ (120 nm cores) with 240 nm shell. The images highlight the formation of centered and homogeneous core-shell architectures across a broad range of core dimensions and morphologies

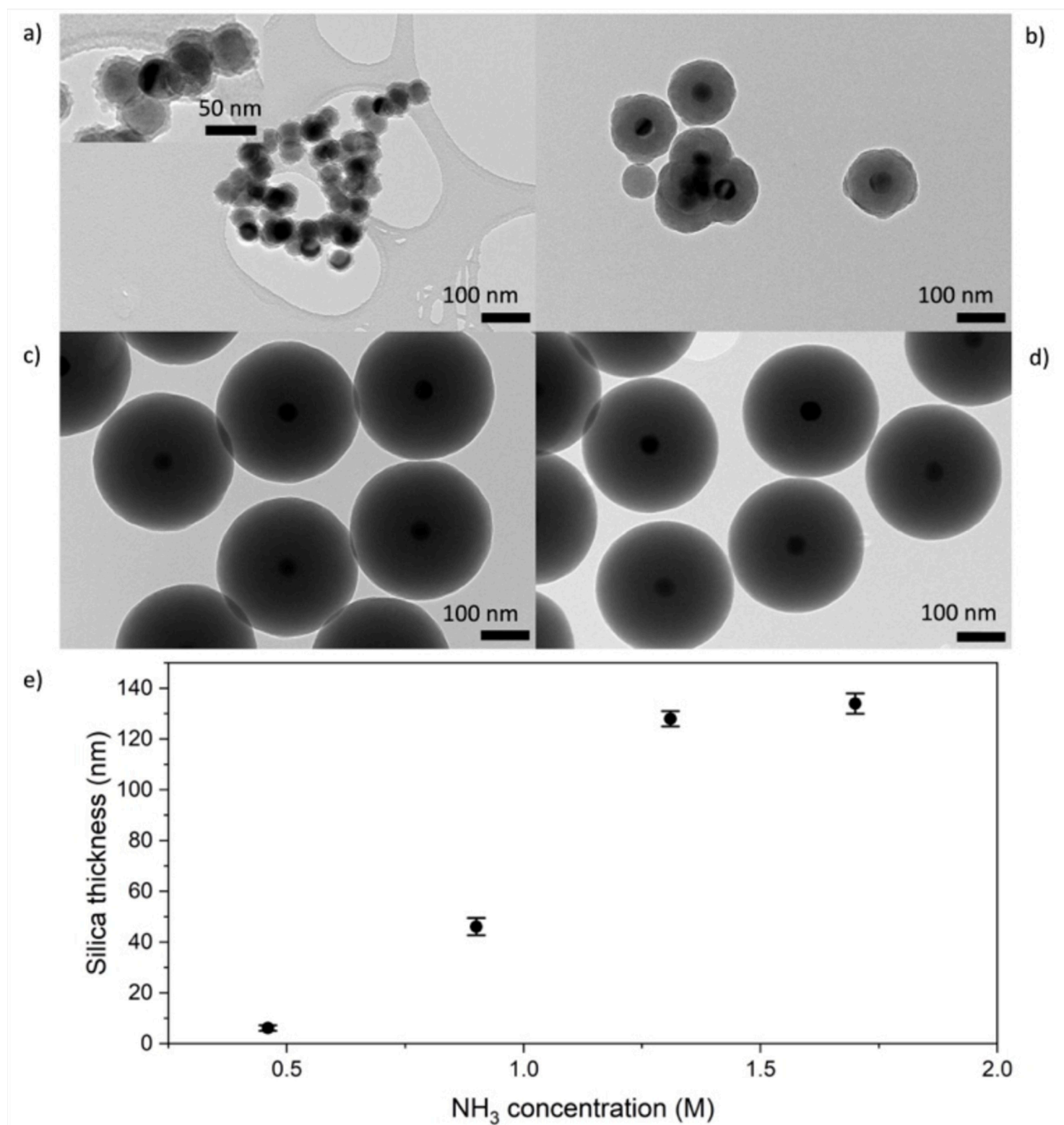


Figure 3

TEM images of 40 nm $\beta\text{-NaYF}_4\text{@SiO}_2$ nanoparticles synthesized using different initial volumes of aqueous NH_3 (29%): a) 0.25 mL (0.46 M), b) 0.5 mL (0.90 M), c) 0.75 mL (1.31 M), and d) 1.0 mL (1.70 M). e) Evolution of the silica shell thickness as a function of the initial NH_3 concentration. All samples were reacted for 24 h at a constant TEOS volume of 0.25 mL. Error bars represent standard deviations from at least 100 particles per sample

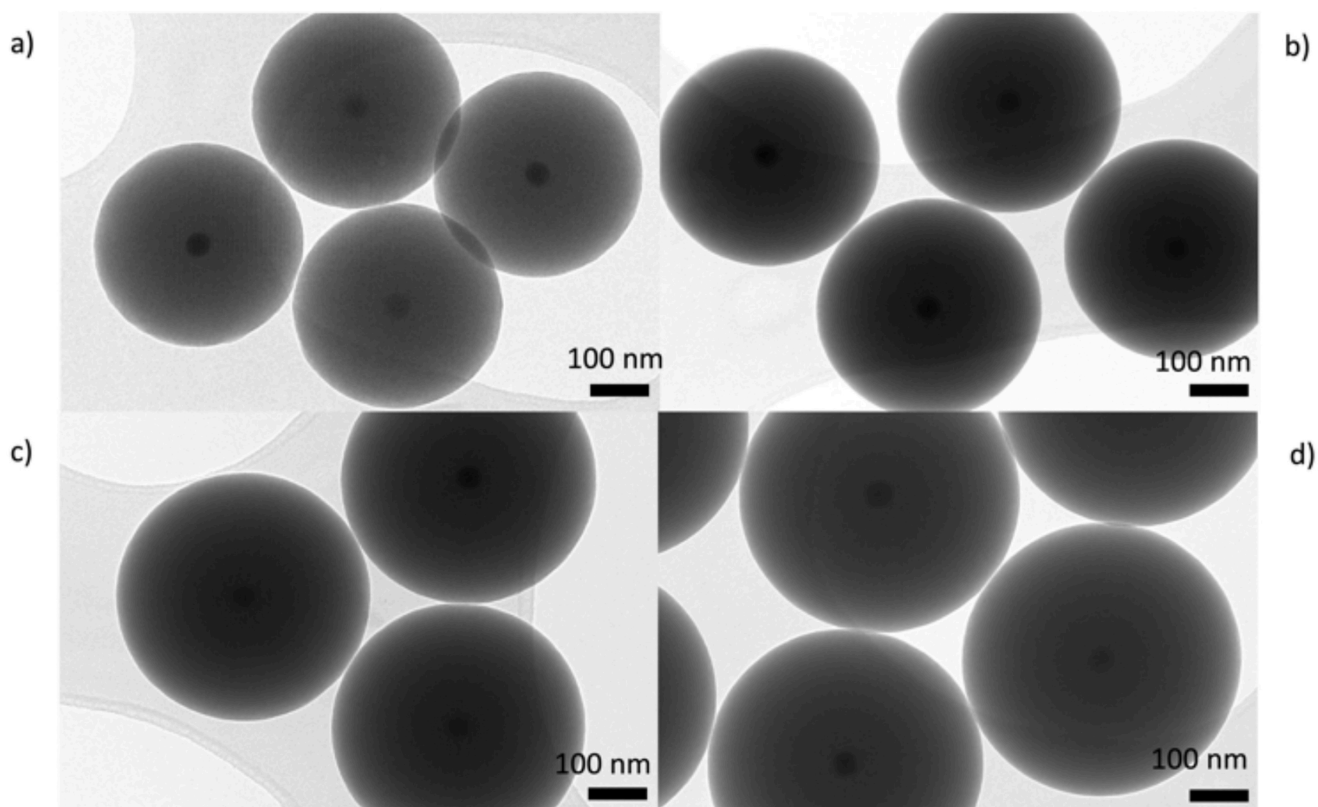


Figure 4

Scalability of silica coating. TEM images showing the increase in shell thickness as a function of TEOS volume: a) 1 mL (150 nm), b) 1.5 mL (170 nm), c) 2 mL (200 nm), and d) 3 mL (230 nm). All samples showed smooth surfaces and relatively uniform silica shells across the tested TEOS volumes, supporting the compatibility of the semibatch Stöber process with increased TEOS volumes

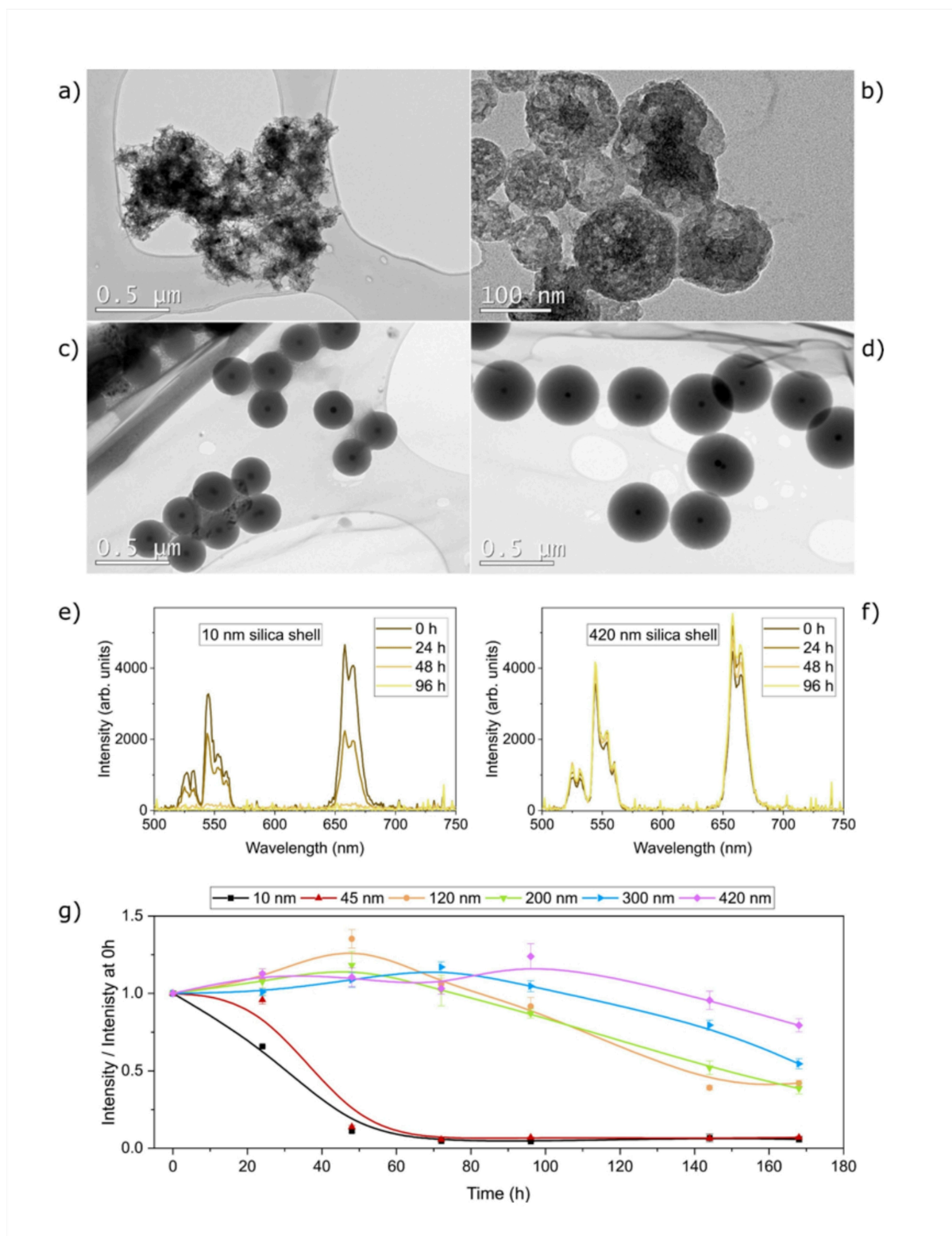


Figure 5

TEM images and emission intensity analysis of 40 nm β -NaYF₄:Yb³⁺,Er³⁺@SiO₂ nanoparticles with varying silica shell thicknesses after 48 h in PBS: a) 10 nm, b) 45 nm, c) 120 nm, d) 200 nm. e) Upconversion luminescence spectra of UCNPs@SiO₂ with 10 nm shell at 0, 24, 48, and 96 h. f) Same for 420 nm shell. g) Normalized emission intensity as a function of time for six shell thicknesses (10, 45, 120, 200, 300,

and 420 nm). Thick shells (300 and 420 nm) retain >75% of initial emission after 168 h. Solid lines are a guide for the eye

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