

# One-pot synthesis of $\text{YF}_3@$ silica core/shell nanoparticles†

Masih Darbandi and Thomas Nann\*

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A new one-pot synthetic method for preparing core/shell  $\text{YF}_3@$  $\text{SiO}_2$  nanoparticles with different morphologies, from spherical to elongated structures (“pearl necklace”), is described; absorbance and photoluminescence spectroscopy reveals intrinsic but no extrinsic defects in the  $\text{YF}_3$ .

Nanoparticles are the building blocks for almost any nanostructure or nanodevice. They frequently display unique size-dependent physical and chemical properties.<sup>1,2</sup> Sometimes nanoparticles cannot be used directly because of certain limitations, such as toxicity, hydrophobicity, interactions with oxygen, *etc.* These problems can often be solved by intermediate layers or shells.<sup>3,4</sup> Therefore, derivatization is a prerequisite for almost any (potential) application of nanoparticles, either to stabilize functional cores or to functionalize (activate) surfaces. Silica is one of the most flexible and robust surfaces. It is chemically inert and does not affect redox reactions at the core surface (except through physical blocking). Moreover, a silica shell is optically-transparent in the visible region, meaning that chemical reactions can be monitored spectroscopically and light emission is not hindered. Furthermore, the ability to control the thickness of the silica shell implies that the separation between neighboring particles can be tuned so that the collective behavior of the particles within a nanostructure can be tailored. The chemistry of such core/shell particles is well known and other functional groups can be added to adopt them into desired applications.<sup>5–7</sup>

$\text{YF}_3$  is an important host crystal for lanthanide-doped phosphors. It provides a wide band gap (>10 eV) and suitable  $\text{Y}^{3+}$  sites where trivalent rare earth elements can be easily substituted without additional charge compensation. Potential applications include, *e.g.*, new laser materials or up-conversion biolabels.<sup>8–11</sup> Furthermore,  $\text{YF}_3$  is an efficient UV phosphor in the near-UV region.

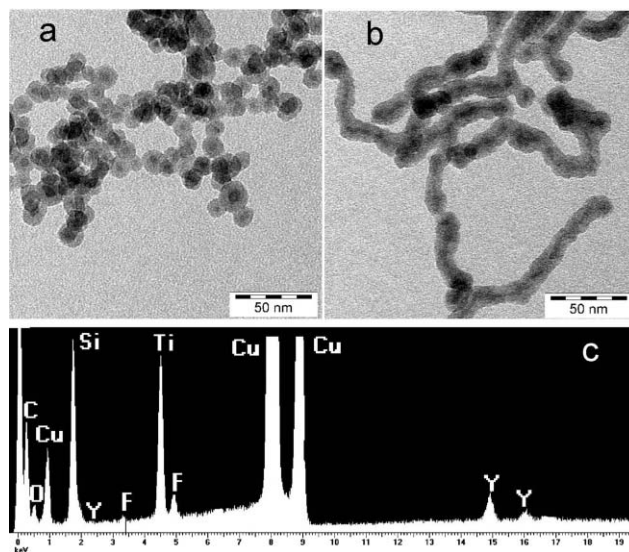
The preparation of nanoparticles within microemulsions has been shown to be a convenient route towards monodisperse particles of controllable size. This method exploits two useful properties: the capacity to dissolve reactants in the water pool and the constant exchange of the aqueous phase among micelles. Thus, by mixing microemulsions containing different reactants, it is possible to perform chemical reactions within reverse micelle water pools by using them as a nanoreactor. This method has been studied for several years and has been widely used for metal, semiconductor and oxide nanoparticle synthesis.<sup>12–14</sup> To the best

of our knowledge, it has not yet been applied to the one-pot synthesis of lanthanide fluoride core/shell nanoparticles.

Herein, we report the first one-pot synthesis of  $\text{YF}_3@$  $\text{SiO}_2$  nanoparticles by means of a microemulsion method.‡ The yielded nanoparticles were characterized by transmission electron microscopy (TEM) and absorption/photoluminescence spectroscopy. It was found, that the morphology of the resulting particles could be tuned from spherical to elongated “pearl necklace” structures. The photoluminescence (PL) spectra revealed the presence of intrinsic, but not extrinsic, defects.

TEM (Zeiss LEO 912 Omega operating at 120 kV) was used to depict the shape and size of the composite nanoparticles, dispersed on a carbon-coated copper grid from ethanolic solutions (Fig. 1; agglomeration on the TEM grids). The core/shell structure of the  $\text{YF}_3@$  $\text{SiO}_2$  nanoparticles can be clearly seen due to the different electron penetrabilities of the cores and shells. Size measurements were performed on randomly selected particles on the TEM micrographs, suggesting that the dark cores have an average thickness of 3.77 nm for spheres and 4.47 nm for “pearl-necklace” structures. The light colored shells have average thicknesses of 3.83 and 4.65 nm, respectively (*cf.* supporting information†).

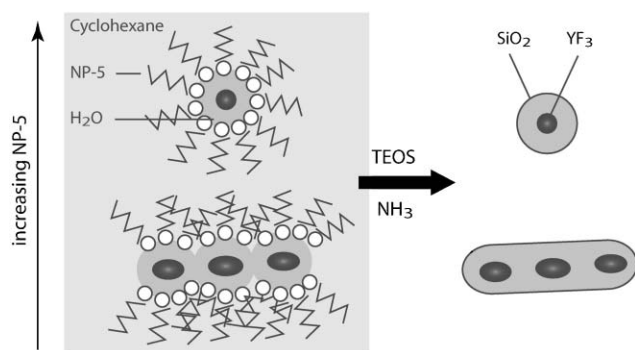
Energy-dispersive X-ray analysis (EDAX, by EDX Oxford) confirmed the presence of Y, F, Si and O in the nanocomposites. Importantly, no chloride was detected. These measurements thus permit the identification of the particles as  $\text{YF}_3@$  $\text{SiO}_2$  (Fig. 1(c)).



**Fig. 1** TEM micrographs of  $\text{YF}_3@$  $\text{SiO}_2$  nanoparticles with (a) high concentration of surfactant and (b) low concentration of surfactant. (c) EDAX spectrum of  $\text{YF}_3@$  $\text{SiO}_2$  nanoparticles.

Freiburg Materials Research Center, Albert-Ludwig University  
Freiburg, Stefan-Meier-Strasse 21, D-79104, Freiburg, Germany.  
E-mail: thomas.nann@mf.uni-freiburg.de

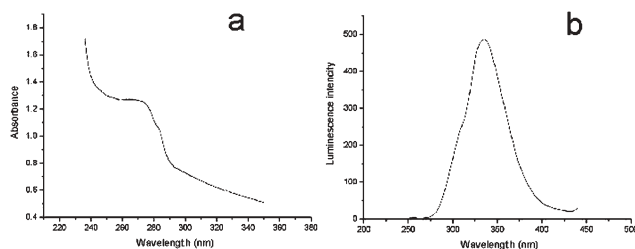
† Electronic Supplementary Information (ESI) available: More TEM and EDAX results, and size distribution histogram. See DOI: 10.1039/b516171a



**Scheme 1** Schematic presentation of the synthesis of  $\text{YF}_3@SiO_2$  in the microemulsion system.

Depending on the preparation conditions, we were able to control the morphology of the resulting nanoparticles from spherical to elongated structures, as shown in the TEM micrographs (Fig. 1). This phenomenon is related to the nature of the microemulsion system: The shape of the nanoreactor's water pool depends on the surfactant concentration because surfactant molecules surround the nanodroplet walls, these walls acting as cages for the growing particles and thereby controlling the average size and shape of the particles during the collision and aggregation process.<sup>15,16</sup> The quantity of reagents available to a reaction occurring within a micelle is limited by the concentrations of the enclosed solutions and the size of the micelles themselves. Since the size of the silica shell depends on the size of the water pool, the size of the shell can be controlled and tuned by changing the water-to-surfactant molar ratio (in general, the higher the ratio, the larger the shell size; cf. Scheme 1).<sup>17,18</sup>

Fig. 2 presents the absorbance and luminescence spectra of  $\text{YF}_3@SiO_2$  nanoparticles (absorbance was recorded with a Perkin-Elmer lambda2 spectrophotometer and luminescence with a Perkin-Elmer LS 45 luminescence spectrometer). A strong absorption band, peaking at 273 nm, is observed, agreeing well with the reported absorption spectra of bulk  $\text{YF}_3$  material. Broad emission characteristics covering the range from 250 to 400 nm were observed. The emission peak at 335 nm corresponds to an intrinsic defect luminescence of bulk  $\text{YF}_3$ . An extrinsic defect emission of bulk  $\text{YF}_3$  at about 400 nm was not observed in our samples, indicating the high purity of the resulting nanocrystals. This fact, as well as a large Stokes shift of the intrinsic luminescence (more than 50 nm) and the large width of the emission bands (near 150 nm), is a strong indication that the observed emission bands can be assigned to a radiative recombination of self-trapped excitons.<sup>19–21</sup>



**Fig. 2** (a) Absorbance spectra and (b) luminescence spectra (excitation at 240 nm) of  $\text{YF}_3@SiO_2$  nanoparticles.

This synthetic process for  $\text{YF}_3@SiO_2$  nanocomposites can readily be reproduced and scaled-up because the W/O microemulsion route is an easy and efficient method for the preparation and encapsulation of nanocrystals over other existing methodologies. Further, considering that the precursor is available for many metal elements (e.g., alkaline earths), we expect that the present one-pot route may be generalized to synthesize many other pure or doped lanthanide fluoride@silica nanoparticles.

In summary, a new synthetic method for preparing  $\text{YF}_3@SiO_2$  nanocomposites in a one-pot system was developed. This method uses water-in-oil microemulsions, in which monodisperse  $\text{YF}_3$  nanocrystals were synthesized in the water nanopool and subsequently silica shells were produced by controlled hydrolysis of TEOS in the water nanodroplets within the same reactor.

Finally, one interesting point to come from this work is that the luminescence source of the  $\text{YF}_3@SiO_2$  nanocomposite was found to be intrinsic and not extrinsic.

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## Notes and references

‡ Experimental:  $\text{YF}_3@SiO_2$  nanoparticles were prepared in two steps, firstly synthesizing  $\text{YF}_3$  nanoparticles by the modification of a literature method.<sup>22–25</sup> Subsequently, silica encapsulation was undertaken within the same reactor (one-pot). In a typical synthesis, a microemulsion was first prepared by mixing 0.5 mL of a 0.04 M aqueous solution of  $\text{YCl}_3$  and the desired amount of NP-5 (polyethylene glycol nonylphenyl ether) in 15 mL of cyclohexane as a continuous phase in a flask under vigorous stirring under ambient conditions (the amount of surfactant was varied from 1.65 g, low concentration, to 4.22 g, high concentration). 30 min after the microemulsion system was formed, 0.5 mL of aqueous 0.04 M  $\text{NH}_4\text{HF}_2$  was added directly to the microemulsion with agitation under ambient conditions. The resulting suspension was clear to the eye. After producing the  $\text{YF}_3$  nanoparticles, 0.1 mL ammonia aqueous solution (33 wt%) was introduced into the microemulsion system, and 30 min later, during vigorous magnetic stirring, 0.1 mL TEOS (tetraethyl orthosilicate) was added to the system as a silica precursor. Silica growth was complete after 24 h of stirring and the  $\text{YF}_3@SiO_2$  composite particles were then precipitated by adding 1 mL acetone into this colloidal solution, followed by washing, in sequence, with 1-butanol, 1-propanol and ethanol. For each washing step and subsequent centrifugation, a sonicator bath was used to completely disperse the precipitate into the corresponding solvent and remove any physically-adsorbed molecules from the particle surfaces. Finally, the as-prepared nanocomposites could be easily redispersed in various polar solvents, such as ethanol and water.

- H. Liu and A. P. Alivisatos, *Nano Lett.*, 2004, **4**, 2397.
- J. Pacifico, D. Gomez and P. Mulvaney, *Adv. Mater.*, 2005, **17**, 415.
- Y. T. Yu and P. Mulvaney, *Mater. Trans., JIM*, 2004, **45**, 964.
- T. Nann, *Chem. Commun.*, 2005, 1735.
- H. Ow, D. R. Larson, M. Srivastava, B. A. Baird, W. W. Webb and U. Wiesner, *Nano Lett.*, 2005, **5**, 113.
- C. Graf, D. L. J. Vossen, A. Imhof and A. Van Blaaderen, *Langmuir*, 2003, **19**, 6693.
- T. Nann and P. Mulvaney, *Angew. Chem., Int. Ed.*, 2004, **43**, 5393.
- Y.-W. Zhang, X. Sun, R. Si, L.-P. You and C.-H. Yan, *J. Am. Chem. Soc.*, 2005, **127**, 3260.
- M. M. Lage, A. Righi, F. M. Matinaga, J.-Y. Gesland and R. L. Moreira, *J. Phys.: Condens. Matter*, 2004, **16**, 3207.
- K. J. Guedes, K. Krambrock and J. Y. Gesland, *J. Phys. Chem. Solids*, 2001, **62**, 485.
- K. J. Guedes, K. Krambrock and J. Y. Gesland, *J. Phys.: Condens. Matter*, 1999, **11**, 7211.

- 12 R. D. Tilley, J. H. Warner, K. Yamamoto, I. Matsui and H. Fujimori, *Chem. Commun.*, 2005, 1833.
- 13 C. Liu, B. Zou, A. J. Rondinone and Z. J. Zhang, *J. Phys. Chem. B*, 2000, **104**, 1141.
- 14 E. Stathatos, P. Lianos, F. Del Monte, D. Levy and D. Tsiourvas, *Langmuir*, 1997, **13**, 4295.
- 15 S. Santra, R. Tapeç, N. Theodoropoulou, J. Dobson, A. Hebard and W. Tan, *Langmuir*, 2001, **17**, 2900.
- 16 P. A. Dresco, V. S. Zaitsev, R. J. Gambino and B. Chu, *Langmuir*, 1999, **15**, 1945.
- 17 T. Mokari, H. Sertchook, A. Aharoni, Y. Ebenstein, D. Avnir and U. Banin, *Chem. Mater.*, 2005, **17**, 258.
- 18 F. Teng, Z. Tian, G. Xiong and Z. Xu, *Catal. Today*, 2004, **93**, 651.
- 19 V. Pankratov, M. Kirm and H. von Seggern, *J. Lumin.*, 2005, **113**, 143.
- 20 J. W. Stouwdam, G. A. Hebbink, J. Huskens and F. C. J. M. van Veggel, *Chem. Mater.*, 2003, **15**, 4604.
- 21 J. Adam, *Chem. Rev.*, 2002, **102**, 2461.
- 22 J. L. Lemyre and A. M. Ritcey, *Chem. Mater.*, 2005, **17**, 3040.
- 23 H. Huang, G. Q. Xu, W. S. Chin, L. M. Gan and C. H. Chew, *Nanotechnology*, 2002, **13**, 318.
- 24 M. H. Lee, S. G. Oh and S. C. Yi, *J. Colloid Interface Sci.*, 2000, **226**, 65.
- 25 D. G. Shchukin and G. B. Sukhorukov, *Langmuir*, 2003, **19**, 4427.

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