SUPPLEMENTARY INFORMATION

Amphiphilic Coatings for Protection of Upconverting Nanoparticles against Dissolution in Aqueous Media

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Synthesis details

Synthesis of UCNPs@OA

β-$NaYF_4$ UCNPs, co-doped with 3.33 at.% of Yb^{3+} and 0.33 at.% of Tm^{3+} ($NaY_{0.78}Yb_{0.20}Tm_{0.02}F_4$), were synthesized with thermal decomposition, using a modified procedure from ref. [1]. A total of 2 mmol of the $LnCl_3$ reagents in a stoichiometric ratio of Y:Yb:Tm = 0.78:0.20:0.02 were mixed with 12 ml OA and 30 ml ODE and heated to 156 °C for 30 min, when a yellow transparent solution formed. After cooling the solution to ~70 °C the solution of NH_4F (8 mmol) and NaOH (5 mmol) in 10 ml of methanol was slowly added. The reaction mixture was stirred at 50 °C for 40 min to evaporate the methanol. After that the mixture was heated to 300 °C in an Ar atmosphere for 1.5 h and finally cooled naturally to room temperature. The as-synthesized UCNPs were collected with the addition of acetone and centrifuging (3000 rcf for 5 min, Eppendorf Centrifuge 5804). They were washed with ethanol and water, and dispersed in cyclohexane or chloroform.

Formation of coatings

UCNP@TPGS were synthesized in a similar way as described previously[2] by applying some modifications. TPGS (~ 100 mg) was immersed in cyclohexane (10 ml) and stirred for 1 h. After the addition of the as-synthesized UCNPs@OA (20-30 mg), the mixture was stirred for another 0.5 h and sonicated for 20 min. After this, 20 ml of water was added to the transparent solution, sonicated for additional 20 min and a white water-in-oil emulsion was formed. The phases were separated by centrifuging (3000 rcf for 5 min) and decanting of the oil phase. The water phase was centrifuged again and the remaining cyclohexane was evaporated at 70 °C for 15 min, resulting in the pure water dispersion of UCNPs@TPGS.

The synthesis of UCNPs@PMAO-BHMT was based on Ref.[3]. A stable dispersion of the as-synthesized UCNPs@OA in chloroform (~12 mg/ml UCNPs) was mixed with a solution of PMAO (0.137 M) in chloroform. The ratio of the PMAO monomer units per UCNPs surface (in nm^2) was ~300. The BHMT

(0.02 M) solution in chloroform with the ratio of BHMT molecules per UCNPs surface (in nm^2) being ~10 was added. After stirring for 0.5 h UCNPs@PMAO-BHMT were precipitated using 0.5–1.0 ml of NaOH solution (1 M). The mixture was sonicated for 2 h. First, the large aggregates and the excess of PMAO-BHMT were removed by decanting, while smaller aggregates were removed by centrifuging (3000 rcf for 5 min) in water. The optically transparent supernatant with UCNPs@PMAO-BHMT was stored.

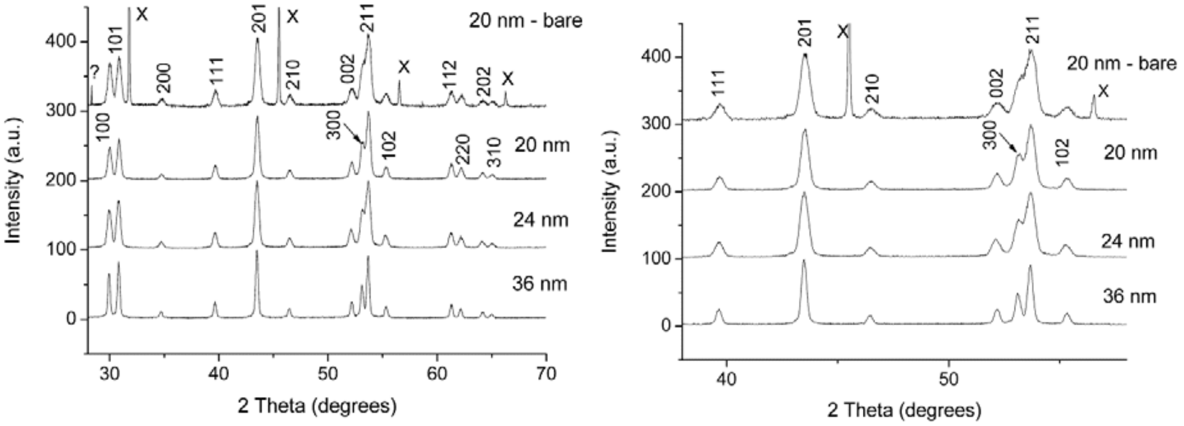

Fig. S1. XRD patterns of the as-synthesized UCNPs@OA of different sizes and of the bare UCNPs (20 nm) with an enlargement on the right-hand side. Indices correspond to space group $P6_3m$ (JCPDS 16-0334), X denotes peaks associated to NaCl (JCPDS 78-0751) and ? denotes unidentified peak.

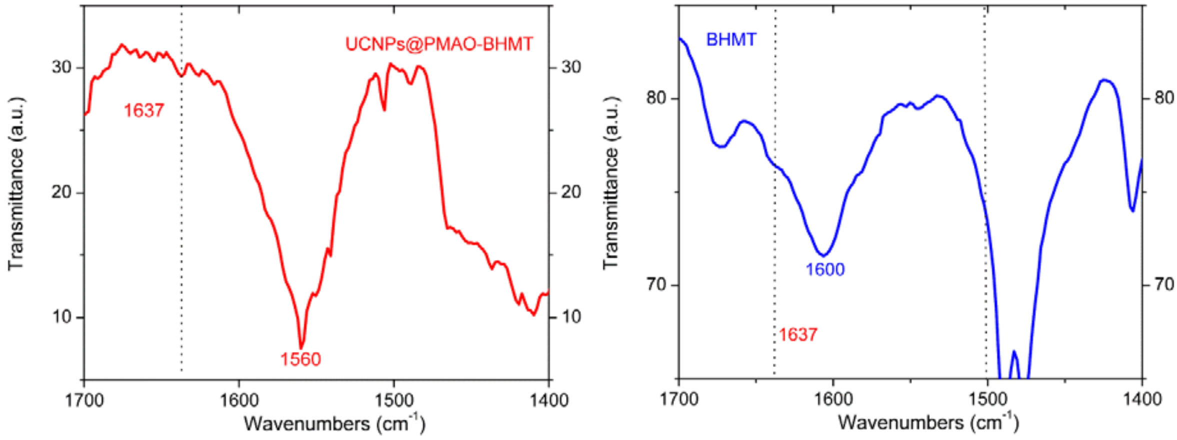

Fig. S2. Enlarged ATR-FTIR spectra, from Fig. 3b in the main document, of the as-synthesized UCNPs@PMAO-BHMT (multiplied by a factor of 5) and BHMT.

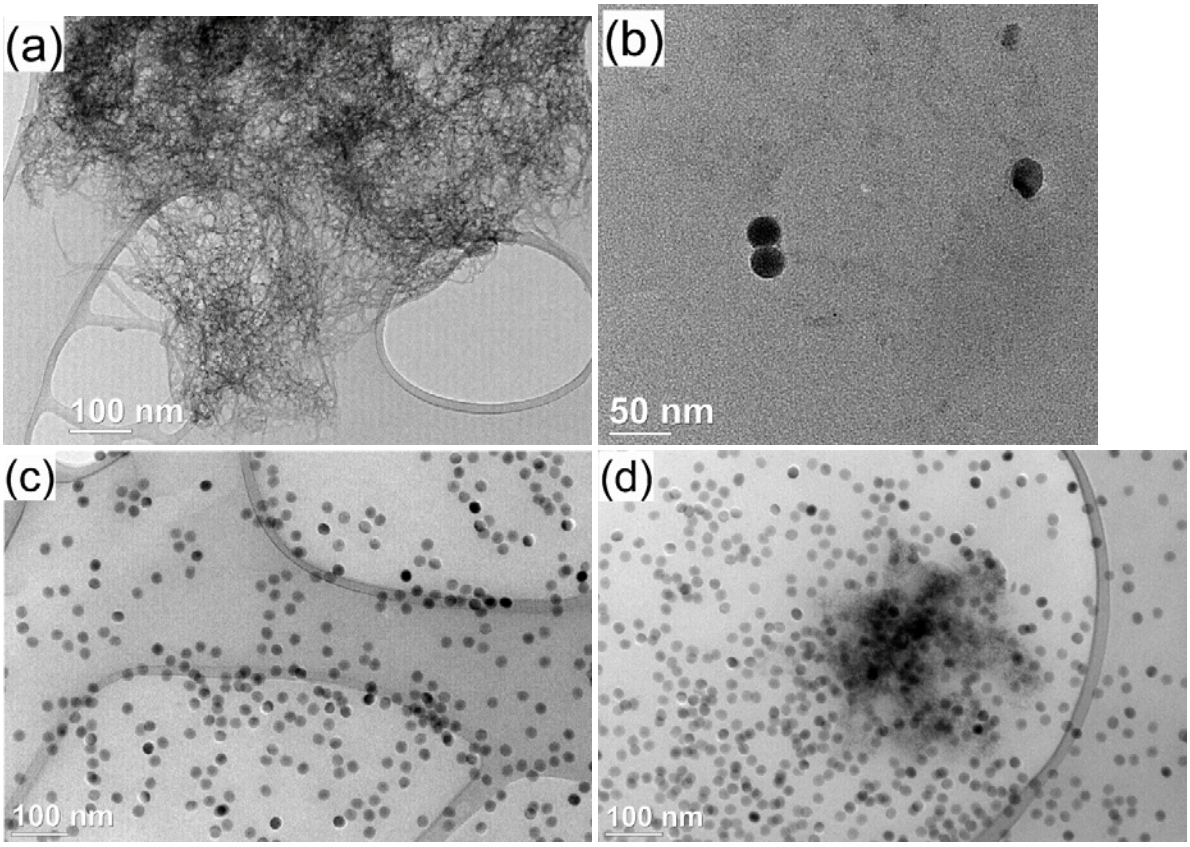

Fig. S3. TEM images of the coated samples aged for two days in PBS at 37 °C: UCNPs@TPGS (a, b) and UCNPs@PMAO-BHMT (c,d). The aged UCNPs@TPGS sample was mostly composed of the thread-like side product (a), with a few remaining particles, shown in (b). On the contrary, the aged UCNPs@PMAO-BHMT was mostly composed of particles (c) and only few areas were spotted with the thread-like side product (d). The side product is amorphous (no distinct SAED) and is composed of Y, Yb, P and O, as determined with EDXS analyses. The images are not of the same magnification – check for different scale bars.

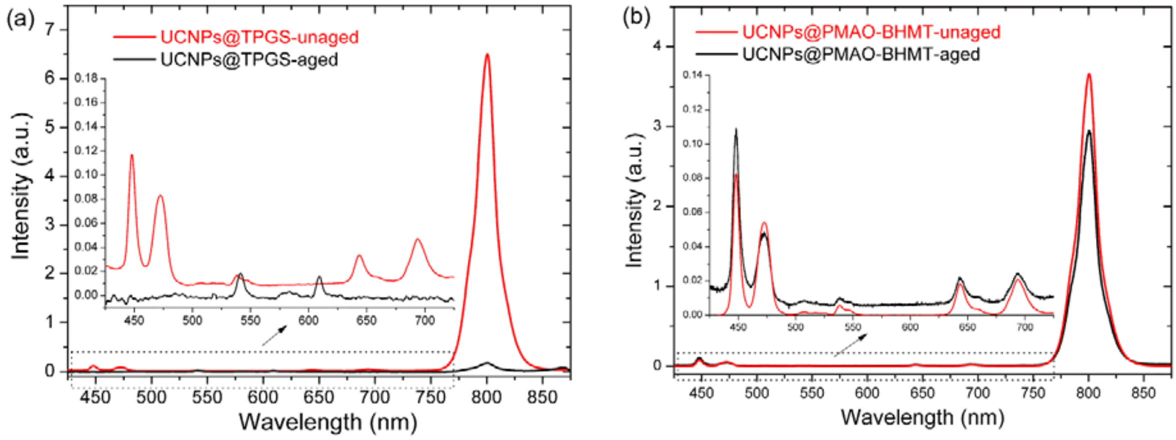

Fig. S4. Fluorescence emission spectra of the unaged and aged UCNPs in PBS at pH = 7.4 and 37 °C for 2 days coated with TPGS (a) and PMAO–BHMT (b).

References

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