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Supporting information

Europium-doped NaGd(WO₄)₂ nanophosphors: synthesis, luminescence and their coating with fluorescein for pH sensing

Mariano Laguna, Alberto Escudero, Nuria O. Nuñez, Ana I. Becerro and Manuel Ocaña*

Instituto de Ciencia de Materiales de Sevilla, CSIC, Américo Vespucio 49, 41092, Isla de la Cartuja, Sevilla, Spain

Estimation of the amount of fluorescein on the NP surface

Table S1: Data from the TG analysis of the citrate capped Eu³⁺(6%):NaGd(WO₄)₂ sample coated PAH-fluorescein.

| Sample | Initial | | Adsorbed water | | Citrate + PAH-F | | Final | |
|---------|---------|-----|----------------|-----|-----------------|-----|----------|------|
| | (RT) | | (up to 200 °C) | | (200 – 500 °C) | | (750 °C) | |
| | Mg | % | mg | % | mg | % | mg | 89.1 |
| NPs@cit | 2.629 | 100 | 0.115 | 4.5 | 0.163 | 6.4 | 2.349 | 89.1 |
| @РАН-F | | | | | | | | |

In the data shown in Fig. 7 the final weight value at 750 °C for the PAH-fluorescein coated NPs was 2.349 mg, which corresponded to 89.1 % of the initial weight. We assume that at this temperature only NP cores are present. For a spherical NP with core diameter d_c = 119 nm, the volume is V_c = $(4\pi/3)\cdot(59.5 \text{ nm})^3 \approx 882.3 \cdot 10^3 \text{ nm}^3$. Given the bulk density of NaGd(WO₄)₄ = 7.18 g/cm³, the mass of one NaGd(WO₄)₂ core thus is m_c = 7.18 g/cm³ · 882.3 · 10³ nm³ ≈ 6.33 · 10⁶ g·(10⁻⁹ m/10⁻² m)³ = 6.33·10⁻¹⁵ g. The number of NPs can be thus calculated:

$$2.349 \cdot 10^{-3} g \cdot \frac{1 \, NP}{6.33 \cdot 10^{-15} g} = 3.71 \cdot 10^{11} NPs$$

By comparing the TG data with the as synthesized NPs (i.e. citrate capped NPs, in which a 4.8 % weight loss was observed between 200 and 500 °C), the amount of PAH-fluorescein is estimated to be 1.6 % (6.4 – 4.8 weight %), in this case 0.0421 mg. The proportion poly(allylamine hydrochloride): fluorescein isothiocyanate is 50:1, meaning that every 3239.4 mg of PAH-fluorescein (50 mmol of PAH monomers · 57 mg/mmol + 1 mmol of fluorescein isothiocyanate · 389.4 mg/mmol) contain 389.4 mg of fluorescein isothiocyanate, then:

$$0.0421\ mg\ PAH-fluorescein \cdot \frac{389.4\ mg\ fluorescein}{3239.4\ mg\ PAH-fluorescein} \cdot \frac{1\ mmol\ fluorescein}{389.4\ mg} = 1.30\cdot 10^{-8}\ mol\ fluorescein$$

Such amount of fluorescein is associated with 3.71·10¹¹ NPs, then:

$$\frac{mol\ fluorescein}{NP} = \frac{1.30 \cdot 10^{-8}}{3.71 \cdot 10^{11}} = 3.51 \cdot 10^{-20}\ mol\ fluorescein\ per\ NP$$

$$3.51 \cdot 10^{-20} \frac{mol\ fluorescein}{NP} \cdot \frac{6.023 \cdot 10^{23}\ molecules}{mol} \approx 21100\ molecules\ of\ fluorescein\ per\ NP$$