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A photo-crosslinking-mediated route towards luminescent supraparticles

Tamires M Oliveira[1], Paulo C. de Sousa Filho[1]

[1]Institute of Chemistry, University of Campinas.
E-mail: t212524@dac.unicapmp.br

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The quest for multifunctional materials exhibiting orthogonal properties drives the development of novel synthesis methodologies providing precise morphological and structural control. An appealing alternative to complex core-shell systems is the controlled aggregation of diverse nanoparticles into submicrometric structures called supraparticles (SPs)[1]. In nanomedicine, there is a growing demand for materials capable of locally monitoring temperature (luminescent nanothermometry) and inducing controlled localized heating under light (photothermal therapy). Furthermore, combination of luminescent and plasmonic particles is particularly attractive for theranostic applications. Prior to controlled aggregation, precise tuning of the surface and spectroscopic characteristics of individual luminescent and plasmonic particles is essential. We prepared[2] β-NaYF$_4$:Yb,Er and NaYF$_4$:Nd, Yb, Er nanoparticles exhibiting characteristic Er^{3+} emission in the green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$)and red ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) regions under 980 and 808 nm excitation, respectively. Additionally, highly-crystalline tetragonal YVO$_4$:Eu^3 particles were obtained by hydrothermal synthesis, showing high-intensity Eu^{3+} emissions ($^5D_0 \rightarrow {}^7F$n, n= 1, 2, 3 and 4) under 270 nm excitation. The luminescent nanoparticles were covered by oleate ligands, which allowed us to further perform the photo-crosslinking step. Finally, gold nanoparticles (AuNP) and nanorods (AuNRs) were also prepared by classical synthesis methods. The preparation of the supraparticles involved an oil-in-water emulsion where the individual NPs were dispersed in cyclohexane in the presence of a UV photo-initiator (HPK), followed by illumination with a commercial UV lamp for 10-30 min at 10, 25 or 50 °C. The chosen composition were: SP1 Y,ErVO$_4$ and Y,EuVO$_4$, SP2 NaGd,Yb,ErF$_4$ and Y,EuVO$_4$, and SP3 NaGd,Yb,ErF$_4$, Y,EuVO$_4$, and AuNP. Dynamic Light Scattering (dls) showed lower size polydispersity for SPs prepared at 25°C illuminated for 30 min, with mean diameters around 250 nm. X-ray diffraction confirmed the presence of tetragonal phase of YVO$_4$ in SP1, and SP2 and SP3 confirmed the coexistence of YVO$_4$ and β-NaLnF$_4$ phases. Infrared (FTIR) analysis indicated the hybrid structure by the presence of oleates covering the surface of vanadate or fluoride particles, confirming the presence of the cross-linked ligands after the production of the SP. *In situ* photoluminescence experiments indicated a progressive quenching of Eu^{3+} emission the formation of the SPs, which is possibly related to the decrease of the total amount of Eu^{3+} at surface sites in comparison to isolated nanoparticles due to the low penetration depth of UV light. The studies showed that it is possible to control the aggregation in a confined environment mediated by a photo-crosslinking process and, as perspectives, additional characterization of the colloidal stability and biologic compatibility of the SPs are necessary for further application.

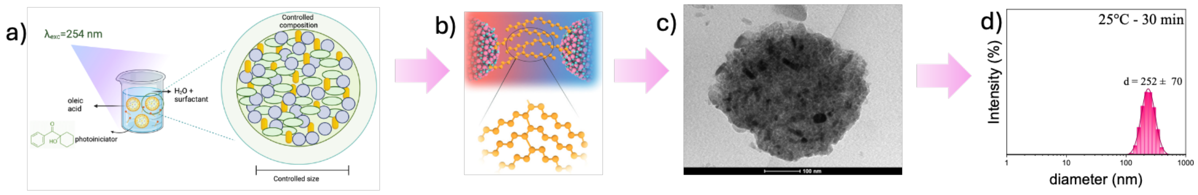

Figure 1. a) Ilustration of the experimental process to obtain the SPs by photo-crosslinking in a confined environment b) Crosslinking between the oleate molecules b) TEM image of SP3, and (d) dls showing the size distribution of the SP3.

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