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Organizador(es):
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Synthesis and characterization of luminescent nanoparticles for application in supramolecular systems

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Abstract

Upconverting nanoparticles (UCNPs) have been drawing attention thanks to its spectroscopic properties which gives them many applications. Combining them with luminescence quenching species, like gold nanostructures (AuNTs), it is possible to develop luminescent supramolecular systems responsive to many analytes, allowing quickly and ultrasensive detection tests. In this work, we prepared $NaYF_4$:20%Yb^{3+},2%Er^{3+} UCNPs with high emission intensity of green and red light and AuNTs of rod-like shape (AuNRs) with plasmon resonance absorption bands matching the wavelength of the UCNPs emission to combine them in a supramolecular system for sensing applications. The synthesis and characterization of these materials will be presented and discussed in this work.

Keywords: upconversion; rare-earth ions; nanostructures.

Introduction

UCNPs are nanomaterials capable of converting low energy radiation into high energy radiation. When compared to traditional phosphors like quantum dots and organic dyes, they have advantages like higher physical and chemical stability, narrow emission peaks and larger anti-Stokes shift. AuNRs are a special type of AuNTs which have two plasmon resonance absorption bands, each one related to its two size dimensions. These bands can be modulated to match the UCNPs emission, having a quenching effect by resonant energy transfer when they are close enough. This UCNP-AuNR system can be employed in sensing devices to detect ions, molecules or even bacteria, according to the modifications made on the UCNP surface.

Experimental Procedure

The UCNPs were prepared using rare earth chlorides, NH_4F and NaOH as precursors, oleic acid as complexing agent and 1-octadecene as solvent.[1] The $NaYF_4$ shell followed a similar method, adding the prepared UCNPs instead of the precursors of doping ions. The $mSiO_2$ shell followed a two-phase procedure,[2] with the aqueous basic phase consisting of cetrimonium bromide (CTAB) and UCNPs@$NaYF_4$, and the organic phase composed of tetraethoxysilane (TEOS) diluted in cyclohexane. The NPs were then washed with a NH_4NO_3 solution to remove the CTAB. Some of these UCNPs went under an amination reaction, using (3-aminopropyl) triethoxysilane (APTES), with triethylamine as a catalyst and ethanol as a solvent, leaving $-NH_2$ groups in the silica surface.[3] The AuNRs were prepared following the seed mediated growth method,[4] making the Au seeds with $HAuCl_4$, CTAB and $NaBH_4$ in water, and the growth solution with CTAB, $HAuCl_4$, $AgNO_3$, ascorbic acid and HCl. The UCNPs upconversion (UC) spectra was measured with excitation in 976 nm. The AuNRs absorption spectra were measured during the reaction until its plasmonic absorption bands matched the UCNPs emission bands. The crystalline structure of the UCNPs was determined by X-ray diffractometry (XRD) and its morphology and size were determined by transmission electronic microscopy (TEM) and with ImageJ software. The AuNRs morphology was determined by scanning electronic microscopy (SEM). The emission quenching tests were done mixing 1 mL of a 0,5 mg mL^{-1} UCNP solution with 100 μL of a 0,17 mM of Au^0 AuNR solution.

Results and Discussion

The XRD diffractogram for the UCNPs@$NaYF_4$ in Figure 1 agrees with other literature patterns,[5] indicating the desired β phase. Figure 2 presents TEM image for UCNPs@$NaYF_4$, and its size distribution. Their medium diameter is 43 nm. The $mSiO_2$ shell was well formed in the UCNPs surface, as shown in Figure 3, with a thickness of 24 nm. Figure 4 shows that the AuNRs have the desired rod-like shape, with a length of 68 nm long and a width of 32 nm.

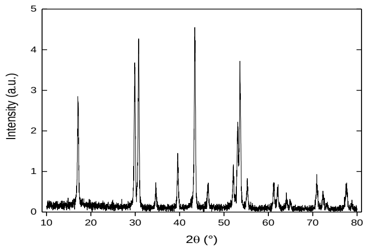

Figure 1: XRD pattern of the UCNPs@$NaYF_4$.

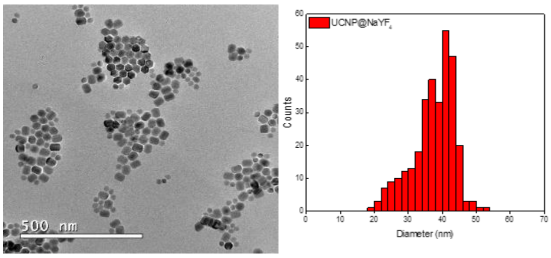

Figure 2: TEM images of UCNPs@$NaYF_4$ and their size distribution.

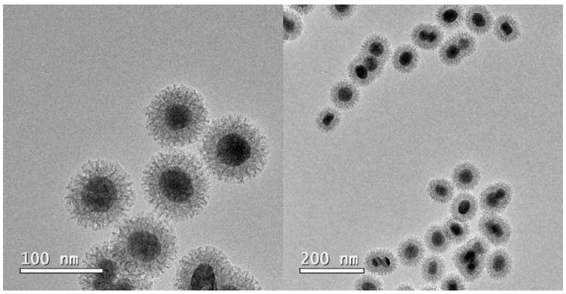

Figure 3: TEM images of the UCNPs@$NaYF_4$@$mSiO_2$.

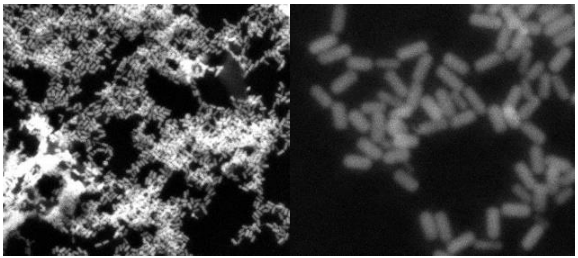

Figure 4: (a) SEM images and (b) TEM images of the AuNRs.

Figure 5 presents the UCNPs emission spectrum compared with the AuNRs absorption spectrum. The two plasmonic absorption bands, the transversal one in 515 nm and the longitudinal in 670 nm, are overlapped with the UCNPs emissions, with peaks in 520, 538 and 652 nm.

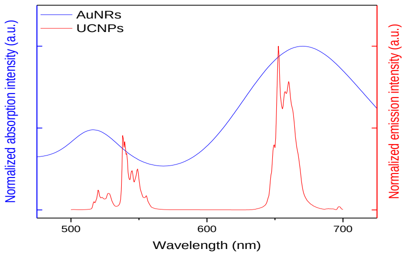

Figure 5: Comparison between the absorption and emission spectra of AuNRs in water and powder UCNPs, respectively. λ_{exc} = 976 nm.

About the UC quenching tests, Figure 6 compares the UCNPs@$NaYF_4$@$mSiO_2$ emission spectra before and after the addition of AuNRs. It is possible to observe a considerable decrease in the signal, indicating the occurrence of energy transfer from the UCNPs to the AuNRs. The quenching effect was 74% efficient to the emission from the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition

(520 nm), 68% efficient to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ emission (538 nm) and 71% efficient to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ emission (652 nm). At last, when the $UCNPs@NaYF_4@mSiO_2$-NH_2 were mixed with the AuNRs, the quenching effect was less intense. This happens because the NH_2 groups lead to a positive superficial charge in the UCNPs (+23 mV), while the OH groups lead to a negative charge (-13 mV),[3] which makes the interaction between UCNP and AuNR less efficient, as the CTAB at the AuNRs surface are also positive. The comparison between the emission spectra of aminated NPs before and after the AuNRs addition is presented at Figure 7. The efficiency of the quenching effect in this case was 67%, 63% e 58% for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ e $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively.

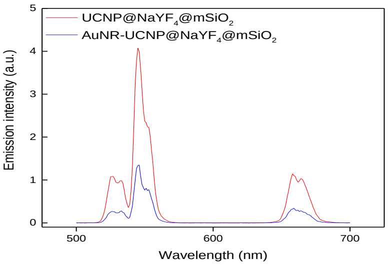

Figure 6: Emission spectra of negative charged UCNPs in the presence and absence of AuNRs. $\lambda_{exc} = 976$ nm.

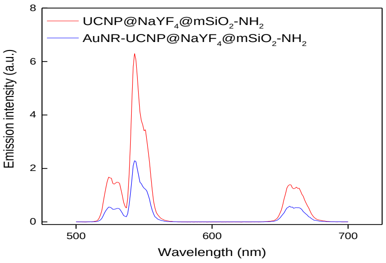

Figure 7: Emission spectra of positive charged UCNPs in the presence and absence of AuNRs. $\lambda_{exc} = 976$ nm.

Conclusions

It was possible to synthesize the desired β-UCNPs, as well as to coat it with $NaYF_4$ and $mSiO_2$. After the $NaYF_4$ shell, the UCNPs has an average size of 43 nm, while the $mSiO_2$ shell has a thickness of 24 nm. The AuNRs absorption bands match the emission peaks of the UCNPs at 520, 538 and 652 nm. The expected quenching effect from the AuNR-UCNP interaction was also observed, and it was affected by the superficial charge of the UCNPs, indicating the possibilities to functionalize the UCNPs to modulate the desired quenching effects, which makes this combination a promising supramolecular system to be employed in sensing devices.

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