

## Luminescence enhancement by energy transfer in core-shell structures

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### Abstract

An energy transfer between the two parts of a nanocomposite was shown in a core-shell made of Tb-doped gadolinium oxide (the core) and polysiloxane (the shell). Polysiloxane is found to act as an *antenna* which absorbs light and transfers the excitation energy to the rare-earth doped oxide, allowing then an enhancement by a factor of 4 of the luminescence of the rare earth cations. Both energy transfer and quenching reduction contribute to the luminescence enhancement observed upon coating. The Letter shows how these relative contributions can be quantitatively discriminated from excitation spectra.

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Coating particles with silica is a promising strategy which presents several advantages in the field of biological [1] and imaging [2] applications. Apart ensuring core protection and water-solubility, the silica shell realizes two crucial functions. The first consists in allowing functionalization by biological groups since silica can be derivatized by organoalkoxysilanes containing reactive organic groups (e.g. amine, thiol, isothiocyanate). These organic functions which are covalently bound to the inorganic network act as anchorage sites for biomolecules. The second which was less extensively studied consists in increasing the optical response of luminescing cores used as optical tags. This latter was recently investigated for two different types of fluorescent inorganic particles: semi-conductors [3,4] and rare-earth (RE) based oxides [5,6]. The enhancement of luminescence brought by coating strongly depends on the nature of the core. It can be significant (about 100%) in the case of Mn-doped ZnS [3] or only slightly pronounced in Eu doped YVO<sub>4</sub>. [5] In some cases as pure Eu<sub>2</sub>O<sub>3</sub> [6] or CdSe/ZnS [4,7], the luminescence is, on the contrary, found

to slightly decrease or severely drop. In all cases, the influence of the coating was explained on the basis of a reduction of the luminescence quenching of the surface hydroxyl groups. However, another physical mechanism could explain the modification of luminescence upon coating. It consists of an energy transfer between the two parts of the core-shell structure, the silica shell acting as an antenna which absorbs the light and transfers it to the core enhancing then its optical response. In this Letter the core chosen is a 5%<sub>at</sub> Tb<sup>3+</sup>-doped gadolinium oxide. It belongs to the family of the lanthanide oxides which received a recent attention in the field of biological application [8,9].

For synthesizing the nanocomposite, a two-step process, described in details elsewhere,[10] was carried out. In a first step, the Gd<sub>2</sub>O<sub>3</sub>: Tb (5%<sub>at</sub>) particles were precipitated by the polyol route [11]. In a second step, a polysiloxane shell was deposited on the lanthanide oxide cores by hydrolysis of a mixture of APTES ((3-aminopropyl)triethoxysilane: H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>-Si-(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) and TEOS (tetraethylorthosilicate: Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>). During the polysiloxane reticulation, a quasi-ideal encapsulation of each core is achieved with a thickness which can be adjusted by varying the amount of precursors. The size of the core/shells is measured by Photon Correlation Spectroscopy (PCS) from the fluctuations of the

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scattered intensity under illumination with a HeNe laser (632 nm). Table 1 details the properties of the core-shells studied in the paper. It shows that the expected shell thickness calculated from the quantity of precursors introduced assuming a polysiloxane volumic mass of  $2 \text{ g} \cdot \text{cm}^{-3}$  [12] coincides perfectly with that deduced by Photon Correlation Spectroscopy (PCS).

Following a strategy already used in the case of a gold/RE oxide composite [13] the most favourable conditions for studying energy transfers between the polysiloxane and the Tb doped gadolinium oxide parts were determined from absorption spectra. Gd-based oxide presents a charge transfer band around 290 nm and has a gap located around 220 nm [14] Due to interband electronic transitions and to localized electric moieties, polysiloxane is found to absorb significantly below 250 nm. An excitation wavelength of 230 nm was then chosen for emission experiments. The luminescence of the core/shell excited at 230 nm is shown in Fig. 1 for different thickness of encapsulation (2.5, 5 and 8 nm) and for two core sizes (3.5 on the left and 7.8 nm on the right). For all core-shells, the luminescence is normalized to the same mass of RE oxide. It is measured for dilution in polyol sufficiently high to ensure that the composite absorption varies linearly with its concentration. The absorption of polyol is predominant so that the effective optical paths are the same for all the samples. As expected the spectra shows that the emission of the  $\text{Tb}^{3+}$  cations is significantly increased when oxide is coated by polysiloxane. The enhancement factor,  $\alpha_D$ , is defined as the ratio of the individual luminescence of the core coated (dotted, solid and bold curves) to that of the core alone (dashed curve).  $D$  indexes the size of the core. For a same thickness, the enhancement  $\alpha_D$  is significantly greater for the smaller core ( $\alpha_{3.5 \text{ nm}} = 7.4$  whereas  $\alpha_{7.8 \text{ nm}} = 3.1$  for a shell thickness,  $e$ , of 8 nm). In accordance with the hypothesis of an energy transfer between the two parts of the core-shell, this result could indicate that only the outer regions of the core (i.e. those located at a low distance from the polysiloxane shell) should contribute significantly to the enhanced emission. In order to demonstrate that this increase of luminescence is actually due to an energy transfer, we verified that the luminescence of the oxide emitter varies in a similar way than the absorption of the polysilox-

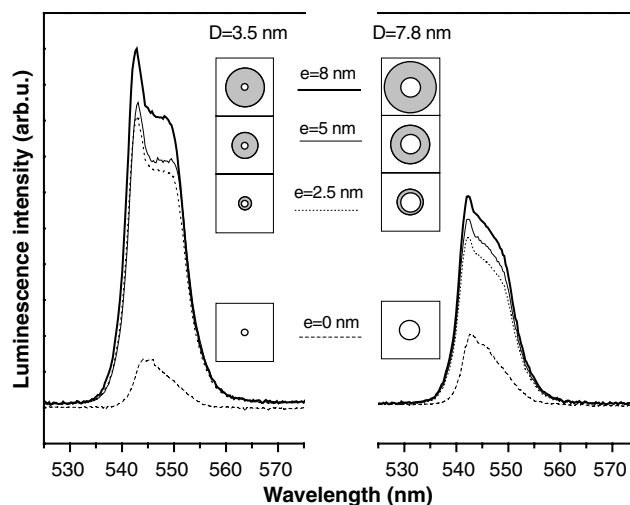


Fig. 1. Emission for excitation at 230 nm of the  $\text{Gd}_2\text{O}_3:\text{Tb}$  cores alone with a size  $D$  of 3.5 nm (left, dashed curve) and 7.8 nm (right, dashed curve) and of the  $\text{Gd}_2\text{O}_3:\text{Tb}$ -polysiloxane core-shells with different thickness  $e$  (2.5 nm : dotted curve, 5 nm : thin solid curve, 8 nm : thick curve). Emission is given after normalization per mass unit.

ane antenna. Fig. 2 which shows the evolution of the emission at 545 nm as a function of the excitation wavelength establishes this correlation. It demonstrates that the enhancement of luminescence is significant only below 270 nm which coincides to the wavelength range where polysiloxane absorbs strongly. Even more interesting is to compare the enhancement induced by the association of the oxide to polysiloxane (this Letter) or gold (a previous paper). [13] Whatever the antenna used, its efficiency is found maximal in the excitation range where its absorption is maximal: below 330 nm for gold and 270 nm for polysiloxane.

The results presented in Figs. 1 and 2 also rules out the explanation involving a reduction of quenching as the only reason to luminescence enhancement. Quenching certainly explains the difference in luminescence observed in Fig. 1 between the two bare cores (in normalized units, the RE oxide with a size of 7.8 nm emits around 1.4 times more than the 3.5 nm one does) since a greater size reduces the specific area of the colloid. However, upon coating, the luminescence of the 3.5 nm core becomes higher than that

Table 1  
Description of the core/shell studied

Core particles		Coating : amount of precursors introduced		Expected shell thickness (nm)	Measured core/shell size (nm)	Measured shell thickness (nm)
Diameter (nm)	Concentration (particles. $\mu\text{m}^3$ )	APTES ( $\mu\text{mol} \cdot \text{l}^{-1}$ )	TEOS ( $\mu\text{mol} \cdot \text{l}^{-1}$ )			
3.5 (1.2)	45	181.2	119.7	2.5	8.5 (2.4)	2.5
3.5 (1.2)	45	758.1	505.6	5.0	13.5 (3.2)	5.0
3.5 (1.2)	45	1966.2	1541.9	7.7	19.5 (4.1)	8.0
7.8 (3.5)	4.5	51.2	33.6	2.5	12.8 (2.8)	2.5
7.8 (3.5)	4.5	160.2	106.8	5.0	17.4 (4.8)	4.8
7.8 (3.5)	4.5	408.6	272.4	8	24.8 (7.9)	8.5

Expected shell thickness are evaluated from the quantity of APTES and TEOS introduced. Measured shell thickness are deduced from core and core/shell sizes obtained by PCS (in parentheses mean standard deviations).

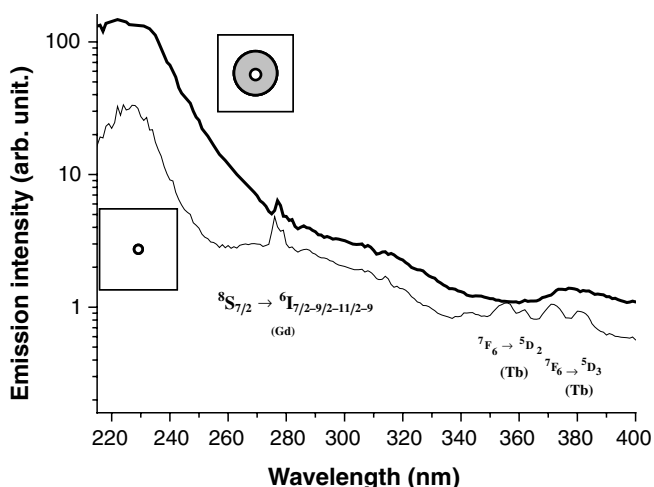


Fig. 2. Excitation spectra monitored at 545 nm for the 3.5 nm oxide cores alone (thin line) and the oxide-polysiloxane core-shells with a thickness of 5 nm (thick line).

of the 7.8 nm one which cannot be explained only by a reduction of quenching: under this latter assumption indeed, the normalized emission of the two cores should be, at best, equal. The excitation spectrum permits to clarify the relative contributions of quenching reduction and energy transfer upon coating. Indeed in the range of the higher wavelengths, the polysiloxane antenna does not absorb so that the quenching reduction becomes the predominant reason to luminescence enhancement. It is clear that in this range the coating-induced enhancement is very limited (less than 80%) and also slightly depends on the wavelength. This fact could lighten controversial literature which reports that for a same material coating can induce different enhancements. Finally, one should use the variation of the luminescence enhancement on the whole wavelength range to roughly evaluate the relative contributions of energy transfer (et) and quenching reduction (qr),  $\alpha_D^{\text{et}}$  and  $\alpha_D^{\text{qr}}$ , to the total enhancement  $\alpha_D$  of a core/shell with a core size  $D$ . This evaluation is made using a simple model in which  $\alpha_D = \alpha_D^{\text{et}} \alpha_D^{\text{qr}}$  and  $\alpha_D^{\text{qr}}$  is given by the enhancement observed between 290 and 330 nm, a range of wavelength for which there is no energy transfer. It is reasonable to assume that  $\alpha_D^{\text{qr}}$  does not depend on the shell thickness (whereas, in the domain where the absorption varies linearly with the concentration,  $\alpha_D^{\text{et}}$  is expected to increase with  $e$ ). For a core size of 3.5 nm:  $\alpha_{3.5 \text{ nm}}^{\text{qr}} = 1.7$  (intensities in Fig. 2 between 290 and 330 nm), then  $\alpha_{3.5 \text{ nm}}^{\text{et}}$  is equal to 3.5, 3.7 and 4.3 for thickness of 2.5, 5 and 8 nm respectively. Similarly, for a core size of 7.8 nm, one finds  $\alpha_{7.8 \text{ nm}}^{\text{qr}} = 1.3$  so that  $\alpha_{7.8 \text{ nm}}^{\text{et}} = 2.1, 2.2$  and 2.4 for  $e = 2.5, 5$  and 8 nm.

The minimum distance between polysiloxane and oxide required to achieve some efficient energy transfer can be estimated by comparing the enhancement induced by the different morphologies of the core/shells. For both core sizes, 3.5 and 7.8 nm, the luminescence is first strongly increased for a coating of 2.5 nm and then only increases

in a slight extent for larger thickness. This indicates that the distance,  $d$ , required to achieve an efficient energy transfer is certainly smaller than 2.5 nm. This distance could be calculated from the comparison between the enhancement factors,  $\alpha_D^{\text{et}}$ , of the two cores using a simple geometrical model in which the cores are embedded in an infinite polysiloxane shell (i.e. with a thickness superior to  $d$ ). In this model, the cores having a diameter  $D$  are schematically divided into two different zones. The first zone with a volume  $\frac{\pi D^3}{6} \left[ 1 - \left( 1 - \frac{2d}{D} \right)^3 \right]$  is the part of the oxide core located at a distance of polysiloxane smaller than  $d$  and having an effective luminescence enhancement of  $\alpha^{\text{et}}$  whereas the complementary zone has no enhancement. The enhancement factor,  $\alpha_D^{\text{et}}$ , of the entire core is then related to the effective one  $\alpha^{\text{et}}$  according to the relation:

$$\left( \alpha_D^{\text{et}} - 1 \right) = \left( \alpha^{\text{et}} - 1 \right) \left[ 1 - \left( 1 - \frac{2d}{D} \right)^3 \right]$$

The two experimental results:  $\alpha_{3.5 \text{ nm}}^{\text{et}} = 4.3$  and  $\alpha_{7.8 \text{ nm}}^{\text{et}} = 2.6$  are now used to calculate  $d$  and  $\alpha^{\text{et}}$ . These  $\alpha_D^{\text{et}}$  values are relative to the larger shell which is the one which corresponds better to the model of an infinite shell. The unknown  $d$  is very sensitive to the values of  $\alpha_D^{\text{et}}$  which are subjected to large uncertainties ( $\approx 30\%$ ). Then one can only conclude that  $d$  is certainly less than 1 nm and that  $\alpha^{\text{et}}$  lies between 2 and 5. In fact if one assumes that  $d \ll D/2$ , one obtains the following relation:  $6(\alpha^{\text{et}} - 1)d = (\alpha_D^{\text{et}} - 1)D$  which indicates that the product  $(\alpha^{\text{et}} - 1)d$  is the only quantity which can be experimentally determined and predicts moreover than the enhancement factor,  $\alpha_D^{\text{et}}$ , must vary as the inverse of the core size. This latter relation is well verified since  $\frac{\alpha_{7.8 \text{ nm}}^{\text{et}} - 1}{\alpha_{3.5 \text{ nm}}^{\text{et}} - 1} = 2.1$  whereas the ratio of the core sizes is 2.2. This agreement confirms the small value of  $d$  indicating then that the transfer mechanism is probably radiationless.[15] For a polysiloxane coating the product:  $(\alpha^{\text{et}} - 1)d$  is equal to  $\approx 2$ . Although significant it is much smaller than that observed in the case of a gold coating where it was found equal to  $\approx 200$  [13]. It is yet in good agreement with the results already reported for RE chelates encapsulated in cage-type ligands [16] or in contact with Ag particles [17].

In this Letter, a clear evidence of an energy transfer between the two parts of a core/shell was proved from the variation of the luminescence enhancement with excitation. This confirms that energy transfer is a general phenomenon which should be expected within all nanoscale particles with suitable absorption and emission properties. Aiming at biological applications, the present result provides directions for developing new efficient tags based on core-shell structures.

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