Comment on "Room-Temperature and Ultrafast Synthesis of Highly Luminescent and Extremely Small Eu^{3+}-Doped YVO_4 Nanocrystals"

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Comment on "Room-Temperature and Ultrafast Synthesis of Highly Luminescent and Extremely Small Eu^{3+}-Doped YVO_4 Nanocrystals" (J. Phys. Chem. C 2023, 127, 5075−5081.)

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In one of its recent volumes, The Journal of Physical Chemistry C published a paper entitled "Room-Temperature and Ultrafast Synthesis of Highly Luminescent and Extremely Small Eu^{3+}-Doped YVO_4 Nanocrystals" (J. Phys. Chem. C 2023, 127, 5075−5081. DOI: 10.1021/acs.jpcc.3c00125).[1] This study focuses on the research field of luminescent rare-earth-doped nanocrystals, a topic that has been present in the literature since approximately 2000 and

continues to be actively explored.[2–9] The primary objective of such studies is to develop synthetic methods that can produce nanocrystals with the highest possible emission yield, as is known for bulk compounds, thereby facilitating novel applications in bio-labeling, displays, and sensors.[10–17]

In this context, the work of Pan and co-workers is noteworthy because it reports an impressive absolute photoluminescence quantum yield (PLQY) of 62% for 3.6 nm YVO_4:Eu^{3+} nanoparticles prepared by a ligand-assisted co-precipitation method.[1] This emission performance is extremely close to the bulk solid (PLQY=70% for 5 mol% of Eu^{3+}).[14] Shortly after, the same group reported in Inorganic Chemistry the synthesis of 2.7 nm $LaPO_4$:Ce^{3+},Tb^{3+} nanoparticles with a PLQY of 74%, an extremely high value for nanocrystals of such a small size.[18]

The great appeal justifying the publication of these works stems from the fact that sub-5 nm oxide-based particles easily prepared at room temperature exhibit emission properties nearly identical to their bulk counterparts. Nevertheless, based on our experience of over two decades in luminescent rare-earth-doped nanocrystals, particularly YVO_4- and $LaPO_4$-based compounds, we are convinced this is a misleading fact. This letter presents three fundamental reasons why extremely small oxide-based luminescent nanoparticles cannot display such a high PLQY. As additional evidence, we reproduced the synthesis reported in the paper, leading to more reasonable results than those reported by the authors.

Firstly, surface is a major source of luminescence quenching in small particles, even overcoming concentration effects.[19,20] Considering that the synthesis was carried out in protic solvents (*i.e.*, water and ethanol) using carboxyl and amine ligands, it is likely that the obtained nanocrystals are covered with species showing high-energy phonons (*e.g.*, OH, NH, and CH groups). These

are well-known to quench the emission of Eu^{3+} via multiphonon relaxation mechanisms.[21] Consequently, nanoparticles generally exhibit a decreased PLQY compared to bulk solids.[7,15,22] Additionally, the authors state that the ligands ensure complete passivation of surface defects by butyrate/butylammonium ion pairs.[18] If this claim were entirely valid, all the spectroscopic properties of the obtained nanocrystals should be similar to those of the bulk material, including the optimal Eu^{3+} concentration. However, the optimal Eu^{3+} concentration (31 mol%) was six times higher than the reported value for the bulk solid (5 mol%).[1,14,22] Such a high value of optimal Eu^{3+} content is commonly reported for nanoparticles as a result of altered energy transfer processes that also lead to the degradation of PLQY.[15,22]

Lattice distortions are a second source of emission quenching. Generally, energy transfer processes after light absorption predominantly occur through exchange interactions,[23,24] which are favored by an efficient overlap of the wave functions. For $YVO_4:Eu^{3+}$, a V-O-Y angle around 170° enhances the σ bonding overlap and explains its outstanding luminescence.[23] However, lattice distortions in nanoparticles caused by crystalline defects or limited size (*e.g.*, oxygen vacancies, reduced vanadium species, dangling bonds, and inhomogeneous strain)[16,25] change the energy migration through decreasing wave function overlaps. This results in an increased non-radiative decay and decreased PLQY. To overcome this issue, treating the solids at very high temperatures (~1000 °C) is crucial. We devised a facile method permitting high-temperature treatments of nanocrystals without aggregation or growth.[22,26] The resulting nanoparticles exhibited a reduced defect density and improved emission performance.[22]

Nevertheless, annealed particles did not exhibit the same bulk performance due to the impact of dielectric effects on the emission yield. This issue is intrinsic to the small size and represents a limitation that cannot be overcome by any surface treatment. It has indeed been shown in several

systems that the radiative decay rate depends strongly on the refractive index of the medium surrounding the particles.[5,8,22] This effect is particularly pronounced for oxide compounds since the refractive index of the medium (solvents or air) is lower than that of the bulk solid. This leads to a significant decrease in the radiative decay rate and emission efficiency. The extension of this decrease depends on the refractive index of the surrounding medium and the volume fraction occupied by the nanoparticles. Clear evidence for such behavior has been reported by Meltzer and co-workers[5] in the case of Eu^{3+}-doped Y_2O_3 nanocrystals immersed in different media and by us in our previous work involving annealed YVO_4:Eu^{3+} nanoparticles.[22]

Based on these arguments, we propose the following reflection to illustrate the consequences of a PLQY of 62% for YVO_4:Eu^{3+} nanoparticles. The emission of Eu^{3+} in YVO_4 arises almost exclusively from the $^5D_0$ state.[6,16] Hence, the PLQY (*i.e.,* overall quantum yield - the ratio between the photon flux emitted and the photon flux absorbed by the sample at a given wavelength) is proportional to and limited by the internal quantum yield (η) of the $^5D_0$ state, which is defined as the ratio between the radiative decay rate (A_{RAD}) and the total decay rate (A_{TOT}) of this emitting state.[15] The total decay rate (A_{TOT}) is given by the reciprocal of the luminescence lifetime (τ, Eq.1):

$$\eta = \frac{A_{RAD}}{A_{TOT}} = \frac{A_{RAD}}{A_{RAD}+A_{NRAD}} = A_{RAD}\tau \qquad \text{(Eq. 1)}$$

Therefore, a PLQY of 62% implies that the internal quantum yield of the $^5D_0$ state must be greater or equal to 62% (η≥ 62%). The results of Pan and co-workers indicate a $^5D_0$ luminescence lifetime of 0.6 ms for that sample showing PLQY of 62%.[1] Consequently, this sample should involve a radiative decay rate at least higher than 1033 s^{-1}, and a non-radiative

decay rate lower than 634 s^{-1}. We will assume this lower limit value of A_{RAD}=1033 s^{-1} for the purpose of our further discussion.

Whilst the non-radiative contribution varies with surface-to-volume ratio, crystallinity, and defect density, the radiative rate mostly depends on the symmetry and local refractive index, thus being less variable for a given phase and structure (*e.g.*, tetragonal YVO_4). An A_{RAD}=1033 s^{-1} value is almost twice the $^5D_0$ radiative decay rates usually observed for YVO_4:Eu^{3+} as nanosized solids, which are around 450-600 s^{-1}.[16,27]

The A_{RAD} value of the $^5D_0$ state can be determined using the integrated intensity (I_{01}) and the rate of spontaneous emission of the magnetic dipole-allowed $^5D_0 \rightarrow {}^7F_1$ transition in vacuum (A_{MD}=14.65 s^{-1})[28,29] in comparison to the integrated intensities of the other $^5D_0 \rightarrow {}^7F_J$ (I_{0J}) transitions (Eq. 2):

$$A_{RAD} = A_{MD} n_{ef}^3 \sum_{J=0-4} \frac{I_{0J}}{I_{01}}, \qquad \text{(Eq. 2)}$$

where n_{ef} is the effective refractive index around the particles. The reported emission spectra are highly similar to other YVO_4:Eu^{3+} compositions found in the literature both in terms of spectral shape and relative intensities.[6,12,16,30,31] So, no alterations on A_{RAD} are expected to arise from the I_{0J} terms, and the I_{0J}/I_{01} intensity ratios can be assumed to be nearly 0, 1, 9, 0.3, and 2 for the $^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2, 3, and 4, respectively) transitions based on our observations and on several previous results.[6,7,12,16,22,27,30,31] Because A_{MD}=14.65 s^{-1} is a constant, the conclusion is that an A_{RAD} value of 1033 s^{-1} must result from a high effective refractive of about 1.79.

Consequently, the volume fraction occupied by the particles (φ) and the refractive index of the dispersing medium (n_{med}) can be taken into account considering that the effective refractive index is given by (Eq. 3):

$$n_{ef} = \varphi n_P + (1 - \varphi) n_{med}, \qquad \text{(Eq. 3)}$$

where n_P is the refractive indices of the solid particles. The refractive index of YVO_4 is expected to be n_P=1.99.[32] Therefore, an effective refractive index of n_{ef}=1.79 requires a high density of particle packing (*i.e.* high φ) or a very high refractive index of the dispersing medium. Even if we assume a high n_{med} due to surface ligands (*e.g.* n_{med}=1.4, which is approximately the refractive index of pure butyric acid or n-butylamine),[33] the volume fraction necessary for n_{ef}=1.79 still should be as high as φ=0.67. This is nearly the random-close packing limit for polydisperse hard spheres with log-normal distribution and radii standard deviation lower than 0.3.[34] These conditions are inconsistent with the narrow size distribution and low aggregation degree reported by the authors, especially considering the transmission electron microscopy. Additionally, the luminescence measurements were performed with powders in air, so n_{med} is probably lower than 1.4.

Hence, unless the obtained particles show an unprecedently high intrinsic refractive index or a significant packing density combined with a high amount of surface ligands providing n_{med} as high as for pure butyric acid/butylamine, a PLQY of 62% is rather unlike to occur for YVO_4:Eu^{3+} particles showing a $^5D_0$ lifetime of 0.6 ms and the characteristic spectral shape described in the paper.

Finally, we evaluated the validity of the published results by conducting experiments with $YVO_4:Eu^{3+}$ nanocrystals containing 40 mol% of Eu^{3+}, as it was claimed to present the highest PLQY. It is worth mentioning that variations regarding synthesis reproductivity are expected, but they do not prevent us from making comparisons of emission yields. The Eu^{3+} emission profile is very similar to that described in the paper (Figure 1a). However, we measured a PLQY of only 21% for the prepared nanocrystals, which obviously contrasts with the reported result (PLQY = 62%). So, we checked the validity of our measurement by experimentally determining the quantum yield of the bulk material, which has a 70% yield for 5% Eu^{3+} doping.[14] The sample prepared by conventional solid-state synthesis exhibited a PLQY of 72%, in excellent agreement with the expected value (Figure 1b).

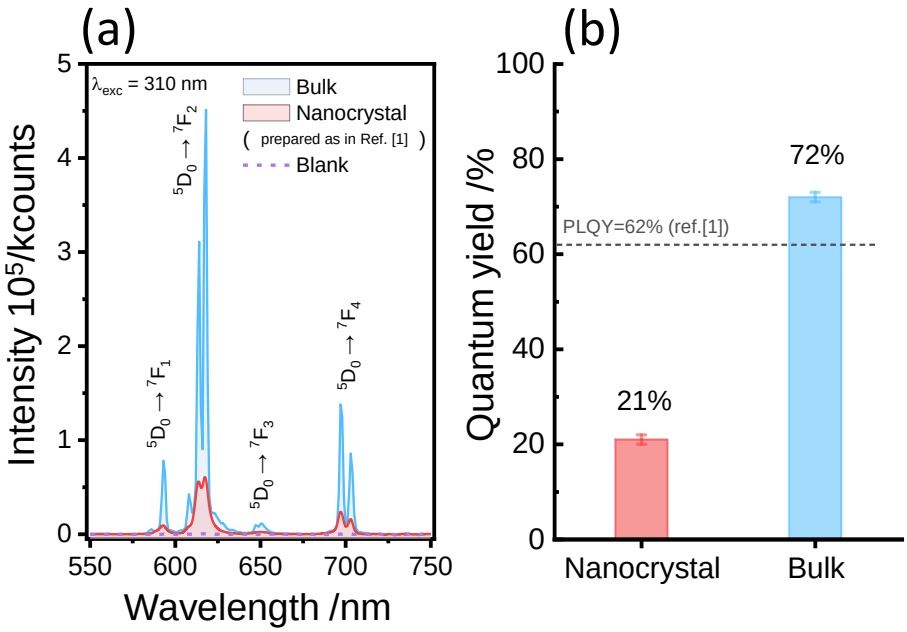

Figure 1. Experimental determination of absolute emission quantum yields (λ_{exc}=310 nm) of $Y_{0.60}Eu_{0.40}VO_4$ nanocrystals prepared by reproducing the methodology described in Ref. [1] (red lines) in comparison to a $Y_{0.95}Eu_{0.05}VO_4$ reference prepared by conventional solid-state synthesis (blue lines): (a) absolute emission intensities, and (b) photoluminescence quantum yields

(PLQY). Errors bars correspond to standard deviations within each triplicate. The measurements were performed with powder samples on a Horiba-Jobin-Yvon Fluoromax-4P spectrofluorometer coupled to an integrating sphere (Horiba Quanta φ) and using a Spectralon® sample cup with coverslip as a blank. The parameters were adjusted to obtain a scattering signal of around 1.3 x 10^6 counts at 310 nm with the blank.

Thus, we confirmed that extremely small $YVO_4:Eu^{3+}$ nanoparticles do not exhibit luminescent performances close to the bulk material. This is because poor crystallinity, surface, and dielectric effects in this size regime limit high emission yields. Additionally, since optimizing emission quantum yield is crucial for the application of luminescent nanocrystals, the present discussion highlights the importance of conducting precise and meticulous measurements, providing all required experimental details, and testing on reference samples. In the work of Pan and co-workers, although the most appealing report is the extremely high emission yield, no details were provided regarding the measurement of PLQY.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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