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Luminescence regulation mechanism of single layer $NaYF_4$: Yb^{3+}, Er^{3+}@ $NaYF_4$ nanocrystals on Au nanolayer supported by anodic aluminum oxide template

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ABSTRACT

A kind of novel hybrid nanostructure of anodic aluminum oxide (AAO) template or Au sputtered AAO template covered by a single layer $NaYF_4$: Yb^{3+}, Er^{3+}@$NaYF_4$ nanocrystals (NCs) was prepared by a facile strategy. Two kinds of available models that include with and without Au nanolayer were suggested for simulations. Significant downconversion luminescence (DCL) enhancement was observed when the supported template changed from single AAO to Au nanolayer covered AAO. A formula for luminescence enhancement factor based on the cavity quantum optics theory was constructed. With luminescence dynamics analyses, the DCL enhancement was ascribe to the main positive influence of excitation enhancement, besides the minor negative impact of the competition among the nonradiative loss of resonant cavity, the higher order mode loss of Purcell factor, and the increase of radiative transition rate. It proposed a new idea for surface plasmon (SP) induced luminescence regulation mechanism exploration.

1. Introduction

In recent years, rare earth doped luminescent nanomaterials have demonstrated appealing potential for novel applications in anti-counterfeiting [1], optogenetics [2], theranostics [3], sensing [4], display [5], photovoltaics [6], and so on. However, the application of rare earth doped luminescent materials especially for upconversion materials was often limited by its low luminescent efficiency, which induced by a small absorption cross-section originated from the parity forbidden *f-f* transition of rare earth ions [7]. Currently, most of the related works are focus on the luminescence enhancement of rare earth doped luminescence materials for catering to their novel applications [8,9]. In contrast, some specific radiative transitions need to be optically inhibited (i.e. luminescence quenching) in other fields, such as stimulated emission depletion (STED) nanoscopy [10,11], environmental monitoring and assessment [12], and immunoassay [13]. Accordingly, accurate and reasonable luminescence regulation turns to be one of the urgent problems for rare earth doped materials.

The collective oscillation of conduct electrons on metallic nanostructure surfaces known as surface plasmon resonance (SPR), can produce strong local field adjacent to the metallic nanostructures in subwavelength scale. The localization results in the near-field enhancement by orders of magnitude, thus the remarkable application in the luminescence regulation of rare earth doped nanomaterials. Recently, a dual-enhancement and precise color tuning of gold nanorod@SiO_2 coupled $NaGdF_4$: Yb^{3+}, Nd^{3+}@$NaGdF_4$: Yb^{3+}, Er^{3+}@ $NaGdF_4$ NCs have been realized by Kang et al, and a reasonable theoretical interpretation based on the electrodynamic simulation has been presented [14]. Differentiated relative contributions of excitation, radiative decay rate and energy transfer enhancements of $NaYF_4$: Nd^{3+}, Yb^{3+}, Er^{3+} NCs on the Au film with ultra-broad plasmonic absorption have been demonstrated by Wang et al [15]. Song et al addressed a significant excitation enhancement of UCL of $NaYF_4$: Yb^{3+}, Er^{3+} NCs induced by Ag nanowire network [7]. An opening-angle-controlled metal nanogap was employed to improve the luminescence of Y_2O_3: Yb^{3+}, Er^{3+} NCs, and the relation between SPR absorption wavelength and the enhancement factor was suggested by numerical simulation [16]. Additionally, a tunable luminescence enhancement of single $NaYF_4$: Yb^{3+}, Er^{3+}, Mn^{2+} nanocrystal has been presented by tailoring scattering and absorption cross sections of Au nanorods, where both

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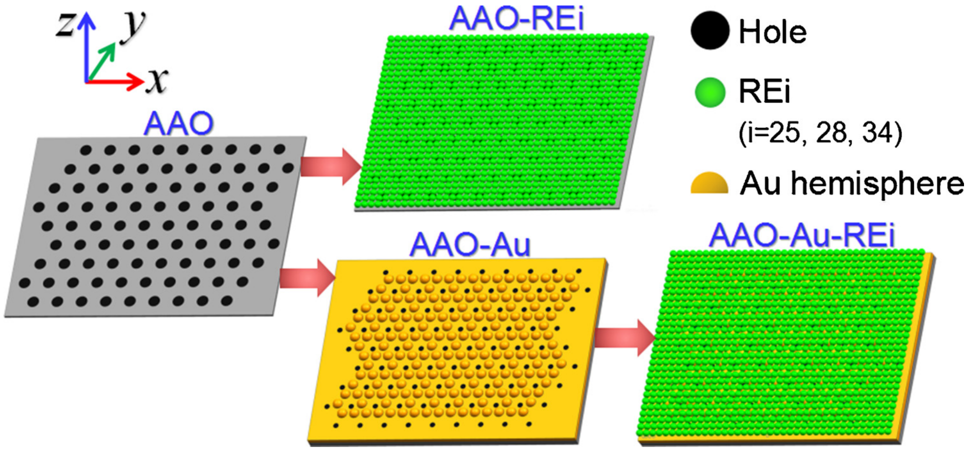

Fig. 1. Schematic diagram for formation of AAO-RE and AAO-Au-RE.

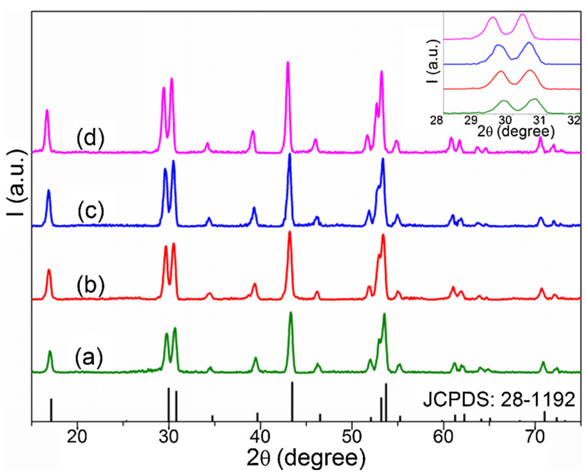

Fig. 2. XRD patterns of sample (a) RE, (b) RE25, (c) RE28, and (d) RE34 (inset: magnification peaks around 30° and 31°).

excitation and emission processes were proved to be accelerated by the SPR effect [17]. Due to the involvement of the synergistic action among excitation photon, luminescent ion and SP, the luminescence regulation mechanism of rare earth doped NCs turns to be very complicated. Furthermore, an accompanied energy transfer from luminescent ion to metallic nanostructure that results in luminescence quenching often appear in the SPR induced luminescence regulation process. To the best of our knowledge, the analytical luminescence regulation mechanism of rare earth doped NCs/metallic nanostructure hybrid system that can be appropriate for both enhancement and quenching has not been addressed.

In this work, a novel hybrid nanostructure of single layer $NaYF_4$: Yb^{3+}, Er^{3+}@$NaYF_4$ NCs supported by periodic arrangement of AAO template or Au sputtered AAO (AAO-Au) template has been constructed by a facile strategy. The theoretical absorption spectra of these two templates can be easily indexed with those for experimental counterparts, which gives a indication of the rationality of the suggest models. Significant upconversion and downconversion luminescence regulations for the single layer NCs have been realized by the introduction of an additional Au nanolayer. An available formula based on cavity quantum optics theory was established, and employed to explain the

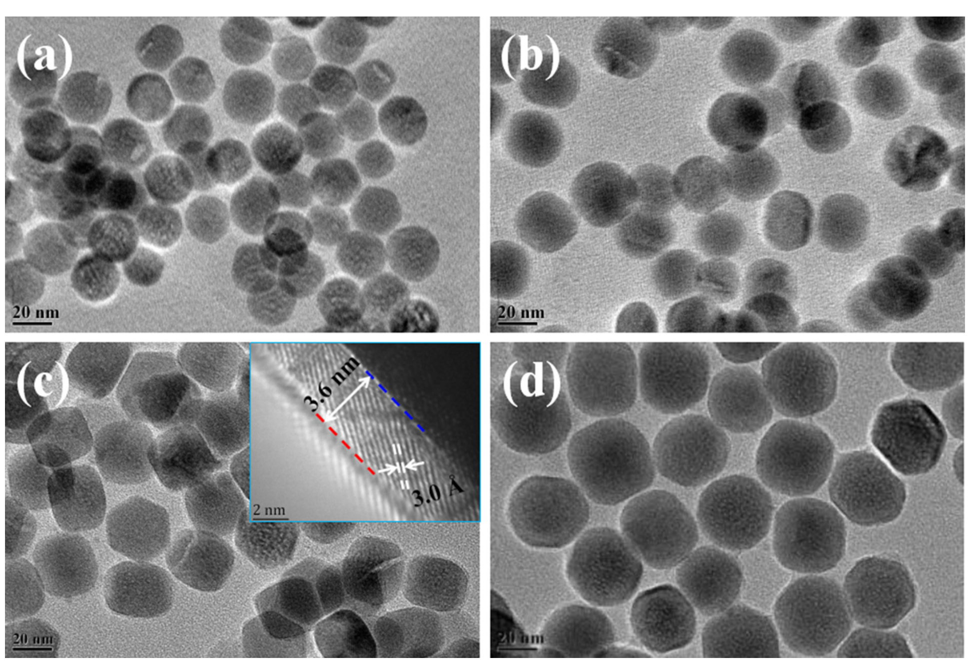

Fig. 3. TEM images of sample (a) RE, (b) RE25, (c) RE28, and (d) RE34 (inset in Fig. 3(c): HR-TEM of sample RE28).