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# Plasmon-enhanced fluorescence of $CaF_2:Eu^{2+}$ nanocrystals by Ag nanoparticles

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ABSTRACT

We report plasmon-enhanced fluorescence in $Eu^{2+}$ doped $CaF_2$ ($CaF_2:Eu^{2+}$) nanocrystals assembled with Ag nanoparticles (NPs) using a simple hydrothermal method. The structure, morphology and composition of the nanocrystals are confirmed by X-ray diffraction (XRD), transmission electron Microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and UV–vis absorption spectrum. Ag nanoparticles are ideal building blocks for plasmonic materials that can exhibit a wide range of unique and potentially useful optical phenomena. Surface plasmon enhancement makes significant contribution to enhance the blue fluorescence emission of $CaF_2:Eu^{2+}$. The enhancement on the Eu emission in visible regions is up to a factor of 12.3-fold. As shown in time-resolved measurements, surface Plasmon Resonance (SPR) can reduce the fluorescence lifetime and increase the quantum yield. Furthermore, with increasing Ag concentration, the fluorescence intensity increases to its maximum and then decreases.



## 1. Introduction

In recent years lanthanide-doped nanomaterials for photonic applications have attracted great attention and been widely investigated for many fields, such as semiconductor [1], UV lasers [2], display [3] and biological labels [4]. What makes nanocrystals special is that each size has a completely distinct set of physical and chemical properties. As nanometer crystals can be precisely prepared now, materials with designed properties can be produced not only by changing their chemical composition but by controlling their sizes [5]. However, the properties of nanometer scale crystals differ from their bulk materials [6]. The nanocrystals with well-defined morphologies and accurately tunable sizes remains a challenge. Their physical and chemical properties vary drastically by geometrical factors such as shape, dimensionality, and size.

So far, the host materials for fluoride nanocrystals have been mainly focused on $NaYF_4$ and $LaF_3$ [7,8]. But, lanthanide doping in these host lattice are induced by a high-intensity pulse laser or have low quantum yield. In contrast, calcium fluoride ($CaF_2$) is very suitable as a host for rare earth ions due to its desirable properties, such as low refractive index, low phonon energy, high laser damage threshold [9–11]. To date, RE-doped $CaF_2$ nanomaterials have attracted more attention because of its robustness among other fluorides. Among the rare-earth ions, $CaF_2:Eu^{2+}$ exhibit excellent properties because of $4f^7$-$4f^6$5d transition and the emission varies from ultraviolet to red region [12]. Particularly, increasing technological and industrial interest is given to research on the luminescence of optical nanomaterials due to their novel optical properties about emission lifetime, luminescence quantum efficiency, and concentration quenching [13]. It has been investigated that luminous efficiency depends on the particle size [14,15]. When particles are prepared in small sizes, the following factors become critical for luminescence intensity: (1) surface defect; (2) ratio between thermalization length of charge carriers and the nanoparticle sizes [16]. The reduction of the nanocrystals size leads to significant luminescence intensity decrease, which limits their further applications. To solve this question, extensive work has been carried out, such as modulating reaction condition [17], coating surfactants or shell [17,18], and preparing composite materials [19]. However, the effect of these enhancement mechanism is not obvious.

By coupling with noble metals on the surface of luminescent

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nanocrystals, luminescence can be enhanced due to Surface Plasmon Resonance (SPR) [20–22]. Surface plasmon enhanced fluorescence has been widely studied and used in various fields starting with classic reports of Drexhage [23]. This can be an effective promoter of fluorescence when optimized to provide a large and highly confined local electric field enhancement that arises from the collective oscillations of the electrons due to resonance [24–26]. In particularly, metal nanoparticles such as gold, silver, and copper nanoparticles can show intense surface plasmon resonance absorption band in UV–vis and near infrared (NIR) region [27,28]. Recently, most researchers have used Ag-NPs with desirable SPR to enhance luminous efficiency. For instance, according Xin Xu's report [29], the visible emission of $Sr_2Si_5N_8:Eu^{2+}$ phosphor can be enhanced by coupling with the localized surface plasmon oscillation of Ag nano-particles. Qiang Shi [30] reported on highly tunable enhancement of red emission from $Mg_{0.1}Zn_{0.9}O$ phosphors by regulation of the LSP resonance of Ag nanoparticles. Hyungduk Ko [31] demonstrated a novel anticounterfeit device based on NIR-to-Vis upconversion luminescence from $\beta$-$NaYF_4:Yb^{3+},Er^{3+}$ enhanced by the Ag nanowires-driven plasmonic effects. Similarly, Wen Xu [32], Hongwei Song [33], and other researchers [34–36] enhanced upconversion emission of $NaYF_4$:Yb, Er nanocrystals by using noble metal. However, among these studies, a large number of researches are about up-converting materials and noble metal with small grain size. There are few reports on down-converting materials with resonance metal.

With this motivation, we report herein a facile one-pot process to synthesize down-converting $CaF_2:Eu^{2+}$ attaching Ag nanoparitcles without any calcination. Using this method, we are able to synthesize nanoparticles with particle size about 60 nm. Meanwhile, a maximum luminescence enhancement of 12.3-fold is observed when the fluorescent intensifier Ag nanoparticles with a relatively large size of 85 nm are used. Tuning by switching between fluorescence enhancements and quenching is shown as a function of the concentration of Ag NPs coated on the surface of $CaF_2$, a parameter easily controlled during synthesis. In reaction process, a reduction of $Eu^{3+} \rightarrow Eu^{2+}$ happens under the catalytically active Ag nanoparticles. In addition, the influences of the reaction time, temperature and pH value are also discussed.

## 2. Experimental

### 2.1. Synthesis of Ag nanoparticles

The nanoparticles were synthesized using method described by P.C.Lee and D.Meisel [37]. Briefly, 45 mg $AgNO_3$ was dissolved in 250 ml boiling water and the solution was kept boiling for half an hour. Under stirring, 1% sodium citrate aqueous solution (5 ml) was rapidly injected into above solution and the mixture was further refluxed for another 1 h. Sodium citrate as a mild reducing agent gradually changed the growth solution from colorless to brownish. The suspension was then cooled to room temperature under stirring and stored at 4 °C for later use.

### 2.2. Synthesis of $CaF_2$: $Eu^{2+}$(2.5%) nanoparticles

$CaF_2:Eu^{2+}$ nanoparticles were prepared by hydrothermal method. The $EuCl_3 \cdot 6H_2O$ were obtained by adding hydrochloric acid to $Eu_2O_3$. In a typical synthesis, 3.40 mmol $CaCl_2 \cdot 2H_2O$ and 0.43 mmol $EuCl_3 \cdot 6H_2O$ were dissolved in 15 ml distilled water under stirring followed by dropwise addition of 15 ml 68.30 mmol $NH_4F$. After a white homogeneous dispersion appeared, a certain amount of Cit-Ag colloids were injected and a well-controlled amount of NaOH solution was added under magnetic stirring to reach different pH values. Next, 0.40 g $NaBH_4$ was added and the mother solution containing white suspension was sealed in 50 ml Teflon-lined stainless steel autoclave. The mixture was treated at different temperature and time. Temperature rate is 10 °C/min. Finally, the obtained suspensions were washed with ethanol and deionized water for several times and dried in a vacuum oven at 60 °C.

### 2.3. Characterization

The XRD measurements of synthesized samples were carried out using a XD-2X/M4600 X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.154056$ nm) at 40 kV and 30 mA in a scan range 10–80°. The morphology and EDS were observed by a JSM-7001F field emission scanning electron microscope (FESEM). A JEOL-2100F High-Resolution Transmission Electron Microscope (HRTEM) operated at 200 kV was used to observe the grain size and examine the lattice fringes. Samples for TEM were prepared by depositing a drop of sample dispersed in ethanol onto a holey carbon–coater copper grid. The photoluminescence (PL) of the powder samples was measured by a Shimadzu RF5301pc fluorescence spectrophotometer. UV–vis absorption spectra were measured using a Shimadzu UV-2550 spectrophotometer with a wavelength range from 200 to 800 nm. The concentration of Ag nanoparticles was analyzed by Varian 810 ICP-MS. EPR spectra were acquired with a Bruker A300-10/12 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed in a ESCALAB 250Xi with an Al Kα X-ray source with constant pass energy of 30 eV.

## 3. Results and discussion

### 3.1. Structure and formation of $CaF_2:Eu^{2+}$ nanoparticles

The composition and crystal phase of the nanocrystals are characterized by XRD. Fig. 1a and b shows the XRD patterns of 2.5mol% $Eu^{2+}$ doped $CaF_2$ nanoparticles with different amount of Cit-Ag nanoparticles and heating temperatures, respectively. Based on the XRD diffraction peaks, the samples are well-crystallized. The diffraction peaks in Fig. 1 could easily be assigned to the (111), (220), (311), (400) and (331) planes of face-centered cubic (*fcc*, space group: Fm3m [38]). There is no impurity peaks observed. These values obtained from all the samples match very well with $CaF_2$ standard JCPDS cards (35-0816). There is no apparent difference observed after $Eu^{2+}$ doping or Cit-Ag nanoparticles addition. The lattice constant for the $CaF_2:Eu^{2+}$ is calculated to be 5.39 Å, which is close to 5.46 Å for pure $CaF_2$ nanocrystals [39]. The $Eu^{2+}$ ions may occupy the $Ca^{2+}$ sites in the $CaF_2$ host lattice. Based on the half-maximum (FWHM) values of the (111) peaks, the mean size of the $CaF_2$ nanocrystals is evaluated to be about 56 nm by Debye–-Scherrer formula [40]. As shown in Fig. 1a, the strong and sharp diffraction peaks indicate that the $CaF_2$ with different amount of Cit-Ag nanoparticles are well crystallized. As heat treatment temperatures rise, the intensity of the diffraction peaks increase significantly (Fig. 1b), which implies a better crystallinity. The broadening of these diffraction peaks is an indication of small size samples.

XPS can be used to check the composition of surfaces, which is carried out in the 0–1300 eV binding energy range to identify the elements on the surface of samples. Fig. 2a depicts the survey of the samples, which indicates that all the samples are mainly consist of Ca, F, Eu, and some impurity elements of C, O. The 2p levels of Ca show the spin-orbit doublet with the binding energies around 348.6 eV ($2p_{3/2}$) and 352.2 eV ($2p_{1/2}$) in Fig. 2b [41]. Moreover, the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ core level binding energies for Ag NPs sample appear at 368.1 and 374.1 eV in Fig. 2c, which are higher than the reference value from J. S. Hammond [42] and Schon, G [43] due to the larger size [44]. However, a broad peak of the Ag $3d_{5/2}$ peaks as