Size-dependent photoluminescent property of hybrid nanoparticles consisted with YVO$_4$:Eu$^{3+}$ and gold

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Abstract. The hydrothermally synthesized YVO$_4$:Eu$^{3+}$ nanophosphors were mixed with gold nanoparticles with different sizes to form hybrid nanoparticles. The microstructure and luminescent properties of all hybrid nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-Visible absorption spectrum (UV-Vis), and photoluminescence (PL) spectroscopy. The growth process of gold nanoparticles prepared by seeding growth method was discussed firstly. Furthermore, the effects of grain size of gold nanoparticles on the fluorescent property of hybrid nanoparticles were investigated in detail. All the emission spectra presented the characteristic red emission of Eu$^{3+}$. The emission intensity of hybrid nanoparticles was increasing with the growing of gold nanoparticles. The influential mechanism was discussed as well.

Keywords: YVO$_4$:Eu$^{3+}$, gold nanoparticles, size-dependent, photoluminescent properties

1. Introduction

YVO$_4$ crystal has been considered as an excellent host material because of its outstanding chemical, thermal, mechanical and optical properties as well as easy to be doped with trivalent rare earth ions [1,2]. Eu$^{3+}$ ions are excellent luminescent centers with the parity forbidden characteristics exhibiting strong red line emissions with high color purity [3]. As a kind of excellent commercial phosphor, YVO$_4$:Eu$^{3+}$ has been widely used in many fields, such as luminescent lamps, solid-state lasers, optical fiber communication systems, flat displays, and photonic devices [4-7].

Recent years, higher requirements of fluorescence materials about stability, brightness, color purity and so on are put forward due to its expansive application in drug delivery, biolabeling and solar cell. Therefore, YVO$_4$:Eu$^{3+}$ phosphor has become a hot research topic because of its high purity and high quantum yield. Currently, the methods to improve the luminescent property of YVO$_4$:Eu$^{3+}$ phosphors are including ions doping [8-11], core-shell structure [12-17], metal enhancing [18-20], and so on.

Metal enhanced fluorescence is a promising method to enhance the luminescent property of lanthanide nanophosphors [21,22]. The highly localized electromagnetic (EM) fields generated around metal nanoparticles (MNPs) are responsible for the enhancement. The EM fields are generated by resonant excitation of conduction electrons in MNPs also known as surface plasmon, upon excitation by incident light [23]. It is suggested that the plasmon absorption band and scattered light of MNPs both contribute to the enhancement process [24]. The MNPs can modify the free-space conditions in ways that increase the incident EM and decrease the radiative decay rate, namely, the MNPs provide more radiative decay pathways and larger radiative decay rates [25].
In this paper, we present a study of a hybrid nanoparticles consisting of YVO$_4$:Eu$^{3+}$ nanocrystals and gold nanoparticles (Au NPs). The fluorescent property of the hybrid nanoparticles with different Au NPs sizes was investigated. The excitation and emission intensity of YVO$_4$:Eu$^{3+}$ nanocrystals were influenced by Au NPs due to the local plasma resonant effect. The details were discussed below.

2. Experimental

All the chemical reagents purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China) were of analytical grade and used as received without further purification.

2.1. YVO$_4$:Eu$^{3+}$ nanoparticles preparation

The YVO$_4$:Eu$^{3+}$ nanoparticles were synthesized by typical hydrothermal method. Firstly, all of rare earth chloride stock solutions of 0.1 M were prepared by dissolving the corresponding metal oxide in hydrochloric acid at elevated temperature. In a typical procedure, the Eu$^{3+}$ concentration in the YVO$_4$ host was 5 mol.%, a certain amount of YCl$_3$ was added into aqueous solution containing 2 mmol of trisodium citrate. Then, 1 mmol Na$_3$VO$_4$ was introduced into the solution. After additional agitation for 1h, the as-obtained mixing solution was transferred into a Teflon bottle held in a stainless steel autoclave, sealed, and maintained at 180$^\circ$C for 24h. As the autoclave cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with ethanol and deionized water in sequence, and finally dried in air at 80$^\circ$C for 12h.

2.2. Au NPs preparation

Au NPs with various diameters were obtained by using classic seeding growth method [26].

2.2.1. Preparation of Gold Seed. A 20 mL aqueous solution containing 2.5×$10^{-4}$M HAuCl$_4$ and trisodium citrate were prepared in a conical flask. Then, 0.3mL ice-cold, freshly solution of 0.1M NaBH$_4$ was added to the above-mentioned solution while stirring. The formatted particles in this solution were used as seeds after the preparation of 2h. (Citrate serves only as a capping agent since it cannot reduce the gold salt at room temperature in this section).

2.2.2. Preparation of Growth Solution. A certain amount of cetyltrimethylammonium bromide (CTAB) and HAuCl$_4$ aqueous solution were stirring under heated condition. And the solution was cooled to room temperature. The detailed process was described in Ref 25.

2.2.3. Seeding Growth. Four groups of 50 mL conical flasks were labeled A, B, C, and D. The appropriate volume of growth solution was mixed with 0.05 mL of freshly prepared 0.1M ascorbic acid solution. Next, the appropriate volume of particle seeds was added while stirring. The volumes of growth solution and seeds solution added in the conical flasks were listed in Table 1.

| Sample name | Ascorbic acid solution (0.1M) | Growth solution | Seed Solution |
|-------------|-------------------------------|-----------------|---------------|
|             | Original | B sample | C sample |
| A           | 0.05 mL | 7.5 mL    | 2.5 mL |
| B           | 0.05 mL | 9.0 mL    | 1.0 mL |
| C           | 0.05 mL | 9.0 mL    | 1.0 mL |
| D           | 0.05 mL | 9.0 mL    | 1.0 mL |

2.3. Synthesis of YVO$_4$:Eu$^{3+}$–Au hybrid nanoparticles
The as prepared citrate-coated YVO₄ nanoparticles were dissolved in deionized water to form suspension, and then four different CTAB-coated Au nanoparticles were added to the suspension. Kept stirring for 2h. The YVO₄:Eu³⁺-Au hybrid nanoparticles were prepared after excess Au colloid was wiped out by centrifugation.

2.4. Characterization methods
The X-ray diffraction (XRD) analysis (XRD-7000 X-ray diffractometer, Shimadzu, Japan) was used to identify the crystalline phases and operated at 40 kV and 40 mA, Cu Kα radiation was used and the goniometer was run from 15° to 80°. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL 3010 transmission electron microscope, using an accelerating voltage of 300 kV. UV-Vis spectra were recorded from 400 nm to 600 nm using a UV-3010 UV-Vis spectrophotometer. The photoluminescence (PL) excitation and emission spectra were recorded with 970CRT fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source.

3. Results and discussion

3.1. Phase, structure and morphology of YVO₄:Eu³⁺ nanoparticles
Figure 1(a) shows the XRD patterns of YVO₄:Eu³⁺ nanoparticles. According to JCPDS standard card No. 72-0861, all peaks are assigned to tetragonal crystalline phase YVO₄ with lattice contents a = b = 7.12 Å and c = 6.29 Å. No other impurity peaks are detected indicating pure YVO₄ powder was prepared and Eu³⁺ doping don’t affect its crystal structure. The morphologies of YVO₄:Eu³⁺ nanocrystals characterized by TEM are presented in figure 1(b). The TEM image indicates that as-prepared YVO₄:Eu³⁺ nanocrystals possess rod-like shape with a length of ~50 nm and a width of ~20 nm. Furthermore, the SAED image (inset as figure 1(c)) reveals the polycrystallinity of YVO₄:Eu³⁺ nanocrystals with spotty diffusion rings indexing to the tetragonal phase of YVO₄.

Figure 1. XRD pattern(a), TEM image(b), and SAED image(c) of YVO₄:Eu³⁺ nanoparticles.

Figure 2. TEM images of Au NPs with four different diameters (a) 8.5±0.6 nm, (b) 10.0±0.8 nm, (c) 24.5±0.8 nm, and (d) 55±0.5 nm. The SAED image of Au NPs.
3.2. Size-dependent Au NPs
The TEM images of Au NPs obtained from A, B, C and D groups were exhibited in figure 2. As can be seen that the products’ diameter is increasing from 8.5±0.6nm, 10.0±0.8 nm, 24.5±0.8 nm to 55±0.5 nm corresponding to A, B, C and D groups, respectively. Otherwise, all the NPs distribute homogeneously and independently, which can be attributed to the feature of CTAB and the negative electrical property of Au NP. The Au NPs with sizes of 8.5 nm and 10 nm (in figure 2(a-b)) present good size distribution and uniform spherical morphology. But the size distribution of the Au NPs with sizes of 24.5 nm and 55 nm (in figure 2(c-d)) become wider and present polygon morphology, which results from the non-uniform adsorption of chlorauric acid on the crystal surface during the step by step reduction process. Furthermore, the SAED image (inset as figure 2(e)) presents bright spot rings, which verify the polycrystallinity of Au NPs. All four products exhibit similar SAED images those are not repeated here.

![Figure 3. UV-Vis absorption spectrum of Au NPs with four different particle size.](image)

For the UV-Vis absorption spectrum of nano dimension, the electron cloud of the particle surface can generate oscillation through the electromagnetic radiation of specific energy absorption. It could produce resonance when the frequency of electromagnetic wave equals to the plasma oscillation. The resonance macroscopically shows the absorption of light by metal nanoparticles, which is seriously affected by the particle size. Figure 3 shows the corresponding UV-Vis absorption spectra of Au NPs with different particle sizes. It can be seen that the plasma absorption band is broadened and the strength is weaken with the increasing of the Au NPs size from 8.5 nm to 55 nm, which means the coupling of plasmon mode is weaken. Meanwhile, the plasma absorption band location is red shifted from 525 to 540 nm due to size shrinkage.

3.3. Morphology of the hybrid nanoparticles
Figure 4 is the TEM image of four kinds of hybrid nanoparticles with different Au NPs’ diameters. As can be seen, the dark particles represent Au NPs, while the light particles represent YVO₄:Eu³⁺ nanoparticles. It also can be seen clearly from the figure 4 (a-c) that the spherical Au NPs with four different sizes and YVO₄:Eu³⁺ nanoparticles distribute alternatively. Some of the Au NPs are attached on the surface of YVO₄:Eu³⁺ nanoparticles due to the Van der Waals’ force. In figure 4 (d), the Au NPs possess the similar size with YVO₄:Eu³⁺ nanoparticles.

3.4. Size-dependent photoluminescent properties
Figure 5 is the excitation and emission spectra of the hybrid nanoparticles consisted with YVO₄:Eu³⁺ nanoparticles and Au NPs at room temperature. All the excitation spectra are monitored at the emission wavelength of 618 nm. It is obviously that the excitation intensity is higher than pure YVO₄:Eu³⁺ nanoparticles, and the intensity increase with the grown of the grain size of Au NPs. The excitation band at 200 ~ 300 nm is caused by energy transition (ET) between VO₄³⁻ and Eu³⁺. And the violent fluctuation of the excitation curve is attributed to the strong reflection of local plasma resonant field around the Au NPs. The excitation spectra are obtained under excitation of 281 nm. Two main identifiable peaks located at 593 nm and 618 nm are connected with ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ characteristic transition of Eu³⁺. Luminescent properties of Eu³⁺ in the crystal lattice are related to the position, when in the non-spatial inversion symmetry, Eu³⁺ exhibit electric dipole transitions (⁵D₀→⁷F₂), however, at the center of the inversion sites, Eu³⁺ exhibits magnetic dipole transitions (⁵D₀→⁷F₁). So in the crystal of as-prepared YVO₄:Eu³⁺ nanoparticles, Eu³⁺ ions occupied the non-spatial inversion sites. The intensity of the main emission peaks is enhanced with the increasing of the Au NPs’ grain size. It can be seen in the figure 3 that with the size reduction of Au NPs, the local plasma resonant field is stronger, but the fluorescent property decreased. According to Lakowicz report [25], the metal enhanced fluorescence is due to at least three known mechanisms: (1) energy transfer quenching, (2) the increasing of the local incident field on the fluorophore, (3) the increasing of the intrinsic radiative decay rate of the fluorophore. In the hybrid nanoparticles, the absorption band of Au NPs is not overlapped with the emission peaks of YVO₄:Eu³⁺ nanoparticles. So the energy transfer quenching is not presented in the YVO₄:Eu³⁺ nanoparticles mixed with smaller Au NPs (8~10 nm). But with the increasing of Au NPs’ size, the local incident field is enhanced. Thus the YVO₄:Eu³⁺ nanoparticles mixed with larger Au NPs (25~55 nm) exhibit enhanced emission intensities. The radioactive decay rate is not detected in this experiment. The schematic diagram of fluorescence enhancement is shown in figure 6.

![Figure 5](image5.png)

**Figure 5.** Excitation and emission spectrum of YVO₄:Eu³⁺ hybrid four sizes Au NPs.

![Figure 6](image6.png)

**Figure 6.** The schematic diagram of fluorescence enhancement.

### 4. Conclusions

In summary, a series of hybrid nanoparticles consisting of YVO₄:Eu³⁺ nanophosphors and Au NPs were prepared and examined for fluorescent property. The excitation and emission intensity were increased with the size growing of Au NPs. This is a result of enhanced reflection of plasma resonant effect of Au NPs.

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