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Preparation and optical properties of Eu(III) complexes J-aggregate formed on the surface of silver nanoparticles

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Abstract

Ag colloidal nanoparticles coated with $Eu(TTA)_3 \cdot 2H_2O$ complexes were prepared, and it was found that $Eu(TTA)_3 \cdot 2H_2O$ complexes J-aggregate was formed on the surface of Ag nanoparticles according to a red shift (18.2 nm) in UV–Vis spectra. However, there had similar excitation wavelength, which was attributed to existence of Ag nanoparticles. Highly luminescent properties of Ag colloidal nanoparticles were observed, and it was believed to result from low energy transfer between Eu(III) complexes and Ag and the large electromagnetic field arising from the excitation of surface plasmon polariton of Ag nanoparticles.

1. Introduction

J-aggregates are characterized by a red-shifted and sharp absorption band relative to the monomer band, a result of exciton delocalization over the molecular building blocks of the aggregate [1–4]. In addition to their uses as photographic sensitizer, the large oscillator strength and fast electronic response of J-aggregate are of interest in many fields, such as modeling energy transfer in photosynthetic reaction center antenna, nonlinear optics related to superfluorescence, and solar photochemical energy conversion [3–8]. Because rare earth complexes show strong ligand-sensitized rare earth characteristic luminescence with excellent monochromacity of bandwidth and lifetime up to several millisecond [9] and these characteristics make them good candidates for advanced optoelectronic materials [10]. Considerable attention has been paid on the theirs J-aggregate formed on bulk metal [11–15]. The J-aggregation of cyanine dyes on the surface of noble metal nanoparticles was reported and showed the enhanced optical properties [16–23]. Rare earth complexes coating on surface of Ag nanoparticle are expected to modulate and improve optical properties owing to the electromagnetic interaction between metal core and rare earth complexes, particularly in the case that absorption frequency of rare earth complexes lies close to the surface plasmon resonance (SPR) of Ag nanoparticles. So here the Ag colloidal nanoparticles coated with rare earth complex of $Eu(TTA)_3 \cdot 2H_2O$ was prepared in the mixture solution of acetone/water, and its optical properties were investigated in detail. Specifically, this offers a unique opportunity to study the interaction between rare earth complex J-aggregates and the laser near-field enhancements and modulate electrochemical properties of Ag colloidal nanoparticles.

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2. Experimental sections

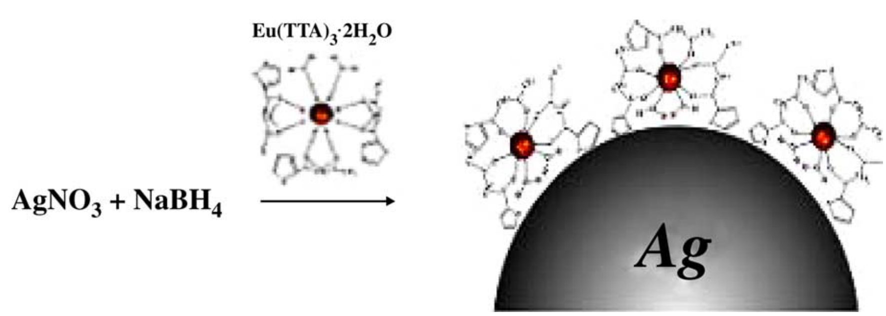
$Eu(TTA)_3 \cdot 2H_2O$ complex was synthesized according to the procedure [24] and its chemical structure was given in Scheme 1. The product was determined by IR spectrum, such as the C=O group at 1614.5 cm^{-1}, CF_3 group at 1357.4 cm^{-1}, C=C group at 1541.8 cm^{-1} and the Eu–O at 638.9 and 579.8 cm^{-1}.

Ag colloidal nanoparticles coated with $Eu(TTA)_3 \cdot 2H_2O$ complex were prepared by reduction of $AgNO_3$ with $NaBH_4$ in the presence of $Eu(TTA)_3 \cdot 2H_2O$ complexes as shown in Scheme 1. $Eu(TTA)_3 \cdot 2H_2O$ (1.0 g, 1.17 mmol) and $AgNO_3$ (67.9 mg, 0.4 mmol) were dissolved in acetone (150 ml) and aqueous (10 ml) solution, respectively. After mixing the two solutions, $NaBH_4$ aqueous solution (20 ml, 0.83 mM) was dropped under vigorous stirring. The color of the solution changed to deep orange immediately after the addition of $NaBH_4$. The reaction solution was left for 12 h with rapid stirring to ensure complete reaction. Then, centrifuging (3000 rpm) gave a brown acetone/water precipitates, and supernatant solution containing excess $Eu(TTA)_3 \cdot 2H_2O$ and $NaBH_4$-derived impurities was extracted. The precipitates were again dissolved into acetone. The purification procedure was repeated for three times. Morphology and size distribution of complex nanoparticles was obtained by using transmission electron microscope (TEM). The samples were also characterized by UV–Vis spectroscopy and fluorescence spectroscopy.

3. Results and discussion

While preparing Ag colloidal nanoparticles coated with $Eu(TTA)_3 \cdot 2H_2O$ complex, it is important to choose solvent for the reaction. The key considerations of solvent for the reaction are: (1) that the solvent can dissolve $Eu(TTA)_3 \cdot 2H_2O$ complex, (2) that the solvent can also dissolve $AgNO_3$ and $NaBH_4$, and (3) the solvent can not form complex with Ag^+. With these considerations, *N*,*N*-dimethylformamide and aqueous/ethanol mixture solution were not chosen for solvent as reported in previous work [25,26], and here acetone/water mixture solution was chosen for the solvent, which was very important to synthesize complex particles with long-term stabilization and monodispersity. Fig. 1a shows that all the particles are almost spherical and that the average size of the particles is 21.5 nm. Size distribution is shown in Fig. 1b, suggesting the good monodispersity. Typical electron diffraction pattern image of Ag colloidal nanoparticles is also shown in Fig. 1c, which shows growing parallel to (1 1 1), (2 0 0) and (2 2 0) planes of cubic silver, indicating the formation of Ag nanoparticles with good crystalline.

Fig. 2 shows UV–Vis absorption spectra of the Ag colloidal solution, confirming further the formation of Ag nanoparticles. A dilute Ag colloidal solution displays a strong absorption in the region of 422.4 nm. This peak must arise from the surface plasmon absorption of the Ag clusters [27]. At same time, the UV absorption



Scheme 1. Preparation of Ag colloidal nanoparticles coated with $Eu(TTA)_3 \cdot 2H_2O$ complexes, and formation of $Eu(TTA)_3 \cdot 2H_2O$ complexes J-aggregate on the surface of Ag nanoparticles.

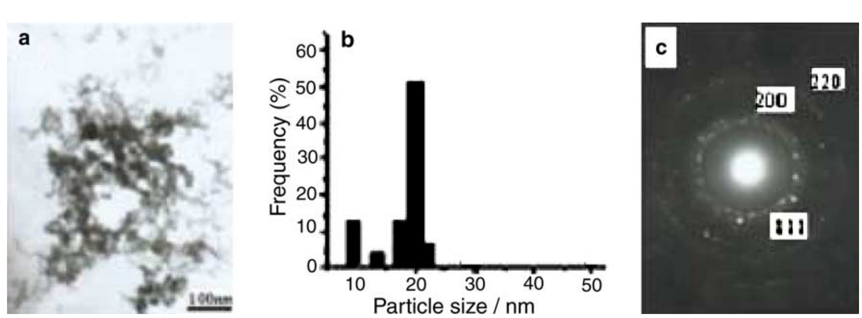


Fig. 1. (a) TEM image of Ag colloidal nanoparticles coated with $Eu(TTA)_3 \cdot 2H_2O$ complexes and (b) its size distribution and (c) electron diffraction pattern.