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Inner filter effect of gold nanoparticles on the fluorescence of rare-earth phosphate nanocrystals and its application for determination of biological aminothiols

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ABSTRACT

A simple, sensitive fluorescent method for detecting biological aminothiols has been developed based on the inner filter effect principle that utilizes $CePO_4:Tb^{3+}$ luminescent nanoparticles as the donor and gold nanoparticles (AuNPs) as the energy receptor. Stable, water-soluble and well-dispersible $CePO_4:Tb^{3+}$ nanoparticles with low photobleaching features were synthesized conveniently by a facile solvothermal method. At the same time, AuNPs with a high extinction coefficient are expected to be capable of functioning as powerful receptor. Based on the complementary overlap between the emission spectrum of $CePO_4:Tb^{3+}$ nanoparticles and the absorption spectrum of Au NPs, an inner filter effect system was constructed. In the presence of aminothiols (such as cysteine), AuNPs interacted with the aminothiols, thereby inducing the aggregation of AuNPs, which induced the fluorescence recovery. In the present work, we developed a turn-on fluorescent assay for the determination of biological aminothiols. Under the optimum conditions, the linear concentration ranges were 1.0×10^{-7}–2.0×10^{-6} M for cysteine, 5.0×10^{-8}–5.0×10^{-7} M for glutathione and 8.0×10^{-8}–1.0×10^{-6} M for homocysteine, respectively. The method is successfully applied to the quantification of biological aminothiols in synthetic samples.

1. Introduction

Recent advances in nanotechnology have shown great promise of nanomaterials in the chemical and biological sensors design [1–4]. Rare-earth phosphate nanocrystals have attracted growing interest for use as luminescent label materials owing to their unique properties, including long lifetimes, high quantum yields (up to 61%), low photobleaching, expected low toxicity, and high chemical stability [5–9]. Among these lanthanide nanoparticles, $CePO_4:Tb^{3+}$ nanocrystals were widely studied due to their unique properties (such as water-soluble, well-dispersible, luminescence stable), and applied in determination and sensing. With the great extinction coefficients, gold nanoparticles (AuNPs) are usually used in the colorimetric-based detection system [10–13]. Recently, AuNPs have been favorably adopted as an active unit in the fluorescent assay [14–20], and the most frequently adopted scheme is based on the ultra-efficient quenching capability of AuNPs to the fluorescence of nearby organic fluorophores through non-radiative energy/electron transfer processes [21]. Moreover, some research groups have constructed fluorescence resonance energy transfer (FRET) between QDs and AuNPs, and have applied the FRET systems to sensitively detect important biological analytes [22–24]. It is noted that the design of these FRET processes would involve the intermolecular connection of QDs with AuNPs at a particular distance or geometry to enable the interaction between them. Unfortunately, it is necessary and important for the AuNPs to be modified or engineered so as to directly contact with or be indirectly linked to special modified QDs. To date, the modifying steps make the method very complicated, time-consuming and expensive, so, consequently restricted their practical applications [25].

In this work, stable, dispersible and unfunctionalized $CePO_4:Tb^{3+}$ nanocrystals were synthesized according to the previously reported methods [26–30]. A strong emission of $CePO_4:Tb^{3+}$ could be seen as a narrow band between 540 and 580 nm. Thus, we present an alternative approach to design fluorescent assays based on the inner filter effect (IFE) of AuNPs on the fluorescence of $CePO_4:Tb^{3+}$,which is conceptually different from the previously reported AuNPs-based FRET systems. In this approach, Au NPs and $CePO_4:Tb^{3+}$ do not need to be modified (or labeled). Notably, this approach does not require the binding of AuNPs with $CePO_4:Tb^{3+}$, which offers considerable flexibility and more simplicity. The low-molecular-mass aminothiols such as cysteine (Cys), homocysteine (Hcy) and glutathione (GSH) play a critical role in many biochemical

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pathways [31,32]. Their concentrations in biological fluids are important for clinical diagnostics of some diseases. In the presence of aminothiols (such as Cys), Au NPs interacted with the aminothiols, thereby inducing the aggregation of AuNPs, which induced the fluorescence recovery. Based on this, a new IFE method was developed for the determination of biological aminothiols.

2. Experimental

2.1. Reagents and instruments

$Tb(NO_3)_3 \cdot 6H_2O$ and $CeCl_3 \cdot 7H_2O$ were purchased from Sigma-Aldrich company, L-cysteine, glutanthione, homocysteine and chloroauric acid ($HAuCl_4$) were purchased from Aladdin company. Sodium tripolyphosphate (TPP) and sodium citrate were prepared by dissolving them in doubly deionized water. Water used throughout was doubly deionized.

The fluorescence spectra were performed using Hitachi F-2500 fluorescence spectrophotometer (Hitachi, Japan) equipped with a quartz cell (1 cm × 1 cm). UV–vis absorption spectra were obtained using a U-4100 spectrophotometer (Hitachi, Japan). The transmission electron microscope (TEM) images of the nanocrystals were acquired using a JEM-2100 transmission electron microscope. (JEOL, Japan). Zeta potential was measured using a Malvern Zetasizer nano ZS90 apparatus (Malvern Instruments, Malvern, United Kingdom).

2.2. Synthesis of $CePO_4$:Tb^{3+} nanocrystals

$CePO_4$:Tb^{3+} nanocrystals were synthesized by using facile and solvothermal technology [8]. $CeCl_3 \cdot 7H_2O$ (4.5 mL, 0.1 mol L^{-1}), $Tb(NO_3)_3 \cdot 6H_2O$ (0.5 mL, 0.1 mol L^{-1}), and sodium tripolyphosphate (TPP, 10 mL, 0.1 mol L^{-1}) were added to 10 mL water, and the solution was thoroughly stirred. Subsequently, the milky colloidal solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 30 mL and heated at 90 °C for 3 h. The system was then allowed to be cooled to room temperature. The final product was collected by centrifugation, washed with ethanol once and with deionized water twice to remove any possible remnants, and then dried in air.

2.3. Preparation of AuNPs

AuNPs were prepared by the citrate reduction method according to the published protocol [33–35]. All glasswares used in these preparations were thoroughly cleaned in aqua regia, rinsed thoroughly in water and dried in the air. Briefly, a sodium citrate solution (1%, 1 mL) was rapidly added to a boiled $HAuCl_4$ (1%, 1 mL) solution under vigorous stirring. The mixed solution was kept for boiling for 10 min, and further stirred for 15 min. The resulting solution was cooled to room temperature, which was stored in the refrigerator (4 °C) and ready for use.

2.4. Fluorescence investigation on the interaction between $CePO_4$:Tb^{3+} nanocrystals and AuNPs

0.5 g L^{-1} $CePO_4$:Tb^{3+} nanocrystals were mixed with different concentrations of prepared AuNPs and equilibrated for 10 min. Then the emission spectra were recorded. The fluorescence data were analyzed by plotting the decreased fluorescence intensity at 550 nm versus the concentration of AuNPs.

2.5. Fluorescent detection of aminothiol

A typical fluorescent analysis was realized by the following steps. First, 3 mL AuNPs (ca. 30 nm) solution, 1 mL HAc (1.3 mM), different volumes of aminothiol (such as Cys) were added into 10 ml volumetric flask. This mixture solution was allowed to react for 15 min at room temperature. Second, 3 mL $CePO_4$:Tb^{3+} (0.5 g L^{-1}) and 1 mL pH 6.0 Tris-HCl buffer solution were added to the above prepared solution, then the mixture was diluted to 10.00 mL with doubly distilled water and then mixed thoroughly. The resulting solution was incubated for 5 min at room temperature before spectral measurements. The instrument excitation and emission slits were set at 2.5 nm, and the fluorescent spectrum and intensity were obtained with excitation wavelength of 307 nm at room temperature.

3. Results and discussion

3.1. Characteristics of AuNPs and $CePO_4$:Tb^{3+} nanocrystals

Fig. 1 shows the TEM images of $CePO_4$:Tb^{3+} nanocrystals (A) and AuNPs (B). From the TEM images, we can see that these nanoparticles appear to be relatively uniform in size.

3.2. The principle of inner filter effect for determination of biological aminothiols

As shown in Fig. 2, the degree of the overlap was effective for fluorescence energy transfer between the fluorescence emission

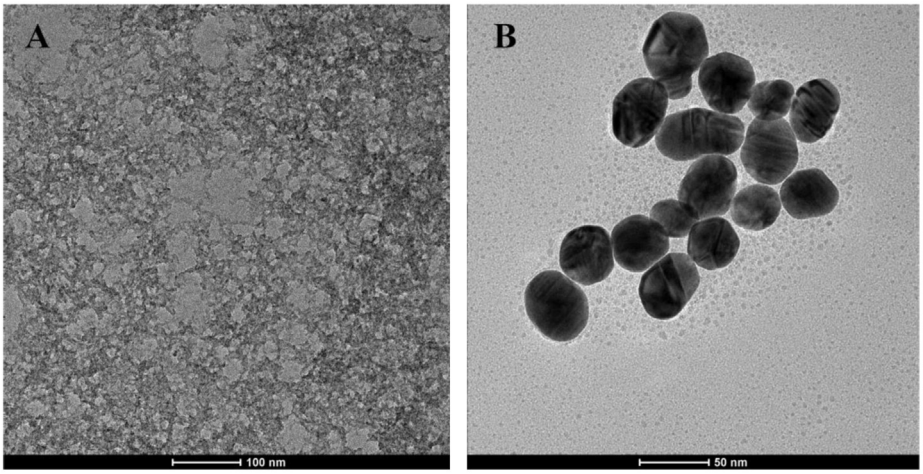

Fig. 1. TEM images of $CePO_4$:Tb^{3+} nanocrystals (A) and AuNPs (B).