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Simple and sensitive detection method for Cobalt(II) in water using $CePO_4:Tb^{3+}$ nanocrystals as fluorescent probes

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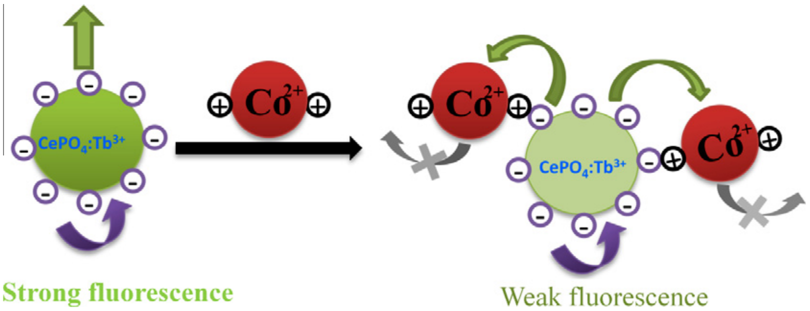
HIGHLIGHTS

- ▶ A new method was developed for determination of Co^{2+}.
- ▶ $CePO_4:Tb^{3+}$ NCs were synthesized and used as fluorescent probes.
- ▶ The probable quenching mechanism is an energy transfer process which from $CePO_4:Tb^{3+}$ nanocrystals to Co^{2+}.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and sensitive method for detecting cobalt by synchronous fluorescence spectrometry technique with a novel fluorescence probe $CePO_4:Tb^{3+}$ has been developed. $CePO_4:Tb^{3+}$ nanocrystals were synthesized in aqueous solutions and characterized by transmission electron microscopy, electron diffraction pattern spectroscopy and spectrofluorometry. When $\Delta\lambda = 210$ nm, the selected synchronous fluorescence is produced at 284 nm. $CePO_4:Tb^{3+}$ nanocrystals were negatively charged under weakly basic conditions (pH = 8.2), which can interact with Co^{2+} via electrostatic interaction. Moreover, there is the spectrum overlap between the emission wavelength of $CePO_4:Tb^{3+}$ NCs and the absorbance of Co^{2+}. So the energy transfer would occur, leading to the quenching phenomenon. The quenching equation of the system was agreed with the Stern–Volmer equation. The linear range and detection limit of Co^{2+} were 5–1.8 μM and 3.5 nM, respectively. The method is successfully applied to the quantification of Co^{2+} in water samples.

Introduction

Cobalt as an essential trace element in body is an important composition of Vitamin B_{12} and other enzymes. It can stimulate the body's bone marrow system, promote the synthesis of hemoglobin and increase the number of red blood cells. Fundamentally it helps women to solve the problem of maintaining beauty and keeping young. The determination of trace amounts of cobalt is of great significance, not only for industry, but for biological study as well. Several techniques have been utilized for cobalt determination, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) [1], flame atomic absorption spectrometry (FAAS) [2], electrothermal atomic absorption spectrometry (ETA-AS) [3], stripping voltammetry [4] and spectrophotometry, the latter being favored for rapid analysis in view of its ease of automation, simple and low-cost instrumentation. Owing to its advantages, a wide variety of spectrophotometric methods for the determination of cobalt have been reported. The main chromogenic reagents are pyridylazo reagents, thiazolylazo reagents, benzothiazolylazo reagents, 8-aminoquinoline derivatives, nitroso dyes, dithizone reagents and the like [5–10]. Unfortunately, most of these methods are not practically usable due to poor sensitivity. It can be circumvented by using fluorophotometirc method, which is less prone to suffering such problem.

Compared with the fluorescence method commonly used, synchronous fluorescence spectrometry (SFS) which was first

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introduced by Lloyd [11–13], gives an important simplification of emission spectra through scanning both the excitation and emission monochromator with a constant difference in wavelength [14]. Because the sensitivity associated with fluorescence is maintained in the synchronous spectra [12], while offering several advantages: spectral simplification, spectral bandwidth reduction and avoiding different perturbing effects, stabilize, SFS serves as a very simple, effective method of obtaining date for several compounds in a single measurement [15].

In recent years, there is increased interest in using rare-earth phosphate nanocrystals as biological luminescence labels and bioimaging probe [16–18] owing to their attractive chemical and optical features, such as long lifetimes, high quantum yields (up to 61%), low photobleaching, expected low toxicity, and high chemical stability [19–21]. In this work, water-soluble and stable $CePO_4$:Tb^{3+} NCs were successfully synthesized. Based on the fluorescence quenching of $CePO_4$:Tb^{3+} by Co^{2+} in terms of electrostatic interaction and energy transfer, a new method which combine $CePO_4$:Tb^{3+} nanoparticles with the synchronous fluorescence spectrometry technique was successfully developed for the convenient and selective determination of trace Co^{2+}.

Experimental

Apparatus and reagents

Fluorescence measurements were performed using a Hitachi F-2500 spectrofluorometer (Tokyo, Japan), with a quartz cell (1 cm × 1 cm). The lifetime measurements were performed with an FLS920 transient/steady-state luminescence spectrometer (Edinburgh Instruments Inc., England) at room temperature. The TEM image and the electron diffraction pattern of the nanocrystals were acquired using transmission electron microscope (TEM, FEI Tecnai G2 20 S-TWIN, USA). The crystal structure was analyzed with a Rigaku RU-200b X-ray powder diffractometer (XRD) using nickel-filtered Cu Kα radiation ($\lambda = 0.14518$ nm) $15° \leqslant 2\theta \leqslant 80°$. Zeta potential was measured using a Malvern Zetasizer nano ZS90 apparatus (Malvern Instruments, Malvern, United Kingdom).

All the chemicals were of analytical-reagent grade without further purification. A stock Cobalt(II) solution (1 mM) was prepared by dissolving $CoCl_2{\cdot}6H_2O$ in water; working standard solution was obtained by diluting the stock solution in water at a final concentration of 10 μM. The buffer solutions were prepared by adjusting 0.1 M HCl with 0.1 M Tris. The stock solutions of $Tb(NO_3)_3{\cdot}5H_2O$ (Sigma), $CeCl_3{\cdot}7H_2O$ (Sigma) and sodium tripolyphosphate (TPP) were prepared by dissolving them in doubly deionized water. Water used throughout was doubly deionized.

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

$CePO_4$:Tb^{3+} nanocrystals were synthesized by the traditional solvothermal technology [11]. $CeCl_3{\cdot}7H_2O$ (4.5 mL, 0.1 mol L^{-1}), $Tb(NO_3)_3{\cdot}5H_2O$ (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 40 mL and heated at 90 °C for 3 h, and then allowed it to cool to room temperature naturally. The final product was collected by means of centrifugation, washed once with ethanol and twice with deionized water to remove any possible remnants, and then dried in vacuum at 40 °C overnight.

Procedure of determination of Co^{2+}

Two milliliter of pH 8.2 Tris–HCl buffer solutions, a certain volume various amounts of Co^{2+} working solution or sample solution, 1 mL of the 0.5 mg mL^{-1} $CePO_4$:Tb^{3+} NCs were added into 10 ml volumetric flask. The mixture was diluted to 10 ml with water, mixed thoroughly and incubated for 30 min at room temperature. Then the fluorescence intensity was measured with 1.0 cm quartz cells of the F-2500 spectrofluorometer. When the $\Delta\lambda = Em - Ex = 210$ nm (scanning began with excitation at 220 nm, emission at 430 nm), the position of the maximum emission of the synchronous fluorescence spectra is 284 nm. The slits of excitation and emission were set at 2.5 nm.

Results and discussion

Characteristics and synchronous fluorescence spectra of $CePO_4$:Tb^{3+} nanocrystals

UV/Vis absorption spectra of the crystalline $CePO_4$:Tb^{3+} NCs exhibit two overlapped bands located around 258 and 273 nm (Fig. 1a), consistent with the reported data for 4f–5d electronic transitions for Ce^{3+}. The emission wavelength of the maximum fluorescence intensity is located at 495 nm corresponded to the $^5D_4$–$^7F_6$ transitions of Tb^{3+} [22] (Fig. 1c). The synchronous fluorescence spectra of $CePO_4$:Tb^{3+} NCs was studied. When the $\Delta\lambda = Em - Ex = 210$ nm, the position of the maximum emission of the synchronous fluorescence spectra is 284 nm (Fig. 1b). From Fig. 1, we can see that the intensity of the synchronous fluorescence was higher than that of the conventional fluorescence. In this assay, the $\Delta\lambda = 210$ nm was selected. The morphology and size of the samples were investigated by using transmission electron microscopy (TEM, Fig. 2). A typical TEM image of the sample reveals that the as-prepared $CePO_4$:Tb^{3+} were well dispersed. The electron diffraction pattern shows that the form of crystals is polycrystalline. Fig. 3 gives the XRD pattern of the $CePO_4$:Tb^{3+} nanocrystals, and the diffraction peaks can match closely with the standard XRD file of $CePO_4$ (JCPDS 32-0199).

Effect of pH

The effect of pH on the synchronous fluorescence signal of the assay system was studied. The F_0 (solid) and F (circle) represented the relative fluorescence intensity of the system in the absence and presence of Co^{2+}. As shown in Fig. 4, the pH had great influence on the synchronous fluorescence intensity. The synchronous fluorescence quenching intensity reached the maximum when pH was 8.2. In order to get a high sensitivity, pH 8.2 was chosen as optimum

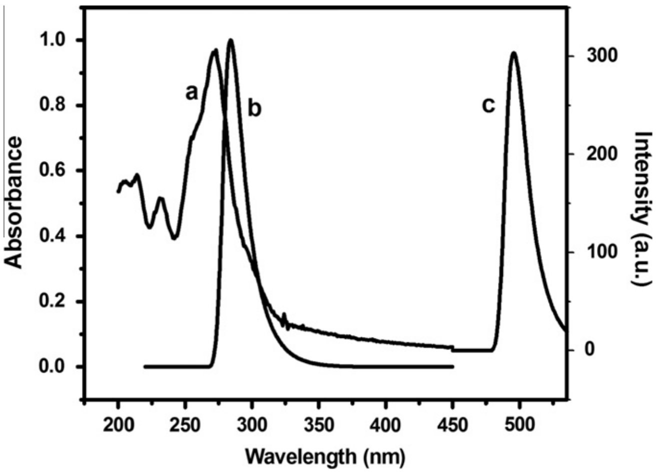

Fig. 1. The absorption spectra (a), the synchronous fluorescence spectra (b) and the conventional fluorescence emission spectra (c) of $CePO_4$:Tb^{3+} nanocrystals.