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## Sensitive determination of chromium (VI) based on the inner filter effect of upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ )

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### ABSTRACT

A new method was developed for selective and sensitive determination of trace chromium (VI) based on the inner filter effect (IFE) of upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) as fluorescence probes. In this study, water-soluble and well dispersible upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) were firstly synthesized by hydrothermal method, and characterized by transmission electron microscopy (TEM) and luminescence spectroscopy. And then, the IFE method was established for determination of chromium (VI). The principle of this assay is based on the complementary overlap of the green emission band of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) with the absorption spectrum of a pink chelate complex (Cr(III)-diphenylcarbazine), which was generated by the quantitative reaction between diphenylcarbazine (DPC) and Cr(VI) in mineral acid solution. Under the optimal condition, the decrease in the upconversion luminescent nanoparticles was proportional to the concentration of chromium (VI) due to IFE. The linear range is  $0.070\text{--}10.0 \times 10^{-6} \text{ mol L}^{-1} \text{ Cr(VI)}$ , and the limit of detection ( $3\sigma$ ) is  $2.40 \times 10^{-8} \text{ mol L}^{-1} \text{ Cr(VI)}$ . The method described here is sensitive than the method of spectrophotometry. This assay was used in the determination of Cr(VI) in water samples.

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### 1. Introduction

Luminescent nanomaterials have been widely studied for two decades because of their unique optical properties [1–3]. Currently, various luminescent nanomaterials such as quantum dots and rare-earth nanoparticles are successfully prepared and have been widely used in chemical, biological and biomedical fields, such as luminescence analysis, bioimaging, immunoassay, and biomedical studies [4–13]. Among these nanomaterials, rare-earth upconversion nanoparticles [13,14] exhibit great potential in certain bioapplications. Upconversion luminescence involves the conversion of two or more low energy photons, usually near infrared (NIR) (typically 980 nm), to higher energy visible emission through multiple photon absorption or energy transfer [15]. Conventional down conversion fluorescent materials, such as organic dyes, metal complexes and semiconductor nanocrystals show visible fluorescence under excitation of UV or blue light [16]. Compared to the conventional down conversion fluorescent materials, upconversion nanoparticles have the following advantages: high light penetration depth in tissues, no photo-damage to living organisms, weak autofluorescence from cells or tissues, low background light and high sensitivity for detection [17–19].

Additionally, these upconversion materials show high quantum yields, narrow emission peak, long lifetimes, large Stokes shifts, superior photostability, high chemical stability and low toxicity. Furthermore, the optical properties of upconversion luminescent materials can be tuned by variation of lanthanide dopants and the host matrix [20,21]. So far, luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) are considered to be the best NIR to visible upconverting materials, and they exhibit great potential in bioimaging and chemical sensing [22,23].

The inner filter effect (IFE) [24–26] is one of non-irradiation energy conversion models in spectrofluorometry, which results from the absorptions of the excitation and emission light or both simultaneously by absorbents in the detection system. The IFE is usually considered as an annoying source of error in fluorescent analysis and should be avoided as far as possible. However, IFE can be useful for the fabrication of the optical sensors for the determination of certain ions [24,27–29]. The advantages of the IFE method are: (1) *no covalent linking between the energy receptor and donor* (not as the fluorescence resonance energy transfer (FRET)), simplifying the synthesis of the fluorescent materials; (2) higher sensitivity of the fluorescent analysis compared to absorption methods because the changes in the absorbance of sensors transform exponentially into fluorescence intensity changes [27]. However, IFE would occur only when the absorption band of the absorbent complementarily overlaps with the excitation or emission bands or with the both of chromophore to some

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extent. Furthermore, the two materials should not chemically interact with each other or show interference effects on their fluorescence properties. Therefore, it is a challenge to develop a new IFE system for some applications. Due to their high chemical stability, the rare-earth upconversion nanoparticles are well suitable to be used as luminescent probes in the IFE system. To the best of our knowledge, much less attention is paid to highly sensitive determination of metal ions based on the IFE of upconversion luminescent nanoparticles.

In this work, stable, water-soluble and well-dispersible luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) with high upconversion efficiency were synthesized by hydrothermal method, and characterized by transmission electron microscopy (TEM) and upconversion luminescence spectroscopy. Under mineral acid condition, diphenylcarbazide (DPC) and Cr(VI) can react quantitatively and generate a pink chelate complex (Cr(III)-diphenylcarbazone). The green emission band of upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) possesses a complementary overlap with the absorption spectrum of the pink chelate complex. Based on this principle, the IFE method was well established for the determination of trace chromium (VI). The effects of certain experimental conditions were investigated, and the probable mechanism was discussed. Under the optimal condition, the upconversion luminescence quenching of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) was proportional to the trace amounts of Cr(VI). This assay was used for the determination of Cr(VI) in water samples.

## 2. Experimental

### 2.1. Apparatus and reagents

Upconversion luminescent spectra were recorded with a F-4500 fluorescence spectrophotometer (Hitachi, Japan), and the excitation source was a 980 nm diode continuous-wave semiconductor laser (Beijing Hi-Tech Optoelectronic Co., Ltd.) with an optic fiber accessory, instead of the Xe source in the spectrophotometer. The UV–vis absorption spectra were recorded by U-3010 spectrophotometer (Hitachi). JEM-2100 transmission electron microscope (JEOL, Japan) was used for characterization of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ).

All chemicals used were of analytical reagent grade and used without any further purification.  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ , NaF, HCl, ethanol, and hexadecyltrimethylammonium bromide (CTAB), Trisodium citrate dihydrate, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).  $\text{K}_2\text{CrO}_4$  and diphenylcarbazide were products of Sigma-Aldrich Chemical Co. (Milwaukee, USA). 0.1000 g of diphenylcarbazide was dissolved in 4 mL anhydrous ethanol, and then diluted to 100 mL with water (prepared freshly each day). All chemicals used were of analytical reagent grade and used without any further purification. Doubly distilled water was used in all the experiments.

### 2.2. Preparation of upconversion luminescence nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ )

The upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) were prepared using the procedure described in the literatures [30,31] with a little modification. Briefly, an aqueous solution of  $\text{YCl}_3$  (2.2 mL,  $0.2 \text{ mol L}^{-1}$ ),  $\text{YbCl}_3$  (0.5 mL,  $0.1 \text{ mol L}^{-1}$ ),  $\text{Er}(\text{NO}_3)_3$  (0.1 mL,  $0.1 \text{ mol L}^{-1}$ ) and trisodium citrate dihydrate (1.75 mL,  $0.1 \text{ mol L}^{-1}$ ) were mixed under vigorous stirring and a white complex was formed. After 5 min, 2.2 mL  $\text{H}_2\text{O}$ , 15 mL ethanol and 0.1 g hexadecyltrimethylammonium bromide (CTAB) were added into the solution. An aqueous solution of NaF (6 mL,  $1 \text{ mol L}^{-1}$ ) was dropped slowly into the complex and

stirred for 1 h. The newly-formed complex precursor solution and 1 mL nitric acid (69%, w/w) were then transferred into a 40 mL autoclave and treated at  $180^\circ\text{C}$  for 4 h, then naturally cooled down to the room temperature. The as prepared products were washed several times with distilled water and absolute ethanol in turn, and finally dried in vacuum ( $-600 \text{ mmHg}$ ) at  $70^\circ\text{C}$ .

### 2.3. Procedure for determination of Cr(VI)

Three hundred and fifteen microlitre of HCl ( $1 \text{ mol L}^{-1}$ ), 1.0 mL of diphenylcarbazide ( $1.0 \text{ mg mL}^{-1}$ ), and various amounts of Cr(VI) working solution or sample solution were added into 10 mL volumetric flask, and then mixed thoroughly. After 10 min, 2.0 mL upconversion luminescent nanoparticles ( $2 \text{ mg mL}^{-1}$ ) were added. The mixture was diluted to 10.00 mL with doubly distilled water and then mixed thoroughly. After 5 min, upconversion luminescence spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer using a 980 nm laser as a light source. All the experiments were performed at room temperature.

## 3. Results and discussion

### 3.1. Morphology and upconversion luminescence spectra of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ )

Fig. 1 displays the TEM image of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ). The nano-particles appear to be relatively uniform in size (mean  $\sim 60 \text{ nm}$ ) and chemical composition.

With the 980-nm diode laser as excitation light source, the strong green luminescence of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) was visible to the naked eye in daylight. Fig. 2a shows the upconversion luminescence spectrum of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ). All spectra show two obvious  $\text{Er}^{3+}$  emission bands. The dominant green emission peak was 551 nm, which was attributed to the transitions from  $^4\text{S}_{3/2}$  to  $^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$  [32]. The weak emission is observed at 650–680 nm, which is originated from the  $^4\text{F}_{9/2}$  to  $^4\text{I}_{15/2}$  transition [33].

### 3.2. The principle for determination of Cr(IV)

In mineral acid solution, diphenylcarbazide (DPC) firstly reacts with Cr(VI) to generate the products of Cr(III) and diphenylcarbazone, and then the two products further react to form a chelate

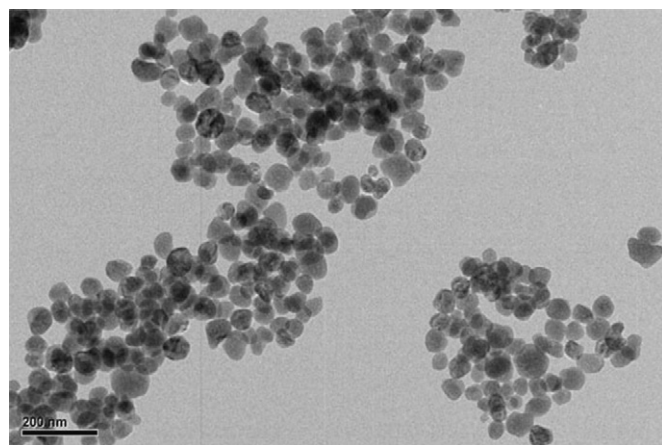


Fig. 1. TEM image of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ).

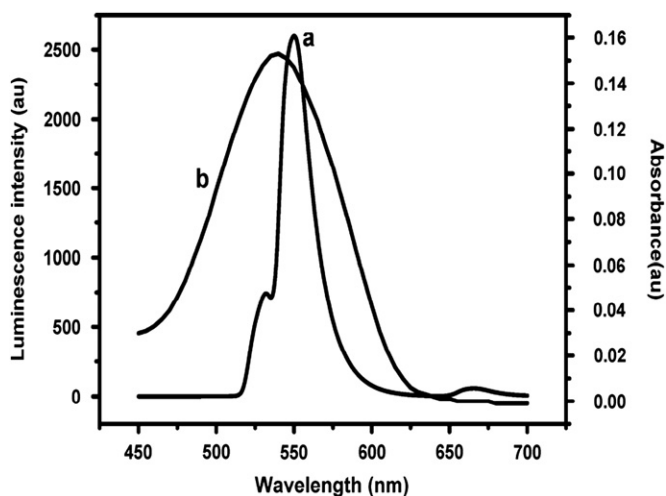
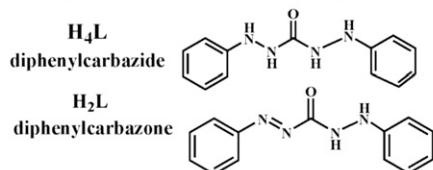
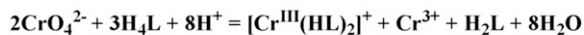


Fig. 2. Upconversion luminescent spectrum of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) (a) and the absorption spectrum of the complex (b). DPC:  $0.10 \text{ mg mL}^{-1}$ ; HCl:  $3.15 \times 10^{-2} \text{ mol L}^{-1}$ ; Cr(VI):  $2.0 \times 10^{-6} \text{ mol L}^{-1}$ .

complex of Cr(III) and diphenylcarbazone. The reactions may be summarized as [34]



To be noted, the direct reaction of Cr(III) with diphenylcarbazone does not occur to any appreciable extent on account of the well known inertness of the Cr(III) aquo-complex. The chelate complex of Cr(III) and diphenylcarbazone is a pink colored chromophore whose maximum absorption wavelength is 540 nm. The absorption spectrum of the chelate complex is shown in Fig. 2b (recorded by U-3010 spectrophotometer). As we can see from Fig. 2, the green emission band of nanoparticles ranging from 520 to 630 nm can complementarily overlap with the absorption spectrum of the chelate complex. Therefore, the luminescence of nanoparticles can be quenched by the chelate complex of Cr(III) and diphenylcarbazone due to IFE. The red emission band ranging from 650–680 nm is not quenched, and the peak of 660 nm can be used as an internal ratio reference (seen in the Fig. 6).

### 3.3. Effect of HCl and diphenylcarbazide

Under the optimum conditions, the absorbance of the pink chelate complex would reach the maximum. The stronger absorption results in higher energy transfer efficiency.

The effect of the volume of HCl on the absorbance of the pink chelate complex was studied and the results are shown in Fig. 3. It can be seen that the absorbance of the pink chelate complex reached the maximum when the volume of HCl ( $1 \text{ mol L}^{-1}$ ) was 315  $\mu\text{L}$ . In this assay 315  $\mu\text{L}$  of HCl ( $1 \text{ mol L}^{-1}$ ) was recommended for use.

The effects of diphenylcarbazide concentration were studied. As shown in Fig. 4, the absorbance of the pink chelate complex reached the maximum and remained unchanged when the

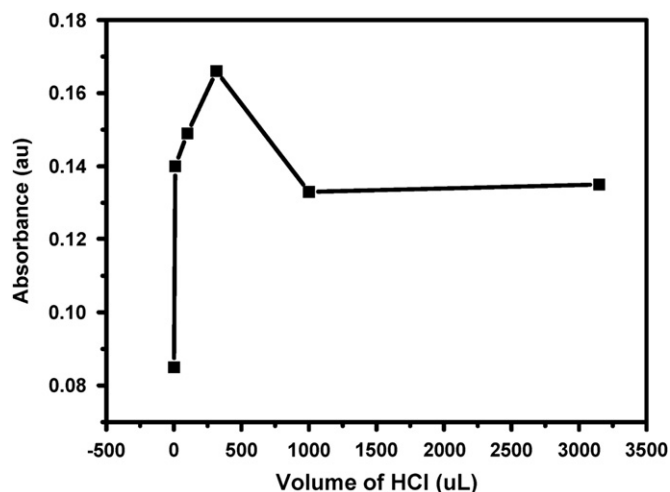


Fig. 3. Effects of the volume of HCl on the absorbance of the complex. DPC:  $1.0 \text{ mg mL}^{-1}$ ; Cr(VI):  $2.0 \times 10^{-6} \text{ mol L}^{-1}$ .

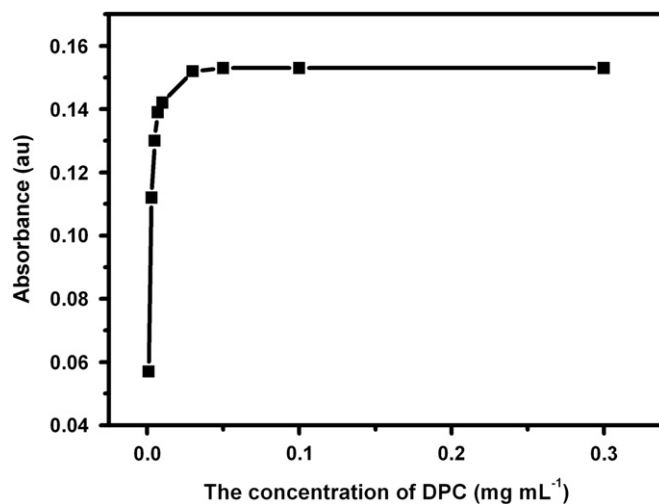


Fig. 4. Effect of the concentration of DPC on the absorption intensity of the complex. HCl  $3.15 \times 10^{-2} \text{ mol L}^{-1}$ ; Cr(VI):  $2.0 \times 10^{-6} \text{ mol L}^{-1}$ .

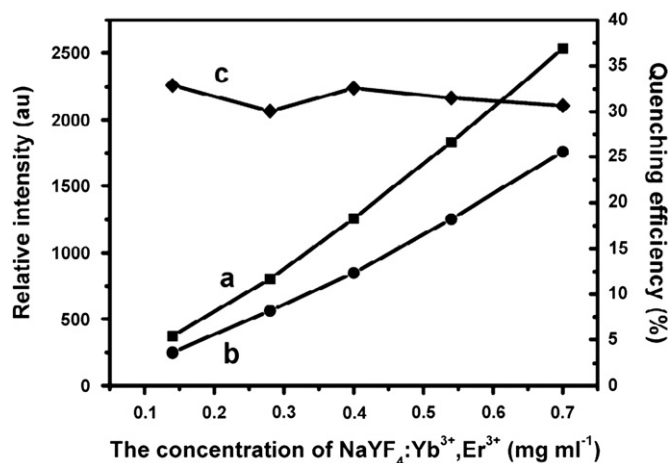
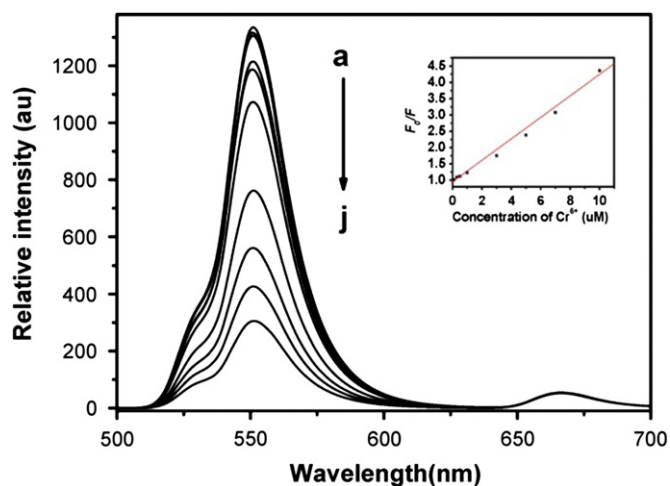


Fig. 5. Effect of the concentration of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) in the absence (a) and presence (b) of  $2.0 \times 10^{-6} \text{ mol L}^{-1}$  Cr(VI) and quenching efficiency (c) against the concentration of  $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ . The Conditions: DPC:  $0.10 \text{ mg mL}^{-1}$ ;  $3.15 \times 10^{-2} \text{ mol L}^{-1}$ .



**Fig. 6.** Luminescence spectra of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) in the presence of  $\text{Cr(VI)}$ : a–j: 0.00, 0.07, 0.10, 0.30, 0.50, 1.00, 3.00, 5.00, 7.00,  $10.00 \times 10^{-6} \text{ mol L}^{-1}$ . Nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ):  $0.40 \text{ mg mL}^{-1}$ ; DPC:  $0.10 \text{ mg mL}^{-1}$ ;  $\text{HCl}$   $3.15 \times 10^{-2} \text{ mol L}^{-1}$ . The inset: Calibration curve for determination  $\text{Cr(VI)}$  with error bar.

concentration of diphenylcarbazide was  $0.050 \text{ mg mL}^{-1}$ . In order to get a high sensitivity and stability,  $1.0 \text{ mL}$  of diphenylcarbazide ( $1.0 \text{ mg mL}^{-1}$ ) was recommended for use.

### 3.4. Effect of upconversion luminescence nanoparticles concentration

The effects of the nanoparticle concentration were studied. As shown in Fig. 5, the luminescence intensity significantly increased, but the quenching efficiency decreased slightly with an increase in the concentration of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ). In consideration of the sensitivity and linear range,  $0.4 \text{ mg mL}^{-1}$  of nanoparticles is recommended in this assay.

### 3.5. Calibration curves and detection limit

Under the optimum conditions, the upconversion luminescence spectra of nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) were recorded in the presence of different concentration of  $\text{Cr(VI)}$  and the results are shown in Fig. 6. The linear regression equation is described by the following equation:  $F_0/F = 0.9484 + 0.3294C$  (where  $C$  is the concentration of  $\text{Cr(VI)}$  in  $\times 10^{-6} \text{ mol L}^{-1}$ ,  $F_0$  is the intensity in the absence of  $\text{Cr(VI)}$ ,  $F$  is the intensity in the presence of  $\text{Cr(VI)}$ ) and the correlation coefficient is 0.995 (shown in the inset figure of Fig. 6). The linear range is  $0.070\text{--}10.0 \times 10^{-6} \text{ mol L}^{-1}$ , and the limit of detection ( $3\sigma$ ) for  $\text{Cr(VI)}$  is  $0.024 \times 10^{-6} \text{ mol L}^{-1}$ . In comparison to the method for the determination of  $\text{Cr(VI)}$  in clean waters by spectrophotometry with diphenylcarbazide [35], in which the limit of detection is approximate  $0.038 \times 10^{-6} \text{ mol L}^{-1}$ , the inner filter effect method described here is more sensitive.

### 3.6. Effect of interference substances

In order to apply the proposed method to the determination of  $\text{Cr(VI)}$ , the effects of foreign ions on the quenching intensity of the system were tested. In the presence of the  $\text{Cr(VI)}$  concentration of  $5.0 \times 10^{-7} \text{ mol L}^{-1}$ , the relative errors in the fluorescence intensity generated by foreign substances are listed in Table 1. As shown in Table 1, most of the species tested caused no interference when existed in the specified molar excesses. The results indicate that the IFE method has a good selectivity.

**Table 1**  
Interference of different species to the determination of  $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Cr(VI)}$ .

Metal ion	Concentration ( $\times 10^{-6} \text{ mol L}^{-1}$ )	Change of fluorescence Intensity (%)
$\text{K}^+$	1000	+3.9
$\text{Na}^+$	1000	+4.2
$\text{Cr}^{3+}$	250	+2.7
$\text{Mg}^{2+}$	100	−1.6
$\text{Ca}^{2+}$	100	+4.8
$\text{Cu}^{2+}$	100	+2.3
$\text{Ni}^{2+}$	100	−1.7
$\text{Pb}^{2+}$	100	+4.0
$\text{Fe}^{3+}$	50	+4.4
$\text{Zn}^{2+}$	50	+4.5
$\text{Al}^{3+}$	50	+3.6

**Table 2**  
Determination of  $\text{Cr(VI)}$  in water samples.

Sample	$\text{Cr(VI)}$ found ( $\text{mol L}^{-1}$ )	$\text{Cr(VI)}$ added ( $\text{mol L}^{-1}$ )	$\text{Cr(VI)}$ found ( $\text{mol L}^{-1}$ )	Recover (%)
Tap water	–	$5.00 \times 10^{-7}$	$4.88 \times 10^{-7}$	97.6
	–	$1.00 \times 10^{-6}$	$9.92 \times 10^{-7}$	99.2
River water	–	$5.00 \times 10^{-7}$	$5.21 \times 10^{-7}$	104.2
	–	$1.00 \times 10^{-6}$	$9.46 \times 10^{-7}$	94.6
Waste water	$7.78 \times 10^{-7}$	$5.00 \times 10^{-7}$	$1.27 \times 10^{-6}$	98.4
	$1.04 \times 10^{-6}$	$5.00 \times 10^{-7}$	$1.53 \times 10^{-6}$	98.0

### 3.7. Analysis of water samples

To test the applicability of the proposed method, the determination of  $\text{Cr(VI)}$  in water samples was performed, and the analytical data are shown in Table 2. The river water samples were collected from Yangtze River, and waste water samples were collected from an industrial effluent collection point in an industrial zone. Waste water was adjusted the pH value to 8.0 and filtered before determination. The recovery of  $\text{Cr(VI)}$  was measured by adding known amounts of  $\text{Cr(VI)}$  in water samples. For each sample, three parallel experiments were repeated, and the recovery of the samples was between 94.6% and 104.2%.

## 4. Conclusions

In this study, we firstly prepared the upconversion luminescent nanoparticles ( $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ ) by using hydrothermal method, and then described a new method for sensitive determination of trace chromium (VI) based on the IFE of upconversion luminescent nanoparticles as fluorescence probes. The effects of certain experimental conditions were investigated, and the probable mechanism was discussed. The linear range of this assay is  $0.070\text{--}10.0 \times 10^{-6} \text{ mol L}^{-1} \text{ Cr(VI)}$ , and the limit of detection ( $3\sigma$ ) is  $0.024 \times 10^{-6} \text{ mol L}^{-1}$ . The IFE method described here has a good selectivity, and is sensitive than the method of spectrophotometry.

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