



## Stripping voltammetric determination of europium via ultraviolet-trigger synthesis of ion imprinted membrane



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### ABSTRACT

To solve the problem that the ion-imprinted membrane modified on glassy carbon electrode (GCE) usually easily falls off, a screen printed electrode (SPE) which has a relative rough surface than GCE, was selected as the base electrode for preparation of an ion-imprinted sensor for determination of Eu(III). The sensor was obtained by modifying SPE successively with carboxylic multiwalled carbon nanotubes (MWCNs-COOH) as signal amplifying element and Eu(III) ion-imprinted membrane (Eu(III)-IIM) as specific recognition material. To avoid damaging SPE by thermal initiation, the Eu(III)-IIM was prepared via radical photopolymerization at 380 nm using azobisisobutyronitrile (AIBN) as initiator. Differential pulse adsorptive stripping voltammetry (DPASV) was used for determination of Eu<sup>3+</sup> by the obtained sensor. After the detection condition was optimized in detail, the sensor showed a linear response to Eu<sup>3+</sup> in the concentration range of  $1.0 \times 10^{-7}$ – $1.0 \times 10^{-3}$  mol L<sup>-1</sup> with the detection limit of  $4.0 \times 10^{-8}$  mol L<sup>-1</sup>. The obtained sensor possesses of good regeneration, stability and practicability, it can maintain more than 95% of its original response after used more than 30 times or stored in the water for two months. The satisfactory results with the relative standard deviation (RSD) of less than 3.5% ( $n = 5$ ) were obtained for the determination of europium in water samples by the novel sensor.

### 1. Introduction

Europium [(Xe)4f76s2] is the only lanthanide ion which possesses both nondegenerate ground <sup>7</sup>F<sub>0</sub> and excited <sup>5</sup>D<sub>0</sub> states and has many industrial application in material science, electronics, and life science due to its favorable metallurgical, optical and electronic properties [1]. The growing applications have resulted in more and more accumulation of europium in environment [2]. However, europium is a harmful element for human body and has bioaccumulation effect along the food chain, people continuous exposed to low concentration of europium also can cause adverse health effect [2]. So development of a method for rapid, sensitive and determination of europium in the environment sample is of great significance.

Various analytical techniques have been used to determine europium ions [3–8]. Compared with techniques, electrochemical method especially for the stripping analysis have been widely recognized as a powerful tool for determination of metal ions due to its low cost, easy operation, good specificity, excellent stability, high sensitivity and low limit of detection [9–11]. However, the electrochemical methods reported in the references for determination of Eu(III) often suffer the

interference of other lanthanide ions or other metal ions such as Ce<sup>3+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup>, because the working electrodes used in these methods such as glassy carbon electrode modified with nafion [12], gold electrode modified with 2-pyridinyl-1-oxide [13] and LaB<sub>6</sub> electrode [14] lack of selectivity for Eu(III). So any progress in improving the selectivity of the electrode material for Eu(III) is highly important in this field.

Molecularly/ion imprinted material are famous for selectivity due to its predetermined spatial structure which is only complementary for certain template. It has been widely used in many areas, such as in analytical chemistry, separation science and pharmaceutical research and so on [15–18]. It has also been certified to be an effective material for improving the sensitivity and selectivity of the electrode [19–21]. As a matter of fact, Alizadeh et al. [22] have developed a Eu(III) ion-imprinted carbon paste electrode. However, they could only used an indirect method for determination of Eu<sup>3+</sup> by using Cu<sup>2+</sup> as probe ions because Eu<sup>3+</sup> is not capable of creation a considerable voltammetric signal on this electrode. Compared with the direct technique, the indirect method usually lacks sensitivity and selectivity. Any factors can disturb the response of the probes such as Cu<sup>2+</sup> can also disturb the

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determination of the analytes such as  $\text{Eu}^{3+}$ . Thus, it is imperative to provide an alternative sensitive and selective procedure for the direct recognition of  $\text{Eu}(\text{III})$ .

The base electrode used for the preparation of ion-imprinted sensor is mainly a glassy carbon electrode (GCE), but a phenomenon often appears in our previous works that the ion imprinted membrane easily falls off from GCE maybe due to its smooth surface. To solve this problem, a screen printed electrode (SPE), a kind of disposable compositive electrode which has the relative rough surface and don't need any complex pretreatment [23], was selected as the base electrode to fabricate a sensor for  $\text{Eu}(\text{III})$  by modifying SPE with carboxylic multiwalled carbon nanotubes as the signal amplifying element. The  $\text{Eu}(\text{III})$  ion-imprinted membrane could prepared via UV-triggered polymerization as the recognition material using either Type I [24,25] or Type II photoinitiators [24,26]. In this work, simple Type I photoinitiator was used and the obtained sensor displayed high selectivity and sensitivity to  $\text{Eu}^{3+}$ . It can be applied in the determination of  $\text{Eu}^{3+}$  in water samples.

## 2. Experimental

### 2.1. Apparatus and instruments

The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) data were carried out with a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China). The electrochemical impedance spectroscopy (EIS) data was performed on Autolab302N (Metrohm, Netherlands). The electrochemical cell was assembled with a conventional three-electrode system: a disposable SPE obtained from Suzhou Mayor Triangle System Biological Cross Science Research Institute Co., Ltd. (Suzhou, China) was employed as the working electrode ( $30 \times 10 \times 0.25$  mm), a  $\text{Ag}/\text{AgCl}$  and a carbon ring were employed as the reference and counter electrode, respectively. All potentials were measured and reported versus  $\text{Ag}/\text{AgCl}$ . The surface morphology was observed on a Nova Nano SEM 450 field emission scanning electron microscopy (FEI, American).

### 2.2. Reagents and chemicals

$\text{EuCl}_3$  were obtained from Chengdu Ada Chemical Reagent Co., Ltd. (Sichuan, China). Acrylamide (AM), 2-acetamidoacrylic acid (EAA) and 2-(allyl sulfur) nicotinic acid (ANA) were purchased from Sigma-Aldrich (USA). Allyl phenoxyacetate (APA) or allyl acetoacetate (AAA) were obtained from Beijing Lark Technology co., Ltd. (Beijing, China). The multiwalled carbon nanotube (MWCN) was obtained from Aladdin Industrial Corporation (Shanghai, China). Ethylene glycol dimethacrylate (EGDMA) was purchased from Suzhou Anli Chemical Factory (Jiangsu, China) and distilled under vacuum to remove the stabilizers prior to use. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Reagent Factory (Shanghai, China) and purified by recrystallization from ethanol before used. The other reagents and solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

The solution ( $0.1 \text{ mmol L}^{-1}$ ) of  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Er}^{3+}$  and other metal ions were prepared by dissolving appropriate amount of their nitrate or chloride in 100 mL deionized water. The working standard solution was obtained by diluting the stock solution with deionized water.

The reagents and solvents used without special illustration were analytically pure grade and used without further purification. Deionized water was produced by a Millipore water system composed of Milli-RO 60 and Milli-QSP.

### 2.3. Preparation of the sample solution

The water samples were obtained from the local Pan Long river and

Green Lake (Kungming, China). After simple filtration by the filter, the water samples can be detected directly by the modified SPE.

### 2.4. Preparation of MWNTs-COOH

0.5 g of multiwalled carbon nanotube and 100 mL of concentrated nitric acid were added into a 250 mL of round-bottom flask. After refluxing at  $120^\circ\text{C}$  for 4 h and then cooling to room temperature, the mixture was filtered and washed with deionized water to neutral. The black powder of carboxylic multiwalled carbon nanotubes (MWNTs-COOH) was obtained after dried in the vacuum oven [27].

### 2.5. Preparation of MWNTs/SPE

Prior to modification, the screen printed electrode was rinsed with plentiful of deionized water for several times at the ultrasonic condition. Then it was immersed in  $0.05 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  solution and scanned several circles used the cyclic voltammetry from  $-0.50$  V to  $+1.10$  V at  $100 \text{ mV s}^{-1}$  under the stirring condition until the stable voltammogram were observed.

1.0 mg of the prepared MWNTs – COOH was dispersed in 1.0 mL of DMF by ultrasonication for 1 h to get a homogenous suspension ( $1 \text{ mg mL}^{-1}$ ).  $2 \mu\text{L}$  of this suspension was dropped onto the working electrode surface of freshly cleaned screen printed electrode and dried under the infrared lamp, then the MWNTs – COOH modified screen printed electrode (MWNTs/SPE) was obtained.

### 2.6. Preparation of $\text{Eu}(\text{III})$ -IIM/MWNTs/SPE and NIM/MWNTs/SPE

The  $\text{Eu}(\text{III})$  ion-imprinted membrane ( $\text{Eu}(\text{III})$ -IIM) and non – imprinted membrane (NIM) were prepared via ultraviolet trigger in situ polymerization technique. The polymerization solution was prepared as follow: Firstly,  $0.0125 \text{ mmol}$  of  $\text{EuCl}_3$  was dissolved in  $30 \mu\text{L}$  of methanol, then  $0.47 \text{ mL}$  of acetonitrile and  $0.05 \text{ mmol}$  of AM were added. After ultraphonic for 5 min and standing for 30 min,  $0.5 \text{ mmol}$  of EGDMA and  $0.04 \text{ mmol}$  of AIBN were added in the mixture. Hereto, the polymerization solution was obtained.  $1.5 \mu\text{L}$  of the above solution was dropped onto the surface of MWNTs/SPE and the polymerization process was proceed under the exposure of UV lamp ( $380 \text{ nm}$ ,  $19.6 \text{ mW cm}^{-2}$ ) for 3 h. After cooling in the refrigerator, the modified electrode was immersed in  $0.6 \text{ mol L}^{-1} \text{HCl}$  and applied potential of  $-1$  V on it to remove the template ion under the stirred condition until no peak current of  $\text{Eu}^{3+}$  was observed. The procedure for preparation of  $\text{Eu}(\text{III})$  ion-imprinted film modified SPE ( $\text{Eu}(\text{III})$ -IIM/MWNTs/SPE) was showed as Scheme 1. The procedure for the preparation of non-imprinted membrane modified SPE (NIM/MWNTs/SPE) were the same as that of  $\text{Eu}(\text{III})$ -IIM/MWNTs/SPE just in the absence of  $\text{EuCl}_3$ . All of the electrodes are stored in water when not used.

### 2.7. Electrochemical characterization

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were used to characterize the modified electrode. CV and EIS measurement were carried out in 10 mL of  $0.1 \text{ mol L}^{-1} \text{KCl}$  solution containing  $5.0 \text{ mmol L}^{-1} \text{K}_3[\text{Fe}(\text{CN})_6]$ . The scan range of CV is between  $-0.2$  V and  $0.6$  V at the scan rate of  $100 \text{ mV s}^{-1}$ . The high and low frequency of EIS is  $10^5$  and  $0.1$  Hz, respectively. DPV measurement was carried out in  $0.1 \text{ mol L}^{-1} \text{HAc-NaAc}$  buffer (pH4.7) containing  $3.0 \times 10^{-5} \text{ mol L}^{-1} \text{Eu}^{3+}$ . The scan of DPV was performed from  $-1.2$  V to  $-0.6$  V at a scan rate of  $100 \text{ mV s}^{-1}$  with the amplitude, pulse width, sampling width, pulse period and quiet time as  $0.05$  V,  $0.05$  s,  $0.0167$  s,  $0.1$  s and  $10$  s, respectively.

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