

Study on Molecularly Imprinted Sensor Based on Photocurrent Response for Ni-complex



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Abstract: A novel molecularly imprinted sensor based on photocurrent was fabricated to detect Ni²⁺. CdTe quantum dots (QDs) were selected as photoelectric material and modified on an indium-tin oxide (ITO) electrode, then the nickel-1-(2-pyridylazo)-2-naphthol molecularly imprinted film was formed on the QDs layer by photopolymerization. While 365 nm ultraviolet light was used as the excitation light, an electron-hole pair could be generated by the QDs. The electron receptor ascorbic acid would form a photocurrent under the excitation of the electron as detection signals. Ni²⁺ was determined according to “gate-effect”. The complex was characterized by Fourier transform infrared spectrum and the CdTe QDs were characterized by ultraviolet absorption spectrum and fluorescence emission spectrum. The time for elution and rebinding, as well as the concentration of ascorbic acid, were also optimized. The experimental results indicated that there was a liner relationship between the photocurrent and the concentrations of Ni²⁺ in the range of 5×10^{-11} – 5×10^{-8} M, with a detection limit of 8.31×10^{-12} M. The sensor had good selectivity, and was applied in real water samples analysis.

Key Words: Molecularly imprinted sensor; Photocurrent; Nickel-1-(2-pyridylazo)-2-naphthol; Quantum dot; Nickel ion

1 Introduction

Nickel, a metallic element, is widely used in various industries. Long-term exposure to nickel residue would increase the risk of dermatological abnormality^[1]. The accumulation of nickel in human body might cause cancer and gene mutation, with a great threat to human health^[2]. The maximum permitted limits of nickel in water were established by the World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) to be 0.07 and 0.04 mg L⁻¹^[3], respectively. Present methods for determination of nickel include atomic absorption spectrometry (AAS)^[4,5], inductively coupled plasma mass spectrometry (ICP-MS)^[6–8], electrochemical method^[9–11], fluorescence^[12], and so on. However, those methods had some disadvantages such as serious interference, low sensitivity, high cost and time-consuming^[13]. With the improvement of living standards,

people have higher requirements for water quality. Development of accurate, efficient and low-cost detection methods for nickel is highly desirable.

Molecularly imprinted sensors have the advantages of highly specific recognition ability and low detection limit^[14,15], which aroused great interest in detecting metal ions^[16,17]. At present, detection methods for metal ions by molecularly imprinted sensors include stripping voltammetry^[18], potentiometry^[19], etc. But those methods usually have relatively low sensitivity. The electrochemiluminescence method^[16] is highly sensitive, but requires expensive instrument and strict detection conditions.

Photocurrent sensor, with the merits of high sensitivity, low detection limit, low background signals, is one of the most sensitive detection methods^[20–22], and has been applied in metal ions detection^[23]. However, these sensors usually had poor selectivity, and ions with the similar characteristics and other materials would interfere with the detection.

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Molecularly imprinted membrane has high selectivity for the analyte, which provide a good solution of the problem. However, till now there has been no report on detection of metal ions using molecularly imprinted photocurrent sensor.

In this study, a highly sensitivity sensor for nickel ion detection was fabricated by combining molecularly imprinted technique with photocurrent. The complex of nickel and 1-(2-pyridylazo)-2-naphthol (PAN) was used as template molecule, and the molecularly imprinted film was formed on indium-tin oxide (ITO) electrode coated by CdTe quantum dots (QDs) through photopolymerization. Ultraviolet (UV) light (365 nm) was used as excitation light, with photocurrent as detection signal. The detection of Ni^{2+} was based on the “gate-effect”. After the elution of the template molecule (Ni-PAN complex) from the molecularly imprinted polymer (MIP), cavities were left in MIP. With the UV-light irradiation, the valence electrons would transit to the conduction band, leaving an electron-hole. The electron receptor in solution could combine with electron through the imprinted cavities, and photocurrent was thus produced. When MIP adsorbed the template molecules, since the imprinted cavities were taken, the number of the electron receptor molecules passing through the cavities would decrease, so did the photocurrent^[24], causing the so-called “gate effect”. Since the photoelectric signal was generated by light excitation, the interferences from electrical excitation could be avoided thus the signal-to-noise ratio and sensitivity were greatly improved.

2 Experimental

2.1 Instruments and reagents

A three-electrode system was used, including an MIP-modified ITO electrode as the working electrode, a Pt wire electrode as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. CHI660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.), KQ3200DE digital ultrasonic cleaner (Kunshan ultrasonic cleaner Instrument Co. Ltd., China), DF-101S heat-collected constant temperature thermostat magnetic agitator (Zhengzhou Great Wall Scientific Industrial and Trade Co. Ltd., China) and AL204 electronic balance (Mettler-Toledo China region) were used in this experiment.

Dimethoxybenzoin was purchased from Aladdin, 1-(2-Pyridylazo)-2-naphthol (PAN) from Shanghai reagent Co., Ltd. and NiSO_4 from Guangdong Reagent Company, acrylic acid from Tianjin Zhiyuan Reagent Company. *N,N*-methylenebis acrylamide, acrylamide and Na_2SO_4 were purchased from Xilong Chemical Company. All reagents used were of analytical grade. Double-distilled water was used throughout the experiments.

2.2 Synthesis of QDs

QDs was synthesized according to reference^[25]. 250 mL 0.0025 M CdCl_2 solution was purged with nitrogen flow for 15 min to get rid of the dissolved oxygen. Then 100 μL mercaptoacetic acid was added under magnetic stirring. pH value of the solution was adjusted to about 10 with 2 M NaOH. Then the mixed solution was purged with nitrogen gas for another 15 min. 0.144 g Te powder and 0.36 g NaBH_4 were placed into a 50 mL three-necked flask, and then 2.5 mL water was added. The mixture was stirred for 20 min at 65 °C until the black Te powder completely disappeared, and purple transparent NaHTe solution was obtained. Nitrogen gas was constantly supplied to the three-necked flask for protection during the reaction process. Then the two solutions were mixed at 95 °C and refluxed for 2 h to obtain the CdTe QDs solution with red wine color.

2.3 Preparation of the Ni-PAN

The Ni-PAN was synthesized according to methods described in references^[26–28]. 1.0 g PAN was dissolved in 50 mL ethanol, and 0.52 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL double-distilled water. The two solutions were added in 100 mL three-necked flask under vigorous stirring. The pH value of mixed solution was adjusted to 7.0 and stirred for another 15 min. A large amount of double-distilled water was added before filtration. The Ni-PAN complex could be obtained by washing the solid product with ethanol and double-distilled water and then dried.

2.4 Preparation of the Ni-PAN sensor

The working electrode was fabricated by cutting the indium-tin oxide (ITO) glass into 5 mm × 10 mm pieces. These pieces were soaked in 0.5 M NaOH solution for 20 min, and then subjected to ultrasonication in ethanol and ultrapure water respectively, and then dried. Then the electrode was immersed in 0.5% aminopropyltriethoxysilane (APTES) ethanol solution for 24 h introduce amine group. At last, it was soaked in *N*-hydroxysuccinimide (NHS)/1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and QDs solution for 4 h to link QDs.

Preparation of the MIP sensor: 0.028 g Ni-PAN complex, 0.009 g acrylic acid, 0.009 g acrylamide, 0.192 g *N,N*-methylene bisacrylamide and 0.003 g dimethoxybenzoin were dissolved in 50 mL acetone as photopolymerization solution. 20 μL photopolymerization solution was dropped onto the ITO electrode surface and exposed to UV-light until the solution evaporated. After repeated for three times, the sensor was stirring washed with methanol-acetic acid (5:1, *V/V*) for 5 min. Then the MIP sensor was obtained.

Preparation of the non-imprinted polymer (NIP) sensor: Other conditions were the same as the MIP fabrication, except for the addition of template molecule Ni-PAN complex.

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