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ORIGINAL PAPER

Carbon nanotube-modified glassy carbon electrode for anodic stripping voltammetric detection of Uranyle

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Abstract A multi-wall carbon nanotube (MWNT) modified glassy carbon electrode (GCE) is described for the measurement of trace levels of uranium by anodic stripping voltammetry. In a pH 4.4 NaAc-Hac buffer containing 0.010 mol L^{-1} $Mg(NO_3)_2$, UO_2^{2+} was adsorbed onto the surface of a MWNT film coated glassy carbon electrode and then reduced at −0.40 V vs. Ag/AgCl. During the positive potential sweep the reduced uranium was oxidized and a well-defined stripping peak appeared at +0.20 V vs. Ag/AgCl. Low concentrations of Mg^{2+} significantly enhanced the stripping peak currents since they induced UO_2^{2+} to adsorb at the electrode surface. The response was linear up to 1.2×10^{-7} mol L^{-1} and the relative standard deviation at 2.0×10^{-8} mol L^{-1} uranium was 5.2%. Potential interferences were examined. The attractive behavior of the new “mercury-free” uranium sensor holds promise for on-site environmental and industrial monitoring of uranium.

Keywords Anodic stripping voltammetry · Uranyle · Carbon nanotube · Modified electrode · Composite film electrode

1 Introduction

Uranium is distributed inhomogeneously in nature. Measurement of uranium levels in aquatic environments is of great importance for environmental safety assessment in nuclear devices and plants. Uranium commonly exists in aqueous solutions in the form of its oxide ion, Uranyle, which exhibits high stability in natural environments such as seawater [1].

Various analytical procedures based on the use of different instrumental techniques have been developed in the past for determination of uranium and other metals in geological samples [2, 3]. Electroanalytical techniques have established themselves as versatile analytical tools for quick and precise determination of trace metals.

Carbon nanotubes (CNTs) represent an increasingly important group of nano materials with unique geometric, mechanical, electronic and chemical properties [4, 5]. Such properties of CNTs make also them extremely attractive in electrochemical detection. Recent studies demonstrated that CNTs can impart strong electrocatalytic activity and minimization of surface fouling onto electrochemical devices [6–8].

Anodic stripping voltammetry (ASV) is one of the most sensitive methods for determination of trace levels of numerous ions. In the past, hanging drop mercury electrodes (HDMEs) and thin mercury film electrodes (MFEs) have been widely used in ASV. Despite the good properties of mercury electrodes (reproducibility, easy surface renewal, high hydrogen over potential, etc.), numerous attempts to replace them with solid electrodes have been undertaken, for they have some intrinsic drawbacks such as toxicity and difficulty in determination of metals such as Ag and Au whose stripping potentials are more positive than those of mercury.

The use of chemically modified electrodes (CMEs) in ASV is an expanding area of investigation. To date, some CMEs have been reported for determination of Uranyle [9–11].

Dueber et al. [12] studied the cyclic voltammetry of uranium oxide in aqueous electrolytes. Their results

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supported a mechanism of a U(VI) to U(V) electron transfer coupled to cation diffusion to form a topochemical insertion compound at the solid electrode–electrolyte interface. They used Li^+, Na^+ and Mg^{2+} as electrolytes. The most apparent difference in the Li^+ and Na^+ electrolytes was a large decrease in the peak current in the oxidative scan direction.

Nafion, a perfluorinated sulfonated cation exchanger, is widely used as an electrode modifier due to its excellent properties such as thermal stability, chemical inertness, mechanical strength and antifouling properties. The objective of the current work was to develop a sensitive and simple electrochemical method for the determination of Uranyle at a multiwall carbon nanotube-Nafion (MWNT-Nafion) composite film electrode, based on the unusual properties of CNT such as its strong adsorptive ability, large specific area and high activity. The MWNT-Nafion composite film modified electrode exhibited strong activity towards the redox reaction of Uranyle and a large increase in the magnitude of the redox peak currents. In pH 4.4 NaAc-Hac buffer containing low concentrations of Mg^{2+}, the stripping peak current of Uranyle increased significantly at the MWNT-Nafion composite film modified electrode in comparison to the bare GCE.

2 Experimental

2.1 Reagents

A stock solution of 1,000 ppm UO_2^{2+} was prepared by dissolving $UO_2\ (NO_3)_2$ (obtained from Merck, Germany) into redistilled water, which was then diluted to various concentrations of working solution. Nafion solution (5 wt.% in lower aliphatic alcohols) was purchased from Aldrich (Germany) and diluted as required in double distilled water. Other chemicals were of analytical grade. All the chemicals were used without further purification. The multiwall carbon nanotube (obtained from the Aldrich, Germany) was synthesized by a CVD method (60 ± 10 nm Ø). Voltammetric experiments were carried out using a Radiometer Analytical POL150 trace analyzer running with Trace Master 5 Software (Radiometer Analytical, France). The cell was a standard three electrode cell. The reference electrode was an aqueous Ag/AgCl (3 mol L^{-1} KCl as electrolyte) (Radiometer Analytical, France). The auxiliary electrode was a platinum wire (Radiometer Analytical, France) and the working electrode was a 2 mm diameter glassy carbon electrode (Radiometer Analytical, France). The surface of the MWNT-Nafion composite film-modified electrode was investigated by SEM (Philips Model XL30, Netherland).

2.2 Preparation of the MWNT-Nafion composite film-modified electrode

The GCE (2 mm, inner diameter) was carefully polished with aluminum on a polishing cloth. The electrode was placed in distilled water and subjected to vibration to remove adsorbed particles. It was then rinsed with distilled water.

16 mg of MWNTs were added to the 5 mL of 0.5% Nafion suspension. A homogeneous and stable suspension of 3.20 mg mL^{-1} MWNT-Nafion was achieved with the aid of ultrasonication for about 10 min. The GCE was coated by casting 20 μL suspension of MWNT-Nafion and dried in an oven at 35 °C.

2.3 Procedure for the detection of Uranyle

The supporting electrolyte contained 0.20 mol L^{-1} acetate buffer (pH 4.4) and 0.010 mol L^{-1} Mg^{2+}. An accumulation potential of −0.40 V was applied to the modified electrode, while the solution was stirred for an accumulation time of 13 min with stirring. Following the preconcentration, stirring was stopped and after an equilibrium time of 10 s, the square wave voltammograms were recorded from −0.40 to 0.40 V at a scan rate of 0.05 V s^{-1} and pulse amplitude of 0.05 V. The parameters were obtained experimentally as optimum values for maximum peak current (data not shown in this paper). All the recordings were done at room temperature with nitrogen maintained over the solution surface.

3 Results and discussion

3.1 SEM image of MWNT-Nafion composite film modified electrode

The SEM image of MWNT-Nafion composite film on the glassy carbon disk is shown in Fig. 1. It is clear that the GCE surface is coated with a homogeneous MWNT film.

3.2 Cyclic voltammetry

Preliminary studies on the electrochemical behavior of Uranyle were performed by cyclic voltammetry. Figure 2 shows the cyclic voltammograms for the reduction of UO_2^{2+} at a scan rate of 0.05 V s^{-1} in pH 4.4 solution containing 0.020 mol L^{-1} $UO_2(NO_3)_2$ and 0.010 mol L^{-1} $Mg(NO_3)_2$ on the MWNT-Nafion composite film modified electrode. The forward potential scan commenced at an initial potential of −0.60 V and its direction was reversed at 0.40 V. As Fig. 2 shows, U(VI) was re-oxidized on the MWNT-Nafion composite film modified electrode,

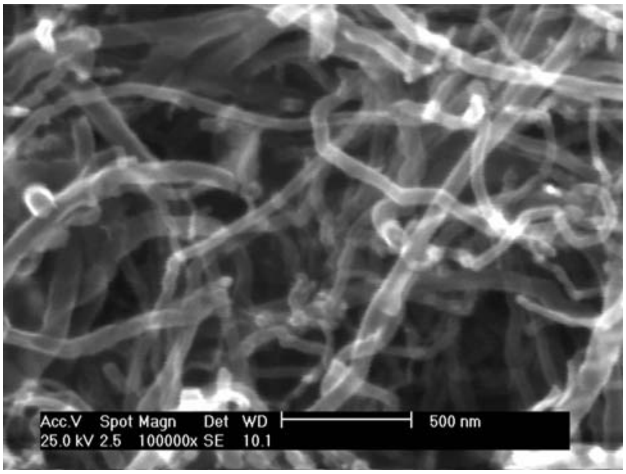

Fig. 1 SEM image of the MWNT-Nafion composite film on the glassy carbon disk electrode

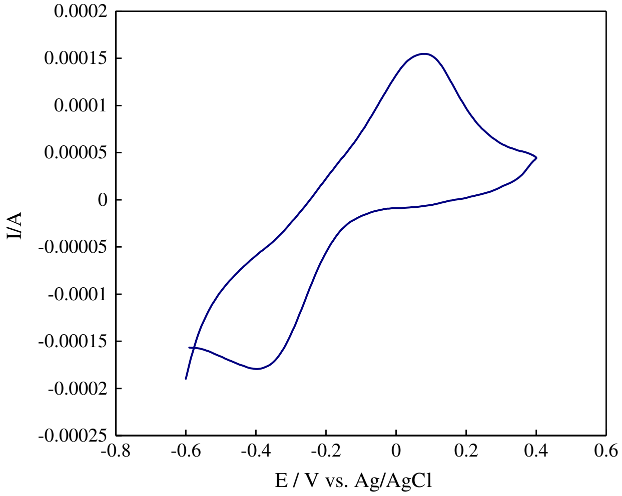

Fig. 2 Cyclic voltammograms for the reduction of UO_2^{2+} at the scan rate of 0.05 V s^{-1} in pH 4.4 solution containing 0.020 mol L^{-1} $UO_2(NO_3)_2$ and 0.010 mol L^{-1} $Mg(NO_3)_2$ on the MWNT-Nafion composite film modified electrode

producing one anodic peak with Epa = 0.07 V and a cathodic peak potential of −0.39 V. The peak separation (0.46 V) was not close to the theoretical value for a “one electron-reversible” wave as in the other work for uranium on the HMDE [13], indicating that the cathodic reduction peak is due to the reduction of U(VI) to U(V). UO_2^+ was reasonably stable at this pH and should be reduced to UO_2 at more negative potentials for the mercury electrode according to the work of Kolthoff and Harris [14]. However, hydrogen evolution commences at about −0.58 V for MWNT-Nafion modified electrodes at pH 4.4.

3.3 Anodic stripping voltammetry

Figure 3 displays the square wave voltammetry of 1.0×10^{-5} mol L^{-1} Uranyle between −0.40 and 0.40 V (vs. Ag/AgCl). Curve a shows the square wave voltammograms of Uranyle in the presence of 0.010 mol L^{-1} Mg^{2+} after 13 min accumulation at −0.4 V on the GC electrode. The voltammograms of Uranyle in the absence (curve b) and presence of Mg^{2+} (curve c) after 13 min accumulation at −0.40 V on the MWNT-Nafion composite modified electrode are also shown. Curve d shows the square wave voltammograms of Uranyle in the presence of Mg^{2+}, without preconcentration on the MWNT-Nafion composite modified electrode. Comparison of the voltammograms shows that the height of the uranium oxidation peak depends on the duration of the preconcentration step and also on the presence of Mg^{2+}, indicating the adsorptive nature of the response.

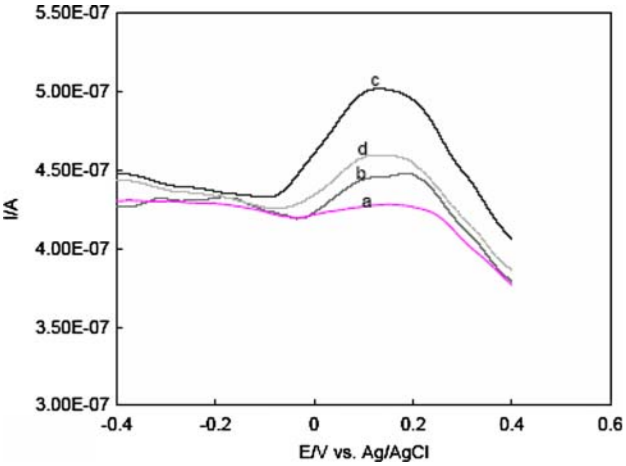

Fig. 3 Square wave voltammograms of 1.0×10^{-5} mol L^{-1} Uranyle in the presence of 0.010 mol L^{-1} Mg^{2+} after 13 min of accumulation at −0.40 V on the GC electrode (a), in the absence (b) and the presence of 0.010 mol L^{-1} Mg^{2+} after 13 min of accumulation time at −0.40 V (c) and also in the presence of 0.010 mol L^{-1} Mg^{2+} without preconcentration on the MWNT-Nafion composite modified GCE (d). The square wave voltammograms were recorded at 0.05 V s^{-1} and the pulse amplitude of 0.05 V in the 0.20 mol L^{-1} acetate buffer (pH 4.4) solution

3.4 Optimization

3.4.1 *Effect of accumulation time and accumulation potential*

The influence of the accumulation potential on the 2×10^{-7} mol L^{-1} uranium (VI) peak current was also tested between −0.40 and 0.40 V. Figure 4a shows the influence of accumulation potential on the uranium peak current; the response increased with potential between 0.0 and −0.40 V due to the increased reduction and accumulation of U(IV) on the electrode surface. In this figure I_{corr} is the difference between the peak current and the base line.

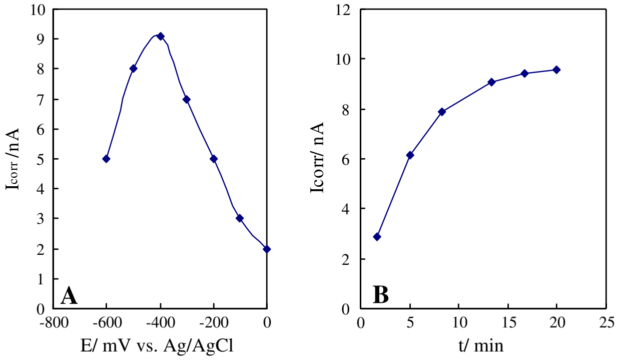

Fig. 4 Effect of accumulation potential (**a**) and time (**b**) on the response to 2 × 10^{-7} mol L^{-1} Uranyle. Accumulation for 13 min (**a**); accumulation potential −0.40 V (**b**). SWV was recorded in a solution containing 0.010 mol L^{-1} Mg^{2+} and 2 × 10^{-7} mol L^{-1} Uranyle (pH 4.4) at 0.05 V s^{-1} and the pulse amplitude of 0.05 V

The peak current decreased at potentials more negative than −0.40 V, because of hydrogen reduction on the electrode surface. All further measurements were carried out with an accumulation potential of −0.40 V.

Under a fixed accumulation potential the stripping peak currents improve as the accumulation time is extended. As expected, the stripping peak currents increased during the first 13 min and then levelled off (Fig. 4b). The curvature presumably indicates that the limiting value of reduced uranium was achieved on the MWNT-Nafion film modified GCE surface when the accumulation time was beyond 13 min. A further increase in accumulation time did not cause saturation. Therefore, the peak currents remained almost constant. Although the sensitivity for lower concentrations improved with increasing accumulation time, the linear range was then diminished.

3.4.2 *Effect of pH*

Various electrolytes (sodium acetate, sodium nitrate and sodium citrate) were tested as a supporting electrolyte. Of these, 0.20 mol L^{-1} sodium acetate gave the best response. The effect of pH was studied in the range 4.0–5.7 (Fig. 5). It was observed that the height of the oxidation peak increased with increase in pH up to 4.4. Then it decreased with further increase in pH (in this figure, I_{corr} is the difference between the peak current and the base line).

Increase in pH to around 4 caused an increase in the extent of UO_2^{2+} hydrolysis to the point where the $(UO_2)_2(OH)_2^{2+}$ concentration became considerable. At a pH of about 4.4, the concentration of $(UO_2)_2(OH)_2^{2+}$ became maximum [15], while its concentration decreased with increase in pH. It seems that $(UO_2)_2(OH)_2^{2+}$ species can be easily adsorbed and reduced on the electrode surface in preference to other species due to the negative charge of the Nafion film.

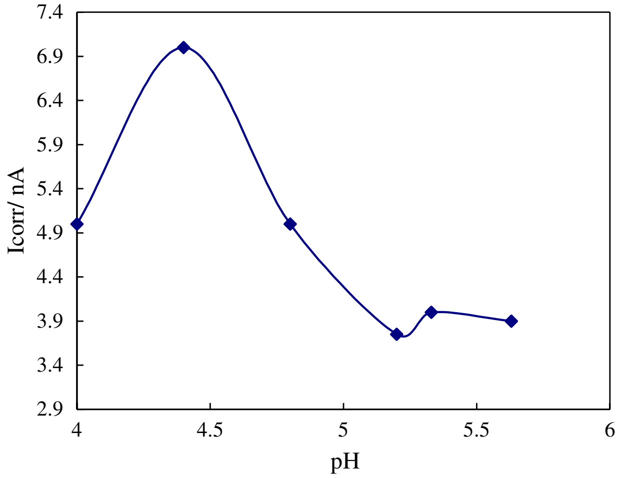

Fig. 5 Effect of pH on the stripping voltammetric response of 1.2 × 10^{-7} mol L^{-1} Uranyle. Square wave voltammograms were recorded at 0.05 V s^{-1} and a pulse amplitude of 0.05 V

3.4.3 *Effect of MWNT-Nafion film thickness*

The voltammetric response of UO_2^{2+} is closely related to the thickness of the MWNT-Nafion film on the GCE surface [16]. The relationship between the amounts of MWNT-Nafion suspension and the stripping peak currents was examined. The stripping peak currents were very high even when 10 µL (MWNT)–2 mg mL^{-1} (Nafion) suspension was used to cast the GC electrode. MWNT is an ideal electrode material with excellent electrical conductivity and large specific surface area. In principle, the stripping peak currents are independent of the thickness of the MWNT-Nafion film.

3.5 Calibration curve

Under the optimum conditions, the oxidation peak current of UO_2 yields well-defined concentration dependence from 5 × 10^{-9} to 1.2 × 10^{-7} mol L^{-1} ($i_p = 0.0353C + 2.188$, $r^2 = 0.968$, i_p in nA, C in nmol L^{-1}) as shown in Fig. 6. The lowest detectable concentration of Uranyle at 1,000 s accumulation was estimated to be 1 × 10^{-9} mol L^{-1}. The relative standard deviation of 10 measurements of 2.0 × 10^{-8} mol L^{-1} Uranyle determined at one single modified electrode was 4.6%. After each measurement, the GC electrode was modified again by the MWNT-Nafion composite film and the R.S.D. of 2.0 × 10^{-8} mol L^{-1} Uranyle was 5.2% ($n = 8$), indicative of excellent reproducibility towards the determination of Uranyle.

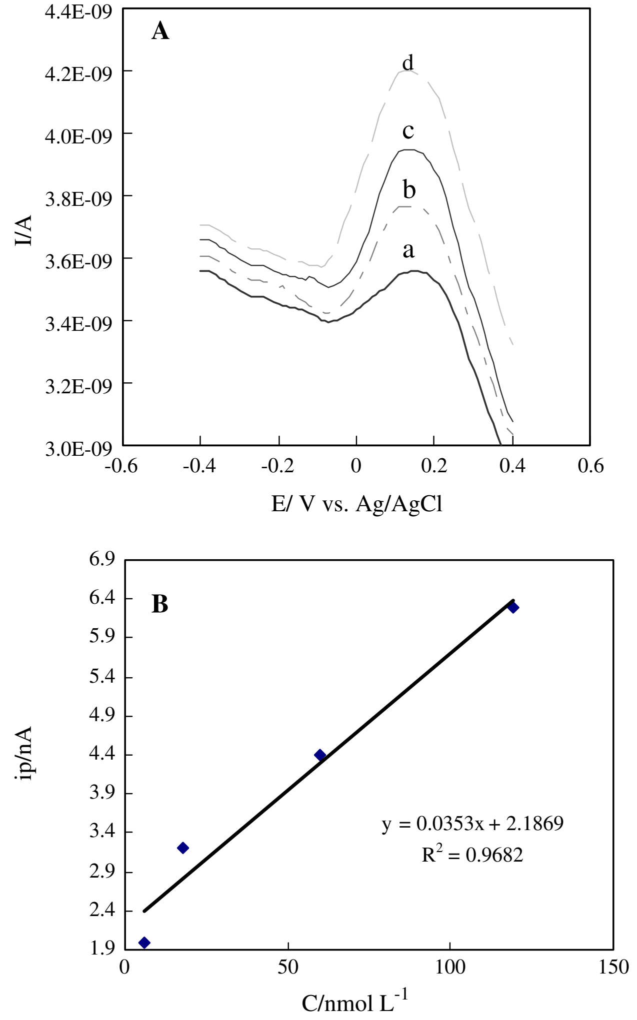

Fig. 6 (**a**) Anodic stripping voltammograms for the concentration of Uranyle: curves ‘a’ = 5×10^{-9}, ‘b’ = 1.7×10^{-8}, ‘c’ = 5.9×10^{-8}, ‘d’ = 1.19×10^{-7}, at an optimal condition of 0.20 mol L^{-1} acetate buffer (pH 4.4) and 0.010 mol L^{-1} Mg^{2+}. The square wave voltammograms were recorded at 0.05 V s^{-1} and a pulse amplitude of 0.05 V. Accumulation time and potential were 13 min and −0.40 V, respectively. (**b**) Calibration curve of Uranyle

3.6 Interferences

The possible interferences of some inorganic species were also tested. The response for 1.0×10^{-7} mol L^{-1} Uranyle was not affected by 300 µg L^{-1} levels of zinc, aluminum, cadmium, bismuth, antimony, cobalt, nickel or vanadium. Common anions including chloride, chlorate and sulphate were tested at 0.002 mol L^{-1} level and none of them had any effect on the response to 1.0×10^{-7} mol L^{-1} Uranyle.

3.7 Determination of uranium in water samples

The MWNT-Nafion composite film modified electrode exhibits high sensitivity towards the determination of Uranyle under optimum laboratory conditions. To show its application in practical analysis the MWNT-Nafion composite film modified electrode was used to detect Uranyle in some synthetic mixtures and real water samples. The data obtained for the water samples spiked with uranium showed good recoveries (Table 1). The method was also applied to the determination of synthetic mixtures. The good recoveries were indicative of the successful applicability of the proposed electrode.

Table 1 Determination of Uranyle in the synthetic and natural water samples ($n = 5$)

Sample	Added (µg L^{-1})	Found (µg L^{-1})	Recovery (%)
Tap water	20	19.6	98
Synthetic sample 1[a]	20	20.3	101.5
Synthetic sample 2[b]	20	19.8	99

[a] Synthetic sample 1: the solution contained Ag, Cu, Cd, Ni, Pb, Zn (150 µg L^{-1}) and 4×10^{-3} mol L^{-1} EDTA

[b] Synthethic sample 2: The solution contained CN^-, SO_4^{2-}, Cu, Ag, Mn (200 µg L^{-1})

4 Conclusion

Anodic stripping voltammetric determination of Uranyle based on accumulation of uranium on a MWNT-Nafion composite film modified electrode can be used to determine trace amounts of this element in the presence of other ions. A dispersion of MWNTs in 0.5% Nafion was cast uniformly on a glassy carbon electrode. This mercury-free thin film electrode was used to detect uranium in aqueous solutions. Cyclic voltammetry showed that the cathodic reduction peak was due to the reduction of U(VI) to U(V). UO_2^+ was reasonably stable at this pH and was reduced to UO_2 at more negative potentials. A plot of peak current versus Uranyle concentration showed a linear relationship (Fig. 6).

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