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Electrooxidation of Se on nanodispersed films of titanium dioxide modified with ZnO and Au

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Selenium electrooxidation process on TiO_2 and TiO_2/ZnO electrodes, modified by gold nanoparticles, was investigated in solutions of sulfuric, chloric and citric acids. It is shown that TiO_2/ZnO/Au electrodes can be used as indicator electrodes at the determination of selenium by anodic stripping voltammetry method. Optimum conditions of selenium (IV) determination are: supporting solution 0,001M H_2SO_4, electroconcentrating potential -(1,3÷1,5) V; time of electrolysis 120 s, scanning speed of potential 20 mV/s.

Introduction

Selenium is an important technological and biological element used both in industry and in medicine[1]. It is used in semiconductor technology, pulp and paper industry, manufacture of fertilizers, nonferrous metallurgy. The main peculiarity of selenium consist in the existence of a nice distinction between its useful and toxic content, which necessitates the use of highly sensitive and accurate techniques for the determination of its concentration. The stripping voltammetry (SV) method satisfies these requirements[2-8], because it has incontestable advantages over other methods: it has a high sensitivity and selectivity, rapid response to changes in the composition of the analyzed object, is easy to automate. This method does not require expensive analytical equipment and can be used in laboratory, industrial and field conditions. Cathodic stripping voltammetry is most frequently employed to determine selenium, using hanging mercury drop electrode, mercury-film electrode, mercury-graphite electrode, thick-film graphite electrode, silver electrode, silver disk electrode as indicator electrodes [2-4]. Disadvantages of the cathodic voltammetry for determination of selenium are the interfering effect of oxygen and the need to remove it from solution during analysis, as well as the use of toxic mercury electrodes. The anodic SV method using gold indicator electrodes has no above disadvantages. However, the complexity of gold electrodes making and their short service life [5-8], as well as the interfering effect of chloride ions, are significant disadvantages of this method, which greatly limits its use in the analysis of real objects for selenium content. This paper presents results of studying TiO_2- and TiO_2/ZnO- electrodes modified by gold nanoparticles, which are easy to make, are cheap and have a long service life for Se (IV) determination by anodic stripping voltammetry method. This method of selenium determination is based on the process of selenium electrooxidation. The method consists in previous electroconcentrating of selenium (0) in cathodic potential range and its subsequent electrodissolution in anodic potential range.

Experimental part

Electrode materials were TiO_2 and TiO_2/ZnO based films doped with Au nanoparticles prepared as described in [9]. Mesoporous TiO_2 and TiO_2/ZnO films were obtained, using titanium tetra-isopropoxide and zinc acetate as metal sources and triblock copolymer Pluronic P123 as templating agent. Gold-modified films were prepared using two techniques. Namely, thermoinduced reduction of Au^{3+} ions added to the precursor as $HAuCl_4$ aqueous solution with the following calcinations at 500^0C signing here as *s–g* and photoreduction of Au^{3+} ions deposited on mesoporous TiO_2 and TiO_2/ZnO films from aqueous solution $HAuCl_4$ under UV-irradiation followed by heat treatment at 20–550 ◦C signing as *ads*. The use of these techniques makes it possible to form in TiO_2 and TiO_2/ZnO films gold nanoparticles of different sizes with different distributions on the surface (*(ads)* – Au NPs are distributed on the surface; *(s-g)* - Au NPs are distributed in the matrix) [10].

The effect of doping Au on the electrocatalytic activity of films in the reaction of selenium electrooxidation were investigated. A current wave, which was observed on anodic voltammograms in the potential range +(0,6÷0,8) V, was used as the analytical signal of selenium (IV). The voltammograms were recorded as follows. The solution under investigation containing Se(IV) ions was placed in an electrochemical cell. A potential (E_e) was applied to the indicator electrode, and electrolysis was carried out for 60...180 s with stirring of the solution. The electrolysis potential was varied between –0,2 and –1,6 V. The current-potential curve of anodic electrooxidation of selenium (0) obtained by electrolysis was recorded with potential variation from 0 to +1.0 V at a rate of 20 mV/s.

The photoelectrochemical properties of the TiO_2/ZnO, TiO_2/Au and $TiO_2/ZnO/Au$ electrodes were estimated using the spectral dependence of the photoelectrochemical current

(i_{ph}) [11]. The i_{ph} spectra were expressed in the units of quantum efficiency (electron/photon).

Results and discussion

The photoelectrochemical characteristics (flat-band potential E_{fb} and band gap energy E_g) of electrodes based on TiO_2 and TiO_2/ZnO films as a function of their composition and the method of modification by gold nanoparticles are listed in **Table 1**. It follows from **Table 1** that the flat-band potential E_{fb} differs insignificantly for the modified samples, which means a small change in the potential drop in the space charge region after the modification. The band gap energy E_g for the modified samples was somewhat different, depending on the method of modification.

Table 1. Values of flat-band potential E_{fb} and band gap energy E_g for TiO_2/Au and TiO_2/ZnO/Au electrodes as a function of films composition in the solution 0,001M H_2SO_4:0,001 M KCl:0,1 mg/L H_2SeO_3.

	Composition	E_{fb}, V	E_g, eV
1	TiO_2/Au$_{(ads)}$	-0.30	3.25
2	TiO_2/1%ZnO/Au$_{(ads)}$	-0.50	3.25
3	TiO_2/4%ZnO/Au$_{(ads)}$	-0.60	3.25
4	TiO_2/3%Au$_{(s-g)}$		3.40
5	TiO_2/1%ZnO/Au$_{(s-g)}$	-0.56	3.60
6	TiO_2/4%ZnO/Au$_{(s-g)}$	-0.56	3.70
7	TiO_2/ Au $_{(s-g)}$ Termo	-0.62	3.60

The increase in E_g values observed for the samples synthesized by sol-gel method can be explained by the Burstein–Moss effect [12], where the apparent band gap of a semiconductor is increased due to the shift of absorption edge to higher energies as a result of all states close to the conduction band being populated.

In [10] we showed that, the maximum observed at around 530–600 nm on the optical absorption spectra of Au containing TiO_2 and TiO_2/ZnO films can be assigned to the surface plasmon resonance (SPR) of spatially confined electrons in Au nanoparticles (NPs), and confirms the reduction of Au^{3+} ions to the Au^0 state. According to the XRD data, TiO_2 and TiO_2/ZnO films had an anatase crystal structure but TiO_2/Au films had an anatase crystal structure with cubic Au crystals [10]. In TiO_2/ZnO/Au$_{(s–g)}$ films, a cubic $Zn_2Ti_3O_8$ phase was also observed. Au NPs with a mean diameter of 10–30 nm were found in TiO_2/Au$_{(s–g)}$ and TiO_2/ZnO/Au$_{(s–g)}$ films prepared by consequent photo- and thermoreduction while the particle sizes of TiO_2/ZnO/Au$_{(ads)}$ samples rose to 100 nm. For the Au containing films obtained by thermoreduction (without UV-irradiation), the particle size near 300 nm are observed [10].

Sulfuric, nitric, perchloric and citric acids were used as a supporting electrolyte for Se (IV) determination by anodic stripping voltammetry. It has been found that selenium (IV) electrooxidation current is affected by the nature of acid anion and pH value of the supporting electrolyte. At pH of supporting solution over 5.5, Se (IV) electrooxidation current is not observed. Decreasing pH solution to 4 leads to an increase in electrooxidation current and its better reproducibility. The largest value of selenium electrooxidation current was observed in sulfuric acid solutions. At an acid concentration in the supporting electrolyte of 0,001M, which corresponds to pH = 3.0, the analytical signal of Se (IV) had the same appearance but a different height in supporting electrolytes based on sulfuric, nitric and perchloric acids, decreasing in the order $H_2SO_4 > HClO_4 > HNO_3$.

Further increase of acid concentration, and hence - decreasing the background solution pH causes an increase the value of the background current and a shift of potential at the onset of dissolution of gold nanoparticles from the electrode surface towards more negative potentials. This leads to a decrease in sensitivity of electrodes and to worse reproducibility of selenium electrooxidation current.

Analytical signal of Se (IV) in sulfuric acid based electrolytes was observed in the potential range + (0,60 – 0,70) V, and for electrolytes based on citric and perchloric acids at in potentials of about + 0.80 V. At these potentials, the anodic voltammograms in selenium-containing solutions exhibited a current wave (**Figure 1**).

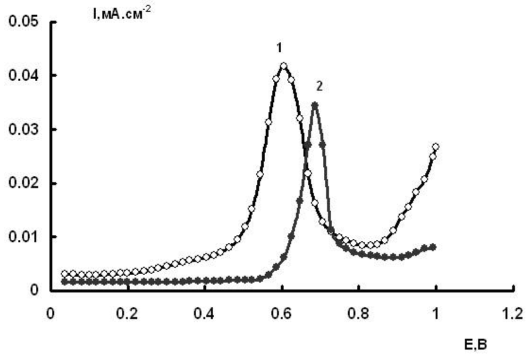

Figure 1. Anodic voltammograms in sulfuric acid solution (0,001M H_2SO_4:0,001 M KCl:0,1 mg/L H_2SeO_3) at electrodes: 1–TiO_2/1%ZnO/$Au_{(s\text{-}g)}$; 2–TiO_2/4%ZnO/$Au_{(s\text{-}g)}$.

The anodic polarization curves were recorded after cathodic electroconcetration of solutions at potential of -1.2 V (vs silver-chloride electrode) for 2 min. The current wave on anodic polarization curves at potentials of (0.6 ÷ 0.8) (**Figure 1**) is an analytical signal of Se (IV) and is caused by electrooxidation of Se^0,

$$Se^0 + 3H_2O - 4e \leftrightarrows H_2SeO_3 + 4H^+, \qquad (1)$$

which is formed in the investigated solution as a result of cathodic electroconcentration [13].

It has been found that selenium electrooxidation potential and analytical signal height of selenium dependent on the modification method and the composition of films, which were used as sensitive layer of working electrode (**Table 2**).

Table 2. Values of selenium electrooxidation potential E_{Se0} and selenium electrooxidation current I_{Se0} for TiO_2/Au and TiO_2/ZnO/Au electrodes as a function of films composition in the solution 0,001M H_2SO_4: 0,001 M KCl: 0,1 mg/L H_2SeO_3.

	Composition	E_{Se0},V	I_{Se0}, mA
1	TiO_2/$Au_{(ads)}$	> 0.70	-
2	TiO_2/1%ZnO/$Au_{(ads)}$	> 0.70	-
3	TiO_2/4%ZnO/$Au_{(ads)}$	> 0.70	-
4	TiO_2/3%$Au_{(s\text{-}g)}$	0.72	$1,5\cdot10^{-3}$
5	TiO_2/1%ZnO/$Au_{(s\text{-}g)}$	0.60	$4,2\cdot10^{-2}$
6	TiO_2/4%ZnO/$Au_{(s\text{-}g)}$	0.70	$3,1\cdot10^{-2}$
7	TiO_2/ $Au_{(s\text{-}g)}$ Termo	-	-

As seen from **Figure 1**, decreasing of ZnO content from 4% to 1% in TiO_2/ZnO/Au films with a uniform distribution of gold nanoparticles in the matrix of the film leads to shift of selenium electrooxidation potential E_{Se0} towards more negative values and to increase in the selenium oxidation current I_{Se0} (**Table 2**, samples 5 and 6; **Figure 1**).

At the electrodes of the compositions $TiO_2/ZnO/Au_{(ads)}$ and $TiO_2/Au_{(ads)}$ (**Table 2,** samples 1-3) with Au nanoparticles, distributed on the surface of films and at the electrodes $TiO_2/Au_{(s-g)}$ (**Table 2**, sample 4) with Au nanoparticles distributed in the matrix, the selenium electrooxidation current wave overlapped with the current wave of dissolution of gold nanoparticles from the electrode surface, which is manifested at potentials of > 0.8 V in sulfuric acid based electrolytes (**Figure 2**). The electrodes containing 1% ZnO in $TiO_2/ZnO/Au$ films with a uniform distribution of gold nanoparticles in the matrix of the film showed the best catalytic activity (**Table 2**, sample 5).

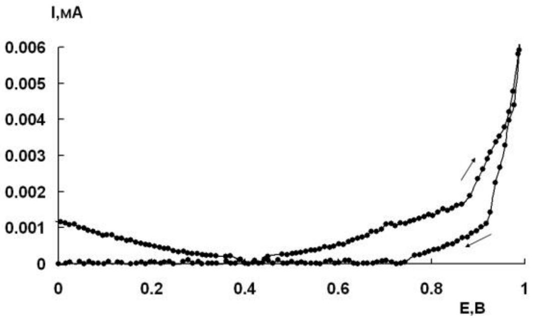

Figure 2. Anodic voltammograms (forward and reverse scan) for $TiO_2/Au_{(ads)}$ electrodes with gold nanoparticles distributed over the surface of films (**Table 1,** sample 1) in sulfuric acid based electrolyte (0,001M H_2SO_4 : 0,001 M KCl: 0,1 mg/l H_2SeO_3).

The decrease in the activity (I_{Se0}) of TiO_2 and TiO_2/ZnO samples with gold nanoparticles distributed on the surface (**Table 2**, samples 1-3) in comparison with the samples 5 and 6 (**Table 2**) may be a result of enlargement of gold NPs and their nonuniform distribution on the surface, since it has been found that the smallest size of gold NPs localized in the near-surface layer of the film is observed for $TiO_2/ZnO/Au_{(s-g)}$ films [10]. For $TiO_2/ZnO_{(s-g)}$ electrodes with gold nanoparticles distributed in matrix, the flat-band potential does not change on increasing ZnO content from 1 to 4% (**Table 1,** samples 5 and 6), whereas the band gap energy increases from 3.6 to 3.7 eV. This indicates a shift in the position of the valence band in the anodic side and may point to a better catalytic activity of these materials compared to unmodified TiO_2 in photooxidation processes, which was confirmed by us in selenium electrooxidation reaction as an example.

The electrooxidation current depended on selenium concentration, electroconcentration conditions and electrolyte composition.

Thus, the use of TiO_2/ZnO electrodes modified by gold NPs makes it possible to determine the selenium (IV) content in solutions by anodic stripping voltammetry. Optimum conditions of selenium (IV) determination are: background solution 0,001M H_2SO_4, electroconcentrating potential -(1,3 – 1,5) V; time of electrolysis 120 s, scanning speed of potential 20 mV/s. By means of this method it is possible to determine the concentration of Se (IV) within (0,02-0,40) mg/L.

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