

Determination of Pb^{2+} ions by square-wave anodic stripping voltammetry using silver nanoparticles grown on indium tin oxide substrate

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Silver (Ag) nanoparticles with a pure face-centred cubic phase were grown on indium tin oxide (ITO) substrate via the electrodeposition method. The products were characterised by scanning electron microscopy, energy-dispersive X-ray analysis and X-ray diffraction. Ag nanoparticles deposited on the ITO substrate were first used as an electrode for the electrochemical analysis of lead ions. A linear response was observed for Pb^{2+} in the range of 0.1–8 μM . The linear regression equation was $I = 0.129 + 0.368C$ (unit of C is μM) and the correlation coefficient was 0.9993. The detection limit was 70 nM Pb^{2+} ($S/N = 3$). The results open new possibilities for the fabrication of novel electrodes for the construction of simple, low-cost and reliable electrochemical sensors for the quantification of trace levels of Pb^{2+} .

1. Introduction: Lead is employed in piping, welding alloys, paints, ammunitions and accumulators, and is considered to be one of the most toxic pollutants. Lead poisoning is a medical condition caused by increased levels of plumbum (lead) in the blood [1]. Lead can inhibit brain development, and can cause reproductive toxicity, cardiovascular effects and renal malfunction. Accordingly, controlling the level of lead ions in the environment is both necessary and challenging. During past decades, the detection and quantification of lead ions of environmental pollutants in potable water and natural waterways have generated increasing interest in the development of novel sensors [2–5]. Conventional techniques used for the determination and quantification of heavy metal ions, such as inductively coupled plasma, anodic stripping voltammetry, chromatography, atomic fluorescence spectrometry and atomic absorption spectrometry, are expensive and rather cumbersome [6, 7]. Electrochemical sensors, being compact, highly efficient and sensitive, are more suitable for simple measurements and for rapid and express analyses [8]. Recently, the selective detection of Pb^{2+} through electrochemical techniques has aroused great interest in many areas. Electrochemical stripping analysis of heavy metals using a carbon-modified electrode was first carried out by Fan *et al.* [9], which demonstrated the good applicability of the sensor to the determination of Pb^{2+} in sewerage samples. A novel carbon paste ion selective electrode with fast response time and long-term stability was prepared by Ganjali *et al.* [10], which was used to determine the concentration of lead ions in waste water and black tea samples. An electrochemical DNA-based sensor for the detection of Pb^{2+} was developed based on ionic liquid-supported CeO_2 nanoparticles–carbon nanotubes composite with the thrombin-binding aptamer as a molecular recognition element. The sensor exhibited high sensitivity and selectivity [11].

Nanomaterials have attracted great interest because of their catalytic, thermal, and unique optical and electrical properties [12, 13]. Recently, noble metal nanomaterials have been extensively used in the construction of electrochemical sensors [14, 15]. The gold nanoparticle–chitosan composite film electrodeposited on the glassy carbon electrode surface showed high stability and excellent electrocatalytic activity when used as a glucose non-enzymatic sensor [16]. Gold nanowire assembling architecture with a high surface-to-volume ratio was developed by Guo *et al.* [17]. The obtained sensor exhibited good electrocatalytic activity towards

the reduction of H_2O_2 . Ag nanoparticles were electrochemically grown on polyaniline films for the purpose of a sensitive non-enzymatic glucose sensor. The novel Ag/polyaniline-based sensor shows great potential applications in electrochemical sensor development [18]. Ag nanorods with remarkable electrocatalytic activity for H_2O_2 reduction can also be prepared by a simple hydrothermal process without harmful chemicals, templates or surfactants [19]. To the best of our knowledge, there are few reports that discuss the detection of Pb^{2+} ions with Ag nanomaterial electrodes. In this Letter, we report a simple electrochemical deposition method for the production of Ag nanoparticles on an ITO substrate at room temperature, and Ag nanoparticle electrodes have been applied to detect Pb^{2+} ions. Our method opens new possibilities for the fabrication of novel Ag nanoparticle electrodes for the construction of inexpensive, simple and reliable electrochemical sensors for the detection of Pb^{2+} ions.

2. Experimental

2.1. Sample preparation: The Ag nanoparticle electrodes were prepared by the electrodeposition method. A conventional three-electrode cell system was used, including an indium tin oxide (ITO) conducting glass (ITO, $1 \times 2 \text{ cm}^2$) as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The electrochemical experiments were performed on a CHI660C electrochemical analyser (CHI, Chenhua, Shanghai, China). ITO was put into 0.01 M AgNO_3 solution and the Ag nanoparticles were grown on the ITO electrode by a potentiostatic method applying a cathodic potential of -0.7 V for 180–360 s. After electrodeposition, the ITO electrode was washed with deionised water and dried in air at room temperature.

2.2. Characterisation: The surface morphologies of samples were characterised using scanning electron microscopy (SEM, Hitachi S-4700 with an accelerating voltage of 15 kV). The crystal phases of the products were analysed by X-ray powder diffraction (XRD) using a Thermo ARL SCINTAG X'TRA X-ray diffractometer with graphite monochromatised $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 80 mA. The composition of the obtained samples was analysed by an energy dispersive X-ray detector (EDS) using a Thermo Noran VANTAG-ESI.

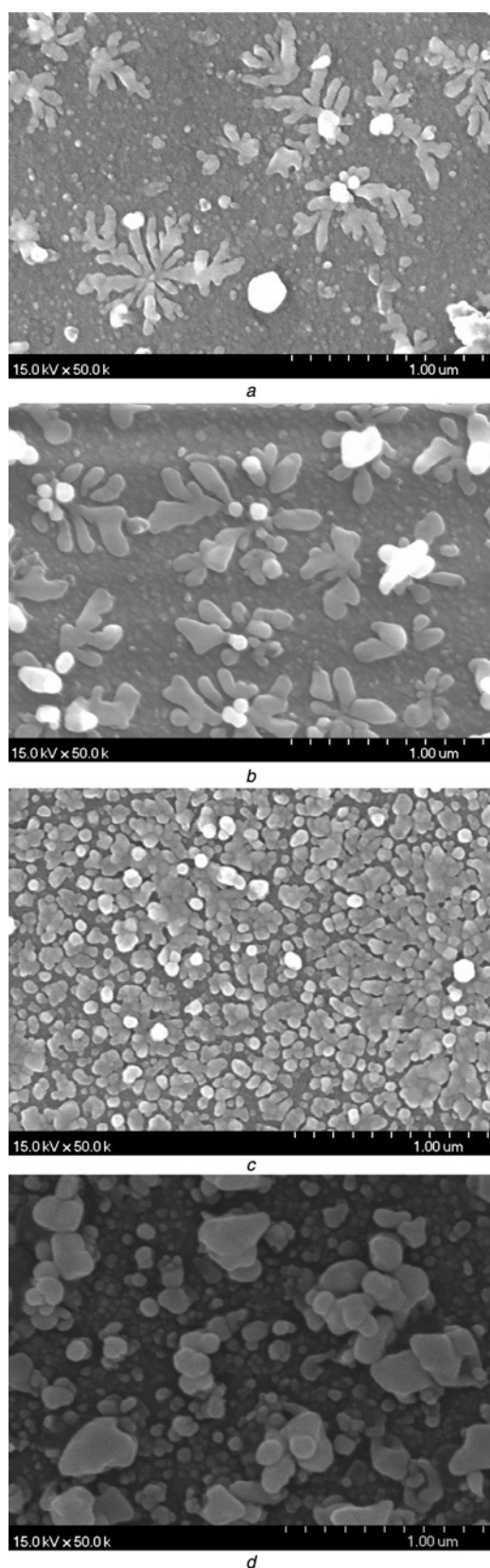


Figure 1 SEM images of Ag nanoparticles prepared by electrodeposition for different times

a 180 s
b 240 s
c 300 s
d 360 s

2.3. Electrochemical measurement: The electrochemical measurements were measured in a CHI600C three-electrode

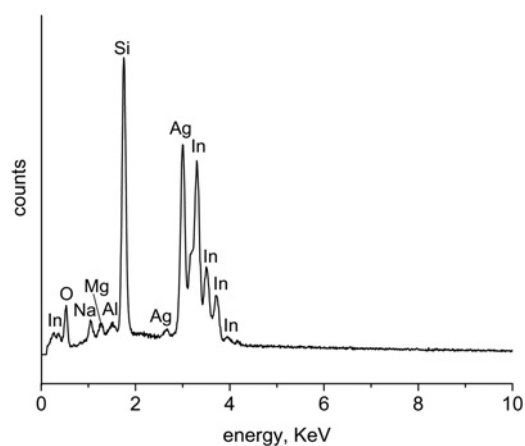


Figure 2 EDS patterns of Ag nanoparticles deposited on ITO substrate

electrochemical analyser, in which a platinum wire, an Ag/AgCl electrode and an Ag nanoparticle electrode were used as the counter, reference and working electrodes, respectively. The preconcentration of Pb^{2+} proceeded in 15 ml 0.1 M KNO_3 solutions for 2 min while holding the electrode at -1.0 V and stirring the solution. After 30 s of equilibration period, the square wave anodic stripping voltammetry measurements were performed in the potential range of -0.7 to -0.3 V with a frequency of 50 Hz, an amplitude of 40 mV and a potential step of 4 mV.

3. Results and discussion: The morphology and particle sizes of the Ag nanoparticles grown on ITO was investigated by SEM. The SEM images of the obtained products after different times of electrodeposition are shown in Fig. 1. Fig. 1a is the SEM image of the obtained products after 180 s of electrodeposition. As can be clearly seen, some Ag nanoparticles with sizes ranging from 100 to 200 nm were obtained. The SEM image of the obtained products after 240 s of electrodeposition is shown in Fig. 1b. It can be seen that the Ag nanoparticles were gradually deposited on the ITO substrate. The pattern of Fig. 1c indicates that more Ag nanoparticles were deposited on the ITO conducting glass substrate after 300 s. As shown in Fig. 1d, Ag nanoparticles with sizes ranging from 100 to 350 nm are spread on the ITO substrate after 360 s of electrodeposition. The surface morphology and particle sizes of the obtained Ag nanoparticles under different electrodeposition times demonstrate that the deposition time has controlled the size and density of Ag nanoparticles on the ITO substrate.

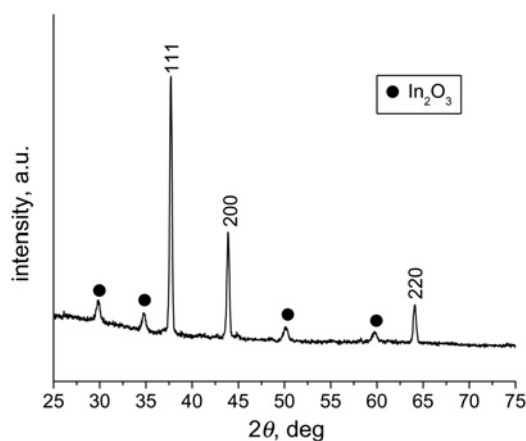


Figure 3 XRD patterns of Ag nanoparticles grown on ITO substrate

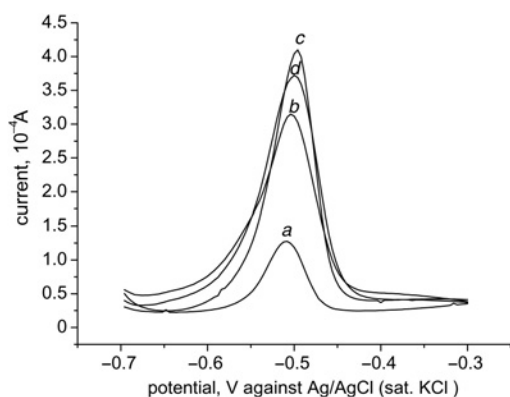


Figure 4 SWASVs of Pb^{2+} at obtained Ag nanoparticles under different times of electrodeposition: 180 s (trace a); 240 s (trace b); 300 s (trace c); 360 s (trace d)

Experimental conditions: deposition/measurement solution: 0.1 M KNO_3 solutions containing $10 \mu\text{M}$ Pb^{2+}

EDS analysis was employed to determine the composition of Ag nanoparticles deposited on the ITO substrate. The EDS patterns of the obtained Ag nanoparticles after 300 s of electrodeposition are shown in Fig. 2. The figure reveals that the main elements in the samples are Ag, and Si, Na, Mg, Al, In from ITO.

The crystal phase of the samples was analysed by powder X-ray diffraction. Fig. 3 shows the XRD patterns of the Ag nanoparticle electrode prepared by electrodeposition for 300 s. The distinctive diffraction peaks such as (111), (200), (220) in Fig. 3 can be readily indexed to face-centred cubic silver with the lattice parameter $a = 4.084 \text{ \AA}$. The results are in good accordance with the standard

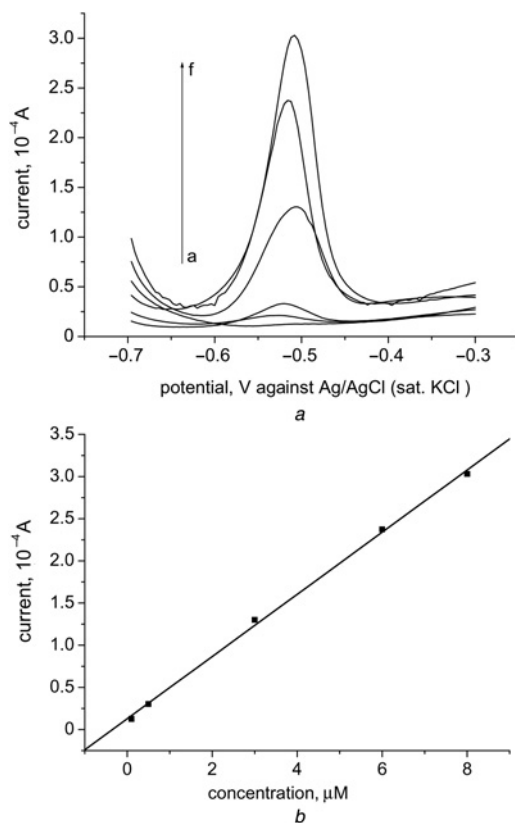


Figure 5 SWASVs for standard additions of Pb^{2+} of $0.1\text{--}8 \mu\text{M}$ (Fig. 5a), and linear relationship between peak current and concentration of Pb^{2+} (Fig. 5b)

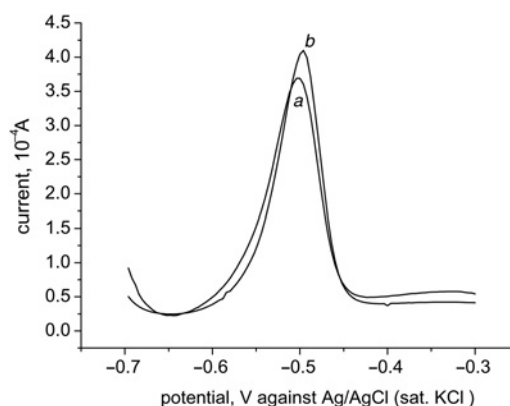


Figure 6 SWASVs for addition of Na^+ , K^+ , Ca^{2+} and Zn^{2+} ($10 \mu\text{M}$, each) (trace a) and SWASVs corresponding to detection of $100 \mu\text{M}$ Pb^{2+} (trace b)

values (JCPDS 04–0783). No silver oxide phase can be detected, indicating the high purity of the final products.

Fig. 4 shows the square wave anodic stripping voltammograms (SWASVs) of Pb^{2+} at the Ag nanoparticles prepared by electrodeposition. All Ag nanoparticles obtained after different times of electrodeposition exhibit well-defined anodic peaks of Pb^{2+} . The peak potential of Pb^{2+} at the Ag nanoparticle electrode are -0.512 V . As can be clearly seen, the Ag nanoparticle electrode prepared by electrodeposition for 300 s exhibited the strongest anodic peak current of Pb^{2+} . On the basis of the SEM analysis of Ag nanoparticle electrodes, the strongest anodic peak current may be attributed to its smaller particle size and higher density. The smaller particle size and higher density are favourable for increasing the interface area between Ag nanoparticles and the electrolyte, which can facilitate the preconcentration of lead. The strongest peak currents are beneficial for the determination of Pb^{2+} .

Fig. 5 displays SWASVs at the Ag nanoparticle electrode prepared by electrodeposition for 300 s at various concentrations. The peak currents of Pb^{2+} increase linearly with the concentrations of Pb^{2+} in the range of $0.1\text{--}8 \mu\text{M}$. The linear regression equation was $I = 0.129 + 0.368C$ (unit of C is μM) and the correlation coefficient was 0.9993. The detection limit was 70 nM Pb^{2+} ($S/N = 3$).

The selectivity of the Ag nanoparticle electrode was evaluated with four species: Na^+ , K^+ , Ca^{2+} and Zn^{2+} . As shown in Fig. 6, the signal obtained from the mixture of metal ions was slightly lower than that obtained from the pure Pb^{2+} solution. This suggests that these species had no obvious interference in the detection of lead ions.

4. Conclusion: In summary, we demonstrated a sensitive lead ion sensor based on Ag nanoparticles deposited on the ITO substrate. Ag nanoparticles were synthesised on an ITO substrate by simple electrodeposition in a single step. The surface morphology, particle size, composition and structure of Ag nanoparticles were characterised by SEM, EDS and XRD. The developed nanoAg sensor had excellent sensitivity for Pb^{2+} detection. A linear response was observed for Pb^{2+} in the range of $0.1\text{--}8 \mu\text{M}$, and the detection limits are 70 nM for Pb^{2+} . This method is inexpensive, simple and reliable, thus it could be extensively applied in many fields for the detection of Pb^{2+} .

5 References

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