

Nitrate sensing based on Pd-Sn bimetallic composite: a comparison between a bulk electrode and a microband electrode array

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Published in *Micro & Nano Letters*; Received on 5th January 2016; Accepted on 23rd February 2016

This work presents a bulk electrode and a microband electrode array for electrochemical nitrate sensing in acidic medium. The microelectrode array is fabricated on silicon wafer by micro electro-mechanical system technique. Electrodeposition was carried out to modify tin onto the bulk palladium electrode and thus formed Pd-Sn bimetallic composite. On the microelectrode array, Pd and Sn were successively deposited to obtain a double-layer composite. The performance of the two kinds of electrodes towards nitrate sensing was investigated and compared. The microelectrode array showed better sensitivity and repeatability than the bulk electrode. The results are consistent with the unique properties of the microelectrode array in electrochemical analysis such as high current density and low background noise.

1. Introduction: Nitrate contamination of ground and surface water has been of interest to scientific communities and the public because of its potential hazard to health [1]. To perform detection and qualification of nitrate, researchers have developed kinds of techniques such as spectrophotometry, electrochemistry, fluorimetry, mass spectroscopy, capillary electrophoresis and chromatography [2]. However, some conventional techniques including spectrophotometry, capillary electrophoresis and chromatography usually require large instruments, complex procedures and multiple reagents. Nitrate samples are manually taken from water sources to labs for analysis in practice [3].

Electrochemical methods can be more viable because they are relatively simple and cheap, and electrochemical sensors can be assembled into a portable device. Electrodes are employed in this method and modification materials onto the electrodes are usually required [4]. A wide variety of materials such as Cu [5], Ag [6], Sn [7] and some bimetallic materials including PdCu [8], PdSn [9] and PtRh [10] have been investigated for nitrate reduction, among which PdSn is believed to have strong catalytic activity [11]. However, many of the bimetallic materials have been limited to nitrate removal [12–15]. Their effects on nitrate sensing have not been fully investigated.

Microfabrication has been an efficient manufacturing technique for microelectrodes, which possess many favourable properties in comparison with bulk electrodes. These properties comprise reduced iR drop, low background noise and high current density. To overcome the small absolute current of a single microelectrode, microelectrode array with the advantages of microelectrode is developed to obtain a satisfactory output signal [16]. These properties have thus captured much interest in the field of electrochemical, biochemical and environmental analysis.

In this work, tin was deposited on a bulk Pd electrode and Pd-Sn composite was developed onto a microband electrode array. Pd-Sn acted as the sensing material for nitrate determination on both electrodes. Nitrate was determined by linear sweep voltammetry (LSV) in 0.01 M HClO₄ electrolyte. In order to compare the analytical performance of the two kinds of electrodes, sensitivities and repeatabilities were examined. The aim of this Letter is therefore to investigate on the advantages of microelectrodes in electrochemical analysis over bulk electrodes.

2. Experimental section: All solid reagents were of analytical grade and were used without further purification. Ethanol,

chlorhydric acid (36–38%) and sulphate acid were obtained from Beijing Chemical Works; SnCl₂, NaCl, HClO₄, KNO₃ and tin granular were obtained from Sinopharm Chemical Reagent Co. Ltd; PdCl₂ was obtained from Sigma-Aldrich; solutions were prepared by dissolving the solid reagents in deionised water with a resistivity of 18 M Ω ·cm obtained from Millipore Direct-Q 3 UV system. The deionised water was also used for washing the electrodes and containers of the solutions.

The three-electrode system was used for the electrochemical experiments in this work. The working electrodes were a bulk Pd electrode and a microband electrode array. The bulk electrode was a PTFE-shrouded palladium disk electrode with a diameter of 2 mm. The microband electrode array was fabricated by micro electro-mechanical system technique in our lab. Platinum was deposited on silicon substrate and then patterned by lift-off process to form the microband array structure. The length of the microband was 2000 μ m and the width was 10 μ m. The gap between the bands was 50 μ m. The total number of the bands was 50. The microband electrode array was defined by a layer of SU-8 negative photoresist, thus exhibiting a fixed effective area of 1 mm². The counter electrode was a PTFE-shrouded platinum disk electrode with a diameter of 3 mm. A KCl saturated Ag/AgCl electrode acted as reference, and all potentials reported are referred here. All electrochemical experiments were controlled by electrochemical measurement system CHI620e. The data were analysed using CHI620e electrochemical analyser software. An optical microscope was used to preliminarily observe the surface of the electrode. Scanning electron microscopy (SEM) and energy dispersive spectroscopy analysis of the deposited layer was performed using an S-4800 field emission scanning electron microscope produced by Hitachi (Japan).

The bulk Pd electrode was polished with 0.3 μ m-diameter alumina-particles till mirror-shine was achieved before experiments. It was then rinsed with copious deionised water to ensure a clean surface. The deposition bath was 20 mM SnCl₂ + 0.1 M HCl, prepared by dissolving SnCl₂ powder in concentrated HCl solution. Electrodeposition onto the electrode was performed by cyclic voltammetry (CV) from –0.45 to –0.58 V for 20 cycles with a scan rate of 0.05 V/s. After electrodeposition, the bulk electrode was rinsed with deionised water and dried for nitrate determination in another electrochemical cell.

Before electrodeposition of sensing materials onto the bare microband electrode array, it was electrochemically pretreated by

CV for 5 cycles in 0.05 M H₂SO₄. The potential range was -0.4 to 1.2 V and the scan rate was 50 mV/s. A stable cyclic voltammogram was finally obtained to verify a clean state of the electrode surface. The deposition of sensing materials was carried out in two steps. The microelectrode was first modified in 20 mM PdCl₂ by chronoamperometry at -0.56 V for 100 s. The deposition bath was prepared by dissolving PdCl₂ in 1 M NaCl. The microelectrode with the palladium layer was then cycled in 20 mM SnCl₂ + 0.1 M HCl between -0.45 and -0.58 V for 20 cycles. Hence the Pd-Sn double layer was acquired on the microbands.

The bulk electrode and the microelectrode were both examined in 10 ml aqueous solutions (pH 2) containing 0.01 M HClO₄ and KNO₃ with different concentrations. Determination of nitrate was performed by LSV. The potential range was set to be -0.47 to -0.73 V with a scan rate of 0.05 V/s. The first few voltammograms were neglected till the reduction potential and the current response both became stable.

3. Results and discussion: Coelectrodeposition was rejected as it is difficult to prepare a deposition bath simultaneously containing tin and palladium salt. Therefore deposition of tin was directly carried out on bulk Pd electrode and successive deposition of palladium and tin was carried out on the microbands. Hence, Pd-Sn double-layer was acquired on both the bulk electrode and the microelectrode array. The morphology of the Pd-Sn composite on the microbands was examined by SEM, as was shown in Fig. 1. Palladium and tin particles were piled up like gravels on the surface of the microbands. Palladium particles assembled at the

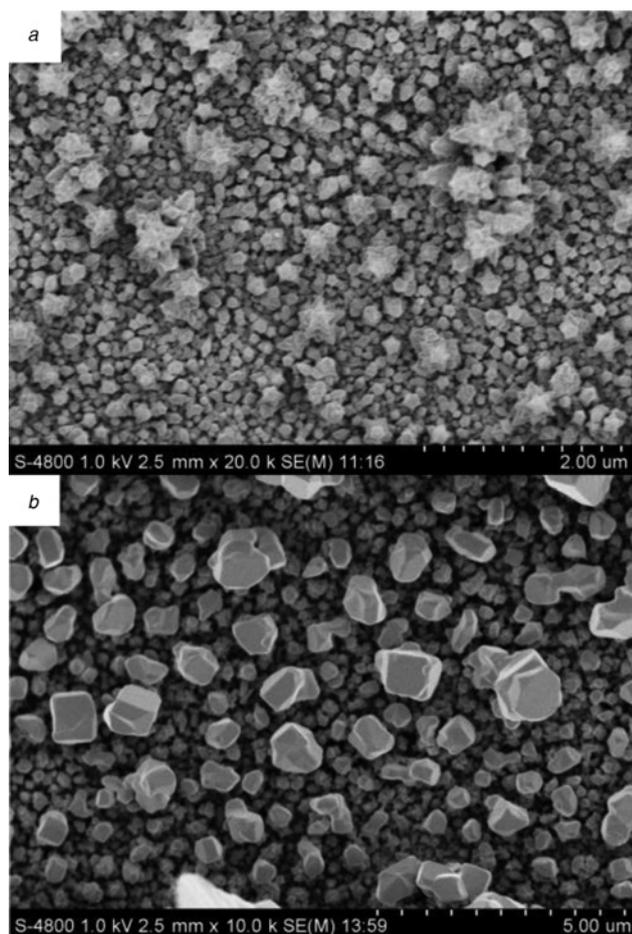


Fig. 1 View of modification layer on the microband electrode array under SEM
a Palladium modification layer after the first-step deposition
b Palladium-tin modification layer after the second-step deposition

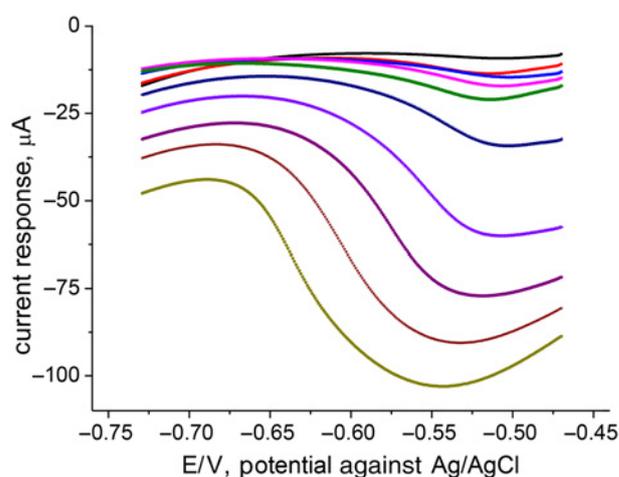


Fig. 2 LSVs of the bulk electrode towards different nitrate concentrations (concentration increasing from up to down)

bottom and tin particles were scattered in the upper layer. Synergy of palladium and tin and plentiful active sites were achieved in this structure, which were beneficial to the analytical performance of the electrode used as a nitrate sensor.

LSVs of the bulk electrode and the microband electrode array in electrolytes with varied nitrate concentrations ranging from 0 to 50 mg/l were recorded in Figs. 2 and 3. Solutions containing 0, 1, 2, 3, 5, 10, 20, 30, 40, 50 mg/l KNO₃ were prepared and detected, respectively. Nitrate was electrochemically reduced on Pd-Sn and the reduction current increased with the ascending nitrate concentration. The microelectrode exhibited a distinctly larger absolute current despite its smaller electrode area. The reduction peak appeared around -0.51 V, where there was current response even in blank electrolyte owing to the dissolved oxygen reduction. The oxygen level in electrolytes with varied concentrations were almost the same as room temperature was controlled, and therefore its current response kept relatively stable and could be regarded as background. The calibration curve displayed in Fig. 4 indicates that good linearity ($R^2 = 0.999$) was obtained from 0 to 20 mg/l for both electrodes. The bulk electrode (curve b) showed a sensitivity of 80 $\mu\text{A}/(\text{mg/l}\cdot\text{cm}^2)$ with the limit of detection (LOD) estimated to be 0.23 mg/l ($S/N=3$). The microelectrode array (curve a) exhibited a sensitivity of 423 $\mu\text{A}/(\text{mg/l}\cdot\text{cm}^2)$ with a smaller LOD of 0.17 mg/l ($S/N=3$). The microband electrode array showed significant advantage in sensitivity over the bulk electrode, which supported

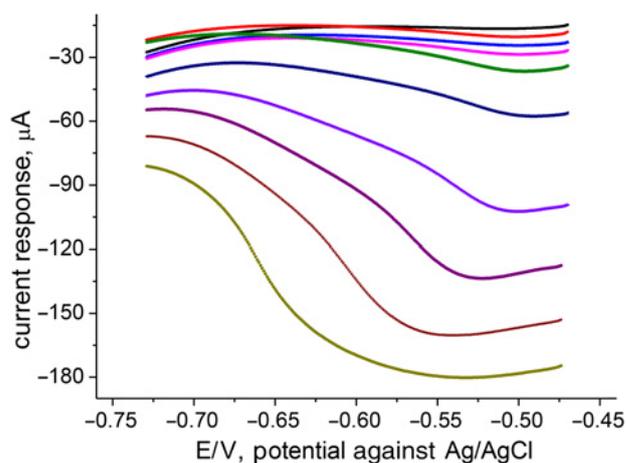


Fig. 3 LSVs of the microelectrode towards different nitrate concentrations (concentration increasing from up to down)

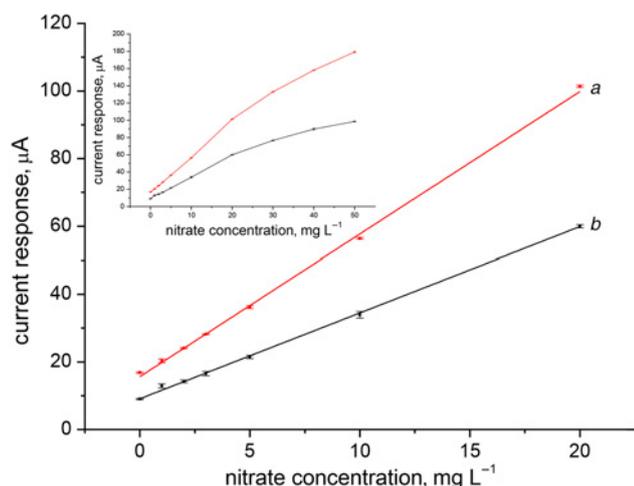


Fig. 4 Calibration plot of microelectrode array (curve a) and bulk electrode (curve b) for nitrate sensing. The inset shows current responses on both electrodes in full range from 0 to 50 mg/l

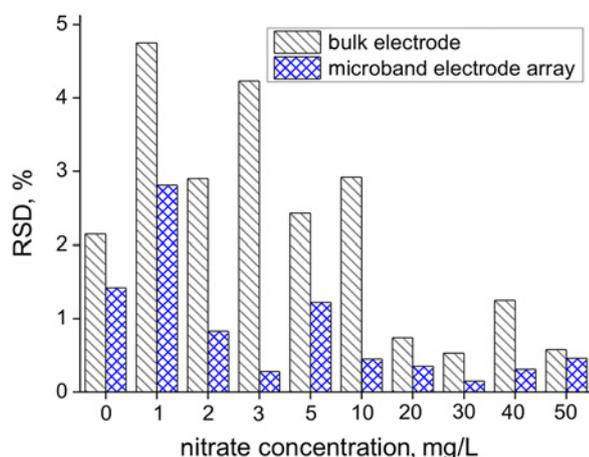


Fig. 5 Comparison of the repeatabilities between the microelectrode array and the bulk electrode

the theory that current density of a microelectrode is higher than a bulk electrode.

The repeatabilities of the two electrodes were examined by analysing the repeated current responses (at least 3 times for each concentration) to nitrate samples. As indicated in Fig. 5, the relative standard deviation (RSD) is always no bigger than 5%. The microelectrode array showed even smaller RSD, namely better repeatability than the bulk electrode. The results reflect that there was lower background noise when the microband electrode array was applied for detection.

4. Conclusion: In this work, a bulk electrode and a microband electrode array were applied to nitrate sensing. Palladium-tin bimetallic composite acted as sensing material on the electrodes and displayed satisfactory analytical performance towards nitrate.

Linearity was obtained in the range from 0 to 20 mg/l. The sensitivity of the microband electrode array was over 4 times larger than the bulk electrode, which supports the idea that microelectrode possesses high current density. The RSD of the microband electrode array was distinctly lower than that of the bulk electrode for each concentration, reflecting a low background noise. These experiment results supported that microelectrode array has advantage over bulk electrode in electrochemical analysis.

5. Acknowledgments: This work was supported by National Natural Science Foundation of China with grant no. 61302034 and no. 61134010 and 973 program no. 2015CB352100.

6 References

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