

Short Communication

Synthesis of Palladium Nanoparticles on the Surface of Gold Electrode for Determination of Dissolved Oxygen in Water

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Received: 4 July 2014 / Accepted: 28 August 2014 / Published: 29 September 2014

In this paper the electrochemical technology was performed for synthesis of palladium nanoparticles on the surface of gold electrode using EDTA as a stable reagent. Electrochemical behavior of oxygen at palladium nanoparticle modified gold electrode was investigated. It was demonstrated that the gold electrode modified with palladium nanoparticles is a simple and effective sensor for obtaining highly sensitive determination of oxygen in water.

Keywords: palladium nanoparticles; gold electrode; oxygen; water

1. INTRODUCTION

Dissolved oxygen (DO) is a key parameter characterizing wastewaters and assessing the state of environment. The sufficient concentration of DO is critical for the survival of most aquatic plants and animals [1]. The different methods have been reported for the determination of oxygen, including electrochemical techniques, titrimetric method, and optical methods. Titrimetric and electrochemical techniques are recommended as standard techniques [2, 3]. Among these methods, the oxygen sensor is an effective method for determination of oxygen because of its high sensitivity, low cost and possibility of miniaturization. However, the direct oxygen reduction at the solid electrodes is slow and requires a high potential, hence the study of electrocatalytic reactions of oxygen are important in the electroanalysis. Numerous sensors such as polymeric nickel–salen film coated platinum electrode [4], CdS modified screen printed carbon electrodes [5], multielectrolytic modified carbon electrode [6], NiCu alloy electrode [7], cobalt tetrasulphonated phthalocyanine (CoTSPc) immobilized in a poly-l-

lysine (PLL) film modified glassy carbon electrode (GCE) [8], polypyrrole/magnetite hybrid modified electrode [9] have been applied to determine DO.

Noble metal nanoparticles applied in various fields, such as catalysis, chemical sensing, bio-labeling or photonics, and palladium nanoparticles (PNs) are particular attractive. There are many methods to synthesize the modified electrode with desired PN composition, dimension and shape, such as palladium nanocube [10], palladium nanoparticles (PdNPs)-graphene nanosheets [11], carbon nanotubes (CNTs) supported palladium-iron bimetallic nanoparticles [12], carbon supported palladium-iron nanoparticles [13] and triangular shaped palladium nanoparticles decorated nitrogen doped graphene [14].

The electrochemical synthesis of metal nanoparticles is a conventional method to control the size, interparticle distance and shape of PNs [15-17], which could be controlled by not only the depositing time but also the different electrodes.

In present work, the electrochemical technology was applied for the synthesis of excellent repeatability and reproducibility PNs on the surface of gold electrode (GE) for DO. Electrochemical behavior of DO at PN modified electrode was investigated. The prepared sensor for determination of DO has many advantages such as easy preparation, high activity, simple operation, low cost, and no pollution.

2. EXPERIMENTAL

2.1. Regents

4.00g.L⁻¹ PdCl₂ were prepared by dissolving of 0.4000g PdCl₂ in the mixtures of 10.00ml of 37% (w/v) HCl and 90.00ml of H₂O. 2.00 g.L⁻¹ 10.00g.L⁻¹ NH₄Cl was prepared by dissolving 10.0000g NH₄Cl in double-distilled water (pH=7.00). Double-distilled water was used throughout. All reagents were analytical grade.

2.2. Instrument and Characterization

For all electrochemical experiments a CHI660B Electrochemical Analyzer (CHI, U.S.A.) was employed. The electrochemical cells consisted of a three electrodes, the PN modified electrode, platinum wire, and saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. A TP350 oxygen analyzer (China) was performed for determination of DO in water. The PN composite was characterized by scan electron microscopy (SEM) (Guanwta FEC 450, FEI, U.S.A.).

Before modification the GCE, GE and GPE were polished with 0.05μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water, and sonicated in ethanol and doubly distilled water for 10 min, sequentially. Then the GE was cycled between -0.35 and 1.5 V (scan rate 4000 mV. s⁻¹) in 0.1 M H₂SO₄ aqueous solution for 20 times until achieving the reproducible responses, and sonicated in doubly distilled water for 10 min, sequentially.

2.3 Prepared PN modified electrode

The PNs were deposited at -0.3V for 30s on the surface of GE, GCE or GPE that was immersed in the solution containing 1.00ml of 4.00 g.L⁻¹ PdCl₂, 1.00ml of 2.00 g.L⁻¹ EDTA.Na₂ and 1.00ml of H₂O, respectively. The obtained modified electrode was washed in doubly distilled water. Before the voltammetric measurements, the modified electrode was cycled between -0.6 and 0.6 V (scan rate 100 mV. s⁻¹) in 10.00g/L NH₄Cl buffer solution of pH 7.0 for several times until acquiring the reproducible responses.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammograms of EDTA-Pd

The cyclic voltammograms (CVs) of EDTA-Pd at bare GCE in the solution containing PdCl₂, HCl and EDTA are shown in Fig.1, the reduction peak and oxidation peak were observed at -0.126 and 0.189V, respectively, which could be ascribe to the reduction of Pd-EDTA and oxidation of Pd, respectively.

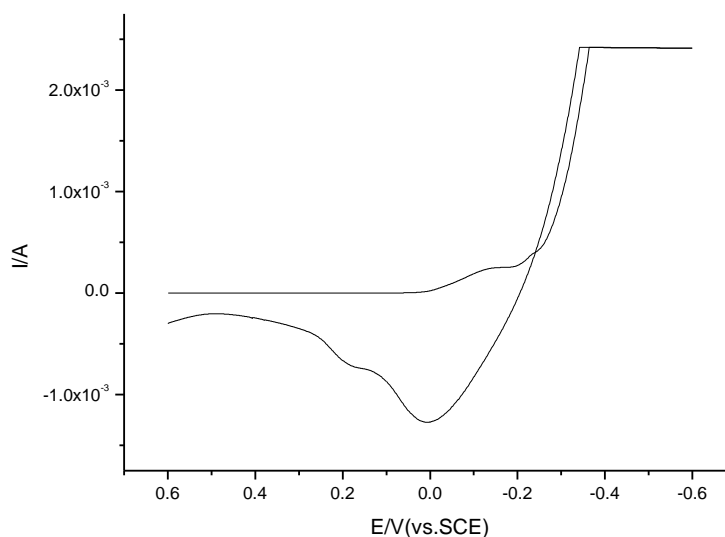


Figure 1. CVs of EDTA-Pd at GCE; Scan rate: 100mV/s.

3.2. Assembling processes of PNs on the surface of bare electrode

The assembling processes of PNs on the surface of bare electrode are shown in Fig. 2. The reduction currents of EDTA-Pd on the surface of bare electrode decrease, indicating that PNs on the surface of GCE were obtained.

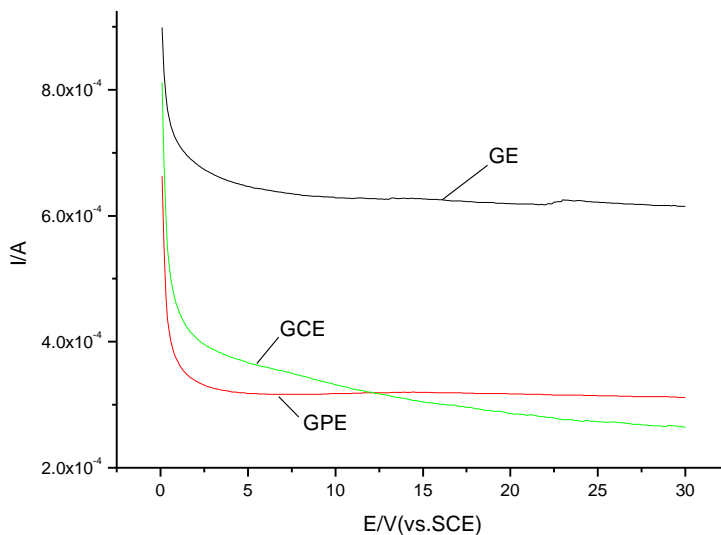


Figure 2. Electrochemical assembling processes of PNs on the surface of GE, GPE and GCE; initial E: -0.30 V; final E: -0.30 V; sample interval: 0.1s; quiet time: 0s; run time: 30s.

3.3. SEM imagine of PNs

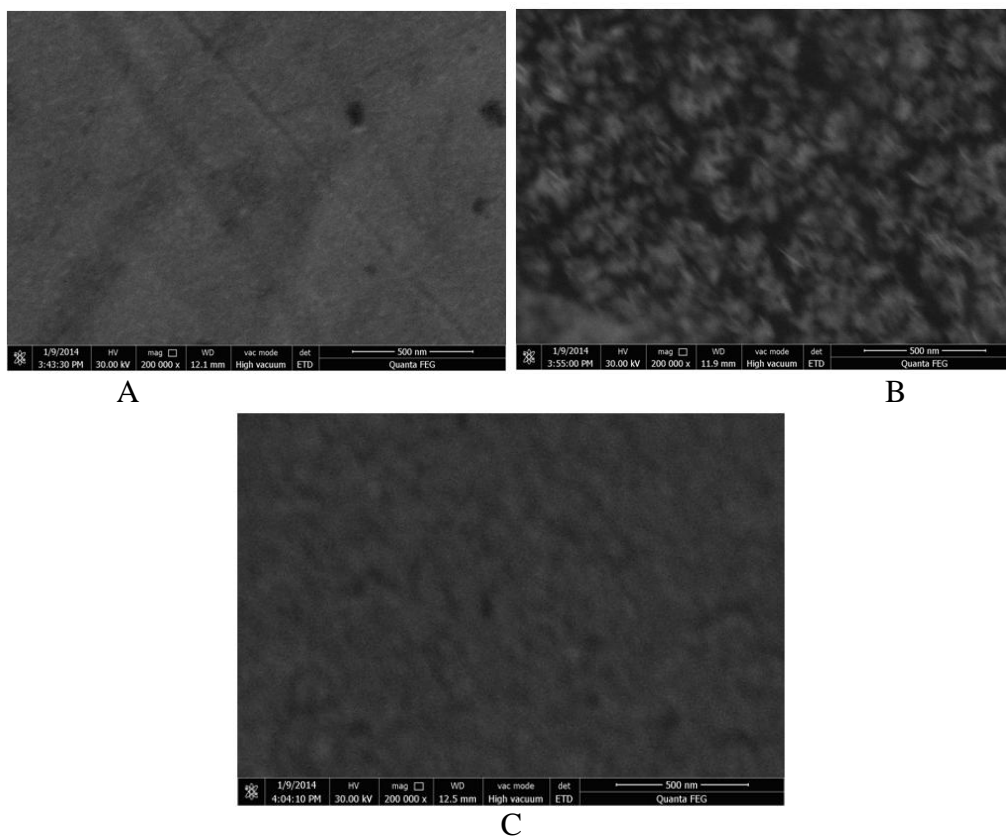


Figure 3. SEM imagine of PNs on the surface of (A) GE (B) GPE and (C) GCE

SEM is applied to confirm the formation of a layer of the film on the surface of bare electrode.

Many PNs on the surface of GE, GPE and GCE were observed in Fig. 3. The SEM image of like-snowflake PNs on the surface of GPE is shown in Fig. 3B, the similar shape of PNs on the surface of GCE was observed. The phenomena indicated that PNs had been assembled on the bare electrode surface. However, the PNs on the surface of GE are different to those on the surface of GCE and GPE, more and smaller PNs on the surface of GE were found (Fig. 3A).

3.4. CVs of DO at the modified electrode

In order to find the sensitive modified electrodes for the determination of DO, the CVs of DO at the modified electrode in 10.00g.L^{-1} NH_4Cl solution of pH 7.0 are shown in Fig.4. A typical curve for DO is shown in Fig. 4A and it is clear that a well formed reduction wave, $E_{1/2} = 0.062$ V vs. SCE and a good limiting current plateau, is found, which is in agreement with the previous work [18]. The reduction peak of DO at PN/GE was observed at -0.051 V, the reduction current of DO was more than that of bare GE, and after the oxygen in 10.00g.L^{-1} NH_4Cl was driven off by N_2 for 10min, the current of GN/GE decreased, indicating that the PN modified GE promoted the electrochemical reduction of DO by considerably accelerating the rate of electron transfer.

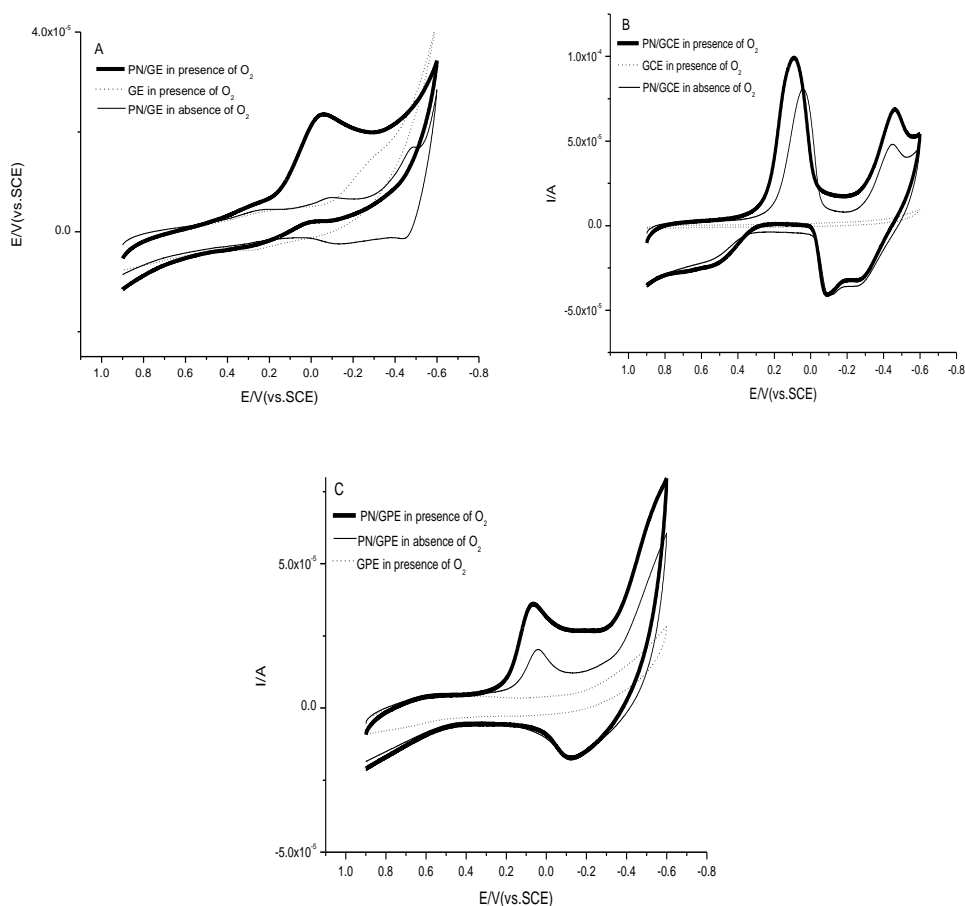
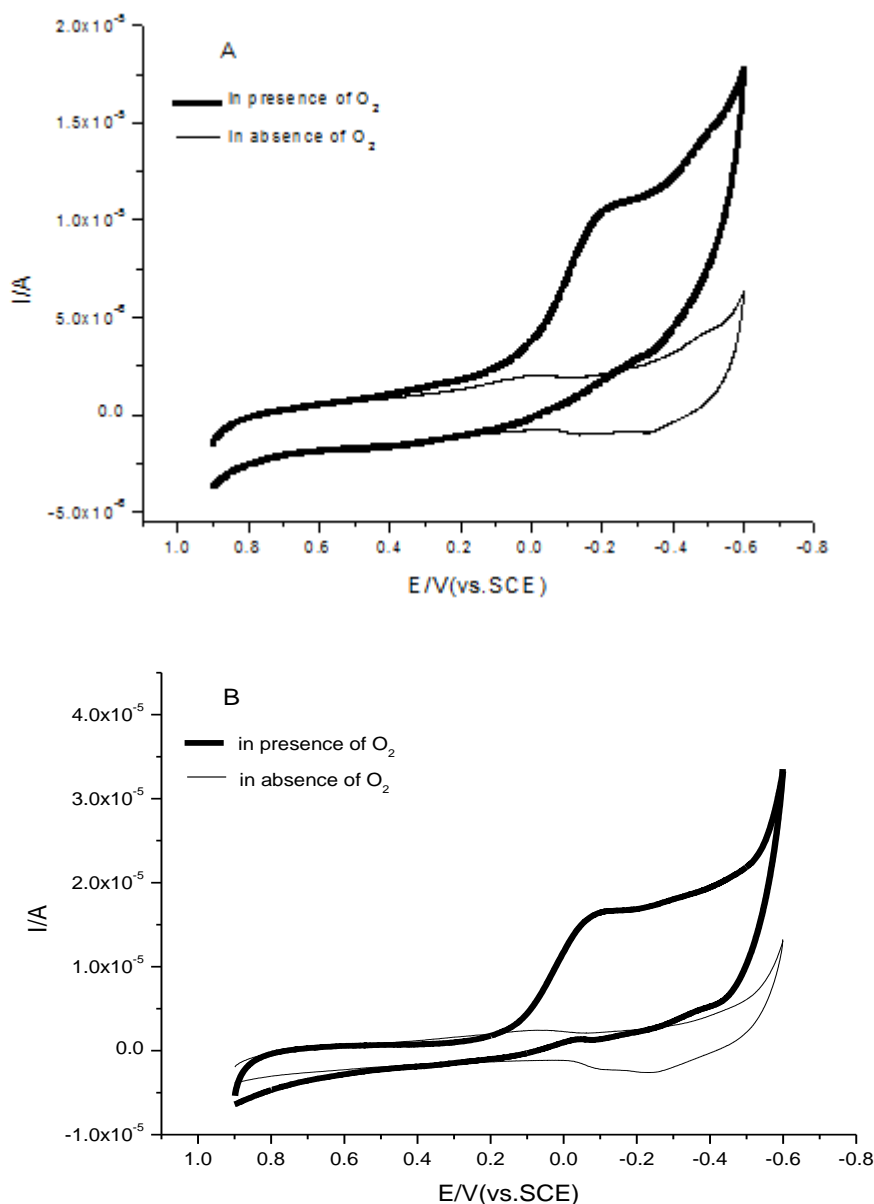


Figure 4. CVs of DO at PN modified electrode and bare electrode; Scan rate: 100.0 mV. s^{-1} ; Supporting electrolyte: 10.00g.L^{-1} NH_4Cl .

However, the reduction peaks of GN/GCE and GN/GPE in 10.00g.L^{-1} NH_4Cl solution were found at 0.093V and 0.064V , respectively, and after the oxygen in 10.00g.L^{-1} NH_4Cl solution was driven off by N_2 for 10min, the peaks shifted to negative direction (Fig.4B and 4C), which were not consistent with that of GN/GE, indicating that the structures of GN/GCE was different to that of GN/GCE and GN/GPE. Therefore, GN/GE was selected to determine the DO in samples.

3.5. Application

The contents of DO in sample were determined by the cathode electricity of CVs in Fig.5. The standard solution (STD) and samples were prepared by added 0.1000g NH_4Cl into 10.00ml of double-distilled water and samples, respectively.



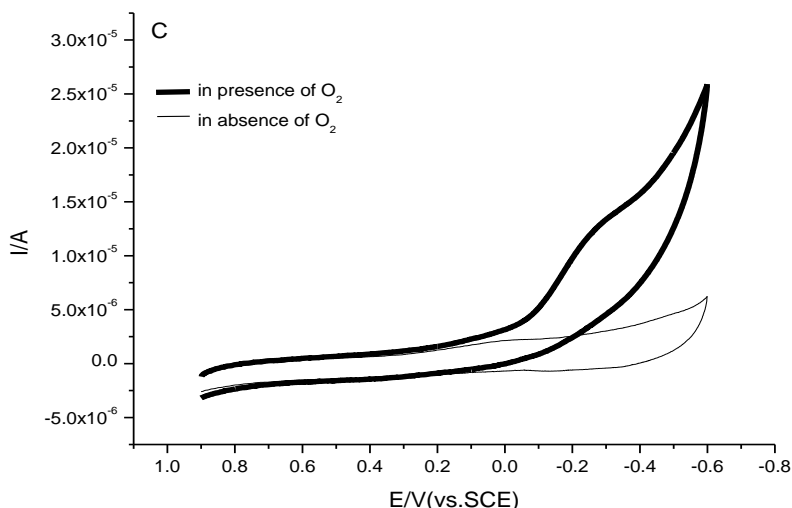


Figure 5. CVs of PN modified GCE in standard solution and samples. Scan rate: 100.0 mV. s⁻¹. Supporting electrolyte: 10.00g.L⁻¹ NH₄Cl.

The contents of DO in STD and samples at 25°C and 1atm were also detected by oxygen analyzer, and contents of DO of sample could be calculated as

$$\frac{Q_{STD} - Q_1}{Q_S - Q_2} = \frac{C_{STD}}{C_S}$$

Where Q_{STD} and Q_S are the cathode electricity corresponding to the STD and sample in present of O₂, Q_1 and Q_2 are the cathode electricity of corresponding to the STD and sample driven off O₂ by N₂ for 10min, and C_{STD} and C_S represent the contents of DO in STD and samples, respectively.

The contents of DO in STD and samples at 25°C and 1atm, detected by the cathode electricity of O₂ and oxygen analyzer, are listed in Table 1, the contents of DO in samples are good in agreement with those detected by oxygen analyzer.

Table 1. Contents of DO in STD and sample

Sample	Q(×10 ⁻⁴ C)						$\bar{x} \pm t_{p,f} \text{ gy}^{-1/2}$ (mg/L, p=95%, n=6)	
							This work	Oxygen analyzer
STD	1.405	1.455	1.374	1.388	1.402	1.411		8.100±0.21
STD driven off O ₂	0.536	0.543	0.546	0.550	0.563	0.524		
lake water	0.966	0.960	0.950	0.976	0.976	0.970	4.56±0.24	4.46±0.26
lake water driven off O ₂	0.498	0.478	0.489	0.470	0.487	0.469		
tap water	0.980	1.002	0.987	0.989	1.001	0.978	5.65±0.18	5.74±0.28
tap water driven off O ₂	0.394	0.384	0.392	0.389	0.400	0.371		

The influence of some salts was tested. The results show 100-fold of K^+ , Na^+ , Fe^{3+} , Fe^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , PO_4^{3-} , SO_4^{2-} , F^- , S^{2-} , Ca^{2+} and Mg^{2+} , 50-fold of NO_3^- , SO_3^{2-} , $S_2O_3^{2-}$ and NO_2^- did not interfere the determination.

To assess the applicability of the proposed method, on using the PNs modified GE daily and storing under ambient conditions over a period of 2 weeks, the electrode retained 97.8% of its initial peak current response for a DO concentration of 8.00mg/L, which shows long-term stability of the film modifier on the surface of GE. The results indicate that the modified electrode has an excellent repeatability and reproducibility.

4. CONCLUSIONS

In conclusion, it was demonstrated that modification of GE with PNs is a simple and effective method for obtaining highly sensitive, excellent repeatability and reproducibility electrode for determination of DO. High sensitivity of the PN modified GE are promising for the determination of DO in water.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the National Science Foundation of China (grant No. 51175245), the Open Science Foundation for Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials (grant no. JSKC13126), the Open Science Foundation for Jiangsu Key Laboratory for Biomass- based Energy and Enzyme Technology (grant No. JSBEET1207), and the Science Foundation for Huaiyin Normal University (grant no. 11HSGJBZ13).

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