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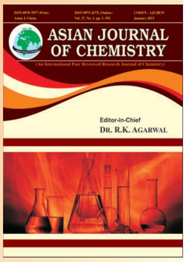

Assembling of Platinum Nanoparticles on the Surface of Glassy Carbon Electrode using Different Electrochemical Method and its Catalysis for Oxygen

Y.Z. SONG[1,*], WEIHAO SONG[2,*], X. ZHANG[1], W. CAO[1], L. ZHOU[1], L. QIAN[1] and A. GE[1]

[1]Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huai An 223300, P.R. China
[2]Nanjing Foreign Language School Xianlin Campus, Nanjing 210023, P.R. China

*Corresponding authors: E-mail: songyuanzhi@sina.com; mike_sung@sina.com

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In this paper, the platinum nanoparticles on the surface of glassy carbon electrode were synthesized by linear sweep voltammetry, differential pulse voltammetry, cyclic voltammetry and amperometric response, respectively. Electrochemical behaviour of oxygen at platinum nanoparticle modified glassy carbon electrode was investigated. It was demonstrated that the modification of glassy carbon electrode with platinum nanoparticles prepared by linear sweep voltammetry is a simple and effective method for obtaining highly sensitive sensor for determination of oxygen.

Keywords: Platinum nanoparticle, Electrochemical synthesis, Oxygen.

INTRODUCTION

Platinum nanoparticles are particular attractive for numerous investigations due to the applications in the field of sensors[1-5]. There are many methods such as chemical, electrochemical, sonochemical and photo-induced methods to synthesize platinum nanoparticles with desired composition, dimension and shape[6-11]. The applications of platinum nanoparticles depend strongly on the particle size, the amounts, the interparticle distance and the shape of the platinum nanoparticles. Therefore, the controlling preparation of platinum nanoparticles is very important and significant for the sensitive sensors.

The electrochemical synthesis of platinum nanoparticles is a conventional method to control the size, the amounts, the interparticle distance and the shape of platinum nanoparticles. The platinum nanoparticles can be prepared by many electrochemical technologies such as linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), normal pulse voltammetry (NPV), differential normal pulse voltammetry (DNPV), square wave voltammetry (SWV), amperometric response (i-t), *etc*[12]. These methods control not only the depositing time but also the depositing potential mode.

In present work, four electrochemical technologies were used for the synthesis of platinum nanoparticles on the surface of glassy carbon electrode (GCE). Electrochemical behaviour of oxygen at platinum nanoparticle modified glassy carbon electrode was investigated.

EXPERIMENTAL

H_2PtCl_6 (4 g L^{-1}) and cetyltrimethylammonium bromide (CTBA, 2 g L^{-1}) were prepared, respectively. Double-distilled water was used throughout. 0.10 M phosphate buffer solution was prepared by dissolving 0.1 mol NaCl and 0.10 mol Na_2HPO_4 in the double-distilled water of 1000 mL and adjusted desired pH values with 6 mol L^{-1} HCl or 1 mol L^{-1} NaOH aqueous solution. All reagents were analytical grade.

For all electrochemical experiments a CHI660D electrochemical analyzer (CHI, U.S.A.) was employed. The electrochemical cells consisted of a three electrode, a platinum nanoparticle modified glassy carbon electrode, a platinum wire and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. The platinum nanoparticle composite was characterized by scan electron microscopy (SEM) (Guanwta FEC 450, FEI, U.S.A.).

Before modification the glassy carbon electrode was polished with 0.05 μm alumina slurry on a polishing cloth, rinsed thoroughly with doubly distilled water and then sonicated in ethanol and doubly distilled water for 10 min, sequentially. The platinum nanoparticles were deposited on the glassy carbon electrode that was immersed in the aqueous solution of mixtures of 4 g L^{-1} $H_2PtCl_6{\cdot}6H_2O$ (1 mL), 3 g L^{-1} Na_2CO_3 (1 mL) and 2 g L^{-1} CTAB (1 mL). The obtained platinum nanoparticle modified glassy carbon electrode was washed in double 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 0.1 M phosphate buffer solution of pH 7.3 for several times until acquiring the reproducible responses.

RESULTS AND DISCUSSION

Cyclic voltammograms (CVs) of $PtCl_6^{2-}$ at glassy carbon electrode in the aqueous solution of H_2PtCl_6 and CTAB are shown in Fig. 1, a reduction peaks are observed at 0.005 V, which can be ascribed to the reduction of $PtCl_4^-$.

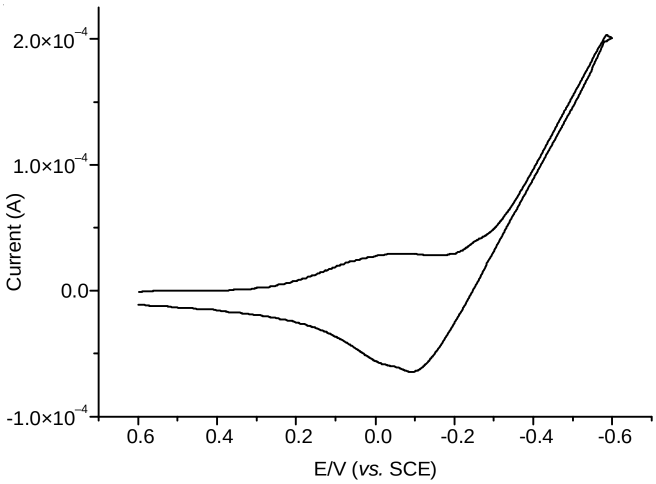

Fig. 1. Cyclic voltammograms of $PtCl_6^{2-}$ at glassy carbon electrode; initial E: 0.60 V; final E:- 0.60 V; quiet time: 2s; Scan rate: 100 mV/s

The assembling processes by cyclic voltammogram are shown in Fig. 1. The other electrochemical assembling processes of platinum nanoparticles on the surface of glassy carbon electrode are shown in Fig. 2. The similar reduction peaks of $PtCl_6^{2-}$ were found by differential pulse voltammetry and linear sweep voltammetry.

SEM is applied to confirm the formation of a layer of the film on the glassy carbon electrode surface. The SEM image of platinum nanoparticles on the surface of glassy carbon electrode is shown in Fig. 3, many platinum nanoparticles on the surface of glassy carbon electrode were observed. It was found that the size of platinum nanoparticles on the surface of glassy carbon electrode prepared by cyclic voltammogram and linear sweep voltammetry are smaller than those prepared by differential pulse voltammetry and i-t method.

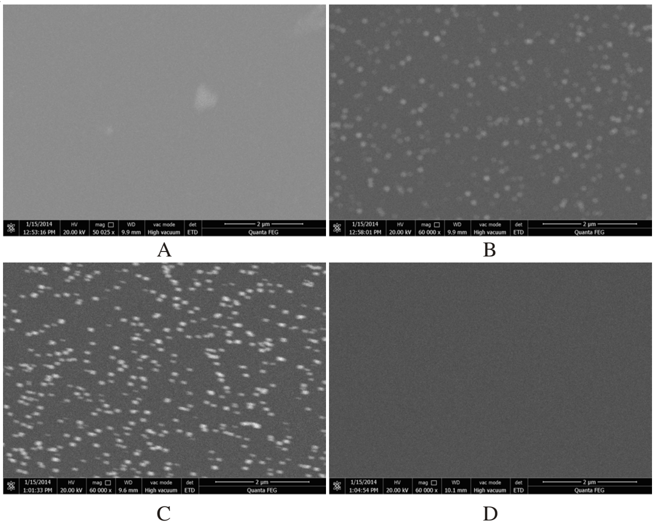

Fig. 3. SEM imagine of platinum nanoparticles on the surface of glassy carbon electrode prepared by (A) cyclic voltammogram, (B) differential pulse voltammetry, (C) i-t and linear sweep voltammetry method

The cyclic voltammograms of modified glassy carbon electrode in the $K_3Fe(CN)_6$-$K_4Fe(CN)_6$ system are shown in Fig. 4. Compared with the bare glassy carbon electrode, the PN/GCE prepared with linear sweep voltammetry shows the highest peak currents due to the varying potential of linear sweep voltammetry, which is different from those of differential pulse voltammetry, cyclic voltammogram and i-t[12], the smaller platinum seeds on surface of glassy carbon electrode prepared by linear sweep voltammetry could be obtained due to the linear increase voltage. The anodic-cathodic peak separations are approximately 148 and 241 mV for the PN/GCE prepared with linear sweep voltammetry and bare glassy carbon electrode, respectively.

In order to search for the sensitive modified electrode, the cyclic voltammograms of oxygen at the modified glassy carbon electrode were described. The oxidation peaks for oxygen at PN/GCE in PBS of pH 7.3 are observed at 0.081 V (Fig. 5), after removing O_2 in water with bubbling N_2 for 10 min, the currents at the peak of 0.081 V decreased, indicating that the reduction peak at 0.081 V was ascribed to the reduction of O_2 in water. However, no reduction peak at 0.081 V for oxygen at bare glassy carbon electrode was found. Compared with the PN/GCE prepared by linear sweep voltammetry, the

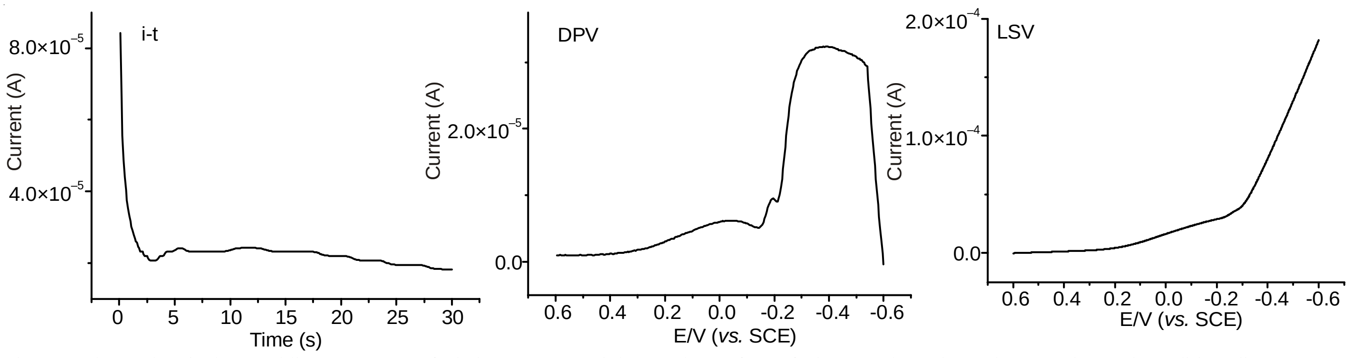

Fig. 2. Electrochemical assembling processes of platinum nanoparticles on the surface of glassy carbon electrode; Experimental condition: linear sweep voltammetry: initial E: 0.60 V; final E :-0.60 V; quiet time: 2s; scan rate: 100 mV/s. differential pulse voltammetry: initial E: 0.60 V; final E: -0.60 V; increase E: 0.004 V; amplitude E: 0.05 V; pulse width: 0.06 V; pulse period: 0.2s; sample width: 0.02s; quiet time: 2s; scan rate: 100 mV/s. i-t: initial E: -0.20 V; final E: -0.20 V; sample interval: 0.1s; quiet time: 0s; run time: 30s

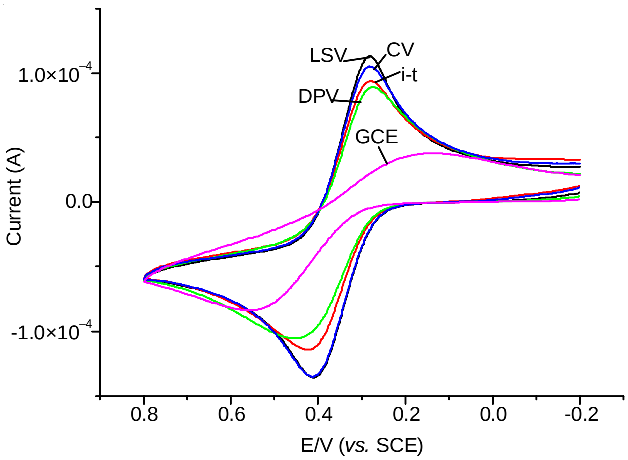

Fig. 4. Cyclic voltammograms of $K_4[Fe(CN)_6]$ (5 mM) at platinum nanoparticle modified glassy carbon electrode and bare glassy carbon electrode; Scan rate: 100 mV s^{-1}

reduction potential for oxygen is less than that of oxygen at bare glassy carbon electrode and other modified electrode, and the peak current of oxygen at PN/GCE prepared by linear sweep voltammetry is more than those of oxygen at other modified electrode due to the larger surface area of smaller platinum nanoparticles.

The results indicated that the platinum nanoparticle modified electrode prepared by linear sweep voltammetry promoted the electrochemical reduction of oxygen by considerably accelerating the rate of electron transfer and was more sensitive for determination of O_2 in water.

Conclusion

In conclusion, it was demonstrated that modification of glassy carbon electrode with platinum nanoparticles prepared by linear sweep voltammetry is a simple and effective method for obtaining highly sensitive electrodes for determination of oxygen.

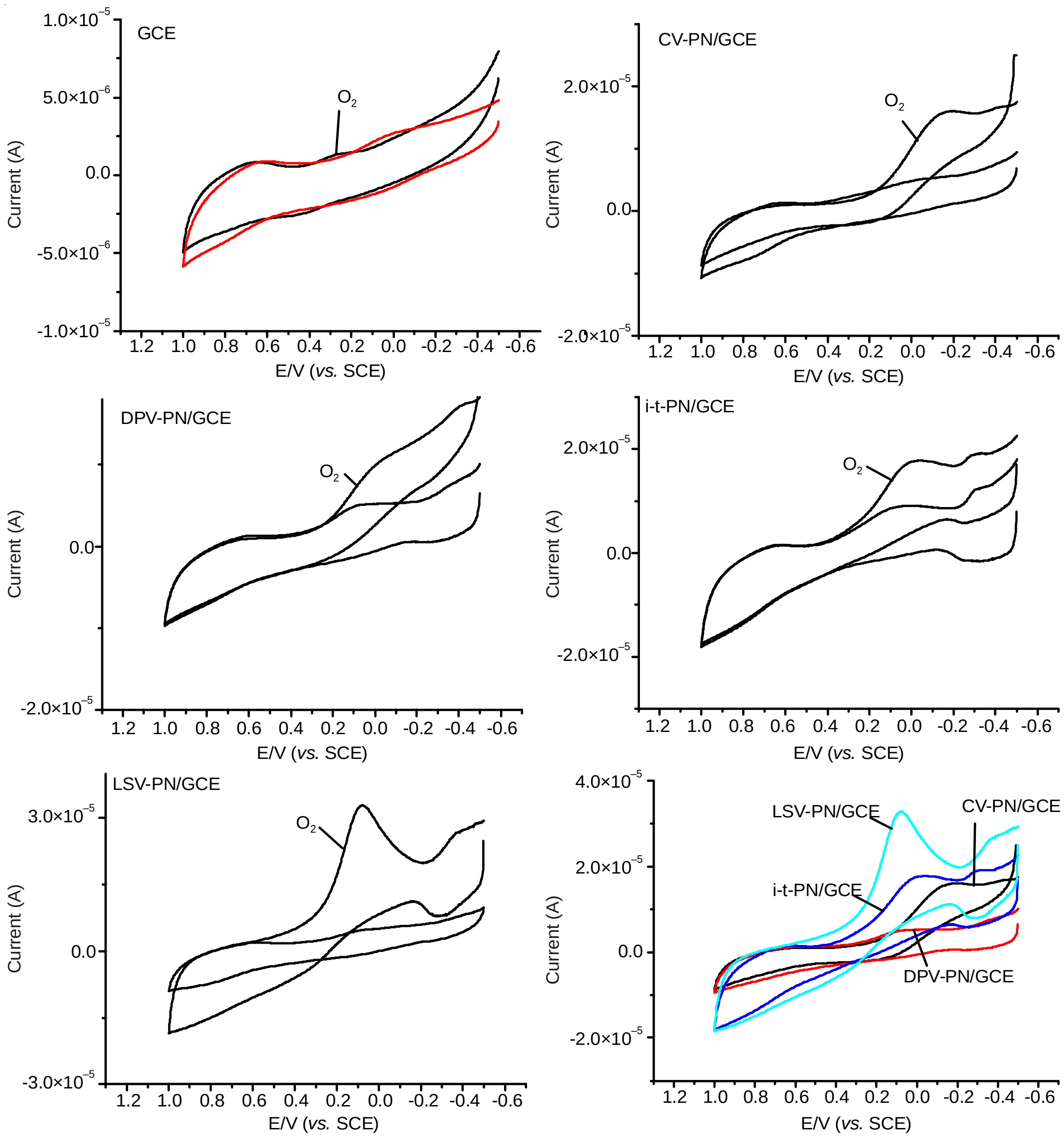

Fig. 5. Cyclic voltammograms of 20 mg L^{-1} oxygen on platinum nanoparticle modified glassy carbon electrode and bare glassy carbon electrode (3). Scan rate: 100 mV s^{-1}. Supporting electrolyte: 0.10 M phosphate buffer of pH 7.3

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