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Catalytic Oxygen Reduction on Silver Nanoparticle Modified Glassy Carbon Electrode with 1, 4-Naphthoquinone

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ABSTRACT

The electrochemical reduction of oxygen was studied on silver nanoparticle (AgNP) modified glassy carbon electrode with 1,4-naphthoquinone in the pH range 1.0 – 13.0 by employing cyclic voltammetric, chronoamperometric and chronocoulometric techniques. The stability of the modified electrodes was examined. The influence of pH on the electrochemical and catalytic behaviour of the modified electrode with naphthoquinone was studied, and pH 7.0 was chosen as the optimum working pH by comparing the shift in oxygen reduction potential. The 1,4-naphthoquinone-adsorbed silver nanoparticle modified glassy carbon electrodes possess excellent electrocatalytic abilities for oxygen reduction with over potential 608 mV greater than that at a bare glassy carbon electrode.

1. Introduction

Electrocatalytic reduction of oxygen finds variety of applications in electrochemical technologies [1] due to its involvement in energy conversion and storage [1–3]. The current research involves the utilization of modified electrodes [4–6]. In this way, a number of compounds such as manganese oxide [7], copper [8], ruthenium-iron cluster [9], metal phthalocyanine [10], metal macrocyclic complexes [11], titanium silicates [12], Au nanoparticle [13], anthraquinone [14–17] and naphthoquinone [18, 19] derivatives have been proposed as electrocatalysts for the reduction of dioxygen to water or H₂O₂. Catalysis of dioxygen reduction was investigated by Golabi and Raoof at the surface of carbon paste electrodes modified by 1,4-naphthoquinone and some of its derivatives [19]. The electrochemical reduction of dioxygen with 1,4-naphthoquinone catalysed by riboflavin has also been studied by Manisankar et al. [18]. However, naphthoquinone/silver nanoparticle modified glassy carbon electrode has not been used for the study of dioxygen reduction.

In the present investigation, the electrochemical behaviour of 1,4-naphthoquinone at silver nanoparticle modified glassy carbon electrode (AgNP/GCE), the stability and efficiency of such combination in the electrocatalysis of dioxygen reduction were examined by cyclic voltammetry, chronoamperometry and chronocoulometry along with the determination of diffusion coefficient.

2. Experimental Methods

2.1 Chemicals

1,4-Naphthoquinone (NQNE) was purchased from Sigma Aldrich. All other chemicals were analytical grade (99%), used without further purification. The experimental solution of 1,4-naphthoquinone in 50% alcohol was prepared. The buffer solutions of pH 1.0 to 13.0 were prepared by using highly pure chemicals and doubly distilled water and the pH of

the media were measured by using Hanna pH-meter. During the experiments, 99.99% pure nitrogen and oxygen gases were used.

2.2 Apparatus

The cyclic voltammetric, chronoamperometric and chronocoulometric studies were carried out using CHI650C Electrochemical workstation (CH Instrument, USA) at room temperature. A conventional three-electrode system was used which consists of a bare GCE or AgNP modified GCE (AgNP/GCE) as working electrode, a platinum wire as counter electrode and a silver electrode as reference electrode was kept in the cell solution containing NQNE.

2.3 Modification of Electrode

GCE was modified with AgNPs. Prior to the electrochemical deposition, the GCE was well polished with alumina powder (0.05 μm), rinsed and ultra-sonicated in double distilled deionized water. 10 μL of the AgNP solution was placed on the polished GCE surface and kept in sunlight to evaporate the solvent.

3. Results and discussion

The electrochemical reduction of oxygen of AgNP/GCE with 1,4-naphthoquinone (NQNE) was studied in the absence and presence of oxygen in different pH media between 1.0 and 13.0.

3.1 Voltammetric Behaviour of Modified GCEs with NQNE

Cyclic voltammograms of AgNP/GCE in the solution of 1,4-naphthoquinone display a single redox couple under deaerated condition. The voltammograms were performed at various scan rates of 20, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650 and 700 mVs⁻¹ which indicate that the cathodic peak currents vary with scan rates. While increasing the scan rate, there is an increase in peak separation which confirms the quasi-reversibility of the electron transfer process. The cyclic voltammetric response for NQNE at AgNP/GCE of scan rates 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs⁻¹ was represented in the Fig. 1. The inset shows the linear variation of cathodic peak current (*I*_{pc}) with the square root of scan rate (*v*^{1/2}).

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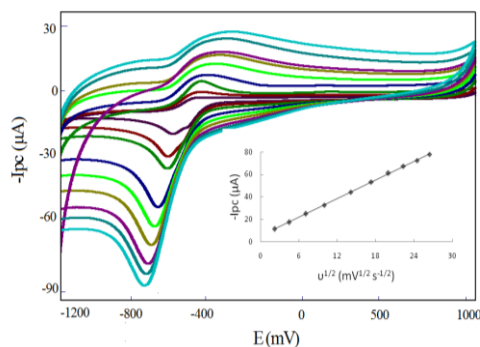


Fig. 1 Cyclic voltammograms of NQNE at AgNP/GCE (pH 7.0) under de-aeration at scan rates 20, 50, 100, 200, 300, 400, 500, 600 and 700 mVs⁻¹

3.1.1 Effect of pH

The voltammetric peak potentials depend on pH for all the 1,4-naphthoquinone. Three distinct linear portions with different slope values were observed indicating the different forms of anthraquinone. The pH-potential diagram for NQNE at AgNP/GCE was given in the Fig. 2. At low pH (1 to 4) values, NQNE involves two-electron three-proton reduction process. In the intermediate pH range, the compound undergoes two-electron, two proton process. At pH above 10, the electrode surface reaction is a two electron, one proton process.

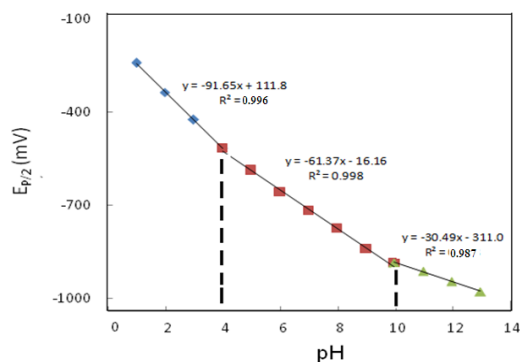


Fig. 2 pH-potential diagram for NQNE at AgNP/GCE

3.1.2 Stability of the Modified Electrode

The stability of the AgNP modified electrode in the presence of 1,4-naphthoquinone and its electrochemical behaviour was examined. The modified electrode was immersed in acidic medium (pH 1.0) with NQNE for 40 h and in neutral medium (pH 7.0) containing NQNE for 30 h and then cyclic voltammograms were recorded. A slight decrease with no changes in the peak current or separation of the peak was obtained in both the media. In addition, after 100 cycles of repetitive scanning (Fig. 3), there were no changes in the peak current or separation of the peak in cyclic voltammograms at scan rate 20 mVs⁻¹ in pH 7.0.

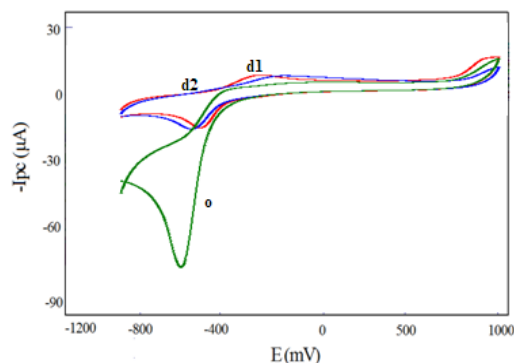


Fig. 3 Cyclic voltammograms of NQNE at AgNP/GCE under deaerated at the beginning (d₁), oxygen saturated (o) and again deaerated (d₂, dashed line) conditions at pH 7.0. Scan rate 50 mVs⁻¹

3.1.3 Surface Coverage

The surface coverage of the AgNP modified electrode with 1,4-naphthoquinone was determined from the cyclic voltammograms at scan rate 50 mVs⁻¹ by using the relation $\Gamma_{nq} = Q/nFA$, where Q is the charge

consumed, n is the number of electrons involved, F is the Faraday constant (96500 Cmol⁻¹) and A is the geometric area of (0.0314 cm²) of glassy carbon electrode. The calculated surface coverage value of NQNE at AgNP/GCE was 1.34 x 10⁻⁸ molcm⁻².

3.2 Catalytic Reduction of Oxygen at the Surface of Modified Electrodes

3.2.1 Effect of pH

The electrocatalytic reduction of oxygen at bare GCE and AgNP/GCE with NQNE was studied in different pH media from 1.0 to 13.0. Due to their different kinetic behaviour, the displacement may be unequal [20]. The optimum pH was found to be 7.0 for the modified electrode where the cathodic peak reached its maximum current with the maximum shift in oxygen reduction potential (ΔE) and the anodic wave was completely vanished. NQNE combined with AgNP/GCE causes a shift in the oxygen reduction potential of about 608 mV at pH 7.0.

Fig. 4 shows the cyclic voltammograms of NQNE in pH 7.0 on AgNP/GCE in the presence and absence of oxygen. It implies that there is a large enhancement in the cathodic peak current for NQNE at the AgNP/GCE in the presence of O₂, while the corresponding anodic peak has disappeared indicating the electrocatalytic reduction of oxygen that occurs.

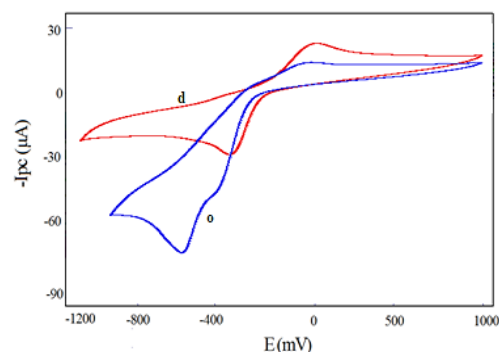


Fig. 4 Cyclic voltammogram of [CuBAAP(DMG)Cl₂] complex in acetonitrile at 300 K (0.1M TBAP). Scan rate 100 mVs⁻¹

3.2.2 Effect of Scan Rate

The variation of cathodic peak current with scan rate was studied at various scan rates of 20, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650 and 700 mVs⁻¹ under aeration. The cathodic peak current (I_{pc}) varies linearly with square root of scan rate ($v^{1/2}$) which clearly confirms the diffusion controlled process for oxygen reduction in presence of NQNE at AgNP/GCE.

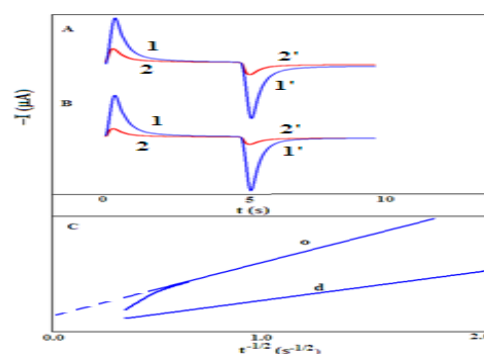


Fig. 5 Chronoamperograms for NQNE at AgNP/GCE in pH 7.0 by double potential step- technique at an initial potential of -100 mV and final potential of -800 mV vs silver electrode. (A) 1,1' for AgNP/GCE in presence of NQNE in O₂ saturated buffer, 2,2' as 1, 1' for the bare GCE. (B) 1,1' for AgNP/GCE in presence of NQNE under deaerated condition, 2,2' as 1, 1' for the bare GCE. (C) Plots of current vs. t^{-1/2} for the above modified GCE under aerated (o) and deaerated (d) conditions

3.3 Chronoamperometric Studies

The Double potential-step chronoamperometric studies were carried out for bare GCE and modified GCE with NQNE in deaerated and aerated condition at optimum pH 7.0 at an initial and final potential of -100 and -800 mV respectively. Chronoamperogram of NQNE at bare GCE and AgNP/GCE in the absence and presence of oxygen is given in Fig. 5. The net electrolysis current I_{net} was determined by point to point subtraction of the background current in the presence and absence of oxygen. Under deaerated condition, a plot of net current against t^{-1/2} shows a straight line

which extrapolates close to origin. From the slope of I vs $t^{-1/2}$ under deaerated condition, the diffusion coefficient values of NQNE was determined using the Cottrell equation,

$$I = n F D^{1/2} A C_{nq} \pi^{-1/2} t^{-1/2}$$

$$\text{Slope} = n F D^{1/2} A C_{nq} \pi^{-1/2}$$

where C_{nq} is the concentration of 1,4-naphthoquinone used, D is the diffusion co-efficient of 1,4-naphthoquinone and A is the geometric area of glassy carbon electrode (0.0314 cm²). The calculated D values is 13.6×10^{-9} cm²sec⁻¹.

3.4 Chronocoulometric Studies

The chronocoulometric studies were carried out on bare GCE and modified GCE with NQNE in deaerated and aerated condition at optimum pH 7.0 by using double potential technique at an initial and final potential of -100 and -800 mV respectively. The chronocoulometric response of NQNE at AgNP/GCE in pH 7.0 is shown in the Fig. 6. Under deaerated condition, the reversible peaks were observed. But under aeration, a large enhancement in the charge of forward peak and nearly a flat line was observed which indicates the irreversible electrocatalytic reduction of oxygen. The number of electrons (n) involved in the reduction of NQNE at the optimum pH was calculated from the slope of Q versus $t^{1/2}$ under deaeration condition using the Cottrell equation,

$$Q = 2n F A C D^{1/2} \pi^{-1/2} t^{1/2}$$

where $C = 1.25$ mM, $A = 0.0314$ cm² and $D = 1.57 \times 10^{-5}$ cm²s⁻¹. The number of electrons involved in the reduction of NQNE (n_{nq}) and the number of electrons involved in oxygen reduction (n_{o_2}) were 2.02 and 2.05 respectively.

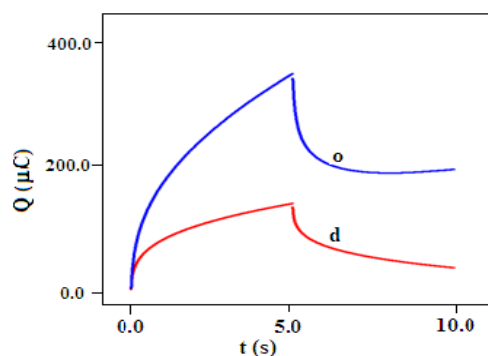


Fig. 6 Chronocoulometric curves of NQNE at AgNP/GCE in pH 7.0 under deaeration (d) and aeration (o)

4. Conclusion

1,4-Naphthoquinone has been used as catalyst for the reduction of dioxygen at bare GCE and silver nanoparticle modified glassy carbon electrode. Cyclic voltammetric, chronoamperometric and chronocoulometric techniques were employed to study the electrochemical and catalytic behaviour of AgNP/GCE in combination with

NQNE. The modified electrode gives higher oxygen reduction potential shifts as compared with bare GCE. A larger potential shift (608 mV) was observed at pH 7.0 and which is chosen as optimum pH. Thus, the AgNP/GCE with NQNE can be used as oxygen sensors. The diffusion coefficient, surface coverage and the number of electrons involved were determined.

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