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Electrodeposition of tantalum on carbon black in non-aqueous solution and its electrocatalytic properties

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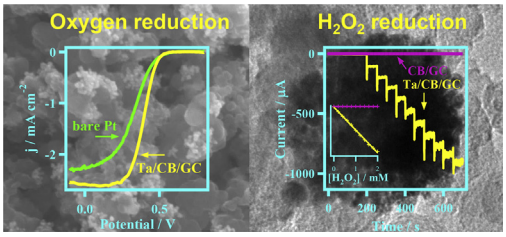
HIGHLIGHTS

- We electrodeposited Ta nanoclusters (Ta/CB/GC) in acetonitrile at room temperature.
- The Ta/CB/GC showed better or comparable performance to bare Pt for ORR.
- The Ta/CB/GC showed high sensitivity for reduction of hydrogen peroxide at pH 7.4.
- The Ta/CB/GC showed possible simultaneous detection of ascorbic acid and dopamine.
- We extended the applicability of Ta electrode material for various electrocatalytic reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we synthesized tantalum (Ta) nanoclusters on carbon black (Ta/CB) via simple electrodeposition in non-aqueous solvent, acetonitrile (ACN) at ambient temperature. Transmission electron microscopy (TEM) images showed that the electrodeposited Ta nanoclusters consisted of tiny Ta nanoparticles. X-ray photoelectron spectroscopy (XPS) result represented that the outermost Ta formed the native oxide on Ta/CB due to its ambient exposure to air. Electrochemical catalytic properties of prepared Ta/CB on glassy carbon electrode (Ta/CB/GC) were investigated toward reductions of oxygen and hydrogen peroxide, and oxidations of ascorbic acid and dopamine. For oxygen reduction reaction (ORR) in acid, Ta/CB/GC represented a decent electrocatalytic performance which was better or comparable to bare Pt. The operational stability in acidic condition was maintained up to 500 repetitive potential cycles presumably due to the protective native Ta oxide layer. Ta/CB/GC also showed high amperometric sensitivity (4.5 ($\pm 0.1_6$) mA mM^{-1} cm^{-2}, $n = 5$) for reduction of hydrogen peroxide in 0.1 M phosphate buffer solution (PBS, pH 7.4). In addition, Ta/CB/GC was demonstrated for the possibility of simultaneous detection of ascorbic acid and dopamine using differential pulse voltammetry (DPV).

1. Introduction

Tantalum (Ta) has attracted attention for many applications such as coating material [1], capacitor [2], and biomedical material [3,4] because of its characteristic properties. The excellent corrosion resistance in most acids and high melting point enable Ta to be

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applied in components exposed to harsh chemical conditions [5]. In addition, Ta has great biocompatibility without any inflammatory response and stable natively-formed passive oxide layer which contributes to in vivo corrosion resistance [6]. Moreover, Ta is more economical compared to other metals used as electrocatalysts such as platinum, gold, palladium, and iridium, etc.

According to Pourbaix diagram of Ta, the reduction potential of Ta species is more negative than that of H_2O [7]. In aqueous system, reduction of H_2O precedes that of Ta precursor as the applied potential is scanned toward a negative direction, and therefore the generated H_2 gas from H_2O reduction decreases the deposition efficiency of Ta. In addition, commonly used Ta precursors, tantalum halides, are known to be unstable in the presence of water [8–10]. Thus, Ta has been electrodeposited in non-aqueous media [11–13].

Electrodeposition in non-aqueous solutions has been investigated in the last few years because these media have wide electrochemical potential windows free from water and/or air involved electrochemistry [12]. Ionic liquids and molten salts were widely used as non-aqueous media for electrodeposition of metals [12–16]. Although many processes have been developed to decrease the production cost of ionic liquids, typical ionic liquids still remain expensive [17]. Additionally, molten salts have high melting points, so they require high operating temperatures, resulting considerable energy costs and serious material's incompatibilities [18].

Group IV and V transition metals, including Ta, are chemically stable under acidic atmosphere so that materials based on these metals have been reported as oxygen reduction reaction (ORR) catalysts in acidic condition [19–21]. Ta as an electrocatalyst has been rarely studied for the preparation method and catalytic activity, regardless of its plausible applicability for various areas. In this study, we synthesized Ta nanoclusters via a rather facile method: Ta was electrodeposited on carbon black loaded glassy carbon electrode (CB/GC) with potentiostatic technique at room temperature using a cheap and common non-aqueous solvent, acetonitrile. The quality of the prepared Ta electrodes (Ta/CB/GC) with various deposition potentials and potential-holding times was tested toward ORR in acidic condition with linear sweep voltammetry. Thus, an optimized condition was chosen for Ta electrodeposition. The stability of as prepared Ta/CB/GC electrode for ORR in acid was also tested with repetitive potential cycling. In addition to the ORR activity, we examined the electrochemical performances of Ta/GB/GC for H_2O_2 reduction; and oxidations of ascorbic acid and dopamine. In previous reports, lithium or europium doped Ta-based electrodes were studied for electrochemical oxidation of ascorbic acid in KCl solution (not physiological condition) [22,23], and MgO-modified graphene-Ta wire was used for simultaneous determination of ascorbic acid, dopamine, and uric acid in which bare Ta electrode, however, did not respond to the analytes [24]. Within confinement of our knowledge, it is the first attempt that investigates catalytic activities of pure Ta without any secondary metals for redox reactions of H_2O_2, ascorbic acid and dopamine.

2. Experimental

2.1. Reagents

Tantalum pentachloride ($TaCl_5$) was purchased from Alfa Aesar. Acetonitrile (ACN), tetrabutylammonium perchlorate (TBAP), sodium phosphate monobasic, sodium phosphate dibasic, D-(+)-glucose, L-ascorbic acid (AA), 4-acetamidophenol (AP), dopamine hydrochloride (DA), and uric acid (UA) were purchased from Sigma-Aldrich. Vulcan XC-72 R carbon black (CB) was obtained from Fuel cell store. All chemicals and solvents were of analytical grade.

2.2. Electrodeposition of Ta on CB

Before electrodeposition, 10 μL of CB mixture (2 mg/mL in water) was loaded on glassy carbon (GC) disk electrode (diameter of 3 mm) and dried in an oven at 40 °C for 20 min, which was repeated one more time. The CB modified electrode was coated with 10 μL of Nafion solution in ethanol (0.05 wt %). The prepared electrode was used as the working electrode; and gold wire and $Ag/AgNO_3$ electrode were used as the counter and reference electrodes, respectively. The potential applied to $Ag/AgNO_3$ reference electrode was calibrated with respect to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium redox couple system. All potentials (vs. $Ag/AgNO_3$) were converted to the values vs. SCE. The potential values denoted in this work are vs. SCE, unless otherwise specified.

Electrodeposition of Ta was conducted in an argon-filled glove box because the potential limit of ACN and $TaCl_5$ precursor for Ta deposition was extremely sensitive to air and moisture. Ta was electrodeposited on a CB modified glassy carbon (CB/GC) electrode from a solution of 1 mM $TaCl_5$ and 0.1 M TBAP (supporting electrolyte) in anhydrous ACN under continuous stirring with potentiostatic method using BAS100B (BAS Inc., IN, USA). After the electrodeposition, electrodes were washed with ACN. The optimum potential and time for the deposition were chosen by measuring the catalytic activity for ORR. Other electrochemical performances were investigated for the Ta/CB/GC electrode prepared with the optimized condition.

2.3. Characterizations

For field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F) were used to examine the morphology of Ta electrodeposited on CB. The composition of Ta/CB was investigated with energy dispersive X-ray spectroscopy (EDS). The

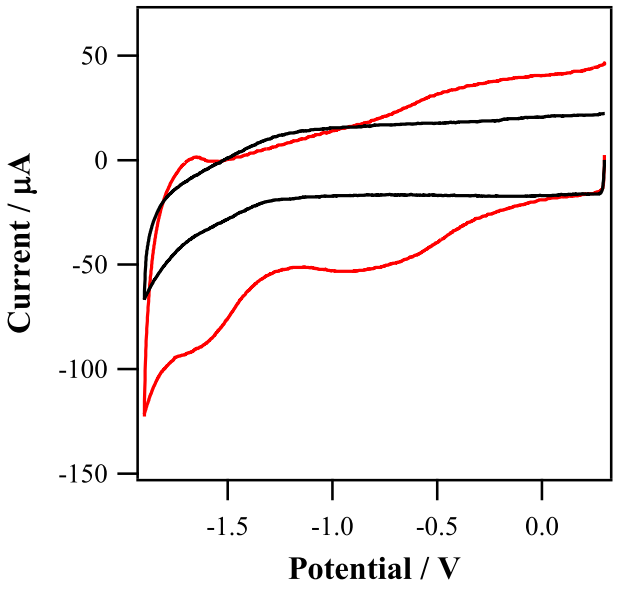

Fig. 1. Cyclic voltammograms at carbon black loaded glassy carbon (CB/GC) electrode in ACN containing only 0.1 M TBAP (black line) and in the additional presence of 1 mM $TaCl_5$ (red) with a scan rate of 50 mV/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)