Electrochemical synthesis of palladium (Pd) nanorods: An efficient electrocatalyst for methanol and hydrazine electro-oxidation

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ABSTRACT

Synthesis of palladium (Pd) nanostructures with unique shapes is crucial due to their shape dependent electrochemical activity. In the current investigation, we demonstrate the electrochemical synthesis of rod-like Pd nanostructures with the assistance of nicotinamide adenine dinucleotide (NAD^+). As-synthesized Pd nanorods were used as electrocatalysts for electrochemical oxidation of methanol and the development of highly sensitive platform for hydrazine detection. Additive NAD^+ played an important role in the morphology tuning of Pd nanostructures. Results of morphological study demonstrated the growth of Pd nanorods with an average size of 150 nm. The as-synthesized Pd nanorods had excellent electrocatalytic activity toward oxidation of methanol in alkaline pH and hydrazine oxidation in neutral pH. These Pd nanorods catalyzed the electrooxidation of methanol at −0.17 V with much better tolerance, excellent stability, and oxidation of hydrazine at −0.075 V. The Pd nanorod-based sensing platform delivered a low detection limit of 5 nM, sensitivity of $0.78 \pm 0.02\,\mu A\,mM^{-1}cm^{-2}$, and stable response toward hydrazine sensing without any interference from potential interferents such as Na^+, K^+, NO_2^-, BrO_3^-, or Pb^{2+} ion. Their electrochemical performances were found to be highly dependent on the morphology of Pd nanostructures.

1. Introduction

Shape-controlled synthesis is an important research area because of morphology-dependent physiochemical properties of inorganic nano-materials [1,2]. Among various nanomaterials, Pd nanostructures with diverse shapes have received much attention because of their potential applications in various fields of science and technology [3–9]. Traditionally, colloidal approach has been extensively used for the synthesis of Pd nanostructures of diverse shapes [10]. However, for practical applications, these nanostructures need to be assembled on different substrates either by spin-coating or drop-casting technique [11]. Unfortunately, nanostructure assembled substrate obtained by these methods suffers from weak physical or chemical interaction between nanomaterial and the substrate surface [12–20]. Therefore, development of simple methods to obtain nanomaterial integrated substrate is highly essential. Electrodeposition offers the best solution to these aforementioned problems due to several advantages over wet-chemical method [21–23]. By electrodeposition, the morphology of the nanostructure could be tuned by tuning electrochemical parameters. In addition, nanomaterial integrated substrate could be achieved easily without using any additional immobilizing reagents or costly equipments [24]. Following this strategy, palladium nanoplate arrays [12], tetrahexahedral NCs [25], dendritic nanowire [26], pine needle-like micro/nano-leaves [27], highly ordered nanowire arrays [28], single-crystal Pd nanothorns [29], thorn clusters [30], micro/nano structures with dendritic, cactoid, splintery flowers-like and spinous flowers-like morphology [31], nanorods [32], flower or pinecone-like morphology [33], nanotrees arrays [34], nanourchins [35], trapezohedral and concave hexoctahedral [36], concave-disdyakis triacontahedral [37], nanoflake [38], and triangular rods [39] have been synthesized. Recent studies have demonstrated that the presence of different additives in electrolyte solution plays an important role in the electrochemical growth of Pd nanostructures [40–42]. For example, the electrochemical synthesis of Pd nanodendrites using additive ethylenediamine has been

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demonstrated [40]. Direct electrodeposition of urchin-like Pd nanostructures using sodium nitrite as an additive has also been reported [41]. In another study, Xu et al. have demonstrated electrochemical synthesis of vertically aligned Pd nanoneedles in the presence of additive sodium bromide and trisodium citrate [42].

Energy crisis and environmental pollution need sufficient amount of energy to be produced in greener means. To address these issues, direct methanol fuel cells (DMFCs) have emerged in recent years as potential candidates capable of converting chemical energy into electrical energy. Since anodic oxidation of methanol is the main electrode reaction in DMFCs, development of highly efficient electrocatalyst for electrochemical oxidation of methanol is highly essential to further advance in fuel cell technology. Noble metal Pt has been extensively utilized as electrocatalyst in the development of DMFCs. However, its high cost and surface poisoning by electro generated CO-like intermediate species hinder its application in DMFCs commercialization [43,44]. To address this problem, exploration of non-Pt catalysts is indispensable but a tough task. Recent investigations have demonstrated that, as an electrocatalyst for methanol electrooxidation, Pd is an appropriate substitute to Pt because of its low cost, abundance, higher tolerance against electrogenerated CO-like species, and better stability [45–47]. Therefore, developing new approaches for shape controlled synthesis of Pd nanostructures and their application as electrocatalyst toward electrochemical oxidation of methanol has become a hot topic, particularly for electrochemists.

In addition, hydrazine is well-known for its potential application in fuel cells, weapons, pesticide making, chemical preparation, rocket fuel, pharmaceutical application, and photography industry [48,49]. Despite of its wide variety of potential applications, hydrazine has been recognized to be extremely harmful to human health as it damages liver, brain, kidney, and DNA. In addition, it affects the nervous system [50]. Considering these adverse effects of hydrazine to human health, there is an urgent need to develop simple and sensitive analytical techniques for precise detection of hydrazine [50]. Up to date, several analytical techniques have been developed for the detection of hydrazine. Among them, electrochemical detection has emerged as an efficient alternative because of its simple operation and high sensitivity. Conversely, the requirement of high overpotential for hydrazine oxidation on the conventional electrode is a major drawback. To overcome this, mediator modified electrochemical interface has been used [51–53]. However, poor stability due to peeling out of the mediator from the electrochemical interface hinders its application. To address this issue, electrochemical interfaces modified with various metal nanoparticles including Pt, Ag, Au, and Pd have been developed and used in electrochemical detection of hydrazine [48]. Among those, Pd nanoparticles are recognized as prospective electrocatalysts for electrochemical detection of hydrazine [54]. Although Pd-nanoparticle based electrochemical interfaces have shown their potential in electrochemical sensing of hydrazine, exploration of highly active Pd nanostructures with high catalytic activity and excellent stability toward hydrazine sensing is desirable.

Considering the importance of Pd nanostructures in the electrochemical oxidation of methanol and hydrazine, in the current investigation we have attempted for the direct electrodeposition of catalytically active Pd nanorods using NAD^+ as an additive. Although a handful of reports are available on additive-assisted electrochemical growth of Pd nanostructures in which additives play a major role as shape regulating agent, to the best of our knowledge, no report is available describing the application of NAD^+ as an additive in direct electrodeposition of Pd nanorod. The as-synthesized Pd nanorods were then utilized as the electrocatalyst in the electrochemical oxidation of methanol and electrochemical sensing of hydrazine. Compared to Pd nanostructures synthesized in the absence of NAD^+, Pd nanorods synthesized using NAD^+ showed excellent electrocatalytic activity toward oxidation of methanol and hydrazine. The function of deposition potential, pulse width, and concentrations of NAD^+ and H_2PdCl_4 during

electrochemical growth of Pd nanostructures were also investigated in details. The current study not only demonstrates a facile approach for direct electrodeposition of Pd nanorods, but also opens up the possibility for NAD^+ to be used as a shape regulating agent in direct electrodeposition of other metal nanostructures.

2. Experimental

2.1. Materials

H_2PdCl_4 and NAD^+ were purchased from Sigma-Aldrich. Methanol, hydrazine, H_2SO_4, H_3PO_4, Na_2HPO_4, NaH_2PO_4, and all other chemicals were of analytical grade and used as received. ITO plates were obtained from HS technologies, Korea. Millipore water was used to prepare all solutions. All electrochemical experiments were performed in an argon atmosphere.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a PANalytical High Resolution XRD (PW 3040/60) with Cu Kα radiation (λ ≈ 1.54 Å) operated at 40 kV and 30 mA. Surface morphology of Pd nanostructure was recorded through field emission scanning electron microscopy (FE-SEM) via JSM-6701F (JEOL, Japan). TEM images and high-resolution TEM (HR-TEM) images were recorded using a field emission transmission electron microscope (FE-TEM; JEOL JEM-2200 FS, Japan). Electrochemical measurement was carried out using computer-controlled CHI660D and CHI760D electrochemical analyser (CH Instruments, Austin, TX, USA). Measurements were performed with two-compartment three-electrode cell using glassy carbon (GC) as working electrode, Pt wire as auxiliary electrode, and Ag/AgCl (3 M NaCl) as reference electrode.

2.3. Synthesis of Pd nanorods

Pd nanorods were synthesized with direct electrochemical deposition approach using ITO plates as working electrode. Typically, amperometric technique was employed for the synthesis of Pd nanorods. Pd nanorods were electrodeposited onto ITO surface at a potential of −0.2 V for 2000s from a electrolyte solution containing 5 mM H_2PdCl_4 and 150 mM of NAD^+ in 0.5 M H_2SO_4.

3. Results and discussion

3.1. Characterization of Pd nanorods

3.1.1. XRD analysis

Pd nanostructures were characterized by X-ray diffraction technique. XRD patterns obtained for Pd nanostructures synthesized with or without NAD^+ are shown in Fig. 1. The XRD profile of Pd nanostructures synthesized in the absence of NAD^+ showed four peaks at 40.1°, 47.1°, 68.1°, and 82.2° corresponding to (111), (200), (220), and (311) planes of face-centered-cubic (fcc) Pd, respectively. Similar peaks were also observed for Pd nanostructures synthesized in the presence of NAD^+. Moreover, the peak corresponding to (111) plane was more predominant than other crystal planes. This indicates that Pd nanostructures preferentially grow in the (111) direction.

3.1.2. FESEM analysis

Pd nanostructures synthesized electrochemically at a deposition pulse width of 2000s in the absence or presence of 150 mM NAD^+ were characterized by FESEM measurement. Results are shown in Fig. 2. Rod-like Pd nanostructures were observed when NAD^+ was introduced to the electrolyte (Fig. 2 (a)). These Pd nanorods had an average size of 150 nm in length. Close investigation of the FESEM image showed the presence of some irregular shaped Pd nanoparticles along nanorods.