Catalysis Today 211 (2013) 137–142

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Fabrication of Ir nanoparticle-based biosensors by plasma electrochemical reduction for enzyme-free detection of hydrogen peroxide

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ARTICLE INFO

Article history:
Received 15 December 2012
Received in revised form 1 March 2013
Accepted 4 March 2013
Available online 24 April 2013

Keywords:
Plasma
Nanoparticle
Biosensor
Hydrogen peroxide
Amperometry

ABSTRACT

We present a plasma-based technique to synthesize iridium nanoparticles (Ir NPs) for enzyme-free detection of hydrogen peroxide (H_2O_2). Solutions of Ir salt precursor are electrochemically reduced by a gaseous, atmospheric-pressure microplasma electrode. As compared to Ir NPs synthesized by chemical reduction, Ir NPs synthesized by plasma electrochemical reduction (PER) are free of metallic impurities such as Na. The resulting electrocatalytic properties of the Ir NPs synthesized by PER are found to be superior, including higher sensitivity and selectivity. Finally, we show that this approach can be extended to the fabrication of flexible Ir NP-based biosensors in a single step.

1. Introduction

Quantitative detection of hydrogen peroxide (H_2O_2) is of critical importance in medicine [1]. For example, H_2O_2 plays a key role in cellular signaling and its level provides a measure of cell function [2]. The overproduction of H_2O_2 has been linked to oxidative stress and decline of organ systems [3] and can lead to the onset and advancement of various diseases including cancer [4], diabetes [5], and cardiovascular [6] and neurodegenerative [7] diseases. H_2O_2 is also a byproduct of enzymatic reactions, such as the oxidation of D-glucose to D-gluconic acid by glucose oxidase, and can be used as an indicator of metabolic conditions in the body [8].

Several spectroscopic methods have been developed for H_2O_2 detection including infrared/Raman spectroscopy [9–11], mass spectrometry [12,13], and colorimetric [14,15] or fluorometric probes [16,17]. Recently, electrochemical methods based on enzyme catalysis have been reported that are more direct, rapid, sensitive, and selective due to the specificity of the interaction between the enzyme and H_2O_2 [18]. However, enzymes usually come from natural sources, making them limited and costly, and can become unstable in certain environments and lose their activity [19,20]. Alternatively, metal nanoparticles (NPs) have been proposed as more stable electrochemical catalysts for H_2O_2 sensing [21–25]. In particular, Ir NPs have attracted considerable interest due to their high conductivity and high electrocatalytic activity for H_2O_2 oxidation [26–29]. Moreover, Ir incorporated with other metals (e.g. Pd, Ru, or Cu) could greatly improve the sensitivity and selectivity between H_2O_2 and interfering species, such as ascorbic acid (AA) and uric acid (UA) [30].

Despite this promise, synthesis of Ir NPs remains a challenge. Ir NPs have been typically prepared by chemical reduction of an Ir salt, such as $IrCl_3$, in solution by a strong reducing agent such as sodium borohydride ($NaBH_4$), hydrazine, or dimethyl formamide, that pose serious environmental and biological risks, the latter of which could be a problem for in vivo applications [31–33]. In addition, it remains unclear if high-quality NPs in terms of chemical purity and crystallinity are produced by these methods which could ultimately impact their catalytic activity and biosensor performance.

Here, we show that Ir NPs synthesized by a recently developed plasma electrochemical reduction (PER) technique exhibit superior electrocatalytic activity and selectivity for H_2O_2 sensing than the more typical chemically-synthesized NPs. Our laboratory has pioneered PER which involves the formation of an atmospheric-pressure microplasma jet at the surface of an aqueous solution to electrochemically reduce metal cations to solid metal (zero oxidation state) NPs without the need for chemical reducing agents [34–36]. In this study, we carefully compare the material and electrocatalytic properties of Ir NPs synthesized by PER and chemical reduction (CR). Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) reveal that Ir NPs produced by PER are crystalline and impurity-free, while Ir NPs prepared by CR contain metallic impurities such as Na from the synthesis

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http://dx.doi.org/10.1016/j.cattod.2013.03.023

process. Electrochemical characterization confirms a significant enhancement in the amperometric response for Ir NPs synthesized by PER with a sensitivity of 451 μA/(cm^2 mM), as compared to 187 μA/(cm^2 mM) for the Ir NPs synthesized by CR. The Ir NPs synthesized by PER also exhibit higher selectivity, with a reduced current response to interfering agents such as AA and UA. An additional advantage of PER is that the technique can be extended to the preparation of metal NPs as a thin film [37–39]. As proof-of-concept, we demonstrate the single-step fabrication of a flexible Ir NP-based biosensor capable of detecting H_2O_2.

2. Experimental

Ir NPs were synthesized by either PER or CR of $IrCl_3{\cdot}xH_2O$ (Sigma–Aldrich Co.). Both approaches were carried out at ambient conditions, i.e. room temperature and atmospheric pressure. To synthesize Ir NPs in solution by PER, a direct current (dc), atmospheric-pressure microplasma was formed in a flow of Ar (30 sccm) using a stainless-steel capillary tube (O.D. = 0.159 cm × I.D. = 180 μm × 5 cm length, Restek, Inc.) at the surface of an aqueous solution containing 1 mM $IrCl_3$ in deionized water. Ir NPs were synthesized with and without a stabilizer agent, citric acid, which was added to the initial solution at a concentration of 1 mM. A platinum foil (Pt) was immersed in the solution as the counter-electrode. The microplasma was ignited and operated by a negatively-biased dc power supply (Keithley, Inc., Model 246). In a typical experiment, the microplasma required ~2 kV to ignite and 1 kV to operate at a constant current of 4 mA. Experiments were carried out for 1 h.

Ir NPs were synthesized by CR using a standard procedure involving $NaBH_4$ [24,40]. Briefly, a solution containing 1.8 mM $IrCl_3$ and 1 mM citric acid was titrated to pH = 7.0 by adding 100 mM NaOH dropwise. Then, 10 mM $NaBH_4$ was slowly added dropwise until the amount of electrons released by the $NaBH_4$ reaction with water was ~1.4 times the theoretical value required to completely reduce Ir^{3+}.

TEM was performed with a Techai F300 at 300 kV. TEM samples were prepared by drop casting the solutions of Ir NPs onto carbon-coated Cu grids. XPS analysis was carried out with a PHI VersaProbe. The synthesized Ir NPs were mixed with carbon black in ethanol, drop cast on Si substrates, and dried in room air overnight. The presence of carbon in the samples allowed us to correct the XPS spectra by the position of the C ls peak (284.5 eV). A monochromatic $Al_{K\alpha}$ (1486.6 eV) source with a spot size of 400 μm was used to acquire all spectra. Films were sputtered by a 3 kV Ar^+ ion beam (Physical Electronics FIG-5) to remove any coating that could cause shifts in the spectra due to charging. The sputtering rate was calibrated to be 7.6 nm/min by using a 100 nm tantalum oxide (Ta_2O_5) film.

Electrodes for electrochemical characterization were prepared by dispersing the solutions of Ir NPs on active carbon black powder (Vulcan XC-72) at a catalyst loading of 20 wt%. The mixtures were washed with excess ethanol, centrifuged, and dried in a vacuum oven at 60 °C overnight. Afterwards, 8 mg of the electrocatalysts were dispersed in 200 μL of ethanol and 100 μL of 5 wt% Nafion in water and sonicated for 30 min. 8 μL of this solution was deposited onto glassy carbon (0.5 cm diameter, AFE2M050GC, Pine Instrument) and dried in ambient air for 3 min. Cyclic voltammetry (CV) was carried out with an electrochemical workstation (Model 660B, CH instrument). The three-electrode system consisted of the Ir NPs dispersed on carbon powder and deposited on glassy carbon as the working electrode, an Ag/AgCl reference electrode, and a Pt-mesh counter electrode. The working electrode was operated at a rotational speed of 900 rpm in 0.1 M PBS at pH 7.4 with 0.15 M KCl as supporting electrolyte. Scans were obtained from −0.2 V to 1.0 V at a rate of 50 mV/s. Amperometry was performed at an applied potential of +0.6 V by incrementally adding H_2O_2 in increasing amounts from 0 to 10 mM. The steady-state current was obtained by waiting ~100 s between each successive addition.

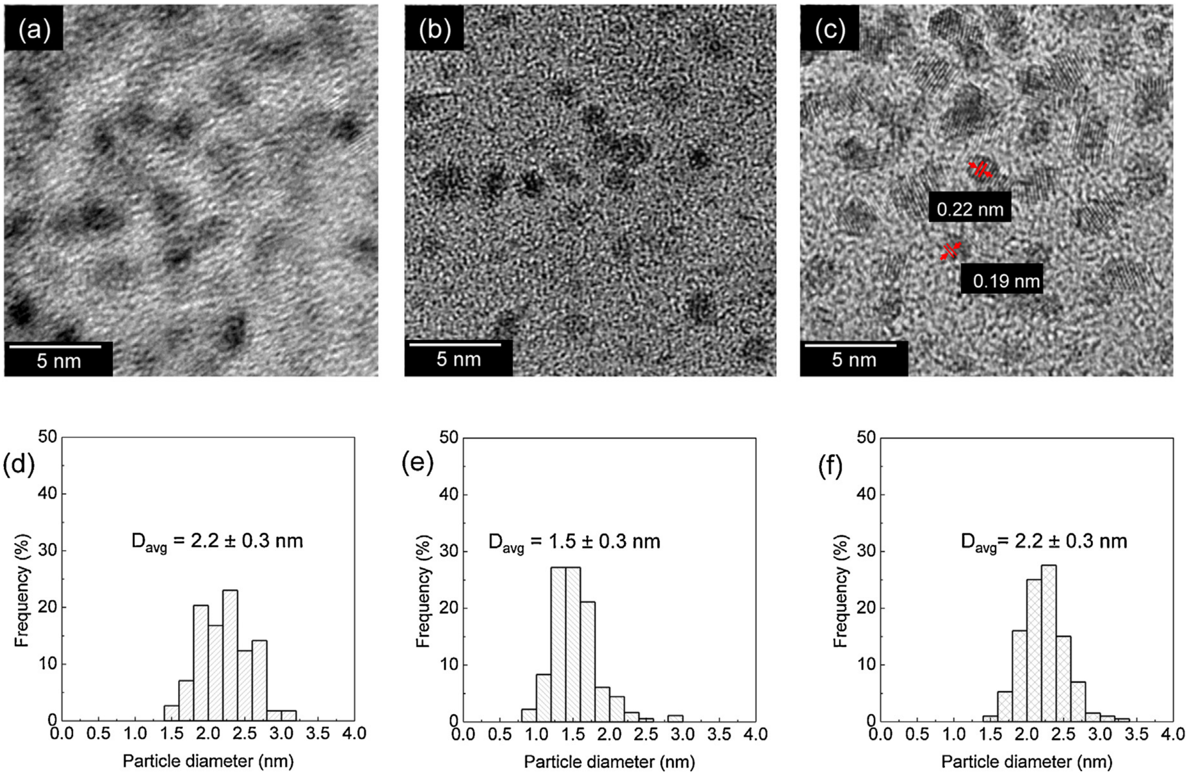

Fig. 1. Representative TEM images of Ir NPs synthesized by (a) CR and (b) PER. In (c), a TEM image of Ir NPs synthesized by PER without citric acid is shown. Lattice spacings of 0.22 and 0.19 nm corresponding to Ir (1 1 1) and Ir (2 0 0), respectively, are evident. Histograms of the particle size distributions obtained from TEM analysis of Ir NPs synthesized by (d) CR, (e) PER, and (f) PER without citric acid.