



Efficient electrochemical regeneration of nicotinamide cofactors using a cyclopentadienyl-rhodium complex on functionalized indium tin oxide electrodes

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ABSTRACT

Functionalized ITO electrodes are used to regenerate NADH using $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (Cp^* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) electrochemically in a buffer solution. Amino- and mercapto-functionalized electrodes featured higher activity and stability for electrocatalytic generation of NADH than a bare ITO electrode. Effect of metal nanoparticles was also studied on modified ITO electrodes and the addition of platinum nanoparticles even resulted in improved activity. The electrochemical regeneration was somewhat affected in the presence of dioxygen, but not significantly. In addition, a conversion of carbon dioxide was carried out utilizing the electrochemically generated NADH and formate dehydrogenase to produce formic acid.

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1. Introduction

In view of the significant concern regarding the depletion of fossil fuels in the near future, the development of renewable energy is a major challenge to address the problem of abundant and environmentally benign energy required for global growth. One of the energy conversion pathways that has aroused the interest of scientists is the development of efficient catalytic systems that can yield chemical energy in the form of a reducing potential such as dihydronicotinamide adenine dinucleotide (NADH). NADH produced during photosynthetic processes is the chemical equivalent of solar hydrogen as a fuel. NADH is used as a cofactor in various biological reactions performed by many important redox enzymes [1–7]. The application of some enzymes for regioselective and enantioselective synthesis has been examined at the expense of NADH regenerated chemically and electrochemically [8–10]. Therefore, development of efficient regeneration methods for NADH based on a renewable energy source is of substantial interest.

An organometallic rhodium complex has been frequently employed as an efficient catalyst for hydride transfer during

chemical and electrochemical formation of NADH to selectively reduce NAD^+ . Several electrochemical NADH regeneration systems have been reported using Rh catalysts to study electron transfer phenomena. Schmid et al. reported non-enzymatic electrochemical production of NADH using a Rh catalyst on a glassy carbon electrode (GC) [10]. Bulk electrolysis of NAD^+ carried out with a Rh catalyst in the absence and presence of platinum nanoparticles (PtNPs) generates enzymatically active 1,4-NADH [10,11]. PtNPs have also been reported to act as a photosensitizer as well as a catalyst during photocatalytic regeneration of NADH [12]. In those studies, PtNPs were used in a homogeneously dispersed solution. Electron transfer between catalyst and electrode during bulk electrolysis occurs within a short distance from the electrode surface. Understanding a relationship between functional groups on the electrode with fast electron transfer to the metal catalyst is required for an efficient electron transfer reaction between a metal catalyst and an electrode. Here, we report the efficient reduction of NAD^+ to the enzymatically active NADH using $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ (Cp^* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) on amino- and mercapto-modified indium tin oxide (ITO) electrodes in aqueous media. The modified ITO electrodes accelerated the generation of NADH in the presence of metal nanoparticles. Furthermore, NADH produced in situ in this system converted carbon dioxide to formic acid in the presence of formate dehydrogenase (FDH).

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2. Experimental

2.1. Materials and instrumentation

Water was purified with a MilliQ purification system. All reagents purchased from Aldrich were used without further purification. The working electrode was tin-doped indium oxide (ITO) obtained from Delta Technology, Inc. (USA). $[\text{Cp}^*\text{Rh}(\text{bpy})\text{Cl}]^{2+}$ was prepared according to previously published methods [13,14]. PtNPs were prepared by polyvinylpyrrolidone (MW = 10k) reduction of potassium tetrachloroplatinate (K_2PtCl_4) as reported [15,16]. A hot aqueous mixture of K_2PtCl_4 (11.5 mM, 120 mL) was reacted with polyvinylpyrrolidone (3 g) for 4 h. The size and distribution of Pt nanoparticles were examined by TEM and dynamic light scattering (Malvern, Zetasizer Nano ZS). Au nanoparticles were prepared from H_2AuCl_4 (11.5 mM) with sodium citrate, as reported [17]. The concentration of PtNPs was measured by total reflection X-ray fluorescence (TXRF) analysis (S2 PICOFOX, Bruker, Germany).

A three-electrode cell consists of a glassy carbon working electrode ($\varnothing=3$ mm), an auxiliary platinum wire, and an Ag/AgCl reference electrode. Cyclic voltammograms were recorded on a CH instrument potentiostat (CHI630C). Bulk electrolysis and coulometry were carried out in phosphate buffer, using ITO electrodes (electrochemical surface area; 0.32 cm^2). Potentiostatic electrolyses were performed in a thermostated 3 mL electrolysis cell gas-tighten with septum. A degassed solution (1 mL) was electrolyzed at -0.80 V (vs Ag/AgCl). The faradaic yield was estimated from the amount of regenerated NADH during the time needed for a charge to pass through the cell.

UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer. Transmission electron microscopy (TEM) images were recorded on a JEOL 2010FX electron microscope operating at 200 kV. Atomic force microscopy (AFM) images were obtained using a Digital Instruments Dimension 3100 scanning force microscope in tapping mode with an Olympus cantilever (spring constant in the range $33.2\text{--}65.7\text{ N m}^{-1}$ and resonant frequency of $277.3\text{--}346.3\text{ kHz}$).

2.2. Preparation of functionalized ITO electrodes

ITO electrodes were cleaned with Alconox solution, propanol, and water with 15 min sonication, followed by drying at 50°C . The cleaned substrates were pretreated in a mixture of $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ (30%)/ NH_4OH (30%) (v/v/v=5:1:1) at 70°C for 1.5 h to ensure the presence of hydroxyl groups on the surface. The substrates were then washed with water and dried at 50°C for 30 min. The activated ITO electrodes were immersed in an ethanol solution containing 2% of 3-aminopropyltriethoxysilane or 3-mercaptopropyltriethoxysilane for 12 h to produce organosilane monolayer [18]. The functionalized ITO electrodes were then washed thoroughly three times with copious amount of ethanol and dried at room temperature.

2.3. Electrocatalytic NADH generation

The typical electrochemical generation of NADH was carried out using 0.1 mM $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$ and 0.4 mM NAD^+ in the absence and presence of metal nanoparticles (20 nm) in 0.1 M phosphate buffer (pH 7.0) at room temperature. The aqueous reaction solution was degassed before electrolysis in a gas-tight electrochemical cell equipped with three electrodes (Pt wire, counter electrode). The production of NADH was determined by UV absorption at 340 nm after background substration ($\epsilon=6220\text{ cm}^{-1}\text{ M}^{-1}$). The data points were obtained from the average of three independent measurements. The current efficiency for NADH formation

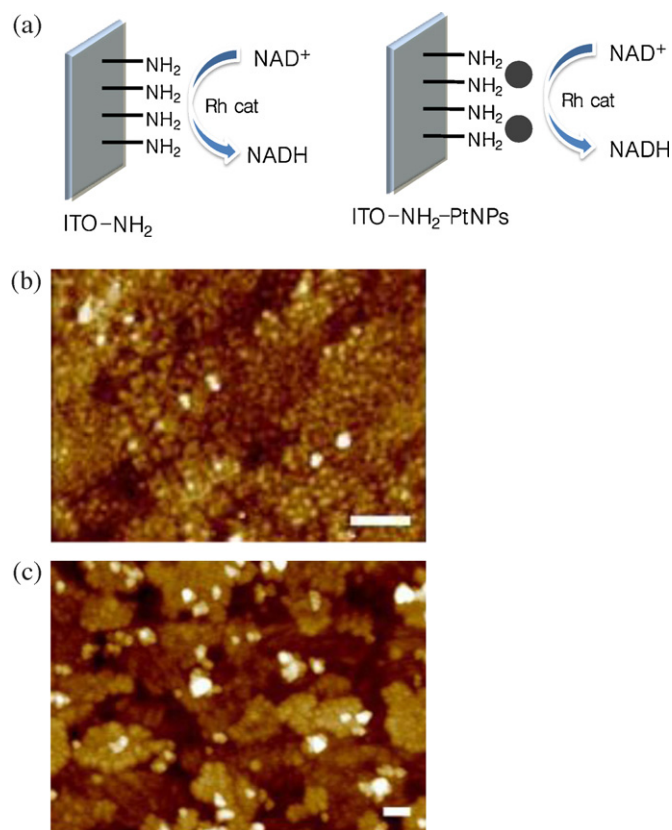


Fig. 1. (a) Scheme for amine-functionalized indium tin oxide (ITO-NH₂) and platinum nanoparticle (PtNP)-loaded ITO electrodes. Electrochemical regeneration of NADH using a Rh catalyst on modified ITO electrodes. Scanning tunneling microscopy of (b) PtNPs loaded on ITO-NH₂ and (c) AuNPs loaded on mercapto-functionalized ITO (ITO-SH). Scale bars = 50 nm.

was calculated by dividing the total number of electrons stored in NADH by the amount of consumed charges.

2.4. Electrochemical CO₂ reduction

The typical electrochemical production of formic acid from CO₂ was performed in a one-compartment cell on bare and functionalized ITO electrodes under inert atmosphere at room temperature. The reference electrode was a commercially available Ag/AgCl electrode. The reaction solution composed of 0.1 mM $[\text{Cp}^*\text{Rh}(\text{bpy})(\text{H}_2\text{O})]^{2+}$, 0.4 mM NAD^+ , formate dehydrogenase (FDH, 3 units) in 1.0 mL phosphate buffer (0.1 M , pH 7.0). The reaction solution was thoroughly deaerated via bubbling CO₂ 30 min prior to and during the experiments. Formic acid was analyzed and quantitated by HPLC (Youngin, Korea, YL9100) using a column (Inertsil ODS-3V, $5\ \mu\text{m}$ $4.6\text{ mm} \times 150\text{ mm}$) and 0.01% phosphoric acid solution as eluent.

3. Results and discussion

ITO electrodes functionalized with amino and thiol groups were prepared with 3-aminopropyl-triethoxysilane and 3-mercaptopropyl-triethoxysilane, respectively, using activated ITO electrodes as reported previously [19]. Then, a solution of 5 nm PtNPs was placed on the amino-functionalized ITO electrode (ITO-NH₂) to afford the formation of a PtNP layer (Fig. 1a). As shown in Fig. 1b, the nanoparticles on the PtNPs-loaded ITO-NH₂ were well dispersed. Additionally, mercapto-functionalized ITO (ITO-SH) loaded with 13 nm gold NPs was also prepared, as shown in scanning tunneling microscopy (Fig. 1c). ITO-NH₂, ITO-SH, and

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