



Hydroxyapatite wrapped multiwalled carbon nanotubes composite, a highly efficient template for palladium loading for electrooxidation of alcohols



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HIGHLIGHTS

- A new catalyst was proposed for alcohol electrooxidation.
- A high catalytic activity was obtained for electrooxidation of ethylene glycol.
- Efficient oxidation was obtained even for high concentrations of ethylene glycol.
- The electrocatalyst showed high tolerance toward high concentrations of ethylene glycol.

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ABSTRACT

A new electrocatalyst is introduced by loading palladium nanoparticles on the unique structured composite of hydroxyapatite and multiwalled carbon nanotubes. The structure and morphology of the designed electrocatalyst are characterized by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The efficiency of the resulted nanostructure is explored toward the electrooxidation of some common alcohols in alkaline media. The electrooxidation of ethylene glycol (EG) is explored more extensively which provides a large peak current density (more than $1810 \text{ mA mg}^{-1} \text{ Pd}$). Surprisingly, the efficiency of oxidation is maintained even for relatively high concentrations of EG. In terms of the current density and the onset potential, significant improvements are observed for the proposed structure versus hydroxyapatite free catalyst. The high efficiency of the proposed electrocatalyst is explained via the presence of hydroxyl rich surface of hydroxyapatite which causes a more effective oxidation of alcohols over the loaded Pd nanoparticles.

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1. Introduction

DAFCs introduce the alternative power sources especially for portable electrical consumers. Alcohols are more easily handled in comparison to hydrogen and have a higher volumetric energy density compared to the common fuels such as gasoline [1]. Among these, direct methanol (MeOH) and ethanol (EtOH) fuel cells (DMFCs and DEFCs) have been widely explored [2–4]. However, the improvement of fuel cells based on the heavier alcohol fuels are of great importance because of their less toxicity, volatility and flammability. Today especially the bioresource based polyalcohol

fuels such as ethylene glycol (EG) and glycerol have been attracted great attentions [5,6]. The energy density (per unit volume) of these alcohols are comparable with ethanol. In addition, some products of oxidation process of these alcohols are themselves valuable chemicals [7].

One of the promising catalysts for both anodic and cathodic reactions at DAFCs is palladium (Pd). Pd-based catalysis in alkaline media could be introduced as an efficient alternative for platinum catalysts [8]. The design of more efficient Pd catalysts as well as the improvements in the anion exchange membranes, are key factors for the growth of DAFCs as an efficient type of low temperature fuel cells [9]. However, especially in the field of nanocatalysis, the support plays a crucial role in the total performance of the designed catalyst [10]. Therefore, supporting Pd nanoparticles (Pd NPs) on the stable, porous and/or high surface area materials with favorable

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electrical conductivity is demanding. In addition to commonly used carbon black supports, carbon nanotubes (CNTs) are widely applicable to construct the electrocatalysts in DAFs [11,12]. The immobilization of Pd catalyst on CNTs had been numerous performed via various routes to attain the higher utility, better dispersity and to enhance the overall performance of the electrocatalyst [13–16]. The higher activity of Pd supported multiwalled carbon nanotubes (MWCNT) in comparison to carbon black and carbon nanofibers as supports was previously observed by Zheng et al. [17] for ethanol oxidation reaction.

Hydroxyapatite (HA) is a bioceramic which could be easily modified by sorption of various metals onto its structure [18]. Numerous publications on using HA in the field of catalysis especially in the case of supporting Pd NPs are present [19–21]. However, the application of HA for immobilization of metallic ions or NPs in the field of electrocatalysis is rare [22,23]. Due to HA hydration and its highly hydrophilic nature, a favorable ionic conductivity for HA layer in direct contact with aqueous electrolytes, is attainable [24,25]. The successful application of HA as a filler in construction of polymer membranes for direct alcohol [26,27] as well as the direct borohydride fuel cells [28] have been reported. The enhancement in ionic conductivity of membranes were reported by using HA as filler. However, optimizing the HA to polymer proportion was required [26].

On the other hand, the enhancement in the conductivity of HA for application in electrochemical devices, could be achieved by its composition with CNTs as a uniquely structured conductive phase. However, the chemical composition as well as the structural features, has crucial roles in the final physicochemical properties of the composite. The precise control of chemical and structural features could be attainable by applying a proper method for the synthesis of CNT-HA composites [29]. Previously, the synthesis of a unique structured nanocomposite, based on HA and MWCNTs via microwave assisted solid state metathesis route has been introduced by our group [30]. Surprisingly, a better charge transfer rate (in solution) than the pristine carbon nanotubes have been observed for the as synthesized HA/MWCNT composite [30]. Additionally, the proposed composite has been successfully applied in the construction of a sensitive electrochemical sensor for the detection of trace amounts of heavy metal ions [31]. It could be expected that the loaded NPs on the HA/MWCNT composite, represent a good electrocatalytic activity.

This work, represents the electrocatalytic activity of a designed catalyst based on the HA/MWCNT composite as a novel support by loading Pd NPs via the electrooxidation of common alcohols (particularly EG). Due to the presence of both HA and MWCNTs, as well as the known favorable electrochemical performance of the HA/MWCNT composite, the improved characteristics as anode material for DAFs could be expected.

2. Experimental

2.1. Materials and apparatus

Palladium (II) chloride anhydrous (PdCl_2 , 60% Pd) was supplied by Fluka. KOH, CaCl_2 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, methanol, ethanol, 1-propanol, 2-propanol and 1,2-propanediol were purchased from Merck. Ethylene glycol and glycerol were supplied by Riedel-de Haen. Multiwalled carbon nanotubes (MWCNTs), (diam. \times L 110–170 nm \times 5–9 mm, purity \geq 90%) were purchased from Aldrich.

Electrochemical experiments were performed by applying a PGSTAT302N electrochemical system (Eco-Chemie, Utrecht, The Netherlands) using a three electrode system; an Ag/AgCl/KCl(3M) reference electrode, a platinum wire counter electrode and a glassy

carbon working electrode (GCE), (Azar electrode Co. 0.2 mm diameter and the geometrical surface area of 0.1256 cm^2). Transmission electron micrograph (TEM) was taken with Zeiss - EM10C - 80 KV and XRD spectra were obtained by D8ADVANCE type (BRUKER-Germany).

2.2. Synthesis procedures

MWCNTs were activated via flash oxidation by application of $700 \text{ }^\circ\text{C}$ for 15 min under the air atmosphere [32]. The HA/MWCNT composite was prepared via the solventless solid state metathesis procedure as previously explained by authors using activated MWCNTs [30]. Briefly, desired amounts of CaCl_2 and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ with the Ca/P stoichiometric ratio of 1.66 were finely mixed with the appropriate amount of activated MWCNTs. The composite was synthesized after 3min of microwave irradiation (900 W) of the mixture. The final product was attained after three times of washing by doubly distilled water followed by drying at $100 \text{ }^\circ\text{C}$ overnight.

Loading of Pd on the as prepared HA/MWCNT composite was achieved via simple impregnation method. The formation of Pd NPs was attained via chemical reduction of adsorbed Pd ions. For this purpose, 10 mg of the as synthesized composite was soaked in 5 ml of Pd^{2+} solution with required concentration (by dissolving PdCl_2 and KCl in deionized water) for 24 h. After removing non-adsorbed Pd ions via three times of washing with deionized water, a 15 ml of a solution containing 10 mM of NaBH_4 was added quickly and the mixture was stirred for an hour. After three times washing with deionized water to remove the excess amount of reducing agent, the product was dried overnight under vacuum at $40 \text{ }^\circ\text{C}$. For comparison, the loading of Pd NPs was done on carboxyl functionalized MWCNTs and HA NPs with the same method and under the same conditions (denoted as Pd/MWCNT and Pd/HA samples, respectively).

2.3. Electrode preparation

Pd/HA/MWCNT electrocatalyst was casted on the GCE for electrochemical experiments. The GCE was polished at first with $0.3 \mu\text{m}$ alumina powder and sonicated in water/acetone and water, respectively. Finally, the surface of GCE was anodized at 1.2 V for 300 s. GCE surface modification was performed via casting of $2 \mu\text{l}$ of 1 mg/ml suspension of Pd/HA/MWCNT electrocatalyst in water. After drying in air, $2 \mu\text{l}$ of 0.25% of Nafion solution (optimized value) was casted on the electrode and left to dry.

2.4. Electrochemical procedures

Cyclic voltammetric analyses (CVs) were performed under the scan rate of 50 mV/s from -0.8 V to 0.5 V vs. Ag/AgCl. In order to attain a steady behavior, the tenth cycles of CVs have been used for better comparison in all figures. Solution of 1 M of KOH was used as alkaline electrolyte. Before each experiment, all of the solutions were purged for at least 25 min with high purity argon. All of the electrochemical experiments were also performed under argon atmosphere. Chronoamperometric experiments were performed under the most favorable potential of -0.250 V and solution stirring rate of 200 rpm.

3. Results and discussion

3.1. Structural characterization of Pd/HA/MWCNT composite

Fig. 1 represents XRD spectra of HA/MWCNT and Pd NP loaded HA/MWCNT composite. The characteristic peaks of Pd at

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