



# Controllable synthesis of hydroxyapatite-supported palladium nanoparticles with enhanced catalytic activity

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## ABSTRACT

A multi-stage electrochemical method was developed to synthesize palladium (Pd) nanoparticles supported on hydroxyapatite (HA) coatings. In the first stage, a dense coating of HA nanocrystals was synthesized from an aqueous electrolyte solution onto a titanium cathode surface through a galvanostatic process. The HA-coated titanium electrode was then used as the cathode for the electrochemical reduction of  $\text{Pd}^{2+}$  from aqueous solution. A synthesis approach using two sequential electrochemical reduction reactions was found to be more effective in producing uniform coatings of Pd nanoparticles than a single stage reduction. In the first step, a higher voltage was applied to the cathode for a short time to promote the nucleation of Pd nanoparticles. A lower voltage was then applied for a longer time in the second stage to promote the growth of the Pd nanoparticles. The size and size distribution of the Pd nanoparticles were controlled by adjusting the duration of the first and second stages of electrochemical reduction. The resulting HA supported Pd nanoparticles demonstrated significantly higher catalytic activity than commercial Pd nanoparticles in the degradation of methyl orange by  $\text{NaBH}_4$ . The high surface area and the complex oxidation states of the HA-supported Pd nanoparticles are believed to account for the enhanced catalytic activity.

## 1. Introduction

Metal nanoparticles can provide superior activity and selectivity in catalysis applications compared to bulk catalysts [1]. Metal nanoparticles have a high surface-to-volume ratio, and the size and surface composition of nanoparticles are controllable by a variety of synthesis methods. Palladium (Pd) and Pd-based nanomaterials have been shown to be versatile and selective catalysts [2–4]. Pd nanoparticles have a wide variety of catalytic applications, such as carbon-carbon bond forming reactions [5, 6], selective oxidation of alkanes [7], oxidation of primary alcohols in alkaline media [8, 9], and cross-coupling reactions of organoboron compounds [10]. One of the main challenges in the application of Pd and other metal nanoparticles as catalysts is particle aggregation that can lead to a significant decrease in catalytic performance [1]. One way of reducing particle aggregation is by immobilizing Pd nanoparticles on a suitable support. Immobilization of Pd nanoparticles on a support also makes it easier for separation from the reaction medium and recovery.

Hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , HA), the main inorganic component of human bones and teeth, has been demonstrated as a promising catalyst support material for metal nanoparticles because of its high adsorption capacity, ion-exchange ability, and adjustable acid-

base properties which can prohibit side reactions [11, 12]. Recently, Rakap et al. reported that HA supported Pd or Co nanoclusters displayed high efficiency and reusability in hydrogen generation from the hydrolysis of ammonia-borane [13, 14]. HA-supported Ru nanoparticles have also been used for hydrolytic dehydrogenation of ammonia-borane [15]. However, the synthesis procedures in these studies were time-consuming and offer little control over the size and loading of metal nanoparticles. For example, in one of the synthesis methods of HA-supported Pd nanoparticles, the precursor  $\text{Pd}^{2+}$ -exchanged HA was obtained by stirring HA and  $\text{Pd}(\text{NO}_3)_2$  solution for 3 days [14]. The size of the obtained Pd nanoparticles was small but the work did not show control over the size of the Pd nanoparticles. Therefore, it is desirable to develop a facile synthesis method in which the size and loading of metal nanoparticles can be easily tuned.

In the present study, a simple electrochemical technique was applied to reduce  $\text{Pd}^{2+}$  and form Pd nanoparticles on a HA nanocrystal support layer. The obtained Pd nanoparticles have a small size and uniform distribution. In addition, the size, size distribution, and loading of the Pd nanoparticles could be controlled by adjusting the deposition time. The catalytic activity of the synthesized HA-supported Pd nanoparticles was demonstrated by catalyzing the reduction of methyl orange (MO) in the presence of  $\text{NaBH}_4$  in aqueous solution. The results

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show that the prepared Pd nanoparticles possess much higher catalytic activity than commercial Pd nanoparticles of similar size. It is believed that the synthesis process and the interaction between the Pd nanoparticles and the unique HA support give rise to the significant enhancement of catalytic activity.

## 2. Experimental procedure

### 2.1. Materials

HCl (37%) and KCl (99.7%) were purchased from Mallinckrodt Chemicals. Sodium chloride ( $\geq 99.0\%$ ),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  ( $> 99\%$ ),  $\text{K}_2\text{HPO}_4$  (99.99%),  $\text{PdCl}_2$  (99.9%), tris(hydroxymethyl)-amino methane ( $> 99.8\%$ ),  $\text{NaBH}_4$ , NaOH, Pd nanoparticles ( $< 25$  nm particle size,  $\geq 99.5\%$ ) and methyl orange were all purchased from Sigma-Aldrich. Silver nitrate was obtained from Ameresco. Titanium (Ti) plates (10 mm  $\times$  10 mm  $\times$  0.89 mm) and platinum foils (25 mm  $\times$  25 mm  $\times$  0.127 mm) were purchased from Alfa Aesar.

### 2.2. Electrochemical crystallization of HA

For the electrochemical synthesis of HA nanocrystals, a pre-cleaned Ti plate was used as the cathode, and a platinum (Pt) foil was used as the anode. The electrolyte solution comprised 1.3 mM  $\text{CaCl}_2$ , 0.84 mM  $\text{K}_2\text{HPO}_4$ , and 138 mM NaCl, 50 mM tris(hydroxymethyl)-amino-methane. The solution pH was adjusted to 7.2 using HCl. The solution was heated to 95°C under continuous stirring. The electrodes were immersed in the solution and kept at a distance of 1 cm, followed by application of a constant current with the current density of 12.5 mA/cm<sup>2</sup> for 4 min. After the reaction, the HA coated Ti plate was rinsed with deionized water and dried in air.

### 2.3. Electrochemical deposition of Pd nanoparticles on HA nanocrystals

For electrochemical deposition of Pd nanoparticles, the HA coated Ti plate obtained above was used as the cathode, and a Pt foil was used as the anode. The electrolyte solution consisted of 1 mM  $\text{PdCl}_2$  and 5 mM KCl. The electrodes were immersed in the solution and held apart by 1 cm. Then a potentiostatic reaction was carried out at room temperature to electrochemically reduce  $\text{Pd}^{2+}$  and deposit metallic Pd nanoparticles. For the single-stage method, a constant voltage of either 3.2 V or 5.4 V was applied to the electrodes for 195 s. For the two-stage method, an electric potential of 5.4 V was first applied for a shorter time, followed by application of a 3.2 V potential for a longer time. The electrochemical reaction was carried out at room temperature. Afterwards, the sample was taken out from the solution, rinsed with deionized water, and dried in air.

### 2.4. Sample characterization

A Zeiss-Leo DSM982 field emission scanning electron microscope (FESEM) equipped with energy dispersive X-ray spectrometer (EDS) was used to investigate the morphology and composition of the samples. The oxidation state of the obtained Pd nanoparticles was examined by a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (XPS), equipped with a monochromatic Al anode X-ray gun ( $K\alpha = 1486.6$  eV). The crystal structures were determined by X-ray diffraction (XRD) with a Philips PW3020 XRD spectrometer using Cu  $K\alpha$  radiation ( $\lambda = 1.5418$ ). The light absorbance of methyl orange solution was measured by a UV/Vis spectrometer (Lambda 900, Perkin Elmer). In order to determine the loading of Pd nanoparticles on HA coatings, the samples were dissolved in aqua regia, and the solution was examined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer).

### 2.5. Catalytic activity of HA-supported Pd nanoparticles

The reduction of methyl orange in the presence of  $\text{NaBH}_4$  was used to demonstrate the catalytic activity of Pd nanoparticles supported on HA nanocrystals. The sample containing Pd nanoparticles was immersed in a solution containing 0.01 mg/mL methyl orange, 10 mM NaOH, and 2 mM  $\text{NaBH}_4$  at room temperature and with continuous stirring. The degradation of methyl orange occurred immediately after the sample came into contact with the solution. A small amount of solution was taken out every minute for light absorbance analysis at 465 nm. For control experiments, a bare HA coating without Pd deposition was used to carry out the reduction of methyl orange. For a second control, 78  $\mu\text{g}$  of commercial Pd nanoparticles was dispersed in deionized water by sonication, and deposited onto the HA coating by evaporative deposition. The reduction of methyl orange using the commercial Pd nanoparticles was carried out under the same conditions used for the electrochemically synthesized Pd nanoparticles.

## 3. Results and discussion

### 3.1. Electrochemical reduction of $\text{Pd}^{2+}$ to $\text{Pd}^0$ on the surface of HA crystals

The electrochemical synthesis of HA from aqueous electrolyte solution is a well established technique that can be used to selectively coat the cathode surface with HA in a standard two-electrode setup [16]. In the first stage of synthesis, a nanoscale coating of HA was formed on a Ti cathode surface following a procedure previously reported [17]. The resulting electrochemically synthesized HA nanocrystals are shown in Fig. 1 (a). The crystals are rod-shaped with a length of approximately 500 nm on average and uniformly coat the Ti electrode surface. Although HA is considered to be a dielectric material, it has measurable DC conductivity near room temperature [18], and the conductivity increases significantly under applied field strength of greater than  $10^4$  V/cm [19]. Despite the low electrical conductivity of HA, the nanoscale thickness of the electrochemically synthesized HA enables significant electron transport through the coating. In recent work, our group has demonstrated the cathodic electrochemical reduction of silver ions to form metallic Ag nanoparticles directly on the surface of the HA coatings [20, 17]. In the present study, the electrochemical reduction of Pd was first attempted following a procedure similar to that previously used for synthesizing Ag nanoparticles. The HA-coated Ti substrate was immersed in a solution containing 1 mM  $\text{PdCl}_2$  and 5 mM KCl. Then, a constant voltage of 3.2 V or 5.4 V was applied to the electrodes for 195 s. The reaction resulted in Pd particles being deposited onto the surface, as shown in Fig. 1 (b) and (c). For the 3.2 V sample, a small number of large nanoparticles were observed on the tips of the rod-shaped HA nanocrystals after the reaction while almost no nanoparticles were deposited on the sides of the HA crystals. For the 5.4 V sample, on the other hand, a large number of tiny nanoparticles which are barely observable were uniformly deposited on the HA coating.

The images in Fig. 1 (b) and (c) suggest that the higher voltage of 5.4 V promotes nucleation of numerous Pd nanoparticles on the HA surface, while the lower voltage of 3.2 V promotes slow growth of larger Pd particles and clusters at the tips of HA crystals. It was hypothesized that a more effective approach would be to carry out the synthesis in two stages. The first stage is a short duration at the higher voltage to promote the formation of Pd nanoparticles on the surface. The second stage is a longer time at the lower voltage to promote growth onto the Pd nanoparticles formed in the first stage. To test this hypothesis, a reaction was carried out in which 5.4 V was applied for 15 s, then 3.2 V was applied for 180 s. This two stage synthesis method was inspired by the “double-pulse” technique shown to be effective in the electrochemical synthesis of uniform silver nanoparticles [21]. Although the overall reaction time was kept fixed at 195 s total, the resulting Pd

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