

## Facile and Rapid Synthesis of Microwave Assisted Pd Nanoparticles as Non-Enzymatic Hydrogen Peroxide Sensor

Ozlem Sahin<sup>1,\*</sup>, Hilal Kivrak<sup>2</sup>, Arif Kivrak<sup>3</sup>, Hilal Çelik Kazıcı<sup>2</sup>, Orhan Alal<sup>2</sup>, Dilan Atbas<sup>2</sup>

<sup>1</sup>Chemical Engineering Department, Selcuk University, 42031, Konya Turkey

<sup>2</sup>Chemical Engineering Department, Yüzüncü Yıl University, 65081, Van Turkey

<sup>3</sup>Department of Chemistry, Yüzüncü Yıl University, 65081, Van Turkey

\*E-mail: [hilalkivrak@gmail.com](mailto:hilalkivrak@gmail.com), [hilalkivrak@yyu.edu.tr](mailto:hilalkivrak@yyu.edu.tr)

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Carbon supported Pd catalyst was prepared with microwave-assisted polyol method (M-Pd@C) and investigated sensing activity for non-enzymatic hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Moreover, M-Pd@C and Pd@C catalyst which synthesized via polyol method (P-Pd@C) were compared to each other in terms of electrocatalytic activity. X-ray diffraction (XRD), X-ray photo electron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate structural and morphological properties of these catalysts. Furthermore, electrochemical measurements were performed via cyclic voltammetry (CV), chronoamperometry (CA) techniques. CV results exhibited that M-Pd/C catalyst showed perfect electrocatalytic activity in terms of reduction of H<sub>2</sub>O<sub>2</sub>. M-Pd/C catalyst showed a fast response of less than 7 s with a linear range of 5.0×10<sup>-3</sup>-11.0 mM and a relatively low detection limit of 1.2 µM amperometric response. M-Pd/C catalyst exhibited great selectivity for detecting H<sub>2</sub>O<sub>2</sub> in the existence of several hindering species such as uric acid and ascorbic acid.

**Keywords:** Pd nanoparticles, microwave assisted polyol method, non-enzymatic, hydrogen peroxide sensor

### 1. INTRODUCTION

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is a well-recognized oxidant and it could obtain from by-product of various oxidase enzymes. On the other hand, it was used as essential mediator for several analysis such as environmental, food, clinical, pharmaceutical, industrial and environmental analysis [1, 2]. Moreover, H<sub>2</sub>O<sub>2</sub> is very crucial indicator in terms of oxidative stress and it used as precursor for formation of hydroxyl radicals which are greatly reactive and hazardous. Consequently, it is clear that

there is an increasing demand for fast, reusable, high sensitivity, cost-effective and safety  $H_2O_2$  sensors.

Particularly, application of the electrochemical method using an enzyme modified electrode is widespread. Because it is precise, uncomplicated and fast analytical process. The activity of the immobilized enzymes affect the sensitivity of these sensors. Nevertheless, one prevalent disadvantage of enzymatic sensors is inadequate stability arising from the structure of the enzymes, since enzymes are easily deformable in term of thermally and chemically during production, storing, or utilization.

Several analytic methods such as spectrophotometry [3], chromatography [4], chemiluminescence [5], colorimetry [6] and electrochemistry [7-9] are suitable for assignment of  $H_2O_2$ . Among these methods, electrochemical sensors are attractive choice, due to their simplicity, practicality, and low-cost. On the other hand in the recent past, publications related to enzyme-free electrochemical sensors became plentiful.

Many kinds of nanomaterials have been used for constructing enzyme-free  $H_2O_2$  electrochemical sensors [10-12]. Metal NPs, peculiarly transition metal NPs, are well-recognized as great catalysts, because their properties are in harmony with multiple oxidation states and their adsorption property is suitable for other materials. Moreover, owing to their nano-size, they show unprecedented benefits of mass transport improvement, high effective surface area and size controlled electrical activity, which are beneficial in improving determination performance for  $H_2O_2$ .

Noble metals for making NPs for enzyme-free sensing of  $H_2O_2$  include Pt [13], Pd [14-16], Au [17], and Ag [18] etc. Among these NPs, palladium is usually preferred to modify the electrodes because it has excellent electrocatalytic activity and is relatively inexpensive [19].

PdNPs usually prepared by electrochemical deposition [20-23] or chemical reduction [22, 24] methods for sensing applications. However, the most difficult challenge for researches is to control the particle size. In this respect, controlled size and shape metal particles can be prepared via polyol synthesis. The polyol process which is carried out with conventional heating take a long preparation time while microwave heating is selective and has more advantage in terms of time and energy consumption. Therefore, microwave assisted polyol is a unrivaled method so as to prepare nanoparticles with the aforesaid superiority.

In this work, a novel electrochemical sensor is prepared via assisted microwave irradiation with polyol process, a well-established way performed for monodisperse metal powders, includes a redox reaction between a metallic compound and a liquid polyol (ethylene glycol). Nevertheless, microwave irradiation is a method which has been applied lots of implementations in synthetic chemistry and has been reported to have many superiorities rather than traditional synthesis methods. When the materials which have microwave absorbing properties get heated, the presence of side reactions can be extinguished. Furthermore, microwave irradiation enable to perform reproducibility tests and accelerate the synthesis, so it is a crucial advantage in terms of time.

This work points out the significance of the performed microwave heating technology so as to synthesize the Pd catalyst. The essential aim of this work is to demonstrate the influence of microwave and the advantage of this novel method is to find out against other conventional techniques. The Pd catalyst modified electrode was tested for non-enzymatic detection of  $H_2O_2$ .

## 2. EXPERIMENTAL

### 2.1. Preparation of electrocatalysts

20 wt% Pd-containing Pd/C catalysts were synthesized via microwave-assisted polyol method in polyol solution with PdCl<sub>2</sub> as a precursor salt. Concisely, Vulcan XC-72 Carbon Black was treated via 4.0 M HNO<sub>3</sub> (thank to this operation, it was provided increasing of hydrophilic functional groups) and impregnation method was applied with 1 mL of 0.0565 M PdCl<sub>2</sub>. Then it was combined with 4 mL 0.12 M KBr. 5 mL 0.05 M NaOH was added drop by drop under magnetic stirring, after ultrasonic treatment for 1 h. PdCl<sub>2</sub>, KBr and NaOH were solved in glycerol or other solvents and the solution was inserted a microwave reactor (Anton Paar monowave 300) and then heated for 2 min at 130 °C. Eventually, filtration and washing with distilled water and ethanol were employed the samples. It was dried in a vacuum oven for 2 hours. The other 20 wt% Pd-containing Pd/C catalysts were prepared by following the same procedure except microwave heating. Instead of microwave heating, the catalyst slurry was refluxed at 130 °C under argon atmosphere during 2 h. Then the sample filtered, washed, and dried.

### 2.2 Characterization of electrocatalysts

X-ray diffraction (XRD) patterns of the M-Pd/C catalyst were collected between  $2\theta = 10.0\text{--}85.0^\circ$  with  $0.05^\circ$  intervals on a Bruker D 8 Advance X-ray diffractometer using Cu-K $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) as a radiation source. Surface information of M-Pd/C and P-Pd/C catalysts was recorded by X-ray photoelectron spectroscopy (XPS, SPECS) using X-ray tube working at 15 kV and 350 W with Mg-K $\alpha$  ( $h\nu = 1253.6 \text{ eV}$ ) unmonochromatized radiation. A transmission electron microscope (TEM) was used for characterization of the M-Pd/C catalyst in terms of its morphological properties.

### 2.3. Preparation of working electrode

The surface of the glassy carbon electrode polished with alumina before electrode preparation and the electrode was prepared following procedure. 5 mg catalyst was added in 1 mL Aldrich 0.5% Nafion® solution so that catalyst ink was obtained and 5  $\mu\text{L}$  of the ink was overlaid the surface of the glassy carbon electrode. Drying process was employed to prepared electrode at room temperature in order to eliminate the solvent.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out on a CHI 660A electrochemical workstation with a three-electrode system comprising an Ag/AgCl, a platinum wire electrode and modified GCE ( $\Phi=3 \text{ mm}$ ) which used as the reference electrode, the auxiliary electrode and the working electrode, respectively. All potentials in this study were mentioned according to reference electrode. Prior to experiments, deaeration of the electrolytes process is applied by means of bubbling with high-purity nitrogen for 30 min. Cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) experiments were performed in a phosphate buffer solution at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization results

XRD pattern of M-Pd/C catalyst is illustrated in Figure 1. XRD pattern of this catalyst exhibits a diffraction peak at around  $20^\circ$  value, related to the (002) reflection of the structure of hexagonal carbon (JCPDS card no 75-1621). Furthermore, XRD pattern of M-Pd/C catalyst have (111), (200), (220), and (311) planes, revealing that this catalyst Pd face-centered cubic (fcc) structure (JCPDS card no 46-1043).

In this study, Pd oxidation state and the interaction between carbon support and palladium metal were determined by XPS. Figure 2a and Figure 2b shows the XPS survey spectra of M-Pd/C and P-Pd/C catalysts, respectively. XPS survey spectra were dominated by Pd and C signals. For M-Pd@C, the atomic percentages predicted from XPS are given as 75.7% for C1s, 19.5% for O1s, 4.5% for Pd 3d, and 0.3% Br 3d on the Figure 2a. In addition, XPS survey spectra of P-Pd/C catalyst given in Figure 2b shows that 65 % for C1s, 26.9 % for O1s, and 7.3% for Pd 3d, 0.3 % for Br 3d, 0.5% for S 2p. One can see that trace amount of Br and S peaks are observed for both of the catalyst. These impurities come from the reducing agents used during the preparation.

C 1s spectra of M-Pd/C and P-Pd/C catalysts are given in Figure 3. C1s peaks are detected at the binding energy ranges of 284.3 eV for M-Pd/C and 284.4 eV for P-Pd/C catalysts. The charging effects were corrected by using the C 1s peak, as reference for all samples at a binding energy (BE) of 284.5 eV. Hence, the O1s and Pd 3d spectra shift 0.2 eV for M-Pd/C and 0.1 eV for P-Pd/C catalysts. Figure 4 illustrates O1s spectrum of M-Pd/C and P-Pd/C catalysts. One can see that the O1s peaks appear at 533.6 eV for M-Pd/C and 532.5 eV for P-Pd/C catalyst. Figure 5 shows the Pd 3d core level spectra of M-Pd/C and P-Pd/C for high and low energy bands. Considering M-Pd@C, an intensive doublet is noticed 335.3 and 340.7 eV, indicating the metallic Pd. These doublet binding energies are 335.2 and 340.5 eV for P-Pd@C. Pd 3d<sub>5/2</sub> core level spectra shifted from the probable 335.3 eV to 335.2 eV for M-Pd/C catalyst compared to P-Pd@C. One could notice that Pd 3d<sub>5/2</sub> peak shifts slightly (+0.1 eV) to higher binding energies, indicating that the electronic structure of Pd are different for these catalysts [25]. As a result, oxidation state of the catalyst changes when microwave assisted synthesis route is used [25].

The 500 nm, 100 nm, and 50 nm magnification TEM images of the synthesized M-Pd@C, catalysts are shown in Figure 6a-d. Particles are not homogeneously distributed. There are two types of particles: (i) particles which have a high particle size and (ii) particles have small particle size clearly seen at 50 nm magnification images. The existence of particles having high particle size could be ascribed to the existence of Pd oxide particles on the surface. On the other hand, smaller particles on the surface could show the existence of metallic Pd.

## 3.2. Electrochemical performance

### 3.2.1. Cyclic voltammetric studies

The electrochemical properties of Pd/C electrodes were studied in 0.1 M phosphate buffer solution, using cyclic voltammetry recorded between  $-0.7$  to  $0.8$  V vs. Ag/AgCl at scan rate of  $50 \text{ mV s}^{-1}$ . The cyclic voltammograms of glassy carbon electrode modified P-Pd/C and M-Pd/C in the absence and presence of  $\text{H}_2\text{O}_2$  in 0.1 M phosphate buffer solution at pH 7.5 is presented in Fig. 7. P-Pd/C and M-Pd/C modified electrode showed no obvious peak in the absence (curve a) of  $\text{H}_2\text{O}_2$  (Fig. 7A). In the presence of  $\text{H}_2\text{O}_2$ , the electrode shows excellent catalytic activity toward  $\text{H}_2\text{O}_2$  without using any enzyme at  $-0.3$  V. However, the reduction current of M-Pd/C modified electrode was much higher

compared with that of P-Pd@C. Moreover, H<sub>2</sub>O<sub>2</sub> reduction current increased with increasing the concentration of H<sub>2</sub>O<sub>2</sub>, as shown in Fig. 7C. The increase in peak current is pointed out that M-Pd/C catalyst has higher electrocatalytic activity towards H<sub>2</sub>O<sub>2</sub> than P-Pd/C catalyst. This result is attributed to the presence of small sized Pd nanoparticles observed at TEM images. These small nanoparticles increase the effective surface area of the catalyst [26-28]. Hence, the catalytic activity enhanced and current response of microwave assisted Pd increased.

### 3.2.2. Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) was used to study the interfacial properties at Pd/C modified electrodes in N<sub>2</sub> saturated 0.1 M phosphate buffer solution. The frequency range was between 0.02 and 100000 Hz with signal amplitude of 10 mV. The Nyquist plots of (a) bare, (b) M-Pd/C and (c) P-Pd/C glassy carbon electrodes was presented in Fig. 8. The diameter of the semicircle corresponds to the electron transfer resistance (R<sub>ct</sub>) at the electrode. The impedance spectrum of bare GCE exhibits an almost straight line, which implies the characteristic of a diffuse limiting step of the electrochemical processes. After surface modification with Pd/C, the semicircle appeared which indicates that the nanocatalysts have been attached to the electrode surface. It can be seen that the R<sub>ct</sub> value of M-Pd/C modified electrode obtained as 2600 Ω (curve b) which is smaller than that for the P-Pd/C (R<sub>ct</sub>= 5600 Ω, curve c), indicating that the microwave preparation method for Pd/C facilitates electron transfer between the electrode and the redox probe.

### 3.2.3. Chronoamperometric studies

The performance of the M-Pd/C modified electrode was further evaluated by chronoamperometric method. Fig. 9 shows the amperometric responses of M-Pd/C modified electrode for successive additions of H<sub>2</sub>O<sub>2</sub> into the stirring phosphate buffer solution at -0.30 versus Ag/AgCl. The M-Pd/C modified electrode responds rapidly to the changes in H<sub>2</sub>O<sub>2</sub> concentration, producing steady-state signals less than 7 s. The right upper inset of Fig. 8 shows the corresponding calibration curve for H<sub>2</sub>O<sub>2</sub> analysis. The M-Pd/C modified electrode showed a linearly increased amperometric responses to H<sub>2</sub>O<sub>2</sub> ranging from 5.0×10<sup>-3</sup> to 11.0 mM with a correlation coefficient of 0.999 and the detection limit of 1.2×10<sup>-3</sup> mM when S/N was 3. Moreover, the sensitivity calculated for the system was found to be 206.67 μA mM<sup>-1</sup> cm<sup>-2</sup>. For comparison, the analytical parameters obtained with different Pd NPs based H<sub>2</sub>O<sub>2</sub> sensors are listed in Table 1, including applied potential, linear range, sensitivity, and detection limit.

**Table 1.** Comparison of the performance of different H<sub>2</sub>O<sub>2</sub> sensors

| Catalyst         | Applied Potential (V) | Linear range (mM) | Sensitivity (μA mM <sup>-1</sup> cm <sup>-2</sup> ) | Detection Limit (μM) | Reference |
|------------------|-----------------------|-------------------|---|----------------------|-----------|
| PdNP-GNs/GCE     | -0.30 (SCE)           | 0.1–10            | 313.4   | 0.05                 | [15]      |
| Pd NPs/GCEs      | -0.11 (SCE)           | 0.001–6.0         | 50.9  | 0.34                 | [16]      |
| PdNP/GCE         | -0.4 (SCE)            | 0.001–3.0         | 70.8  | 0.32                 | [19]      |
| Pd/CNF/CPE       | -0.20 (Ag/AgCl)       | 0.0002–20         | 4.15  | 0.2                  | [20]      |
| Pd-PEI/GO/GC     | -0.25 (SCE)           | 0.5–459           | 0.2   | 2.5                  | [21]      |
| PdNP/MCV/GC<br>E | -0.20 (Ag/AgCl)       | 0.0001–6.1        | 228.5   | 0.079                | [24]      |
| Pd@C/GCE         | -0.30 (Ag/AgCl)       | 0.005–11          | 206.67  | 1.2                  | This work |

It can be seen that M-Pd/C modified electrode shows comparable and even better analytical performance in literature in one or more categories.

The stability of the M-Pd/C modified electrode was investigated. The response current of the modified electrode was measured at intervals of one week and kept in 0.01 M phosphate buffer solution (pH 7.5) at room temperature ( $25 \pm 1^\circ\text{C}$ ) when not in use. The M-Pd/C modified electrode current response to electrocatalytic reduction of  $\text{H}_2\text{O}_2$  was found to remain at 94.6% of its initial current value after 27 days, indicating good long-term stability. The relative standard deviation (RSD) of the current response to 0.5 mM  $\text{H}_2\text{O}_2$  was 4.7% for 6 successive measurements which proved that the sensor also had good repeatability. Moreover, the amperometric measurements with the independently prepared six electrodes showed an acceptable reproducibility with a relative standard deviation of 4.5% for the current determined at 0.5 mM  $\text{H}_2\text{O}_2$ . Finally, in experiments, the selectivity of the sensor was tested by studying the effects of possible interference species such as ascorbic acid (AA), uric acid (UA), catechol (CA) and dopamine (DA). These experiments were conducted with successive additions of 0.1 mM  $\text{H}_2\text{O}_2$ , AA, UA, DA, CA and  $\text{H}_2\text{O}_2$ . It is seen that these interference species give negligible signal changes, as shown in Fig. 10. As has been mentioned above, microwaved synthesis increases the surface area, facilitating the electron and mass transfer.

The practical applicability of the prepared sensor in real sample was also examined. The commercial sample which is used as antiseptic solution is labeled to contain 3% w/v of  $\text{H}_2\text{O}_2$ . The commercial solutions were diluted 100 times in phosphate buffer solution; the diluted samples were analyzed with the M-Pd/C modified electrode by chronoamperometric method. The concentration of  $\text{H}_2\text{O}_2$  was calculated using the present sensor and  $\text{KMnO}_4$  titration method. The results obtained are presented in Table 2. In comparison with titration method, the relative standard deviation (RSD) values for the proposed sensor are lower. The relative standard deviation of each sample for six successive determinations is less than 4.3%. In addition, the recovery ratio on the basis of this method was investigated, and the value is between 100.44 and 97.33%. The recovered ratio shows that the determination of  $\text{H}_2\text{O}_2$  using the M-Pd/C modified electrode is effective and can be applied for the detection of  $\text{H}_2\text{O}_2$  in real samples.

**Table 2.** Determination of  $\text{H}_2\text{O}_2$  in antiseptic solution (n=6) by the present sensor and titration method.

| Sample | This sensor             |                         |              |         | $\text{KMnO}_4$ titration method |                         |              |         |
|--------|-------------------------|-------------------------|--------------|---------|----------------------------------|-------------------------|--------------|---------|
|        | Added ( $\mu\text{M}$ ) | Found ( $\mu\text{M}$ ) | Recovery (%) | RSD (%) | Added ( $\mu\text{M}$ )          | Found ( $\mu\text{M}$ ) | Recovery (%) | RSD (%) |
| 1      | 150                     | 148                     | 98.67        | 4.3     | 150                              | 147                     | 98.00        | 4.7     |
| 2      | 300                     | 292                     | 97.33        | 3.5     | 300                              | 290                     | 96.67        | 3.9     |
| 3      | 450                     | 452                     | 100.44       | 2.7     | 450                              | 443                     | 98.44        | 3.1     |

#### 4. CONCLUSIONS

In summary, Pd/C has been simply prepared both polyol and microwave assisted polyol method. Most importantly, M-Pd/C is found to exhibit good catalytic activity toward the reduction of

H<sub>2</sub>O<sub>2</sub>. This study is significant because it provides us a facile method for the preparation of carbon supported Pd nanocatalyst for sensing and other applications.

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