An electrochemical sensor based on 1,4-benzenedimethaneamine functionalized graphene supported palladium (GO-BDMA-Pd) nanoparticles (NPs) has been synthesized and employed as an efficient electrocatalyst for formaldehyde (HCHO) oxidation reaction (FOR). The physical characterization of the sensor has studied via transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). TEM study has revealed good dispersion of PdNPs onto the GO-BDMA surface. The electrochemical properties of the sensor for FOR have been studied by different electrochemical techniques including cyclic voltammetry, differential pulse voltammetry and chronoamperometry in 1 M KOH. The proposed sensor has shown high sensitivity, good stability and fast response to HCHO. The oxidation peak current has followed a linear relationship with the HCHO concentration in the range of $1 \times 10^{-6}$–$1.8 \times 10^{-2}$ M with limit of detection $3.5 \times 10^{-7}$ M ($S/N = 3$). The experimental data further reveals that the electrooxidation of HCHO by proposed GO-BDMA-Pd sensor inhibits the formation of the poisonous intermediate, such as CO.

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In last few years, small organic molecules like acetic acid, methanol, ethanol and formaldehyde (HCHO) have gathered huge attention due to their potential applications in low temperature fuel cells.1–4 Among these molecules, HCHO has prompted itself as a model to look insight electrooxidation process, a subject of ensured attention in fuel cell technology progression.5 HCHO is an extremely important industrial raw material due to its high purity, relative cheapness and chemical activity. HCHO is found in more than 2000 products6 including soap, shampoo, detergents, and as a sterilizing agent in medicine and pharmacology. Instead, HCHO is also a natural metabolite of living organisms, found in vegetables, fruits, flesh7 and biological fluids of human origin.8 A level of 0.5 to 2 μM was permitted in industrial areas9 because it badly affects central nervous, immune and blood system of humans which could result in stunted growth, blindness and respiratory disorder.7 All these facts convincingly demonstrate the requirement of simple and sensitive method for determination of HCHO in specific biotechnological processes, medicine, environmental control and even for food and drinking water analysis.

Different analytical methods such as, gas chromatography,8 spectrophotometry,9 high performance liquid chromatography10 and electrochemical sensors11 have been reported for HCHO determination in food, air, water and wood. Among these methods electrochemical sensors have been widely researched due to their low cost, sensitivity and simplicity of design and operation. In the area of electrochemical sensors, various metal NPs such as Au, Ag, Pd, and Pt are well-known for their remarkable electrocatalytic properties,12–15 highly effective surface area and extraordinary electron transport nature. Their use as electrochemical interfaces provides a rapid current response and high detection sensitivity. Consequently, the electron transfer between the electrode and the probe molecule is accelerated.16,17 The Pd has high catalytic activities in the electrooxidation of small organic molecules and used as a catalyst in many chemical reactions including alcohol oxidation and oxygen reduction in fuel cells18–20 and sensor reaction.21,22 Pd is preferred over Au and Pt because of its low price, better catalytic activity and higher resistance to CO poisoning than that of Pt.21,24 Metal NPs are not stable enough onto bare electrode; therefore, an appropriate supporting material is required to anchor them to ensure their extended life.12 The choice of a suitable supporting material is an important factor that may affect the performance of supported electrocatalysts, owing to the support-catalyst interactions and surface reactivity.23 A derivative of benzylamine molecules, 1,4-benzenedimethaneamine (BDMA) having two amino linkers on opposite sides acts as a stabilizer for metal NPs. These oppositely positioned –NH2 group are suitable to react with acid group via condensation reaction to form a C–N bond.12,23

Graphene or reduced graphene oxide (rGO) is an extendable 2D carbon sheet, in which carbon atoms are packed in a hexagonal lattice like a honeycomb. Numerous fascinating properties including high specific surface area, excellent mechanical strength and flexibility, and unparalleled thermal and electrical conductivity as well as superior electronic properties are making it as a perfect support material for metal NPs-based nanosized catalysts.24–29 Graphene oxide (GO) is a single layer oxidized derivative of graphene which has abundant functional groups such as, hydroxyl, epoxy, carboxyl and ketone groups.30 Therefore, a reaction between the functional groups of GO and the amine groups of an amine terminated molecule should easily occur. The introduction of a heterocyclic compound onto the graphene sheet yielded a large surface active group to volume ratio, superb thermal stability, good mechanical and electrical properties.30

In this study, we synthesized an electrochemical sensor for the determination of HCHO using BDMA functionalized graphene with PdNPs (GO-BDMA-Pd). The GO-BDMA-Pd was electrochemically reduced which efficiently removed the oxygen containing functional groups from GO and exposed the electronically active material.31 The electrocatalytic behavior of the GO-BDMA-Pd sensor has been studied by several techniques including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CA) in 1 M KOH alkaline solution. The experimental data showed high electrocatalytic activity and good tolerance to CO poisoning giving superiority to many of the previously reported HCHO sensors.

**Experimental**

**Materials and chemicals.**—The graphite powder (~325 mesh 99.999%), BDMA (C8H12N2), sodium borohydride (NaBH4), potassium tetrachloropalladate (II) (K2PdCl4), and HCHO were purchased from Aldrich Chemical Co., South Korea. The KMnO4, H3PO4, H2SO4 and KOH were purchased from Daewoong Co., South Korea. All reagents used were of analytical grade and without further purification. Doubly distilled water was used in the preparation of the aqueous electrolyte solutions. All electrochemical experiments were performed at room temperature. Before all electrochemical experiments the dissolved oxygen was removed from the solution by bubbling high purity argon (Ar).

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*Graphene Supported Palladium for Formaldehyde Oxidation Reaction in Alkaline Media*
Instrumental.— All electrochemical experiments employed one compartment three electrode electrochemical cell with a modified glassy carbon electrode (GCE, 3 mm diameter) as working electrode, a platinum wire as auxiliary electrode and an Ag/AgCl (3 M NaCl solution) served as reference electrode. Electrochemical experiments were performed on a CHI electrochemical workstation (CH instrument, Inc., USA). The morphology of the material was examined using a JEM-2100F JEOL field emission transmission electron microscopy (FE-TEM) and X-ray photoelectron spectroscopy (XPS) measurements were performed on a MultiLab 2000 spectrometer (ThermoVG Scientific, Southend-on-sea, Essex, UK) in an ultra-high vacuum chamber.

Synthesis of GO-BDMA-Pd.— GO was obtained by oxidizing graphite using the improved Hummers method. Briefly, a mixture of concentrated H₂SO₄:H₃PO₄ (360:40 mL) was added to a mixture of graphite powder KMnO₄ (3:18 g) at 50 °C and resulting mixture was stirred for 12 h. The reaction was cooled to room temperature and was transferred onto ice with 30% H₂O₂ (3 mL). The obtained solution was centrifuged and then filtered. The solid material obtained was washed with water and 30% HCl, followed by finally washing with distilled water. Finally GO-BDMA-Pd was obtained after drying the product at 50 °C in vacuum.

Preparation of modified electrode.— A GCE was polished before each experiment with 0.05 μM alumina slurry, washed thoroughly with distilled water and finally rinsed with methanol. For electrode preparation, a GO-BDMA-Pd suspension in water (1 mg mL⁻¹) was mixed with aqueous solution of BDMA (1 mg mL⁻¹) in round bottom flask equipped with a magnetic stirring bar. After 30 minutes stirring, 5 mM K₂PdCl₄ solution (16.324 mg in 10 mL H₂O) was added by continuing stirring followed by the addition of reducing agent 1% NaBH₄ (500 μL) to the solution. The mixture was then continued stirring for 8 hours by providing 130 °C temperatures. After refluxing the black product was washed and filtered three times with distilled water. Finally GO-BDMA-Pd was obtained after drying the product at 50 °C in vacuum for 24 h. For comparison GO-Pd and GO-BDMA were also prepared following same method except BDMA and Pd addition, respectively.

Real sample preparation.— Exactly 1 g of tomato sauce (Ottogi tomato ketchup (43.8% tomato paste), Gwangju, South Korea; collected from local market) was dissolved in 100 mL distilled water and subsequently sonicated for 10 min. This homogeneous solution was then filtered and finally centrifuged for 10 min at 6000 RPM. A clear tomato sauce solution was obtained without addition of extra distilled water which was subjected to analysis.

Results and Discussion

Characterization of the catalyst.— To understand the surface morphology of the as prepared GO-BDMA-Pd catalyst, TEM images were taken at high resolution. Figure 2a shows GO-BDMA sheet while Figures 2b, 2c shows an extraordinary good distribution of 2–3 nm sized PdNPs on the surface of GO-BDMA at different magnifications. Moreover, magnified TEM images also revealed the lattice interplanar spacings of 0.225 nm which represents Pd (111) shown in Figure 2d.

XPS was employed to substantiate the surface compositional analysis and to predict the oxidation state of the metal in GO-Pd, GO-BDMA and GO-BDMA-Pd catalyst. Figure 3a shows the characteristic C1s (~285.08 eV), O1s (~532.58 eV), N1s (~400 eV) photoemission peaks followed by the appearance of several Pd peaks with most distinguished Pd3d peak at 337 eV for GO-Pd and GO-BDMA-Pd. The appearance of N1s peak is in GO-BDMA and GO-BDMA-Pd catalyst due to the functionalization of BDMA with GO. Figure 3b shows C1s core level spectra of the GO-Pd, GO-BDMA and GO-BDMA-Pd catalyst. The spectrum comprises four different components. The peaks at 285.08, 286.12, 287.93 and 289.21 eV corresponds to graphitic sp², sp³ and oxygen containing functional groups such as C–OH and O–C=O, respectively. The O1s core level spectrum in Figure 3c shows the presence of C–OH, O–H and O–C=O bonds at 533.36, 532.16 and 531.24 eV, respectively. The O1s core level spectrum presented in Figure 3d shows a C–NH peak only in GO-BDMA-Pd at 399.47 eV contributed to the higher C1s intensity (68.15%) of the GO-BDMA-Pd on GO-BDMA (64.41%).

Figure 3e shows the doublet Pd3d spectra of GO-Pd and GO-BDMA-Pd. The peak of high energy band (Pd3d₅/₂) and a low energy band (Pd3d₃/₂) at 342.89, 336.2 eV, respectively, for GO-Pd and 341.65, 336.07 for GO-BDMA-Pd indicates the presence of GO-BDMA-Pd in different interacting environment. Furthermore, other weak peaks at 340.83 and 335.55 eV for GO-Pd and 343.35 and 338.12 eV for GO-BDMA-Pd can be assigned to Pd²⁺ ions. It reveals that Pd²⁺ have been reduced to main metallic form Pd⁰ upon chemical reduction by NaBH₄.

Electrochemical study.— The electrooxidation of HCHO at the surface of bare GCE, GO-Pd, and GO-BDMA-Pd was investigated by CV in 1 M KOH solution at 0.05 V s⁻¹ scan rate. Typical results
Figure 3. (a) survey core level regions XPS spectra, (b) C1s, (c) O1s of GO-Pd, GO-BDMA and GO-BDMA-Pd, (d) N1s of GO-BDMA and GO-BDMA-Pd and (e) Pd3d of GO-Pd and GO-BDMA-Pd.

obtained for a potential scan from $-1.2$ to $0.2$ V vs. Ag/AgCl has shown in Figure 4. Addition of $0.03$ M HCHO gave no identical signal for FOR on bare GCE. This indicates that bare GCE has no electrocatalytic activity toward HCHO oxidation at this concentration. On the other hand, the FOR indicating peaks in both forward and backward scans at GO-Pd and GO-BDMA-Pd electrode can be observed in the presence of $0.03$ M HCHO. A well-defined anodic peak was observed in both cases with $75\%$ larger peak current intensity by GO-BDMA-Pd than that of GO-Pd. It signifies that the BDMA benefited the dispersion of PdNPs and provided larger surface area and more active sites to catalyze the oxidation of HCHO. This suggests GO-BDMA-Pd a better catalyst for HCHO oxidation than GO-Pd. The electrochemical response of GO-BDMA-Pd and GO-Pd in the absence of HCHO shows a tiny peak around $-0.4$ attributed to the reduction of $\text{Pd}^{2+}$ to $\text{Pd}^0$ formed during the backward scan (Figure 4 inset).2,3,38 Also, the background current is almost similar at both modified electrodes which suggesting an equal electrochemical behavior of both electrodes.

This corresponds to the following equations (eq.):

$$\text{Pd} + \text{H}_2\text{O} \rightarrow \text{Pd(OH)}_{\text{ads}} + \text{H}^+ + e^- \quad [1]$$

$$\text{Pd(OH)}_{\text{ads}} + \text{Pd(OH)}_{\text{ads}} \rightarrow \text{PdO} + \text{H}_2\text{O} \quad [2]$$

$$\text{PdO} + \text{H}_2\text{O} + 2e^- \rightarrow \text{Pd} + 2\text{OH}^- \quad [3]$$

Adsorption of OH$^-$ usually takes place at lower anodic potential (Eq. 1) whereas the formation of Pd oxides occurs at higher positive potential (Eq. 2). During negative potential sweep, the reduction of Pd oxides shown in (Eq. 3) results in the reactivation of the electrocatalyst surface.

Figure 4. CVs recorded in $1$ M KOH at $0.05$ V s$^{-1}$ scan rate on bare GCE, GO-Pd and GO-BDMA-Pd in the presence of $0.03$ M HCHO, inset: CV on GO-BDMA-Pd and GO-Pd in $1$ M KOH.
Figure 5. Voltammetric response of GO-BDMA-Pd for 0.01 M HCHO in 1 M KOH at various scan rate (0.05, 0.08, 0.12, 0.16, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6, 0.7, 0.8 and 0.9 V s⁻¹), inset: plot of oxidation peak current vs. scan rate (V s⁻¹).

Effect of scan rate toward FOR.—Electrochemical response of GO-BDMA-Pd was investigated in 0.01 M HCHO containing 1 M KOH at various scan rates ranging from 0.03 to 0.9 V s⁻¹. In Figure 5 Peak at −0.16 shows oxidation of HCHO to CO₂ with increase in anodic peak current and slight oxidation peak potential shifting toward more positive value with increasing scan rate.

Figure 5 inset shows a good linear relationship between the oxidation peak current and scan rate (0.05 to 0.9 V s⁻¹) following the linear regression eq. \( i_p = -0.4038 \times [\text{HCHO}] (mM) - 119.27 \) with a correlation coefficient of 0.998 suggest that the oxidation is controlled by an adsorptive process.

Effect of concentration toward FOR.—Figure 6 depicts the voltammetric response of GO-BDMA-Pd electrode in the presence of different HCHO concentrations in 1 M KOH solution at 0.05 V s⁻¹ scan rate. It can be seen that increase in HCHO concentration shifted oxidation peak potential toward more positive value with increase in anodic current. Nobel metals like Pt and Pd are initially good catalyst for electrooxidation of small organic molecules but as the reaction proceeds, formation of CO a poisonous intermediate obstruct the complete oxidation of HCHO is the direct path in which HCHO is directly converted to CO₂ through a dehydrogenation reaction.

According to the below eqs., adsorbed OH⁻ ion onto Pd surface [Pd(OH)ads] (Eq. 1) are involved in the direct oxidation of HCHO to its final product CO₂. In this reaction pathway, Pd(CHO)ads can be directly dissociated into two different intermediates Pd(CO)ads and Pd(COOH)ads through pathway 1 and 2, at pathway 1 produces COads which acts as an electron fouling intermediate and Pd(COOH)ads directly oxidizing to CO₂. This COads species could be desorbed from the surface in a reaction with Pd(OH)ads oxidizing to CO₂ which is actually the resulting of backward peak. It is, however, the ratio of the forward peak current (\( i_f \)) and the backward peak current (\( i_b \)), \( i_f/i_b \), is generally used to determine the poisoning tolerance to the carbonaceous species for Pd catalysts. Also, a higher ratio of \( i_f/i_b \) is attributed to more efficient oxidation and less accumulation of carbonaceous species to the catalysts. The \( i_f/i_b \) of GO-BDMA-Pd (2.3) is higher than that of GO-Pd electrode (1.5). Indicating the GO-BDMA-Pd has much more tolerant toward CO poisoning or the FOR goes through both pathways 1 and 2 with minimal production of CO intermediate. In this regards, it could be rationally assumed that the FOR goes 65% through pathway 1, which producing COads at GO-BDMA-Pd electrode than that of GO-Pd (100%).

\[
Pd + (\text{HCHO})_{\text{sol}} \rightarrow \text{Pd}(\text{HCHO})_{\text{ads}} \rightarrow \text{Pd} + \text{Pd}(\text{CHO})_{\text{ads}} \rightarrow \text{Pd} + \text{Pd}(\text{CO})_{\text{ads}} + \text{Pd}(\text{COOH})_{\text{ads}} \rightarrow \text{2Pd} + \text{CO}_2
\]

Table I. Comparison of the efficiency of GO-BDMA-Pd electrode with some of the previously reported electrode for HCHO oxidation.

| Modified Electrode | Electrolyte   | HCHO (mol L⁻¹) | Current (mA cm⁻²) | Scan rate (mV s⁻¹) | Refs. |
|--------------------|---------------|----------------|-------------------|-------------------|-------|
| Nano Pd           | 1 M NaOH      | 0.02           | 66.96             | 50                | 38    |
| Rh nanostructured | 0.5 M NaOH    | 0.5            | 0.52              | 50                | 40    |
| Nanoporous silver | 0.9 M KOH     | 0.3            | 35                | 20                | 41    |
| Ag/CMK-3 nanocatalyst | 1 M KOH | 1              | 112               | 100               | 42    |
| Ag nanorod catalyst | 1 M KOH   | 1              | 118               | 100               | 43    |
| Ag nanoprisms     | 1 M NaOH      | 0.1            | 4.5               | 50                | 44    |
| BDD                | 0.5 M K₂SO₄   | 0.08           | 82                | 100               | 45    |
| GO-BDMA-Pd        | 1 M KOH       | 0.1            | 50.24             | 50                | This work |
According to Table I, our proposed electrochemical sensor, GO-BDMA-Pd, has a good electrocatalytic response toward FOR while it showed comparatively higher current density (50.247 mA cm\(^{-2}\)) for 0.1 M HCHO.

**Table II.** Comparison of the GO-BDMA-Pd electrode for various parameters with previously reported HCHO electrodes.

| Modified Electrode | Electrolyte                  | Potential (V) | Linear Range (M) | LOD (µM) | Refs. |
|--------------------|------------------------------|---------------|------------------|---------|-------|
| Ti/TiO\(_2\)       | PBS, pH 7                    | 0.8           | 6.7 \times 10\(^{-4}\)–1.48 \times 10\(^{-2}\) | 310     |       |
| Si/SiO\(_2\)/Si\(_3\)N\(_4\) | 2.5 mM BB,\(^{a}\) pH 8.4 | -             | 1 \times 10\(^{-7}\)–2 \times 10\(^{-4}\) | 10      | 13    |
| Pd NW/GCE          | 0.1 M KOH                    | 0.05          | 2 \times 10\(^{-6}\)–1 \times 10\(^{-3}\) | 0.5     | 16    |
| Pd/GC/CV electrode | 0.1 M NaOH                   | -0.06         | 3 \times 10\(^{-6}\)–14 \times 10\(^{-3}\) | 10      | 16    |
| Nano Pd electrode  | 1 M NaOH                     | -0.45         | 0–20 \times 10\(^{-5}\) | 38.6    | 38    |
| Pd-modified TiO\(_2\) | 0.1 M NaOH               | -0.40         | 0–17.7 \times 10\(^{-3}\) | 15      | 46    |
| Pt/Pt/PANI/MWNCS   | 0.5 M H\(_2\)SO\(_4\)       | 0.3           | 1 \times 10\(^{-6}\)–1 \times 10\(^{-3}\) | 0.046   | 47    |
| Pt–Pd–Pt/Nafion    | 0.1 M H\(_2\)SO\(_4\)       | 0.57          | 1 \times 10\(^{-6}\)–1 \times 10\(^{-3}\) | 3       | 48    |
| Ni(OH)\(_2\)/Ni electrode | 0.5 M NaOH         | 0.44          | 70 \times 10\(^{-6}\)–16 \times 10\(^{-3}\) | 20      | 49    |
| GO-BDMA-Pd         | 1 M KOH                      | -0.1          | 1 \times 10\(^{-6}\)–1.8 \times 10\(^{-2}\) | 0.35    | This work |

\(^{a}\)borate buffer

**Figure 7.** Differential pulse voltammetric studies of GO-BDMA-Pd in 1 M KOH with the addition of HCHO concentrations; inset: linear plot of oxidation peak current vs. HCHO Conc. with 5% error bar.

**Figure 8.** Effect of HCHO concentration on chronoamperometric response at the GO-BDMA-Pd electrode at an applied potential of −0.1 V in 1 M KOH; insets: the CA with lower Conc. of HCHO and calibration plot of the current density vs. HCHO Conc. with 5% error bar.

suggests that a very low HCHO concentration could be easily detected by this GO-BDMA-Pd electrochemical sensor.

**Real sample analysis, reproducibility and stability.—**The GO-BDMA-Pd sensor was successfully applied to the determination of HCHO in tomato sauce. At first, 1 mL of sauce sample was added into the 5 mL of 1 M KOH electrolyte and there was no any current increased than blank (Figure 9a) indicating there was no any HCHO. Then, the standard addition method was applied and standard HCHO solution was spiked with three different concentrations (5, 10, and 15 mmol L\(^{-1}\)) into the above (1 mL sauce solution in 5 mL of 1 M KOH) solution. The recoveries were in a range between 98% and 106% with RSDs of 2.3–4.1% (measurement number, n = 3), which indicated that the sensor could be successfully applied to the determination of HCHO in real conditions.

The reproducibility of the proposed GO-BDMA-Pd catalyst was checked in Ar saturated 1 M KOH electrolyte at 0.05 V s\(^{-1}\) scan rate by the addition of 0.01 M HCHO. A series of consecutive 15 measurements showed 3.8% relative standard deviation depicting good reproducibility of the electrode. The long term stability of the electrode was also investigated under same circumstances. The measurements were taken at every three day interval over a period of one month keeping electrode at room temperature. RSD of 5.9% attributed good stability of the electrode.

**Conclusions**

In this study, we combine the advantageous features of BDMA and electrocatalytic properties of Pd with GO and prepared GO-BDMA-Pd catalyst. This chemical sensor was capable of catalyzing HCHO...
oxidation with high sensitivity, broad linear range and good reproducibility. Compared with partially modified GO-Pd catalyst, GO-BDMA-Pd showed significant increase in surface conductivity and electron transfer rate. Moreover, the CO poisoning process has been inhibited to a greater extent which is an important shortcoming of Pd-based electrodes for the oxidation of small organic molecules. These advantages make GO-BDMA-Pd a promising candidate for use in fuel cell, specific biotechnological processes, medicine, environmental control and even for food and drinking water analysis.

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References

1. P. J. Kulesza, I. S. Pietra, I. A. Rutkowska, A. Wadas, D. Marks, K. Klak, L. Stobinski, and J. A. Cox, Electrocim. Acta, 110, 214 (2013).
2. R. Qajri, J. B. Raooof, and S. Safshekan, Electrochim. Acta, 138, 146 (2014).
3. M. S. Ahmed and S. Jeon, J. Electrochem. Soc., 160, 1481 (2013).
4. Y. Yu, W. Su, Z. Yuan, Y. Fu, and J. Hu, J. Power Sources, 286, 140 (2015).
5. H. R. Gerberich and G. C. Seaman, Encyclopedia of Chem. Technol., 11, 929 (1994).
6. M. A. Flyvholm and P. Andersen, J. Ind. Med., 24, 533 (1993).
7. M. S. Ahmed and S. Jeon, Food Chem., 100, 1049 (2007).
8. J. L. S. G. Teixeira, I. S. Leao, I. F. Dantus, L. H. C. Pinheiro, A. C. S. Costa, and J. B. D. Andrade, Talanta, 64, 711 (2004).
9. T. J. Michels, J. Chromatogr. A, 914, 123 (2001).
10. M. A. Ali, M. Gonchar, G. Gyu &., S. Parshak, M. A. Mauret, J. N. Renault, and Y. Kopyan, Biosens. Bioelectron., 22, 2790 (2007).
11. A. Ejaz, M. S. Ahmed, and S. Jeon, Sens. Actuators B, 221, 1256 (2015).
12. X.-H. Cao, M.-M. Zhang, Y.-H. Liu, and W.-B. Nie, J. Electrochem. Soc., 155, 880 (2012).
13. A. R. Fakhari, H. Ahmar, H. Hosseini, and S. K. Movahedi, Sens. Actuators B, 213, 82 (2015).
14. M. S. Ahmed, D. Kin, and S. Jeon, J. Electrochem. Soc., 92, 168 (2013).
15. A. A. Almamman, A. A. Shaikh, N. J. Jassy, T. Akter, and A. A. Mannan, and P. K. Bakshi, J. Electrochem. Soc., 162, 852 (2015).
16. M. S. Ahmed, and S. Jeon., J. Nanosci. Nanotechnol., 13, 306 (2013).
17. C. Bianchini and P. K. Shen, Chem. Rev., 109, 4183 (2009).
18. M. S. Ahmed and S. Jeon., J. Power Sources, 282, 479 (2015).
19. M. S. Ahmed, H. Jeong, J.-M. You, and S. Jeon, Electrochim. Acta, 56, 4924 (2011).
20. M. S. Ahmed, H. S. Han, and S. Jeon, Carbon, 61, 164 (2013).
21. S. Kim, Y. N. Jeong, M. S. Ahmed, J.-M. You, H. C. Choi, and S. Jeon, Sens. Actuators B, 153, 246 (2011).
22. K. Lee, M. S. Ahmed, and S. Jeon, J. Electrochem. Soc., 162, F1 (2015).
23. S. Yasmin, M. S. Ahmed, and S. Jeon, J. Electrochem. Soc., 162, B363 (2015).
24. K. Lee, M. S. Ahmed, and S. Jeon, J. Power Sources, 288, 261 (2015).
25. M. S. Ahmed, D. Kim, H. S. Han, H. Jeong, and S. Jeon, J. Nanosci. Nanotechnol., 12, 8349 (2012).
26. J. Duan, S. Chen, M. Jaroniec, and S. Z. Qiao, ACS Catal., 5, 5207 (2015).
27. J. E. Choe, M. S. Ahmed, and S. Jeon, J. Electrochem. Soc., 163, B113 (2016).
28. M. S. Ahmed, D. Park, and S. Jeon, J. Power Sources.,
29. M. Yun, J. E. Choe, J.-M. You, M. S. Ahmed, H. Lee, Z. Ustundag, and S. Jeon, J. Power Sources.,
30. M. S. Ahmed and S. Jeon, J. Power Sources, 293, 380 (2015).
31. H. S. Han, M. S. Ahmed, H. Jeong, and S. Jeon, Biosensor, J. Electrochem. Soc., 162, B75 (2015).
32. M. S. Ahmed and S. Jeon, J. Power Sources, 218, 168 (2012).
33. J. E. Choe, M. S. Ahmed, and S. Jeon, J. Power Sources, 281, 211 (2015).
34. N. Ochoa, M. Bello, J. Sanchez, M. Valsamo, A. Albornoa, and L. J. Brito, Materials Research, 16, 1209 (2013).
35. T. Tsoufis, G. Tuci, S. Caporalii, D. Gournis, and G. Giambastiani, Carbon, 59, 100 (2013).
36. D. K. Kim, M. S. Ahmed, and S. Jeon, J. Mater. Chem., 22, 16353 (2012).
37. N. Penguan and Y. Qingfeng, Rare Metals, 30, 102 (2011).
38. A. N. Correiaa, L. H. Mascarob, S. A. S. Machadoa, and L. A. Avaca, J. Braz. Chem. Soc., 10, 478 (1999).
39. B. K. Sathe, D. B. Shinde, and V. K. Pillai, J. Phys. Chem. C, 113, 9616 (2009).
40. Z. Li, Z.-X. Lu, B. Li, L. Bai, and Q. Wang, ECS Electrochem. Letters, 4, H24 (2015).
41. L.-B. Kong, R.-T. Wang, X.-W. Wang, Z.-S. Yang, Y.-C. Luo, and L. Kang, Int. J. Applied Physics and Mathematics, 1, 5 (2011).
42. J. Geng, Y. Bi, and G. Lu, Electrochem. Commun., 11, 1255 (2009).
43. V. Bansal, V. Li, A. P. O. Mullane, and S. K. Bhargava, Cryst. Eng. Comm., 12, 4280 (2010).
44. C.-C. Chang, L.-C. Chen, S.-J. Liub, H.-J. Tienc, and H.-C. Changd, J. Chinese Chem. Soc., 53, 839 (2006).
45. Q. F. Yi, F. J. Niu, and W. Q. Yu, Thin Solid Films, 519, 3155 (2011).
46. G. P. Jin, J. Li, and X. Peng, J. Appl. Electrochem., 39, 1889 (2009).
47. Z.-L. Zhou and T.-F. Kang, Microchim. Acta, 164, 133 (2009).
48. J. Zhang, L. Shangguan, S. Shuang, and C. Deng, Russian J. Electrochem., 49, 888 (2013).

![Figure 9. CVs recorded in 1 M KOH at 0.05 V s⁻¹ scan rate on GO-BDMA-Pd in the presence and absence of stock solution of tomato sauce (a); the CVs recorded in stock solution containing 1 M KOH with subsequent addition of 5, 10 and 15 mM HCOH.](image-url)