The effect of defective graphene flake (DGF) as supports for Pd nanocubes (Pd NCs) in the catalysis of D-glucose oxidation reaction (GOR) was studied. The DGF used to support the Pd NCs were prepared via both a sonoelectrochemical method (DGFSECM) and a chemical reduction method (DGFCM). The comparable data supported by the diffraction electron pattern of transmission electron microscopy (TEM) and X-ray diffraction (XRD) spectra evidence that the corners of the Pd NCs faced up toward the both DGF supports, leading to an increase in the XRD intensity of the Pd (111) peak. Additionally, a fair electrochemical comparison of the DGF support effect on GOR catalysis via Pd NCs in a NaOH electrolyte indicated that the DGFSECM-supported Pd NCs (Pd NC/DGFSECM) and DGFCM-supported Pd NCs (Pd NC/DGFCM) demonstrated earlier onset potentials and an overall order of Pd NC/DGFSECM > Pd NC/DGFCM > commercial Pd/C catalyst > Pd NCs for the peak charge accompanying the formation of gluconolactone was obtained. Through the use of a DGFSECM substrate, the electrochemical surface area and charge transfer resistance toward GOR were significantly improved. In addition, as supported by the catalytic activity for GOR, Pd NC/DGFSECM showed remarkable sensitivity and tolerance to foreign substances in the application as a non-enzymatic glucose sensor. Where Pd NC/DGFSECM showed higher two-period sensitivities of 74 and 45.86 μA·mM⁻¹·cm⁻² for 0.25–5 and 5–24 μM D-glucose, respectively. The high recovery in serum sample analyses further confirmed the potential of Pd NC/DGFSECM as glucose sensors. © The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.014160jes] All rights reserved.

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Effect of Defective Graphene Flake for Catalysts of Supported Pd Nanocubes toward Glucose Oxidation Reaction in Alkaline Medium

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Electrocatalytic glucose oxidation reaction (GOR) is of particular interest, and can be applied to a direct glucose fuel cell (DGFC).1–3 Implantable fuel cell (IFC),4,5 and glucose sensor.6–8 Various noble metal materials such as platinum,9,10 palladium,11,12 silver,13,14 and gold15,16 have shown activity and been used as electrodes for electrocatalyzing GOR in an alkaline medium. Among them, Pt is frequently employed as a GOR catalyst16–18 however, there are significant drawbacks for the GOR on its bare surface:19 the poisonous influence of chemisorbed intermediates and the interference of ascorbic acid (AA) and uric acid (UA) in the human body. Therefore, novel catalysts have been investigated to replace Pt catalysts. Wang and coworkers20 conducted exquisite work preparing Au rhombic dodecahedron, octahedra, and nanocubes (NCs) to catalyze alkaline GOR and systematically compared their activities. The study showed that the shape-dependent properties of these Au catalysts mainly originated from the different crystal planes exposed on their nanocrystal surfaces and that (100)-bound Au NCs were more active than the Au rhombic dodecahedral and octahedral catalysts. Some original studies21,22 showed that bulk Pd materials reduced to nanoparticles showed good activity and stability toward alkaline GOR. Recently, based on one growth method using hexadecyltrimethylammonium bromide (CTAB) as a protecting agent, we prepared 27-nm Pd NCs enclosed with (100) facets and octahedral catalysts. Some original studies21,22 showed that bulk Pd materials reduced to nanoparticles showed good activity and stability toward alkaline GOR. Recently, based on one growth method using hexadecyltrimethylammonium bromide (CTAB) as a protecting agent, we prepared 27-nm Pd NCs enclosed with (100) facets and octahedral catalysts. Some original studies21,22 showed that bulk Pd materials reduced to nanoparticles showed good activity and stability toward alkaline GOR. Additionally, utilizing expensive Pd nanocatalysts is an important issue for electrocatalytic devices. Highly dispersed Pd catalysts on a conductive support, commonly carbon black, are used as electrodes for oxidation reactions in fuel cells sealed with formic acid,24–26 glycerol,27 and glucose.21,28 With the helpful carbon powders, the high surface-to-volume ratios of Pd nanoparticles maximize the available surface areas for these electrocatalytic reactions. Graphene flake with a high surface area (ca. 2,600 m²·g⁻¹) 29 is currently the most investigated carbon support as a substitute for carbon black catalyst supports for fuel cell Pd catalysts.30–32 The high degree of sp²-bonded carbon atoms on the graphene flake can lead to effective conductivity and possibly decrease overpotential. In addition, the defect effect of graphene flake as catalyst support is of interest in the electrocatalytic reaction.33–35 Theoretically, the formation of Pt−carbon bonds at graphene support defects can influence the average bond length and thus the strain in the metal catalysts to enhance the stability of Pt catalyst.36 The stronger binding of the metal catalyst to the graphene support leads to increase charge transfer from the cluster to the substrate accompanied by a substantial downshift of the catalyst d-band center, leading to improve CO tolerance of platinum nanoparticles on defective graphene flake (DGF).37 Theoretical calculations further demonstrated that the binding energies, d-band centers, and adsorption energies showed a linear change with the pore size of porous defective graphene support for Pd catalysts. By choosing a graphene support with suitable pore size, Pd catalysts on defective graphene will have similar CO and O₂ adsorption abilities, thus leading to superior CO tolerance.38 Recently, for oxygen reduction reactions (ORRs), Liu and coworkers39 carried out first-principles-based calculations and successfully determined that the defects on a DGF can provide anchoring sites for Pd-based catalysts, increasing their stabilities. This interfacial interaction could further tune the d-band center of these ORR catalysts to weaken O adsorption and promote ORR kinetics. The enhanced activities of defective DGF-supported catalysts can be partly ascribed to the isolated sp²-hybridized bonds (π electrons) and the strong interaction (charge transfer) between the catalysts and the DGF.40 Therefore, the use of defective DGFs for ORR catalysts could be an efficient method for improving reaction kinetics. Previously, we reported a sonochemical method to rapidly prepare defective graphene flakes (DGFSECM), of which surface was dominated by physical defects while they were compared to defective graphene flakes prepared via a chemical reduction method (DGFCM).40 The primary defects on the DGFSECM were C-OH groups.40 In this study, given the goal of developing a highly active catalyst for GOR, we study the support effect of DGFSECM and DGFCM for the catalysis of Pd NCs in GORs. We successfully use electrochemical analyses to perform a comparison between DGFSECM-supported Pd NCs (Pd NC/DGFSECM), DGFCM-supported Pd NCs (Pd NC/DGFCM), and DGF-free Pd NCs when these catalysts were applied to an enzyme-less glucose sensor.

Experimental

Synthesis and materials analyses of Pd NC/DGFSECM and Pd NC/DGFCM.—Before the synthesis of Pd NCs supported on DGFs, the solution containing Pd NCs was prepared. The preparation of the solution containing Pd NCs was based on our previous report41 and is

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described in the supplemental material. The obtained Pd NC solution was centrifuged at 12,000 rpm for 10 min. Then, the Pd precipitate was redispersed in a 1 mL H2O solution, and the solution was centrifuged again at 10,000 rpm. The precipitate was redispersed in a 1 mL H2O solution. The Pd NC solution thus prepared was used for the mixture with DGFs, whose preparation methods are described below.

The DGF was obtained from graphene oxide (GO) using N2H4 as a reducing agent. Initially, GOs were first prepared using a modified Hummers’ method.10,24 Then, 20 mg of the prepared GO powder was dispersed in 100 mL of an aqueous 0.1 M sodium n-dodecyl sulfate (SDS) solution by agitation using a sonicator for a period of 1 h. To remove unreacted graphite powders, the GO solution was centrifuged at 4,000 rpm, and the precipitate was redispersed using deionized water. A 40 mL solution with 4 mg of dispersed GO was prepared. Next, 200 μL of pure NH4OH solution was added to the solution via agitation and sonicated for 30 min. Then, 20 μL of the original N2H4 solution was added to the above solution and stirred for 1 h at a fixed temperature of 95°C for GO reduction. A solution containing DGF was thus prepared. Additionally, to synthesize DGFs, a sono-electrochemical method where SDS was employed as intercalating agent was performed and reported elsewhere.40 The brief description can be referred to the supplemental material.

To purify this mixture and remove some organic compounds (such as SDS and N2H4), the obtained DGF solution was centrifuged at 1,000 rpm and then again at 13,000 rpm. The DGF precipitate was redispersed in a certain H2O solution under ultrasonic vibration for 10 min to generate a liquid with a concentration of ~6 μg/μL. The weight of the DGF powder in the solution was confirmed with a quartz crystal microbalance (QCM; Seiko QCA927). Then, the solution containing DGFs was mixed with the Pd NC solution as described above under ultrasonic vibration for 10 min. Pd NC/DGFs were thus prepared.

The morphologies and structures of the prepared Pd NC/DGFs, Pd NC/DGFs, and unsupported Pd NCs individually were examined using transmission electron microscopy (TEM; JEM-2100 and 2100F CS STEM, JEOL, Tokyo, Japan) and X-ray diffraction spectroscopy (XRD; Bruker D8; Cu anode; 1.5418 Å). The zeta potentials of the prepared Pd NC solution, DGF solution, and DGFs solution for preparing the Pd NC/DGFs and the Pd NC/DGFs were determined by dynamic light scattering (Brookhaven Instruments 90Plus PALS Zeta Potential Analyzer). To estimate precisely the weight percentages of Pd catalysts on the DGF, thermal decomposition analyses of Pd NC-supported DGF (Pd NC/DGF) were carried out using a thermogravimetric analyzer (TGA; TA Instruments; SDT-Q600).

**Electrochemical characterization of catalyzed D-glucose oxidation reactions and Cu UPD and stripping.**—The support effect of DGFs and DGFs on the electrochemical performances of the Pd NCs in the catalysis of GOR was studied by performing a computer-controlled potentiostat (CH Instruments; CHI 62C) with a catalyst-covered glassy carbon electrode (GCE; 0.07 cm2), which was prepared by a drop-casting method using the prepared Pd NC/DGF solution and then heated to 60°C to evaporate the H2O. The weight density of the Pd NCs, acting as active catalysts on the electrode, was 28 μg · cm⁻². All electrochemical measurements were conducted in a N2-saturated 0.1 M NaOH (aq) solution, without or with 5 mM D-glucose, using a three-electrode cell with a catalyst-covered electrode serving as the working electrode, a Pt foil as the counter electrode, and a Ag/AgCl (3 M KCl) reference electrode. To remove any potential interference from any impurities on the Pd NC/DGFs, Pd NC/DGFs and unsupported Pd NCs during the D-glucose oxidation, the catalysts were scanned from −0.9 to 0.25 V using cyclic voltammetry (CV) at a rate of 150 mV · s⁻¹. Then, the redox properties of the catalysts were measured at a scanning rate of 50 mV · s⁻¹. The sensitivities and interference studies of the two Pd NC/DGFs and Pd NCs to glucose were tested in a stirred solution using amperometric measurements at a fixed potential of −0.05 V (vs. Ag/AgCl). In the interference study, the times for the addition of 1 mM D-glucose, 20 μM AA, 60 μM UA, and 2 mM D-glucose were 40, 80, 120, and 160 s after triggering the measurement, respectively. Based on the same loading Pd weight, commercial Pd/C catalysts (Sigma Aldrich; loading Pd: 30 wt%) was used as electrocatalysts in a GOR and glucose sensor and their performance was compared with those of Pd NC/DGF and Pd NCs.

CV experiments for Cu underpotential deposition (UPD) and stripping of the Pd catalysts to determine the electrochemical surface areas (ESAUPD) were performed at a scanning rate of 5 mV s⁻¹ in 0.5 M H2SO4 solution containing 0.05 M CuSO4.

**Results and Discussion**

**Characterizations of Pd NC/DGFs and Pd NC/DGFs compared to individual Pd NCs.**—Figures 1A, 1B, and 1C show TEM images of Pd NC/DGFs, Pd NC/DGFs, and Pd NCs, respectively. As shown in Fig. 1C, the high-yield Pd NCs were prepared and deposited on the TEM copper grid coated with carbon film. The mean edge length of the Pd NCs was 10.9 nm, of which the calculated results based on TEM data are shown in Fig. 1D. After mixing with DGFs and DGFs, the uniform Pd NCs distributed on the DGF were observed, as shown in Fig. 1A. Additionally, the zeta potentials of the DGFs solution and DGFs were measured to be −21.25 and −43.67 mV, respectively. By contrast, the zeta potential in the Pd NC solution was 10.23 mV. The DGFs produced by the interaction of SDS in a sono-electrochemical medium have more negative charges on
their surface. This can confirm the successful deposition of Pd NCs onto the two DGF surface through an electrostatic force. Interestingly, the aggregated Pd NCs, as depicted in Figs. 1A–1B, were observed at the wrinkles of the DGF, especially for DGF_CM, unlike the uniform distribution shown in Fig. 1C. This could have resulted from the folding of flexible DGF after the deposition of the Pd NCs. To ensure the presence of the enclosed facets on the Pd NCs, electron diffraction using high-resolution TEM (HR-TEM) was employed. Figure 1E reveals point pattern and (200) diffraction facets for a single crystalline Pd NC as shown in the inset. This result indicates that the main facet on the prepared NCs exposed for catalyzing GOR is (100).

Figure 2 shows a comparison of XRD spectra for the Pd NCs before and after being supported with DGF_SECM and DGF_CM. In the DGF-free Pd NC spectrum, the pattern shows a strong peak at 46.95° assignable to the (200) diffraction plane of a typical Pd spectrum (JCPDS 65-2867), presenting (100) planes on six facets as confirmed by the electron diffraction result (Fig. 1E). One weaker peak at 40.29° can be assigned to the (111) Pd plane at the truncated corners of some Pd NCs, as evidenced by the arrow in the HR-TEM image (the inset of Fig. 1E). When the Pd NCs were deposited onto the DGF_SECM and DGF_CM, the intensities of the both (111) peak were significantly enhanced and much higher than that of the (200) peak. In particular, the morphology of the Pd NCs (Figs. 1A and 1B) persisted after experiencing the deposition onto the DGFs. Therefore, the reason for the enhancement of the (111) peak resulting from the change of crystalline structures for the Pd NCs can be neglected. As shown in Fig. 1A, the corners and edges of some Pd NCs on the both DGFs faced upward so that the many (111) facets at the corners were detected by XRD spectroscopy. The XRD pattern of the Pd/C was also detected (Fig. 1E). When the Pd NCs were deposited onto the DGF_SECM, as evidenced at the arrow in the HR-TEM image (the inset of Fig. 1E). One weaker peak at 40.29° can be assigned to the (111) Pd plane at the truncated corners of some Pd NCs, as evidenced by the arrow in the HR-TEM image (the inset of Fig. 1E). When the Pd NCs were deposited onto the DGF_SECM and DGF_CM, the intensities of the both (111) peak were significantly enhanced and much higher than that of the (200) peak. In particular, the morphology of the Pd NCs (Figs. 1A and 1B) persisted after experiencing the deposition onto the DGFs. Therefore, the reason for the enhancement of the (111) peak resulting from the change of crystalline structures for the Pd NCs can be neglected. As shown in Fig. 1A, the corners and edges of some Pd NCs on the both DGFs faced upward so that the many (111) facets at the corners were detected by XRD spectroscopy. The XRD pattern of the Pd/C was also detected and shown in Fig. 2. The (111) facet predominates the structure of Pd catalysts in the Pd/C.

**The DGF effect on catalytic properties of cubic Pd catalysts toward GOR.**—Furthermore, in order to precisely study the support effect of DGF on the GOR-catalysis activities and properties for equivalent weights of solid catalysts, the weight percentages of the Pd NCs on the DGF_SECM and DGF_CM compounds were estimated to be 61% and 52.7% using a TGA under an air atmosphere, respectively. The DGF effect on the catalytic activity of Pd NCs toward GOR was initially measured by CV. Figure 3A shows a comparison of the CV curves of the DGF_SECM electrode and the DGF_CM electrode working in the 0.1 M NaOH electrolytes without and with 5 mM D-glucose under a N2 atmosphere. The curve without D-glucose for the DGF_CM shows one reducing peak at −0.37 V and one oxidation shoulder at −0.23 V, whereas the cathodic peak for the DGF_SECM are observed at −0.3 V, which can be attributed to the redox of oxygen-containing groups on the DGF. The faster reduction for chemical defects on the DGF_SECM is obtained. Apparently, the features of the curves for the both DGFs measured in the glucose electrolyte are similar to those in the glucose-free electrolyte, showing that the DGFs are inactive in the catalysis of GOR. The inactivity of DGF in D-glucose oxidation suggests the elimination of any oxidation signal provided by the DGF and that they only have a supporting effect in the oxidation of D-glucose.

Figure 3B shows a CV curve corresponding to Pd NC/DGF_SECM and Pd NC/DGF_CM as compared to DGF-free Pd NCs and Pd/C in a D-glucose-free NaOH solution in a N2 atmosphere. The currents by Pd NC/DGF_CM between −0.55 and −0.9 V are associated with hydrogen adsorption and desorption on the Pd surface and the peak at −0.27 V can be assigned to the reduction of PdO. In the anodic scan, the adsorption of OH− was initially observed at −0.45 V and the significant oxidation current for Pd started from −0.284 V. Compared to Pd NC/DGF_CM, the current by Pd NC/DGF_SECM is greater but the current by Pd NCs and Pd/C is smaller, indicating that Pd NCs can spread out over the DGFs and DGF_SECM which can effectively promote electron transfer in an electrochemical reaction. Additionally, the CV curve for Pd NC/DGF_CM when working in the solution with 5 mM glucose is shown in Fig. 3C: the occurrence of the A1 peak at −0.61 V can be ascribed to chemisorption and dehydrogenation of D-glucose which removed the first hydrogen at hemiacetal carbon 1, similar to the GOR on a Pt catalyst. Note that the suppressed A1 peak for Pd NC/DGF_SECM (Fig. 3C) was located at −0.67 V, earlier than that.
for Pd NC/DGFCM, −0.573 V for Pd NCs, and −0.53 V for Pd/C (Fig. 3C). Following the A1 peak, there was one strong peak (A2) initially at −0.26 V after the adsorption of OH− (−0.45 V) in the curve of Pd NC/DGFCM, as observed in Fig. 3B. At this state, the accumulated hydroxyls adsorbed on the Pd NCs were catalytic to the α-glucose on the catalytic surface. α-Glucose was oxidized to gluconolactone1 as follows:

\[ \text{HOH} + \text{Pd(OH)} \rightarrow \text{HOH} \]

Subsequently, in the cathodic scan, an A3 peak appeared at −0.31 V after the reduction of PdO at −0.21 V, which was earlier than −0.27 V without the occurrence of GOR in the Fig. 3B. This relationship can be suggesting that the active sites suppressed by oxides were available. Previously, the GOR activity of Pd catalysts can be influenced by their preparation process using NaBH4, which caused the insertion of the produced hydrogen into Pd lattice.46 The CV curves (Fig. 1S in the supporting information) for Pd NCs show that the A2 current of the scanning between −0.76 V and 0.25 V was almost equal to that of the scanning between −0.9 V and 0.25 V. These Pd NCs were initially experienced by fast CV scan of 150 mV s−1 from −0.76 V or −0.9 V, as show in Fig. 2S. The unchanged A2 currents indicate that the effect of hydrogen for GOR curves measured from −0.9 V can be neglected. Therefore, the A2 peak can be used as an activity indicator in GOR. The charges for the A2 peaks of Pd NC/DGFCM, can be neglected. Therefore, the A2 peak can be used as an activity indicator in GOR. The charges for the A2 peaks of Pd NC/DGFCM, Pd NC/DGFSEM, Pd NCs, and Pd/C are summarized in Table I. The A2 charges (QA2) for Pd NC/DGFCM and Pd NC/DGFSEM are 939.1 and 685 μC, respectively, significantly greater than 356.4 μC by Pd NCs and 478 μC by Pd/C. The QA2 of Pd NC/DGFCM is 1.37 and 2.64 times greater than those of Pd NC/DGFSEM and Pd NCs, respectively. Simultaneously, the QA2 by Pd NC/DGFSEM is 1.96 times greater than those of Pd NC/DGFCM, Pd NCs, and Pd/C, whereas the significant current was for Pd NC/DGFSEM and Pd NC/DGFCM. The stripping current charge, as indicated by the black section subtracted from double-layer current for Pd NC/DGFCM, was 766.2 μC, greater than 623.08 μC (red section) for the Pd NC/DGFCM, 263.6 μC (blue section) for the DGF-free Pd NCs and 340 μC (green section) for the Pd/C catalysts. Additionally, for electrochemically full coverage of Cu on the Pd (100) substrate and the Pd (111) substrate, the theoretical values are approximately 421 μC·cm−2 and 486 μC·cm−2. Therefore, the ESAUPDs for Pd NC catalysts enclosed with (111) planes and Pd/C catalysts dominated with (111) planes can be calculated from the stripping charges over 421 μC·cm−2 and 486 μC·cm−2, respectively. The ESAUPDs, as summarized in Table I, for the Pd NC/DGFSEM and the Pd NC/DGFCM were thus 1.82 and 1.48 cm2, respectively; the Pd NCs showed an ESAUPD value of 0.626 cm2 and the Pd/C catalyst had 0.7 cm2. Simultaneously, the electrochemical surface areas (ESAUPDs) estimated by integrating the charges of the PdO peaks in the Fig. 3B were 1.86, 1.46, 0.636, and 0.8 cm2 for Pd NC/DGFSEM, Pd NC/DGFCM, Pd NCs, and Pd/C catalysts, respectively. As shown in Table I, the ESAUPDs are consistent with the ESAUPDs. The ESAUPDs of the Pd NCs deposited on the DGFSEM were 1.23 times greater than those of Pd NCs on the DGFCM. It can be thus concluded that one explanation for the increased catalytic power of Pd NC/DGFSEM compared to Pd NC/DGFCM is a greater electrochemical surface area, leading to higher unitization of Pd catalysts. The effect of the DGF support on the catalytic power of Pd NCs towards α-glucose oxidation was further studied by Tafel measurements. Figure 5 depicts a comparison of the Tafel curves of the Pd NCs with and without DGF and Pd/C, and the corresponding kinetic data are summarized in Table I. In the curves of Pd NC/DGFSEM, the rest potential (ER) as defined by zero overpotential was observed at −0.878 V prior to the A1 peak. The ER of Pd NC/DGFCM as well as that of Pd NC/DGFSEM shows an early potential (−0.878 V), confirming that the dehydrogenation of α-glucose is the first elementary step in the mechanism. At ER, the current density can be determined to the exchange current density (j0), which was 4.3 × 10−2 mA·cm−2 under a Tafel slope of 54 mV/dec for α-glucose electrooxidation. Careful study of Fig. 5 revealed that the ER (−0.878 V) for Pd NC/DGFSEM was more negative than the ER (−0.878 V) for Pd NC/DGFCM, the ER was calculated from the stripping charges over 421 μC·cm−2 and 486 μC·cm−2, respectively. The ESAUPDs, as summarized in Table I, for the Pd NC/DGFSEM and the Pd NC/DGFCM were thus 1.82 and 1.48 cm2, respectively; the Pd NCs showed an ESAUPD value of 0.626 cm2 and the Pd/C catalyst had 0.7 cm2. Simultaneously, the electrochemical surface areas (ESAUPDs) estimated by integrating the charges of the PdO peaks in the Fig. 3B were 1.86, 1.46, 0.636, and 0.8 cm2 for Pd NC/DGFSEM, Pd NC/DGFCM, Pd NCs, and Pd/C catalysts, respectively. As shown in Table I, the ESAUPDs are consistent with the ESAUPDs. 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with physical defects reported in our previous study, the Re for the nanocatalysts supported on a carboxylated carbon nanotube. Typically, the electron transfer number (n) involved in an electrocatalytic reaction can be calculated from the Tafel slope (B). Here, \( \beta \) is an asymmetric parameter and is 0.5, F is the Faraday constant, R is the gas constant, and T is the temperature (298 K). Therefore, the n values for Pd NC/DGFSECM and Pd NC were 1.85. The n values of Pd NC/DGFCM and Pd NC were 4.23 and 4.085, respectively. The Re for Pd NC/DGFSECM was 6.38 and 6.2 \( \times 10^{-4} \) \( \text{mA cm}^{-2} \). Adsorption of d-glucose and formed product easily bind to slightly increased. Additionally, as shown in the corresponding TEM images (Fig. S4) for the stability tests, these Pd catalysts didn’t be significantly aggregated and the original morphologies of these Pd catalysts remained. d-glucose and formed product easily bind to and desorb from the surfaces of these Pd catalysts, suggesting high d-glucose-tolerance for all Pd catalysts.

Applications for sensing d-glucose using Pd NCs without and with DGF.—The above electrocatalytic study revealed the effect of DGF for catalyzed with the Pd NC/DGFSECM in comparison to those of the Pd NC/DGFCM, the Pd NCs, and the Pd/C at an applied potential of \(-0.05 \text{ V} \) to allow a steady-state value. Initially, the responding current for Pd NC/DGFSECM was almost equal to those for Pd NC/DGFCM, Pd NCs, and Pd/C after 0.25 mM d-glucose was added to the electrolyte. After sequentially dropping aliquots of d-glucose using Pd NCs without and with DGF—The above electrocatalytic study revealed the effect of DGFSECM on d-glucose oxidation and the potential of the prepared Pd NC/DGFSECM was slightly increased. Additionally, as shown in the corresponding TEM images (Fig. S4) for the stability tests, these Pd catalysts didn’t be significantly aggregated and the original morphologies of these Pd catalysts were retained.

Figure 6. Glucose-sensing properties: (A) amperometric current-time response and (B) corresponding calibration curves of Pd NC/DGFSECM, Pd NC/DGFCM, Pd NCs, and Pd/C in a NaOH (0.1 M) solution after successive injections of different concentrations of d-glucose at an applied potential of \(-0.05 \text{ V} \) (vs. Ag/AgCl/3 M KCl) (weight density of loaded Pd catalysts: 28 \( \mu \text{g cm}^{-2} \), N2 atmosphere).
Table II. Comparison of the sensitivities, linear ranges, and LODs of Pd, Pt, and Au catalysts for non-enzymatic glucose sensing in a NaOH solution.

| Electrode Materials           | Sensitivity (μA mM⁻¹ cm⁻²) | Linear range (mM) | LOD (μM) | Reference |
|-------------------------------|-------------------------------|-------------------|----------|-----------|
| Pd NCs (27 nm)                | 34                            | 1–10              | -        | 23        |
| Pd NPs                        | N. A.                         | 0.07–5            | 10       | 62        |
| Pd NPs/GO                     | N. A.                         | 0.01–5            | 1        | 62        |
| Pd NP (2.1 nm)/multi-walled CNT† | 11.3, 6.3                    | 1–10, 11–20       | N. A.    | 60        |
| Pd NP (3–4 nm)/functional CNT† | 11.4                          | 0–46              | N. A.    | 61        |
| Pt NP (3 nm)/CNT              | N. A.                         | 0–44.6            | 28       | 17        |
| Pt NP (4 nm)/MC              | 8.52                          | 0.005–7.5         | 3        | 63        |
| Au NP/GO                      | N. A.                         | 0.2–2, 2–22       | 0.05     | 64        |
| Pd30Au70 NP (4.8 nm) /C       | 12.1                          | 0–10              | N. A.    | 8         |
| Pd NC/DGFS ECM               | 74, 45.86                     | 0.25–5, 5–24      | 20.6     | This work |
| Pd NC/DGF CM                 | 67.29, 35.57                  | 0.25–5, 5–24      | 27.2     | 5         |
| Pd NCs                        | 42.86, 18.86                  | 0.25–5, 5–24      | 31       |           |
| Pd/C                          | 65, 30.4                      | 0.25–7, 7–20      | 29.4     |           |

*a*carbon nanotube  
*bc*mesoporous carbon  
*cg*raphene oxide

D-glucose into a stirring NaOH solution, the oxidation current on the Pd NC/DGFS ECM increased more steeply than did that on the Pd NC/DGF CM, the DGF-free Pd NC, and Pd/C catalyst and reached a steady-state current within 30 s. As with DGFS ECM, the ability to sense D-glucose of the above Pd NCs became more sensitive, which can be attributed to the high electrochemical surface area and low Rct.

As revealed by the calibration curves shown in Fig. 6B, there were linear current-response relationships for the Pd NCs with and without DGF and Pd/C. The sensitivity when using a catalyst can be estimated from Equation 4:

\[ \text{Sensitivity} = \frac{\text{slope}_{\text{cal}}}{A_{\text{geo}}} \quad [4] \]

Here, \( \text{slope}_{\text{cal}} \) is the linear slope in Fig. 6B, and \( A_{\text{geo}} \) is 0.07 cm², the geometric surface area of the GCE. The sensitivities for the Pd NCs were 42.86 and 18.86 μA · mM⁻¹ · cm⁻² under linear analysis ranges of 0.25–5 and 5–24 mM with correlation coefficients of 0.992 and 0.991, respectively. When Pd NCs were associated with DGFS CM, the sensitivities increased significantly to 67.29 and 35.57 μA · mM⁻¹ · cm⁻² at the same linear ranges. The correlation coefficients in the 0.25–5 and 5–24 mM ranges were 0.986 and 0.991, respectively. Interestingly, the sensitivities using DGFS ECM as a support for Pd NCs can be further improved to 74 and 45.86 μA · mM⁻¹ · cm⁻² under linear analysis ranges of 0.25–5 and 5–24 mM with correlation coefficients of 0.984 and 0.993, respectively. Simultaneously, the sensitivities using Pd NC/DGFS ECM are more sensible than 65 and 30.4 μA · mM⁻¹ · cm⁻² for Pd/C under linear analysis ranges of 0.25–7 and 7–20 mM with correlation coefficients of 0.9952 and 0.9983, respectively. These linear slopes completely cover the normal physiological level of glucose from 3 to 8 mM in human blood. In addition, the limit of detection (LOD) is the lowest concentration of glucose that can be measured with reasonable statistical certainty. Based on the calibration curves (Fig. 6B) and the function for calculating the LOD, the LOD at a signal-to-noise ratio of 3 for Pd NC/DGFS ECM is 20.6 μM, lower than 27.2 μM for Pd NC/DGF CM, 31 μM for DGFS-free Pd NCs, and 29.4 μM for Pd/C. Table II shows a comparison of the sensitivities, linear ranges, and LODs of Pd, Pt, and Au catalysts on various carbon supports used for non-enzymatic glucose sensing in a NaOH solution. A comparison revealed that the Pd NC without and with DGFs show higher sensitivities but a narrower linear range when sensing glucose than the Pd or Pt nanoparticles on carbon nanotubes. The higher sensitivity of Pd NC/DGFS ECM indicates the potential for the use of this electrode in sensing glucose.

For the sensor to be feasible, the effects of several possible interfering substances on the Pd NCs with and without DGF were studied. It is worth noting that these two Pd catalysts show remarkable resistance to foreign substances in the determination of D-glucose. Figure 7 shows a comparison of the current-time curves for Pd NC/DGFS ECM, Pd NC/DGF CM, Pd NCs, and Pd/C at an applied potential of −0.05 V in a NaOH solution with an addition order of 1 mM D-glucose, 20 μM AA, 60 μM UA, and 1 mM D-glucose. The curves of Pd NC/DGF CM, and Pd NCs shows the current were slightly decreased after the addition of UA. The decayed current caused by UA was more obvious under catalysis of commercial Pd/C catalyst. These data are not consistent with our previous result for 27-nm Pd NCs, by which the GOR current did not be interfered by UA. In the curve of Pd NC/DGFS ECM, obviously, the addition of AA and UA did not influence the responding signal of D-glucose and block the active sites on the catalyst. The prepared Pd NC/DGFS ECM catalysts still showed a stable and significant current for D-glucose despite the presence of UA and AA. Careful comparison with Pd NCs revealed that the Pd NC/DGFS ECM showed a higher responding current for D-glucose but was inactive for AA and UA. It also can be concluded that the Pd NC/DGFS ECM electrodes show good selectivity in glucose detection. Subsequently, real sample analyses were conducted for calf serum samples, in which the glucose concentration was determined to be

![Figure 7. Glucose-sensing properties: effect of interference on the current-time curves for sensing glucose using Pd NC/DGFS ECM, Pd NC/DGF CM, Pd NCs, and Pd/C at an applied potential of −0.05 V in a NaOH solution with an addition order of 1 mM D-glucose, 20 μM AA, 60 μM UA, and 1 mM D-glucose.](https://example.com/figure7.png)
Table III. Real sample assays for the detection of glucose mixed with a 0.1 mL calf serum sample. Samples 1–3 were analyzed using Pd NC/DGFSEM, respectively.

| Sample no. | Added glucose (A) (mM) | Mixed serum (B) (mM) | Found (C) (mM) | Recovery (%) | R.S.D (%) |
|------------|------------------------|----------------------|----------------|--------------|----------|
| 1          | 0.3                    | 0.1297               | 0.423          | 98.35        | 1.49     |
| 2          | 0.5                    | 0.1297               | 0.6            | 95.7         | 1.21     |
| 3          | 1                      | 0.1297               | 1.041          | 92.17        | 1.39     |

*The concentration of 0.1 mL of serum added to a 4 mL NaOH (0.1 M) solution.

The detected amounts of glucose were obtained from a mean of three measurements.

Recovery = ((C)/(A + B)) × 100%.

The relative standard deviation (R.S.D) was obtained from the found glucose amounts of three measurements.

Conclusions

A fair comparison between DGFSEM and DGFCM regarding their respective support effects on GOR catalysis via Pd NCs in a NaOH electrolyte indicated that the Pd NC/DGFSEM demonstrated earlier onset potentials, starting from −0.878 V (vs. Ag/AgCl), and an overall order of Pd NC/DGFSEM > Pd NC/DGFCEM > Pd/C > Pd NCs for the A2 charge accompanying the formation of gluconolactone was obtained. Through the use of a DGFSEM substrate, the electrochemical surface area and Rct toward GOR were significantly improved. In addition, as supported by the catalytic characterization for GOR, Pd NC/DGFSEM showed remarkable sensitivity and tolerance to foreign substances in the application as a non-enzymatic glucose sensor, where Pd NC/DGFSEM showed higher two-period sensitivities of 74 and 45.86 μA·mM⁻¹·cm⁻² for 0.25–5 and 5–24 mM glucose, respectively. The high recovery in serum sample analyses further confirmed the potential of Pd NC/DGFSEM as glucose sensors.

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