Catalyst Composites of Palladium and N-Doped Carbon Quantum Dots-Decorated Silica and Reduced Graphene Oxide for Enhancement of Direct Formic Acid Fuel Cells

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ABSTRACT: Pd-based catalysts consisting of Pd nanoparticles on nitrogen-doped carbon quantum dots (N-CQDs) modified silica (SiO₂) and reduced graphene oxide have been synthesized through reduction for use as catalysts for improved formic acid oxidation. The structure, morphology, chemical composition, functional groups, and porosity of the synthesized catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, and Brunauer−Emmett−Teller (BET) spectroscopy, respectively. Their electrocatalytic activities were also evaluated by electrochemical measurements. The differences in the average particle sizes found for Pd/N-CQDs-SiO₂-rGO, Pd/N-CQDs-rGO, and Pd/rGO were 4.81, 5.56, and 6.31 nm, respectively. It was also found that the Pd/xN-CQDs-SiO₂-yrGO composite catalysts (where x and y is 1 to 4) can significantly improve the activity and stability toward formic acid electrooxidation compared with Pd/rGO and commercial Pt/C. The mass activities of Pd/N-CQDs-SiO₂-rGO, Pd/N-CQDs-rGO, and Pd/rGO were 951.4, 607.8, and 157.6 mA g⁻¹, respectively, which was ca. 6−7 times compared with Pd/rGO and approximately 3−4 times compared with commercial Pt/C. With low potential for CO oxidation and high current intensity, the composites of rGO, SiO₂, and N-CQDs into Pd-based catalysts improved the catalytic activity of the prepared catalyst for the oxidation of formic acid in acidic media. The value of the Tafel slope designated that the chief path of the prepared catalysts is the dehydrogenation process. These prepared catalysts exhibit promise toward the development of high-performance Pd-based electrocatalysts for formic acid oxidation.

1. INTRODUCTION

Direct formic acid fuel cells (DFAFCs) are practical energy sources, mostly in portable electric devices with high power density.¹,² DFAFCs have been extensively considered because they are less delicate to formic acid crossover and have a better theoretical voltage (1.48 V).²,³ Hereafter, using extremely selective and active catalysts in the oxidation of formic acid is important. Noble catalyst Pd has been vastly applied in direct formic acid fuel cells owing to its talented catalytic performance in formic acid oxidation.² It is an active metal element for formic acid adsorption and is regularly utilized as an electrocatalyst owing to its high tolerance to acidic condition.¹,⁴

Carbon materials are regularly chosen as support materials for catalyst nanoparticles to diminish the price and are easy to modify for active catalyst loading for the developed efficient fuel cells.⁵,⁶ Carbon supports could increase the diffusion layer thickness, resulting in high resistivity in the mass transfer of analytes.⁵,⁶ The physical and chemical characteristics of carbon supports improve the catalyst performance in the furthest states. Additionally, mixed carbon should increase catalytic activity, as the hybridization of carbon bonds can easily be physically and chemically adapted. Currently, graphene, along with its derivatives as support materials for metal catalysts, is being used for catalytic nanoparticle formation with chemical stability, as it is a remarkable support for electromaterial applications.⁷−⁹ 2D carbon supplies as electrocatalyst supports due to their enormous specific surface area, excellent conductivity and inexpensive production, showing great
promise. The use of reduced graphene oxide (rGO) has been restricted by its poor water solubility due to the lack of hydrophilic groups on its surface. In addition, reducing functional groups on its surface brings about diminishing available fuel anchoring sites. To overcome these obstacles, adding different allotropes of carbon could improve the ability to extend the oxidation reaction. The use of mixed and modified carbon supports would improve the diffusion layer thickness by developing the mass transfer resistivity of analytes and products. Carbon quantum dots (CQDs) are carbon nanomaterials comprising amorphous carbon nuclei with mainly graphitic sp² realms and extraordinary properties, such as excellent water solubility at a small level. CQDs have huge surface functionality, chemical stability, and facile mass scale production and can be used as green, gentle, and low-cost nanomaterials with a wide range of applicability. Therefore, finding compatible carbons and optimizing mixed carbon compositions on the electrode surface results in excellent proficiency in fuel cell reactions.

Metal oxide has been described as an active support for nanostructured platinum and palladium catalysts for water gas shift reactions and other oxidation applications. Silicon oxide (SiO₂) has also been widely used as a support for metallic nanoparticles such as Pd for heterogeneous catalytic applications in oxidation and hydrogenation reactions. The addition of metal oxide to attach strongly catalyst nanoparticles onto the graphene support improved the catalytic activity because of the bifunctional mechanism. The catalytic activity of noble metals, for example, Pt, on graphene catalysts has been demonstrated to be meaningfully enhanced with the use of several oxides, such as Mn₂O₃, MnO₂, TiO₂, and CeO₂. SiO₂ was used to modify the graphene surface to support noble metal nanoparticles with high dispersion.

Reactant or intermediate adsorption on the catalyst surface impacts the catalytic activity. It has been verified that the addition of a second metal could efficiently improve the activity and stability of Pd catalysts. Changed metals and assemblies resulting in particular improvement of the chemical composition and the catalytic activity toward fuel oxidation are given to state density changes close to the Fermi level for specific compositions of the prepared catalysts, which is approved with d-band center theory. Most studies have confirmed that Pd metal shows considerably higher catalytic activity for formic acid oxidation than Pt metal.

However, the main problems of Pd nanoparticle aggregation and the gathering of intermediates on the Pd surfaces through the oxidation of formic acid were observed. The loading of Pd onto metal oxide-modified carbon could improve the catalytic efficiency of the catalyst and increase the catalyst dispersion due to the high active surface area and porous catalyst structure, thereby preventing catalyst nanoparticle agglomeration. To improve its stability, Pd-based catalysts and SiO₂ were prepared, and the prepared Pd-based catalyst was stated to have better activity and higher stability. Finding a synthetic approach that offers practical specifications on electrocatalyst dispersity, catalyst size, and catalyst shape on graphene surfaces is the aim of catalyst nanoparticle formation. Evolutionary methods aim to load high-activity catalyst nanoparticles on support surfaces at a low price, having a huge surface area and high electrical capacity, and to exploit the accessibility of catalyst surface area for electron transfer with excellent fuel mass transport to the electrocatalyst.

In the present work, a catalyst consisting of rGO, N-CQDs, natural SiO₂, and Pd nanoparticles was prepared by a reduction method. The prepared catalysts displayed an electrochemical response in formic acid oxidation, and the high current was enhanced owing to the presence of a N-CQDs-SiO₂-rGO support. The higher mass activity, stability, and mass transfer indicated that the prepared catalyst series on the xN-CQDs-SiO₂-yrGO support could be applied in direct formic acid fuel cells.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. The chemicals in this study were analytical grade and used without further purification. PdCl₂ and graphite powder (Aldrich) were purchased from Sigma–Aldrich. Citric acid monohydrate, NaNO₃, H₂SO₄, HNO₃, HCOOH, H₂O₂ (30%), and ethanol were supplied by Merck. Urea and KMnO₄ were obtained from Ajax Finechem. NaBH₄ was purchased from Fisher Chemical. Nafion (10 wt %, 115) was obtained from Fuel Cell Store, and SiO₂ powder (98.8%) was supplied from the Department of Primary Industries and Mines, Ministry of Industry, Thailand.

2.2. Materials Preparation. GO was synthesized from graphite powder in accordance with the synthesis method described in our previous article. N-CQDs were synthesized according to a thermal approach, and 2.0 g of citric acid monohydrate and 1.0 g of urea were weighed into an Erlenmeyer flask and then dispersed in 30 mL of DI water. The dissolved solution was placed on a hot plate and kept at 120 °C until an orange–yellow solid was obtained. After the solution was cooled to room temperature, the solid was washed with ethanol 2–3 times, redispersed in DI water, transferred to a centrifuge tube, and centrifuged to remove any unreacted and high molecular weight particles. The solution to 250 mL was adjusted with deionized water to obtain 10 mg in 1 mL of N-CQD solution.

2.3. Synthesis of Pd on GO, N-CQDs, SiO₂, and xN-CQDs-SiO₂-yrGO composite. The Pd/1N-CQDs-SiO₂-1rGO catalyst was prepared as follows: 45 mg of GO, 10 mg of SiO₂, 4.5 mL of N-CQDs, and 11 mL of PdCl₂ (1 mg/mL in 0.1 M HCl solution) solutions were dissolved in 100 mL of DI water by sonication for 30 min of each of the components added. Afterward, the mixed solution was transferred onto a hot plate magnetic stirrer and stirred. A 10 mL fresh solution of NaBH₄ (20 mg NaBH₄ /10 mL DI water) was slowly dropped under vigorous stirring, followed by moderate stirring for 2 h. Finally, the Pd/1N-CQDs-SiO₂-1rGO catalyst was collected by centrifugation, washed with DI water several times until the neutral pH of the solution was reached and dried in an oven at 60 °C for 24 h. The other catalysts used in this work, including Pd/rGO, Pd/SiO₂-rGO, Pd/N-CQDs, Pd/SiO₂-N-CQDs, and Pd/xN-CQDs-SiO₂-yrGO with ratios of 1:4 and 4:1 and without SiO₂, were prepared with the same synthesis method. The Pd and SiO₂ loading on all supports was kept at 10 wt %.

2.4. Materials Characterizations. The morphologies, microstructures, and compositions of the as-prepared catalysts were studied by field-emission scanning electron microscopy (FE-SEM, JSM-IT800, JEOL) with energy-dispersive X-ray spectroscopy (EDS) and elemental mapping and high-resolution transmission electron microscopy (TEM/HR-TEM, JEM-2100F, JEOL) with selected-area electron diffraction (SAED). N₂ adsorption and desorption characterization was employed to determine the specific surface areas.
and pore structures of the as-obtained catalysts (Autosorb 1 MP, Quantachrome). The crystallographic structure and composition of the as-prepared catalysts were determined by X-ray diffraction (XRD, Empyrean/Panalytical), attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy (Bruker, INVENIO-S), Raman spectroscopy (T64000, HORIBA Jobin Yvon, France), and X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD system, K-Alpha).

2.5. Electrochemical Measurements. The electrochemical characterization of these as-prepared catalysts was performed on an eDAQ potentiostat (EChem software) with

Figure 1. FT-IR spectra (a and b) and Raman spectra (c and d) of selected as-prepared catalysts.
a conventional three-electrode cell that consisted of Ag/AgCl as the reference electrode, Pt wire as the counter electrode, and a 3 mm glassy carbon (GC) electrode coated with catalysts as the working electrode. The working electrode was prepared as follows: 2 mg of catalyst powder was dispersed in 1 mL of mixed solution containing 625 μL of 5% NaFion 117 solution, 200 μL of ethanol, and 7.375 mL of DI water to the black solution by ultrasonication for 30 min. Consequently, 5 μL of the resulting black suspension was dropped onto the cleaned GC electrode surface and left to dry. Cyclic voltammetry (CV) and CO stripping voltammetry were measured in 0.5 M H2SO4 with a scan rate of 50 mV s⁻¹ to investigate the performance of catalysts and calculate the electrochemical active surface area (ECSA) of Pd catalysts. The electrocatalytic performance of formic acid oxidation was evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA). CV measurement was directed in 0.5 M HCOOH and 0.5 M H2SO4 at a scan rate of 50 mV s⁻¹ to investigate the performance of catalysts and calculate the electrochemical active surface area (ECSA) of Pd catalysts. The electrocatalytic performance of formic acid oxidation was evaluated by cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA). CV measurement was directed in 0.5 M HCOOH and 0.5 M H2SO4 at a scan rate of 50 mV s⁻¹. LSV test was conducted in 0.5 M HCOOH and 0.5 M H2SO4 within an anodic scan (−0.2−1.0 V) at a scan rate of 50 mV s⁻¹. CA measurement was tested at a constant potential of 0.20 V (vs Ag/AgCl) for 3600 s. The electrolyte was purged with pure nitrogen gas for 20 min to eliminate excess dissolved oxygen before the electrochemical measurements.

3. RESULTS AND DISCUSSION

3.1. Physical Characterization. 3.1.1. FT-IR. The chemical bonds and functional groups of the as-prepared GO, N-CQDs, SiO2, and the Pd catalyst composite with N-CQDs-SiO2-rGO supporting materials were demonstrated on the FT-IR spectra, as shown in Figure 1a,b. The characteristic absorption spectra of GO show stretching vibrations for hydroxyls and carboxyls originating from COOH, C−OH, and H2O (~3300−3700 cm⁻¹), carboxyls and/or carboxyls within the overlapping frequency range (C==O, COOH, ~1690−1890 cm⁻¹), carboxyl and/or ketones (COOH, C==O; ~1620 cm⁻¹), and epoxides (C−O−C; ~1370 cm⁻¹ and ~800−900 cm⁻¹).22,23 All the characteristic absorption spectra of GO and rGO show a strong peak, which indicates that the oxygen functional group has undergone chemical reduction and/or more anchor sites. The spectra of N-doped CQDs comprise specific absorption peaks, which relate to the characteristic stretching and bending vibrations of amines and amides attributed to C−N and N−H bonds.24 The broad absorption spectra at ~3000−3300 cm⁻¹ are related to hydroxyls, carboxyl, and the amino groups of −OH, COOH, and N−H. The weak peaks at ~2900 cm⁻¹ correspond to the C−H bond stretching vibrations.25,24 The peaks at ~1600, 1481, 1387, and 1245 cm⁻¹ are attributed to the typical stretching vibrations of C−N and N−H with contributions from N−C==O, heterocyclic C−N−C, N−(C)ø, and C−N−C bonds.23−25 In addition, the absorption peaks at ~1557 cm⁻¹ and between ~900 and 700 cm⁻¹ were attributed to the N−H bending vibration of the primary amino group.24,25 The results indicated that the N-containing groups were created by synthesis between urea and citric acid, and N species were resourcefully doped into the N-CQDs structure. After synthesis of the N-CQDs-rGO composites, the FT-IR spectrum seems to be comparable to the characteristic absorption spectra of N-CQDs and GO. It can be observed that the strength of the N-CQDs-rGO composite material is weak; the peak at approximately 3000–3500 cm⁻¹ is attributed to the stretching vibrations of O−H, COOH, and N−H, and the peaks at ~1600, 1557, 1481, 1387, and 1245 cm⁻¹ correspond to the stretching vibrations of C−N, C==O, C−OH, C−O−C, and C−N and N−H bending vibrations. It was confirmed that the N-containing groups in N-CQDs positively reduced the oxygen content on GO through the reducing agent process. For the spectra of pure SiO2 particles, the absorption spectra are ascribed to the stretching vibrations of Si−O−Si/ Si−O at ~1053, 777, 692, and 453 cm⁻¹.15,26 The peaks at 1053 and 777 cm⁻¹ match the asymmetric stretching vibration and symmetrical stretching vibration of Si−O−Si, respectively, while the absorption peak at 453 cm⁻¹ can be attributed to the bending vibration of Si−O and the shoulder peak at 692 cm⁻¹ is attributed to Pd−O−Si. When Pd nanoparticles were detached on the SiO2 surfaces, the most intense Si−O−Si and Si−OH peaks shifted to lower frequencies, that is, ~1049 cm⁻¹ and 775 cm⁻¹ respectively, resulting in shifts of Si−O−Si and Si−OH bands, representing that Pd nanoparticles were adsorbed on the SiO2 surface. The characteristic absorption spectra of the N-CQDs-SiO2-rGO composites showed stretching and bending vibrations similar to the N-CQDs-rGO and SiO2 spectra, which were composed of hydroxyls, carboxyl groups, alkenes, ketones, amine groups, and silicone at ~3000−3700 cm⁻¹, ~1690−1890 cm⁻¹, ~1500−1600, ~1000−1400, and ~700−400 cm⁻¹, but the absorption spectra had high intensity compared with N-CQDs-rGO; specifically, the peaks at ~3000−3700 cm⁻¹ were ascribed to the stretching vibrations of O−H, COOH, and N−H.25,26 The high intensity at these absorption ranges suggested oxygenation functional groups with involvement from SiO2.25,26

3.1.2. Raman Spectroscopy. In Figure 1(c,d). The characteristic Raman spectra of graphene oxides (GO) as supported materials show three scattering peaks centered at ~1337.2, 1583.9, 2665.1, and 2898.1 cm⁻¹, which match to the D, G, 2D, and (D+G) bands of graphite, respectively.22,26,27 The G-band is reflected by ordered sp² hybridized carbon atoms in the hexagonal structure of graphitic carbons. The D-bands are allocated to disordered sp³ hybridized graphite carbon and/or disordered defects in sp² hybridized carbon atoms.26,27 The 2D band is representative of sp² hybridized carbon−carbon bonds in graphene and can be used to determine the layer number of graphene.22,26,27 Here, the band is perceived to be broadened, ascribed to the fact that the prepared graphene-based carbon support comprises few layers with some defects. The D+G-band is a second-order spectral derivative from the D- and G-band combination, which indicates defects in the carbon atom framework of graphene by the reduction process.27 The D+G-band and the 2D band are broadened, which demonstrates the restoration of graphite structures. Generally, the intensity ratio of the D-band to the G-band (I_D/I_G) is used to describe the defect and/or disorder level of the carbon framework. The I_D/I_G value of the as-prepared catalysts is increased when SiO2 and Pd were reduced on the supported materials. This demonstrates that the SiO2 and Pd nanoparticles bonded on the rGO and/or N-CQDs-rGO hybrid material structure, causing a high number of structural defects.

In addition, the characteristic vibration band of SiO2 is located at ~625 cm⁻¹, which is attributed to the characteristic vibration D2 band of the three-membered silicon ring (Si−O−Si), or homopolar Si−Si and O−O bonds.26,28 Meanwhile, three other bands at ~275.7 (D1; δ_scissoring in extended tetrahedron [SiO4]2−/ [Si4]4−), ~426.1 (D1; and D3; stretching vibrations (ν3) for Si−O−Si associated with
symmetric breathing modes of regular four- and five-membered rings or larger-membered silica rings) and \( \sim 1040.3 \text{ cm}^{-1} \) are assigned to Si–O–Si asymmetric stretching vibrations of tetrahedron SiO\(_4\) which are densified from SiO\(_2\) and correlated with pseudocrystalline structures such as cristobalite, coesite, tridymite, or quartz.\(^{28}\) It is worth noting that all these scattering bands can be observed in the Raman spectra of the catalyst prepared in SiO\(_2\), which is further conclusive evidence that SiO\(_2\), N-CQDs, and rGO coexist in the hybrid material, and the results are consistent with the FT-IR results.

3.1.3. BET. The Brunauer–Emmett–Teller (BET) specific surface area and the pore size distribution profiles of the as-prepared catalysts were examined by nitrogen adsorption and desorption isotherm experiments and are shown in Figure 2. The SiO\(_2\) particles, an assembly of pore types (macropores, mesopores, and micropores), and the isotherm pattern in Figure 2a,b. The as-obtained catalysts possess representative type IV isotherms with obvious H\(_4\) hysteresis loops at relative pressures \( (P/P_0) \) extending from 0.4–1.0, signifying the existence of mesoporous assembly (Figure 2a).\(^{8,20}\) In addition, the adsorption isotherms show that a fast increase in the N\(_2\) adsorbed extent at a relative pressure \( P/P_0 < 0.1 \) and a sharp increase at a relative pressure \( P/P_0 > 0.9 \) disclose the presence of micropores and macropores of the prepared catalysts, respectively. The calculated specific surface areas and total pore volumes of the catalysts are as follows: Pd/rGO (BET; 8.76 m\(^2\) g\(^{-1}\), pore volume; 0.4220 cm\(^3\) g\(^{-1}\)), Pd/SiO\(_2\)-rGO (63.92, 0.1948), Pd/1N-CQDs-SiO\(_2\)-4rGO (101.03, 0.1990), Pd/1N-CQDs-SiO\(_2\)-1rGO (118.32, 0.2813). The BET surface area of Pd/rGO is the lowest, which may be because of restacking of rGO sheets.\(^{8,20}\) As expected, the existence of SiO\(_2\) and N-CQDs in the catalyst composite could possibly discontinue the graphene sheets from being restacked and therefore, bring about high BET surface area and pore volume values related to the Pd/rGO catalyst. The 3D system of SiO\(_2\), N-CQDs, and rGO composite in the Pd-based catalyst system with numerous defects possibly offers highly effective nucleation sites to capably hinder catalyst accumulation. The addition of N-CQDs and SiO\(_2\) onto the GO support stabilizes an entire 3D network catalyst surface. The large specific surface area and pore structure result in an increase in charge usage, a reduction...
in the effective ion diffusion, and an improvement in the physical arrangement of electroactive catalysts, contributing to an increase in the specific capacity of the reaction. The alterations in specific surface areas and pore assemblies for prepared catalysts result in diverse chemical reactions. The high surface area and large pore volume of catalysts implied the exposure of more active sites and the mass transport of reactants and products.

3.1.4. XRD. The XRD patterns of catalysts with N-CQDs display a broad amorphous peak centered at \( \sim 24.4^\circ \) and 43.2\(^\circ\), which is ascribed to highly disordered carbon attributed to the (002) and (101) lattice planes of graphitic carbon and organic carbon. The XRD peaks of catalysts with GO exhibited a peak at \( 2\theta = 10.9^\circ \) with an interlayer distance of 0.8 nm as the interlayer distance of graphite was 0.34 nm (Figure 3). This reveals that numerous oxygen-containing functional groups were inserted between the interlayers. The peak at 10.9\(^\circ\) is less intense after the reduction process, changed by a broad peak at \( 2\theta = 24.3^\circ \) for rGO, with a \( d \)-spacing of 0.4 nm, inferring some reduction of GO to rGO. The crystalline structures of the sharp diffraction of SiO\(_2\) at \( 2\theta = 20.7^\circ, 26.6^\circ, 36.5^\circ, 39.8^\circ, 45.8^\circ, 50.2^\circ, 55.1^\circ, 59.97^\circ, 68.07^\circ, \) and 74.83\(^\circ\) are attributed to the (100), (101), (110), (111), (201), (112), (202), (211), (301), and (302) planes, which correspond to the \( \alpha \)-quartz form mineral reported (JCPDS card no. 46-1045). Quartz, cristobalite, and tridymite are the main phases in silica bricks. The XRD peaks of catalysts with SiO\(_2\) were found at 26.7\(^\circ\) and 39.5\(^\circ\), indicating a hexagonal crystal structure with a lower peak intensity. Amorphous silica shows a much broader diffused XRD peak. Interestingly, SiO\(_2\) was obtained as a sharp peak at ca. 22–30\(^\circ\) showing the high degree of crystallinity of SiO\(_2\) by the physical interaction between silica and metal.

The main peaks of Pd for highly active oxidation were characterized at 39.3\(^\circ\) and 45.4\(^\circ\) due to the phases of Pd(111) and Pd(200), respectively. Nevertheless, the other peaks at 39.3\(^\circ\) and 45.4\(^\circ\) could belong to the cubic and tetragonal structure of PdO. The average Pd and PdO crystallite sizes calculated from the XRD peaks at \( 2\Theta = 39.3^\circ \) and 45.4\(^\circ\), respectively, using the Scherrer equation were 6.87 and 6.01 nm, respectively. The reflection peaks located at \( 2\Theta = 39.3^\circ, 45.4^\circ, 66.5^\circ, \) and 79.9 match the (111), (200), (220), and (311) planes of a fcc Pd lattice, respectively. The diffraction peak (111) of catalysts in Figure 3 was shifted somewhat toward lower at <39.3\(^\circ\) related to Pd/rGO (JCPDS 00-005-0681). The mean crystalline size value (Table S1) was 6.4 nm by means of the Scherrer equation through line broadening of the Pd (111) peak.

3.1.5. Electron Microscopy. Figure 4 and Figure S1 show typical TEM images of Pd and SiO\(_2\) nanoparticle dispersions on N-CQDs and rGO composites. The prepared N-CQDs with spherical and mean sizes of N-CQDs were 3.72 ± 1.08 nm. Pd nanoparticles with a size of 5.67 nm are dispersed on the surface of SiO\(_2\)-rGO nanospheres with an average spherical size in SiO\(_2\) of \( \sim 1 \) \( \mu \)m (SiO\(_2\) powder). The Pd nanoparticles on N-CQDs and rGO are 6.35 and 6.31 nm, respectively, while the Pd nanoparticle size on N-CQDs-SiO\(_2\)-rGO is 4.81 nm, which is rather small. However, some of the Pd nanoparticles are agglomerated for the support without SiO\(_2\) and N-CQDs on rGO. As expected, the energy dispersive X-ray (EDX) spectroscopy and element mapping investigation reveal the presence of the C, O, N, Si, and Pd elements uniformly found.
throughout the N-CQDs-SiO$_2$-rGO supporting materials (Figure 4g–l).

Figure 4c and Figure S1 show the incorporation of Pd within the various supports. With the use of ImageJ software for the measurement, the particle sizes from the TEM are shown in Table S1. The mean crystallite sizes were 4.10 ± 0.77 (Pd/1N-CQDs-SiO$_2$-4rGO), 5.17 ± 1.17 (Pd/1N-CQDs-SiO$_2$-1rGO and Pd/4N-CQDs-SiO$_2$-1rGO), 5.56 ± 1.47 (Pd/1N-CQDs-

Figure 5. (a,b) High-resolution XPS spectra of as-prepared catalysts and (c) C 1s, (d) O 1s, (e) N 1s, and (f) Si 2p of the Pd/N-CQDs-SiO$_2$-rGO catalyst.
4rGO), 5.67 ± 2.09 (Pd/SiO2-rGO), 5.73 ± 1.09 (Pd/SiO2-N-CQDs), 6.31 ± 1.67 (Pd/rGO), and 6.35 ± 1.28 nm (Pd/N-CQDs).

Among catalysts, the nanoparticle shapes are regularly spherical with an average size of 4–6 nm. The selected area of diffraction (SAED) patterns show the diffused rings that designate the polycrystalline N-CQDs (Figure 4e and Figure S2). This agreed with XRD patterns for all catalysts with the N-CQDs indicating a broad diffraction peak at 2Θ = 24.0° and 43.3° for the (002) and (101) planes, which designated the amorphous carbon structure for N-CQDs. The lattice fringes with the calculated interplanar distances were 0.298 nm for catalysts with N-CQD.

The high-resolution transmission electron microscopy (HR-TEM) image of the Pd/N-CQDs-SiO2-rGO is shown in Figure 4d and Figure S2. The image shows interplanar distances of 0.191 and 0.312 nm, agreeing with the Si planes of SiO2. Moreover, the ordered lattice fringes with a constant lattice spacing of 0.223 nm correspond to the Pd (111) plane for the fcc structure, while the interplanar spacing of 0.334 agreed to the C (002) plane. However, the SAED of the prepared catalysts in Figure S2. shows the presence of the (111) and (220) planes of SiO2 nanoparticles and the (111) planes of Pd, indicating the polycrystalline characteristic of the prepared catalyst nanoparticles.

3.1.6. XPS. The elemental composition of the N-CQDs, Pd, SiO2, and rGO was determined by means of XPS. The XPS spectra of the as-prepared catalysts show that the hybrid composited structure was composed by Pd 3d, C 1s, O 1s, N 1s, and Si 2p, core-level spectra in Figure 5, the components well-disposed with the aforementioned EDX and mapping results. The Pd 3d spectra can be deconvoluted into four doublets peaks (Figure 5a,b). The peaks, which individually ascended at ca. (335.8 and 341.3 eV), (336.5 and 342.0 eV), (337.4 and 343.1 eV), (338.7 and 344.4 eV), were ascribed the 3d5/2 and 3d3/2 of metallic Pd0, Pd(OH)ads, PdO(2+), and PdO2(4+), respectively.14,29 Those binding energies of the Pd peaks of Pd/N-CQD-SiO2-rGO had a slightly negative shift...
compared to those of Pd/rGO. These negative shifts are from the electronic structure change ascending from the strong coordination between Pd and SiO₂, N-containing carbon that noticeably decreases in the 3d electron density of Pd, and the smaller size result of Pd nanoparticles. In other words, the negative shift of Pd 3d was associated with a drop in the Fermi level or a rise in d vacancies at valence bonds (3d orbitals). Based on the d-band center theory, an appropriate shift would affect the weak adsorption strength between the Pd surface and the adsorbed species (COads) due to the reduced electron feedback from the Pd surface to the antibonding energy level of the molecule. The C 1s and O 1s spectra were deconvoluted and showed the existence of different bonds in the catalysts (Figure 5c,d). Five types of deconvoluted peaks of C 1s for the as-prepared catalysts were obtained for catalysts Pd/N-CQDs-SiO₂-rGO in Figure 5c, the peak positions were ca. 284.0, 285.0, 285.8, 280.7, and 288.2 eV, associated with the C 1s states in C–OH, C–C/C=C, C–O/C=N–C=NN, C=O/COOH, and HO–C=O bonds, respectively. Four main deconvoluted peaks for O1 s were observed at 531.3, 532.4, 533.7, and 534.9 eV, which indicate the presence of HO–C=O/Pd–O, O=C, C–OH, and O–C groups in the prepared catalyst. Meanwhile, the deconvolution of the N 1s spectrum in Figure 5e shows that two peaks corresponded to pyridine N and pyrrolic N with a binding energy of ca. 309.1 and 400.7 eV, respectively, which is attributed to the N atoms contained in the carbon layer. Electrocatalytic behaviors of various catalysts were first considered by cyclic voltamogram (CV) measurements in a nitrogen (N₂)-saturated 0.5 M H₂SO₄ aqueous solution at a sweeping rate of 50 mV s⁻¹ at room temperature in the potential region of −0.2–1.0 V vs Ag/AgCl as shown in Figure 6. The CVs represent Pd on different compositions of those materials N-CQDs, SiO₂, and rGO in the catalyst system. All the CV curves show three distinguishing potential regions consisting of (1) underpotential adsorption or deposition of hydrogen of −0.2 < E < 0.10 V, (2) the charge of the double-layer region corresponding to the oxygenated groups on the support surface of 0.10 < E < 0.45 V, and (3) the oxidation/reduction (PdO/Pd–OH) on the catalyst surface region of 0.4 < E < 0.75 V.

The CVs of catalysts with diverse support composites show different shapes of H_ads/des and oxide formation/reduction profiles. The CVs of Pd/GO and Pd/N-CQDs, Pd/SiO₂-N-CQDs, and Pd/SiO₂-GO (Figure 6a) provide a double layer for the whole range of scanning, while the CVs of Pd/SiO₂ and Pd/N-CQDs-rGO show less current intensity in all regions (shown here). The Pd/N-CQDs-SiO₂-rGO catalysts (Figure 6b) demonstrated an encouragingly higher and larger current for the hydrogen adsorption/desorption regions compared with Pd/N-CQDs-rGO, Pd/rGO, and Pd/N-CQDs catalysts. This indicated that the SiO₂ and stoichiometric ratio of mixed carbons could provide oxygen-containing species (e.g., −OH) for the oxidation of intermediates, which is promising for improving the catalytic activity and direct electron transfer pathway of hydrogenous fuel such as formic acid or small organic molecules. Similarly, the oxide reduction peaks (Pd–O₂ reduction regions) of ca. 0.4 V are related to the reduction of Pd–OH from a positive sweep over approximately 0.6 V. An observably larger area of the Pd–O reduction peak can be ascribed to the as-prepared SiO₂-composited catalyst developing an electrolyte–electrode available surface area. The oxypyphilic property of the associated metal provided the oxygen-containing species for intermediate removal, and the prepared catalyst had strong attraction with high selectivity pathways for oxygen adsorption. The Pd reduction peak region can be used to evaluate the coverage of active sites in electrochemical reactions. Here, the electrochemical surface area (ECSA) is calculated based on the charge involved in the reduction of the Pd oxide during the negative scan, using the following equation:

\[
\text{ECSA}_{\text{PdO}} = \frac{Q}{(0.420 \times Pd_{\text{m}})}
\]

where Q is the integral of the peak from the reduction of PdO in the potential range of 0.4–0.65 V, Pd_m is the load of Pd on the working electrode, and 0.420 mC cm⁻² is a conversion factor, which shows that the charge of the PdO monolayer can be reduced.

The calculated ECSA values of mixed carbon catalysts for Pd/1N-CQDs-SiO₂-1rGO, Pd/4N-CQDs-SiO₂-4rGO, and Pd/1N-CQDs-4rGO were 52.9, 47.6, 46.3, and 23.4 m² g⁻¹, respectively, whereas those of the single carbon catalysts for Pd/N-CQDs, Pd/SiO₂–N-CQDs, Pd/SiO₂-rGO, and Pd/rGO were 44.2, 40.3, 31.9, and 5.5 m² g⁻¹, respectively, which are also itemized in Figure 6c. Based on a similar Pd (10 wt %) and SiO₂ (10 wt %) loading, catalysts with SiO₂ show a narrow ECSA compared to that catalysts without SiO₂. In addition, the Pd loaded on the mix of N-CQDs and rGO with/without SiO₂ modified surface catalysts were found to have a higher ECSA than that of Pd/rGO, due to the N-CQDs carbon not only having similar spherical and small sized Pd nanoparticles but also aggregating Pd on the supported surface. Although more active sites of those catalysts are quantified than Pd/SiO₂-rGO, Pd/SiO₂-rGO has high dispersibility and high specific active area as observed by SEM–EDS and TEM images. Moreover, the ECSA of Pd on a hybrid material supports that it consists of N-CQDs, SiO₂, and rGO, and the Pd/1N-CQDs-SiO₂-1rGO catalyst was found to have a high ECSA value, which is 2.3 and 9.6 times larger than those of catalysts without SiO₂. Pd/1N-CQDs-SiO₂-rGO and Pd/rGO, respectively (Figure 6c). The high ECSA value of the as-prepared catalysts is attributed to the resulting three features as follows: (1) The N-containing group of N-CQDs, which is a small carbon (ca. 2 nm as seen in TEM), reduced GO to rGO with N-containing groups, which could result in larger areas and provide utilization of more active sites for supported Pd catalysts. (2) Similarly, SiO₂ also played an important role in increasing the surface area and number of accessible catalytically active sites for the catalysts. (3) There was uniform dispersion and ultrasmall Pd NPs on more reachable catalytic sites and high surface areas, which was significant for successful catalytic activity.

In Figure 6a, the Pd/rGO and Pd/SiO₂-rGO catalysts represent a broad region of charge of the double layer, especially Pd/SiO₂-rGO, because SiO₂–rGO contained more oxygenated groups, which are used for Pd bonding and highly active surface sites. However, the Pd/N-CQDs and Pd/SiO₂-N-CQDs catalysts show a narrow double layer on the CVs in
this region less than 5 times compared with Pd/rGO and Pd/SiO$_2$-rGO. Moreover, the oxidation and reduction processes represent the prominent sharp peak in the chemisorption/reduction regions, which is related to Pd nanoparticles on the composite catalysts, as the synthesis process produced Pd interacting on the N-CQDs layer that provided high activity, resulting in the sharp peak Pd chemisorption/reduction process without inhibition of the oxides of SiO$_2$-rGO. Pd/xN-CQDs-SiO$_2$-yrGO catalysts composed of different amounts of N-CQDs and rGO are shown in Figure 6b. The curves signifying CVs are similar to that in Figure 6a. Not only does the rGO catalysts highly loaded with SiO$_2$ content show a wider charge of double-layer area than the catalysts with N-CQDs, but they also show a wider chemical adsorption (Pd−OH)/reduction (Pd−O) area.

3.2.3. Formic Acid Oxidation. The electrocatalysis of the different catalysts was measured in 0.5 M H$_2$SO$_4$ + 0.5 M HCOOH electrolyte with a scan rate of 50 mV s$^{-1}$ at room temperature. Regarding the oxidation reaction for formic acid results shown in Figure 7, the CV curves of all the catalysts displayed two well-defined anodic current peaks: one in the positive sweep and the other in the negative sweep. The forward scan CVs show a prominent current peak at ca. 0.1 V and a shoulder peak at ca. 0.6 V vs Ag/AgCl, which is ascribed to the direct oxidation of formic acid to CO$_2$ (“direct path” or dehydrogenation reaction), and the shoulder peak at ca. 0.6 V is associated with the dehydration reaction. For the reverse scan, CVs show a current peak at ca. 0.2 V vs Ag/AgCl that can be associated with the indirect oxidation of formic acid to the oxidation of CO byproducts (CO intermediate path). Noticeably, the forward scan oxidation peak current density of all the catalysts is much higher than that of the backward scan oxidation peak, signifying good catalytic activity in the dehydrogenation pathway via direct formic acid oxidation (FAO): HCOOH $\rightarrow$ CO$_2$ + 2H$^+$ + 2e$^-$. The hybrid material’s effect of the Pd-based catalysts and SiO$_2$ with N-containing
carbon-supported materials induced activity improvement and the catalytic performance of N-CQDs, rGO, and the material comprising these two types of carbons with and without SiO2 for electrooxidation of formic acid. The peak current is a signal of the catalytic activity of the catalysts. Figure 7a,b shows the Pd nanoparticles with/without SiO2 on hybrid materials composed of N-CQDs and rGO by varying the amount of carbon composition in wt %. The onset potentials of the catalysts are as follows: Pd/1N-CQDs-SiO2-1rGO (−0.115 V), Pd/1N-CQDs-SiO2-4rGO (−0.109 V), Pd/SiO2-rGO (−0.108 V), Pd/4N-CQDs-SiO2-1rGO (−0.99 V), Pd/1N-CQDs-SiO2-4rGO (−0.97 V), Pd/N-CQDs (−0.92 V), Pd/SiO2-N-CQDs (−0.79 V), and Pd/rGO (−0.059 V), respectively. The onset potentials of the catalysts with N-CQDs and SiO2 are rather low compared with those of the catalysts on unmodified rGO support.

The mass activity (MA) and/or specific activity (SA) of Pd nanoparticles on hybrid carbon materials are listed in Table S3, and the MA is ordered as follows: Pd/1N-CQDs-SiO2-4rGO (951.4 mAg−1 Pd) > Pd/1N-CQDs-SiO2-1rGO (905.3 mAg−1 Pd) > Pd/SiO2-rGO (884.9 mAg−1 Pd) > Pd/4N-CQDs-SiO2-1rGO (743.6 mAg−1 Pd) > Pd/1N-CQDs-SiO2-4rGO (607.8 mAg−1 Pd). Moreover, the trend of specific activity (SA) of the prepared catalysts is similar to the MA results presented in Figure 7c. The activity of the Pd/1N-CQDs-SiO2-4rGO catalyst on formic acid oxidation was the highest compared to the other catalysts. The forward oxidation peak of MA on the Pd/1N-CQDs-SiO2-4rGO catalyst was the highest compared to the other catalysts. The activity (SA) of the prepared catalysts is shown in Figure 8. The Tafel slope was calculated in the potential range between −0.12 and 0.00 V. The effect of SiO2 modification on the catalytic mechanism of different supports is shown in Figure 8a. The Tafel slopes for various catalysts are Pd/rGO (79.5 mV dec−1), Pd/N-CQDs (91.8 mV dec−1), Pd/SiO2−N-CQDs (94.4 mV dec−1), and Pd/SiO2-rGO (95.0 mV dec−1). The influence of carbon components (N-CQDs and rGO) and SiO2 hybrids as supporting materials is shown in Figure 8b. Pd/1N-CQDs-SiO2-4rGO (72.5 mV dec−1), Pd/1N-CQDs-SiO2-1rGO (75.2 mV dec−1), Pd/4N-CQDs-SiO2-1rGO (80.9 mV dec−1), and Pd/1N-CQDs-SiO2-4rGO (100.4 mV dec−1). Different Tafel values indicate different catalytic mechanisms and the number of adsorbed reactants in the catalytic process, which are used in the rate determination step.

A Tafel slope value lower than 120 mV dec−1 designated the chief path, as dehydrogenation is the rate-determining step (RDS) through CO2 formation, and a slope value lower than 120 mV dec−1 proposes enhanced dehydrogenation chiefly because of the fewer poisoning species. Herein, Pd nanoparticles supported on rGO and N-CQDs-rGO carbons with/without SiO2 modification confirmed that the Tafel slope value was less than 120 mV dec−1, indicating that the catalytic mechanism was a direct pathway or dehydrogenation.
Obviously, the small value of the Pd/1N-CQDs-SiO2-1rGO catalyst indicates that the charge transfer kinetics of the composite nitrogen-containing carbon and SiO2 hybrid catalyst for the electrooxidation of formic acid is faster and has the highest intrinsic catalytic activity.

3.2.5. CO Oxidation. Further investigation and evaluation of the antipoisoning ability of the prepared catalyst is an important and significant aspect of the high-performance electrooxidation of formic acid catalysts. CO stripping voltammetry experiments were conducted to study the ability to resist COad poisoning and estimate the number of active sites through electrochemically active surface area (ECSA\textsubscript{CO}) (Figure 9 and Figure 6c). The typical CO stripping voltammogram of the prepared catalyst is shown in Figure 9. In the first cycle, the absence of the H\textsubscript{des} peak in the low potential region indicates that CO was successfully adsorbed on the catalytic surface, and there is a CO oxidation peak at a higher potential. In the second cycle, the CO oxidation peak disappeared at the same time, and the recovery of the H\textsubscript{des} peak indicated that the CO adsorbed on the catalyst surface is completely oxidized and eliminated.19,33 According to the CO stripping voltammogram, the lower is the CO oxidation peak and onset potential, the higher is the antipoisoning capability. Based on the influence of SiO2 modification on the rGO and N-CQDs supports loaded with Pd nanoparticles, the initial potential and oxidation peak potentials of the Pd/N-CQDs catalysts are lower than those of Pd/SiO2-N-CQDs, Pd/SiO2-rGO, and Pd/rGO, respectively, (Table S4) and Figure 9a. The results show that the nitrogen-containing carbon N-CQDs and the metal oxide SiO2 have an effective effect on the antipoisoning CO ability in formic acid oxidation. As the results are in good agreement with the hybrid carbon (N-CQDs and rGO) composition with SiO2 of Pd/1N-CQDs-SiO2-1rGO, Pd/1N-CQDs-SiO2-4rGO exhibited a negative shift compared with Pd/1N-CQDs-4rGO (Figure 9b). This indicates the oxophilicity of Si and N-containing carbons, out of which the oxygen species and N derivatives are accessible for CO oxidation via the hybrid surfaces and bifunctional catalytic mechanism. The calculated ECSA\textsubscript{CO} of all catalysts was used to evaluate the active sites by integrating the CO oxidation peaks.19,31,33 The ECSA\textsubscript{CO} of Pd/1N-CQDs-SiO2-1rGO is approximately 43.9 m\textsuperscript{2} g\textsuperscript{-1}, which is larger than those

![Figure 9. CO\textsubscript{ad} stripping voltammograms of single carbon catalysts (a) and hybrid carbon catalysts (b); the catalysts prepared in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution were analyzed at the scan rate of 50 mV s\textsuperscript{-1}.](https://pubs.acs.org/doi/10.1021/acsomega.2c00906)

![Figure 10. Chronoamperometry curves of samples in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution containing 0.5 M HCOOH at 0.2 V (vs Ag/AgCl) for 3600 s.](https://pubs.acs.org/doi/10.1021/acsomega.2c00906)
of Pd/1N-CQDs-SiO2-4rGO (41.8 m² g⁻¹), Pd/4N-CQDs-SiO2-1rGO (4.18 m² g⁻¹), Pd/SiO2-rGO (40.6 m² g⁻¹), Pd/SiO2-N-CQDs (28.9 m² g⁻¹), Pd/N-CQDs (19.7 m² g⁻¹), Pd/1N-CQDs-4rGO (6.8 m² g⁻¹), and Pd/rGO (6.6 m² g⁻¹). The larger ECSA specifies a good distribution of Pd nanoparticles and terminates the mixed material supported by N-CQDs, SiO2, and rGO, thereby contributing to the coverage of active sites and the enhancement of catalyst performance. Consequently, the Pd nanoparticles over the N-CQDs, SiO2, and rGO hybrid material support exhibited mainly enhanced anti-CO poisoning ability and active material, which was useful for the high activity for formic acid oxidation.

3.2.6. Stability. The long-term durability of various catalysts to FAO was further evaluated through chronoamperometric (CA) measurements, as shown in Figure 10. Due to the double-layer charge effect of the adsorption of the intermediate carboxylic acid to the Pd site during the oxidation of formic acid, the current density of all prepared catalysts decayed rapidly in the initial period and stabilized at a pseudo-steady-state. Obviously, compared with all prepared catalysts, the Pd/1N-CQDs-SiO2-4rGO and Pd/1N-CQDs-SiO2-rGO catalysts exhibit a lower decay rate and a higher steady-state current density. The mass activity (MA) after 3600 s measurements was Pd/1N-CQDs-SiO2-1rGO (13.39 mA mg⁻¹Pd), Pd/1N-CQDs-SiO2-4rGO (10.95 mA mg⁻¹Pd), Pd/4N-CQDs-SiO2-1rGO (10.16 mA mg⁻¹Pd), Pd/SiO2-N-CQDs (9.02 mA mg⁻¹Pd), Pd/SiO2-rGO (7.02 mA mg⁻¹Pd), Pd/rGO (5.02 mA mg⁻¹Pd), Pd/1N-CQDs-4rGO (4.58 mA mg⁻¹Pd), and Pd/N-CQDs (4.52 mA mg⁻¹Pd). The value of the Pd/1N-CQDs-SiO2-1rGO catalyst is approximately 2.9 times and 2.7 times higher than that of the Pd/1N-CQDs-4rGO and Pd/rGO catalysts, indicating its excellent ability to maintain catalytic performance.

The excellent catalytic activity and stability of the Pd/1N-CQDs-SiO2-1rGO catalyst toward FAO corresponds to the presence of N-containing carbon and SiO2 in the construction, which can not only immobilize and anchor sites on the Pd nanoparticles with an active phase on the N-CQDs-SiO2-rGO hybrid support but also stimulate the water dissociation process to produce abundant hydroxyl (–OH) sources for the oxidative removal of CO species. In addition, through the mixed carbon-based material structure, the Pd-carbon contact area is improved, and at the same time, the resistance to carbon deterioration is improved under acidic catalytic conditions. Low-CO oxidation of the catalysts could possibly be the formation of Si–O bonds and interaction with the small Pd metal clusters/particles, resulting in an inhibition of CO chemisorption. The XRD result indicated the preparation of a proper catalyst phase with high dispersion (TEM results), and XPS results confirmed the formation of a Pd and Si (XPS) alloy, as a strong interaction between Pd and SiO2, or less CO adsorption was expected as a result of enormous activation; thus, less CO was subsequently adsorbed on the catalyst surface.

4. CONCLUSIONS

By reduction method, Pd/N-CQDs-SiO2-rGO catalysts were prepared to improve the oxidation of formic acid. It was indicated that the synthesis process possibly alters the electronic properties of catalysts containing Pd and SiO2 on the N-CQDs and rGO as a support. This would be attributed to the small size of Pd and SiO2 nanoparticles (particle size in the range of 5–10 nm) dispersed on mixed N-CQDs and rGO supports with the exceptional electronic and physical interactions among Pd, SiO2, N-CQDs, and rGO composites. These catalysts indicate a bifunctional mechanism of composite catalysts to improve the activity toward oxidation. The mass activities of Pd/N-CQDs-SiO2-rGO, Pd/N-CQDs-rGO, and Pd/rGO were 951.4, 607.8, and 157.6 mA g⁻¹, respectively, which was ca. 6–7 times compared with that of Pd/rGO and approximately 3–4 times compared with that of commercial Pt/C. With low potential for CO oxidation and high current intensity, the composites of rGO, SiO2, and N-CQDs into Pd-based catalysts improved the catalytic activity of the prepared catalyst for the oxidation of formic acid and intermediates. The high current densities, intensified durability, and reasonably higher efficiency as compared to Pd/rGO and commercial Pt/C catalysts were also achieved. This prepared catalyst provides potential applications for effective catalyst systems for direct formic acid fuel cells.

ASSOCIATED CONTENT

Supporting Information

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Notes
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