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Intimately coupled hybrid of graphitic carbon nitride nanoflakelets with reduced graphene oxide for supporting Pd nanoparticles: A stable nanocatalyst with high catalytic activity towards formic acid and methanol electrooxidation

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ABSTRACT

A novel nitrogen-rich support material (CNNF-G) consisting of graphitic carbon nitride (g-C₃N₄) nanoflakelets (CNNF) and reduced graphene oxide (rGO) is designed and fabricated for loading Pd nanoparticles. Structural characterizations indicates that the CNNF is formed via splitting decomposition of the g-C₃N₄ polymer on rGO at higher temperatures and the resulting CNNF is intimately coupled to the rGO sheets. The CNNF can provide more exposed edge sites and active nitrogen species for the high dispersion of Pd NPs. It is found that the Pd NPs with an average diameter of 3.92 nm are uniformly dispersed on CNNF-G sheets. DFr computations reveal that CNNF can trap Pd adatom and thus act as a Pd nucleation site at which Pd atoms tend to accumulate to form Pd clusters. The Pd-CNNF-G nanocatalyst exhibits excellent electrocatalytic activity for both formic acid and methanol oxidation reactions, including large electrochemically active surface area (ECSA) values, significantly high forward peak current densities, and reliable stability and durability, far outperforming the Pd-graphene, commercial activated carbon-supported Pd catalyst or Pd-carbon nanotubes. Such a stable Pd/CNNF-G nanocatalyst may bring new design opportunities for high-performance direct formic acid fuel cell (DFAFC) and direct methanol fuel cell (DMFC) in the future.

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1. Introduction

As the depletion of fossil fuels and the increasingly environmental pollution problems, a great deal of research has been performed on how to obtain clean and renewable energy sources as well as their devices [1]. In such an active field, fuel cells have been considered as one of the most promising candidates in recent years because they can convert chemical energy from hydrogenrich fuels to electrical energy with little pollutant emission and high energy conversion efficiency [2,3]. Among the various fuel cell technologies, the direct formic acid fuel cell (DFAFC) and direct methanol fuel cell (DMFC) have attracted plenty of interest due to the storage and transport of these liquid fuels is much easier and safer than that of hydrogen because it does not need to be operated

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at low temperatures and high pressures [4,5]. It is well known that the nature of anode catalysts may heavily affect the performance of DFAFC or DMFC [6], and then much more attention have been dedicated to develop new approaches for preparation of electrochemical active metal NPs supported on advanced materials to improve the performance [7–9].

Recently, Pd-based catalysts have aroused special interest owing to their lower cost, higher activity and stronger tolerance to CO when compared with Pt-based catalysts [10,11]. As has been reported, the structure of Pd NPs, including the size distribution and morphology, can greatly influence the catalytic performance for formic acid or methanol oxidation [12–14]. Inspired by this, tremendous efforts have been made to obtain highly dispersed Pd NPs with a narrow size distribution supported on conductive carbon materials, such as carbon black [15], carbon nanofibers [16], and carbon nanotubes [17] and so on. Apart from other carbon materials, graphene sheets display a myriad of unique chemical and physical properties and can be used as an ideal support material to load and disperse noble metal NPs for high





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performance electrocatalytic or electrochemical devices [12,18-20]. Moreover, based on intensive theoretical calculations and detailed experiments it has been demonstrated that nitrogen doping is an effective approach to tailor the electronic properties of graphene [21-23]. Graphitic carbon nitride (g-C₃N₄) is an appealing class of nitrogen-rich carbon materials, which possesses not only unique features including ideal two-dimensional structure, ultrahigh nitrogen content, large aspect ratio, excellent mechanical resistance and anticorrosion ability in oxidative environments, but also a promising potential in fields ranging from heterogeneous catalysis, energy conversion and storage, to environmental applications [9,24,25]. Especially, because the electron accepting ability of the nitrogen atoms can polarize the adjacent carbon atom and enhance the bonding affinity with adsorbed OOH [26,27], g-C₃N₄-based materials display an excellent electrocatalytic activity for oxygen-reduction reaction (ORR) as a metal-free catalyst [28,29]. On the other hand, we recently developed a covalently coupled hybrid of g-C₃N₄-rGO for supporting Pd nanoparticles [24]. It is found that incorporation of g-C₃N₄ into rGO plays an essential role in changing the nucleation and growth behaviours of Pd nanoparticles, thus resulting in greatly enhanced electrochemical performances of the catalysts for fuel oxidation reactions. Nevertheless, g-C₃N₄ suffers from relatively low electrical conductivity due to its intrinsic porous microstructure, thus the g-C₃N₄ sheets fully covered on the surface of rGO may disturb the electron transport pathways during the electrochemical process.

Inspired by this point, we design a facile approach to fabricate an intimately coupled hybrid of g-C₃N₄ nanoflakelets with rGO (CNNF-G), which can expose much more edge sites and active nitrogen species, facilitating the nucleation and growth of Pd nanocrystals as well as the high dispersion of the resulting nanoparticles. Such unique features are not only favorable for providing fast and barrier-free channels for rapid diffusion of the electrolyte, but also beneficial for the removal of the incompletely oxidized carbonaceous intermediates from the catalyst surface during the fuel oxidation process. As a consequence, the Pd-CNNF-G catalyst displays an excellent electrocatalytic performance towards both formic acid and methanol electrooxidation, including high electrocatalytic activity, unusual poison tolerance, and longterm durability, all of which are superior to the Pd-graphene, Pd-CNT and commercial Pd-activated carbon (Pd-AC) catalysts.

2. Experimental section

2.1. Preparation of Pd-CNNF-G catalyst

Graphite oxide was synthesized from powdered flake graphite by a modified Hummers' method [30]. Specifically, 100 mg GO was dispersed in 100 mL water by ultrasonication. Then, melamine (200 mg) was added into the suspension and the reaction mixture was heated to 80 °C for 2 h to form melamine chemically modified GO sheets (melamine-GO) via a covalent C-N bond. After the water of the mixture was removed through freeze drying, the dried melamine-GO product was then transferred into a crucible and first heated at 550 °C for 2 h under a nitrogen flow, resulting in the polymerization of melamine to form g-C₃N₄ polymer nanosheets and the deoxygenation of GO to yield the reduced GO (rGO). Then the sample was heated to the final calcination temperature of 800 °C for 2 h. At such a high temperature, the g-C₃N₄ polymer nanosheets can be split into many smaller nanoflakelets (CNNF) which are intimately coupled with rGO to form the g-C₃N₄ nanoflakelets/rGO hybrid instead of decomposition due to the protection of graphene. For comparison, the same method was used to prepare rGO without melamine.

Preparation of the Pd NPs-CNNF-G catalyst with 20 wt% Pd was similar to our previous work [24]. Briefly, CNNF-G (10 mg) was ultrasonically dispersed in 100 mL of ethylene glycol to form a uniform suspension. Then 0.025 mL of 0.73 M Pd(NO₃)₂ was introduced to the suspension with magnetic stirring for 2 h. Subsequently, 0.425 mL of hydrazine hydrate solution (50 wt% in water) was added into the mixture with stirring for another 4 h under ambient conditions. The product, denoted as Pd-CNNF-G. was centrifuged, washed with deionized water and freeze-dried. For comparison, Pd NPs supported on rGO and CNT were prepared by the same procedure and were denoted as Pd-rGO and Pd-CNT, respectively. The exact loadings of Pd in Pd-CNNF-G, Pd-g-C₃N₄rGO, Pd-rGO and Pd-CNT samples were measured at 16.08, 17.9, 16.12 and 17.5 wt%, respectively, which agree well with their theoretical metal loading (20.0 wt%). The commercial activated carbon-supported palladium catalyst (Alfa Aesar 38308, Pd 20%, denoted as Pd-AC) was also used without any further treatment.

2.2. Characterization

Powder X-ray diffraction (XRD) analyses were performed using a Bruker D8 Advance diffractometer with Cu K α radiation $(\lambda \approx 1.54 \text{ Å})$. Fourier Transform-IR Spectroscopy (FT-IR) was recorded on a Nicoletis10 instrument (Thermo Nicolet Corporation). Raman spectra of the samples were collected with a LABRAM Aramis Raman Microprobe at wavelength of 532 nm. Field emission scanning electron microscopy (FE-SEM) measurement and elemental mapping were performed on a Hitachi S-3400 N II microscope. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy were carried out on a IEOL JEM-2100 microscope. X-Ray photoelectron spectra (XPS) were recorded using an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Al K α radiation ($h\nu$ = 1486.6 eV). The Brunauer-Emmett-Teller (BET) surface area was obtained by nitrogen sorption experiments conducting at 77K using a Micromeritics TriStar II 3020 automated gas adsorption analyzer. The metal loading of the catalysts was accurately determined with inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian Vista-AX). The TG analyses were carried out on a TGA/ SDTA851e thermogravimetric analyzer under a N2 atmosphere from 30 to 900 °C at a heating rate of $5 \circ C \min^{-1}$.

2.3. Electrochemical activity measurements

Electrocatalytic activities of various catalysts were measured in a conventional three-electrode cell with a CHI 760E electrochemical workstation. A glassy carbon (GC) disk (3 mm in diameter) was used as working electrode, which was polished successively with 1.0, 0.3 and 0.05 μ m alumina slurries before each experiment. Catalysts were applied onto the disk in the form of inks. The ink was a pure water-isopropyl alcohol-Nafion 117 (10:10:1 volume ratio) solution with catalyst concentration approximately 2 mg mL⁻¹. A Pt wire and a saturated calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively.

All electrochemical measurements were performed with the electrolytes of 0.5 M HCOOH in 0.5 M H_2SO_4 solutions and 1 M CH₃OH in 1 M NaOH solutions at 25 °C for DFAFC and DMFC measurements, respectively. The solutions were deaerated by pure N₂ for at least 20 min prior to any measurements. To facilitate comparison of the catalytic activity across samples, the Pd loading on the working electrode were determined by ICP-AES measurements. All electrochemical data were normalized to the actual loading of Pd and all the potentials were expressed with the reversible hydrogen electrode (RHE) by calibrating the SCE to the RHE scale according to the Nernst equation: $E = E^{\odot} - 0.05916^{\circ}$ pH.

2.4. Membrane electrode assembly preparation

Nafion 117 (DuPont) was used as the proton exchange membranes and the pre-treatment of the Nafion membrane was accomplished by successively treating it in a 5 wt.% H_2O_2 solution at 80 °C, distilled water at 80 °C, 8 wt.% H_2SO_4 solution at 80 °C and then in distilled water at 80 °C again, for 30 min each step. Prior to the fabrication of hot-pressed Membrane electrode assemblies (MEA) and catalyst-coated membrane, a carbon cloth was used as Gas diffusion layer for current collector and it also assists in water management.

MEA with a 2.25 * 2.25 cm² active cell area was fabricated using a 'direct paint' technique applied to the catalyst layer. The 'catalyst inks' were prepared by dispersing the catalyst nanoparticles into appropriate amounts of ultrapure water, isopropyl alcohol and 5 wt.% Nafion ionomer solution. For all MEAs in this study, the cathode consisted of commercial Pt/C catalyst at a standard metal loading of 1 mg cm⁻². The anode consisted of carbon supported Pd catalysts with a metal loading of 0.5 mg cm⁻². A carbon cloth diffusion layer (E-TeK) was placed on top of both the cathode and anode catalyst layers. A single cell test fixture consisted of machined graphite flow fields with direct liquid feeds and gold plated copper plates to avoid corrosion (Hephas Energy Co., Itd.). Hot-pressing was conducted at 130 °C and 10 MPa for 120 s.

2.5. Structure models and computational methods

Our calculations were based on DFT with generalized gradient approximation (GGA) [31] for exchange correlation potential. Perdew-Burke-Ernzerholf (PBE) functional was used for the GGA as implemented in Vienna Ab-initio Simulation Package (VASP) [32]. In order to simulate the CNNF-G nanocomposite, a 3×3 graphene supercell was used to match the 1×1 tri-s-triazine unit cell with a small 1.5% strain in graphene. The vacuum space in the third dimension (Z) is 15 Å, which is enough to separate the interaction between periodic images. The structures were relaxed without any symmetry constraints with a cutoff energy of 500 eV, and the convergence criteria of energy and force were set to 1×10^{-5} eV and 0.01 eV/Å, respectively. Reciprocal space was represented by a Monkhorst-Pack special *k*-point scheme [33] with $3 \times 3 \times 1$, and $5 \times 5 \times 1$ grid meshes for structure relaxation self-consistent field (SCF) computations, respectively.

3. Result and discussion

3.1. Structural characterization

The structures of the samples were characterized by means of Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and powder X-ray diffraction (XRD). As shown in Fig. S1, in comparison with rGO, CNNF-G shows a typical breathing mode of tri-*s*-triazine units at 807 cm⁻¹ as well as its stretching modes in the range of 1000–1600 cm⁻¹ [34,35]. With regard to the intense peak of tri-*s*-triazine units, it is speculated that the g-C₃N₄ polymer nanosheets on rGO can be split into some smaller nanoflakelets, which intimately interact with rGO to form the g-C₃N₄ nanoflakelets/rGO nanohybrid (CNNF-G) at higher temperatures (Fig. 1).

Raman spectra (Fig. 2a) provide the further information on the structure of the resulting smaller g-C₃N₄ nanoflakelets in CNNF-G. The G bands of the GO, rGO, and CNNF-G appeared at 1590.2, 1580.6 and 1582.5 cm⁻¹, respectively. As compared with GO, the significant downshift of the G band of rGO can be ascribed to the restoration of the π -conjugated structure during pyrolysis [36]. While slight upshift of the G band of CNNF-G can be observed relative to rGO. As will be seen in the XPS analysis, p-type doping is the dominant part in CNNF-G and therefore its G band shifts to higher frequency as compared to rGO, which is consistent with the phenomena of upshift in p-type doped and downshift in n-type CNTs and graphite [37–39]. Apart from the shift of G band, the intensity ratio of D band to G band (I_D/I_G) is another characteristic feature that is often used to estimate the disordering degree of graphene-based materials. It is found that the I_D/I_G ratios are 1.12, 1.24 and 1.40 for GO, rGO and CNNF-G, respectively. The increase of I_D/I_G ratio is due to the effect of g-C₃N₄ nanoflakelets on the structural disorder and the high baseline of g-C₃N₄ in the region of the D band.

Fig. 2b shows the X-ray diffraction (XRD) patterns of GO, PdrGO, Pd-CNNF-G and $g-C_3N_4$. The diffraction peak of GO at 10.5° can be indexed to (002) facets, corresponding to a layered structure with a basal spacing of 0.84 nm [40]. Upon the formation of Pd-rGO or Pd-CNNF-G nanocompsites, the characteristic (002) peak shifts to a higher angle as a result of the deoxygenation/reduction of GO during the pyrolysis process [41]. Pd-CNNF-G shows a broad peak of (002) diffraction at 26.5°, corresponding to a *d*-spacing of 3.40 Å calculated according to Bragg's equation, slightly larger than that of Pd-rGO (3.36 Å). This indicates that the modification of CNNF on



Fig. 1. Illustrations of the formation process of the Pd-CNNF-G catalyst.



Fig. 2. (a) Raman spectra of g-C₃N₄, CNNF-G, rGO and GO, (b) XRD diffraction patterns of g-C₃N₄, Pd-CNNF-G, Pd-rGO and GO.

the surface of rGO may cause the loosening of layers along the caxis with fewer structural defects. Besides, no typical diffraction peak of rGO (002) or g-C₃N₄ (002) is observable, revealing that g-C₃N₄ nanoflakelets are evenly growing on both sides of rGO nanosheets and. Furthermore, the intensive diffraction peaks at 39.8°, 46.2° and 67.7° are corresponding to the (111), (200) and (220) planes of the face-centered-cubic (fcc) Pd lattices (JCPDS no. 46-1043), respectively, suggesting a good crystallinity of Pd NPs in the hybrid.

The morphologies of various catalysts were characterized by TEM. As shown in Fig. 3a, CNNF-G has a two-dimensional structure with some wrinkles, which is similar to the typical morphology of graphene. While upon the graphene sheets, the homogeneous distribution of $g-C_3N_4$ nanoflakelets can be recognized only when



Fig. 3. (a) TEM image of CNNF-G, (b) TEM image of Pd-CNNF-G, (c) HRTEM image and Pd NP size distribution of Pd-CNNF-G, (d) selected area electronic diffraction pattern (SAED) of Pd-CNNF-G, (e) TEM image and the elemental mapping images of Pd, C, and N elements.

observing carefully due to the similar transparency of CNNF and graphene. To further confirm this, the corresponding energy dispersive X-ray (EDX) spectrum was also carried out (Fig. S2), and there are only four elements in the product, C, N, O, and Cu (the Cu signals come from the copper grid), and the nitrogen content of the CNNF was calculated to be 4.5 at %. On the other hand, it is clearly seen from Fig. 3b that metallic Pd NPs are uniformly dispersed on the surface of CNNF-G sheets while Fig. 3c reveals lattice fringes with crystal plane distances of 0.223 nm, attributed to the spacing of the (111) planes in face-centered cubic (fcc) Pd, respectively. Selected-area electron diffraction of the Pd-CNNF-G displays a set of ring-like diffraction patterns (Fig. 3d), corresponding to the Pd (111), (200), (220) planes, which correlate well with the XRD results. Further inspection by elemental mapping discloses that the Pd-CNNF-G architecture contains C, N and Pd as the main components, and the elements are homogeneously distributed over the entire area of the catalysts (Fig. 3e). This could be attribute to the presence of $g-C_3N_4$ nanoflakelets on the surface of rGO, which possesses π -bonded planar C-N-C-layers along with their incompletely condensed amino groups in the carrier, making it possible to enhance the adhesion between Pd NPs and the support and effectively stabilize highly dispersed Pd NPs and prevent their agglomeration [42]. In contrast, as presented in Fig. S3, it can be seen that Pd NPs supported on rGO, CNT or AC have larger sizes with aggregation to some extent, suffering from their relatively weak interactions of metal and support. The statistical size distribution histograms obtained by measuring 200 randomly chosen particles (Fig. 3c, Fig. S3) demonstrate that the average particle sizes are about 3.9 nm, 5.8 nm, 7.0 nm and 4.6 nm for Pd-CNNF-G, Pd-CNT, Pd-rGO and Pd-AC, further suggesting that the CNNF-G facilitates the formation of smaller-sized Pd NPs with higher dispersity. Moreover, the adsorption and desorption isotherms of nitrogen on the Pd-CNNF-G or Pd-rGO hybrid exhibit a typical IUPAC type IV isotherm, implying the existence of mesoporous structure (Fig. S4). Compared with Pd-rGO, the Pd-CNNF-G hybrid possesses a much higher specific surface area of $360.4 \text{ m}^2 \text{g}^{-1}$ with an average pore diameter of 7.55 nm and a pore volume of $0.926 \text{ cm}^3 \text{g}^{-1}$, thereby not only offering rich absorption sites but facilitating charge transfer across the electrode/electrolyte interface as well.

X-ray photoelectron spectroscopy (XPS) was used to further characterize the elemental composition and the valent state of the elements in Pd-CNNF-G and Pd-rGO. Fig. 4a presents the survey spectrum of the XPS analysis. No peaks of other elements except C, O and Pd were observed for Pd-rGO, by contrast, there was the coexistence of C, N, O and Pd in Pd-CNNF-G. Percentages of the individual elements based on XPS analysis are listed in Table 1. The C1s XPS spectrum of Pd-rGO can be deconvoluted into three



Fig. 4. (a) XPS survey spectra, (b) N 1s, (c) C 1s and (d) Pd 3d core-level XPS spectra of Pd-CNNF-G and Pd-rGO.

components (Fig. 4b): the sp²-hybridized C-C (284.6eV), C-OH (286.1 eV) and HO—C=O (289.0 eV) groups, respectively [43]. While the C1s XPS spectrum of Pd-CNNF-G gives two additional peaks at 285.7 eV and 287.3 eV, which can be assigned to C=N and C-N bonding configurations [24], revealing the existence of C-N species in the Pd-CNNF-G nanocomposites. The broad and asymmetric N 1s spectrum can be divided into three peaks at 398.3, 399.5 and 400.8 eV (Fig. 4c), corresponding to pyridinic N, pyrrolic N and graphitic N, which are well consistent with the g- C_3N_4 sample [44,45]. It should be noted that the content of the pyridinic N together with pyrrolic N in the N-containing species reaches as high as 62.4% (Table S2) and such N atoms can serve as metal-anchoring sites facilitating the nucleation and subsequent growth of metal nanoparticles [26]. Compared with the g-C₃N₄ nanosheets (Fig. S5), the increase of the graphitic N gives an indirect evidence of the formation of the g-C₃N₄ nanoflakelets and the covalent interaction between g-C₃N₄ and rGO, which makes CNNF-G more stable during the electrocatalysis process. Moreover, theoretical studies of N-doped carbon nanotubes indicate that the substitution of C atoms with graphitic N is considered as n-type doping, whereas pyrrolic and pyridinic N may be taken as p-type doping [46-48]. Accordingly, p-type doping is dominant in the Pd-CNNF-G system. As shown in Fig. 4d, the splitting pattern of Pd 4d band contains two pairs of doublets: the intensive doublet (335.8 and 341.0 eV) may be assigned to metallic Pd and another doublet (337.1 and 342.9 eV) corresponds to the +2 oxidation state of Pd [42,49]. Similar results were obtained for Pd-CNNF-G, however, its Pd 3d binding energies were slightly shifted to lower values (Table S4). According to the previous study, lower binding energies of supported Pd species are related to stronger interaction between support and Pd NPs [50]. As will be seen later, the stronger coupling between Pd NPs and CNNF-G gives rise to enhanced electrocatalytic performance towards methanol and formic acid oxidation.

3.2. Theoretical calculations

In order to better understand the effects of g-C₃N₄ nanoflakelets on Pd atom adsorption, DFT computations were performed to investigate the adsorption energy and geometry of Pd atom on graphene and CNNF-G. An adsorption location map and the optimized geometry structures for Pd adsorption on CNNF-G are illustrated in Table S6. As was found for CNNF-G, Pd atoms preferentially bind at hollow sites with strongest adsorption, E_{ads} = 2.82 eV, roughly thrice that for Pd adsorption on graphene $(E_{ads} = 1.035 \text{ eV})$. Interesting, the g-C₃N₄ nanoflakelets' effect on Pd adatoms is unique. Pd adatoms moved significantly from their starting positions and relaxed toward the interlaver between CNNF and rGO to forming a most stable structure (Fig. S8a-b). This well traps Pd adatom, making it able to keep in contact with the substrate of rGO. Subsequently, it could act as a Pd nucleation site at which Pd atoms will tend to accumulate and form Pd clusters (Fig. S8c-d).

When the rGO sheet modified with CNNF, the entire CNNF-G are slightly charged with respect to the graphene sheet, and upon Pd adsorption, it acts to redistribute charge. As Fig. 5 show, an intensive electron increase zone (yellow isosurface) can be observed from the differential charge density. Combine with the overlap located at the Fermi energy in the PDOS (Fig. S9), it is suggestive of that the CNNF-G well acts to tether Pd adatom to the substrate, thus reducing Pd cluster migration and agglomeration,

Table 1	
C, O, N and Pd content (at%) of the samples according to X	PS analysis.

Samples	С	0	Ν	Pd
Pd-CNNF-G	80.8	10.8	5.8	2.6
Pd-rGO	85	12.6		2.4

which is attributed to the interaction of the d orbitals (Pd) and the sp² lone pair orbitals (N). Moreover, the electronic effect of formic acid or methanol molecule on Pd-CNNF-G and Pd-rGO was also considered (Fig. S10).

3.3. Electrochemical analysis

The electrochemically active surface area (ECSA) provides straightforward information regarding the number of electrochemically active sites per unit mass of catalyst [51]. Fig. 6 shows the CO stripping voltammograms for different electrodes in 0.5 M H_2SO_4 solution at a scan rate of 50 mV s⁻¹ at 25 °C. A well-defined stripping peak of CO_{ad} at the potential of *ca*. 0.95 V can be observed for each catalyst. The ECSA values are estimated supposing that the charge required to oxidize a full monolayer of CO on Pd is 420 mC cm^{-2} [52]. As listed in Table 2, the Pd-CNNF-G catalyst exhibits an ECSA value as high as $91.2 \text{ m}^2 \text{ g}^{-1}$, which is more competitive than the one of Pd-rGO ($60.5 \text{ m}^2 \text{ g}^{-1}$), Pd-AC ($39.8 \text{ m}^2 \text{ g}^{-1}$), Pd-CNT (56.3 $m^2 g^{-1}$), or recently reported state-of-the-art Pd-based nanomaterials such as formic acid-reduced Pd/graphene $(56 \text{ m}^2 \text{g}^{-1})$ [12], Pd/DNA-modified graphene $(82.2 \text{ m}^2 \text{g}^{-1})$ [53], Pd/WC modified graphene $(81.22 \text{ m}^2 \text{g}^{-1})$ [54], oriented (111) Pd nanocrystals/graphene (29 m² g⁻¹) [19], porous worm-like Pd nanotubes $(17.7 \text{ m}^2 \text{ g}^{-1})$ [55], Pd/nitrogen-doped acetylene carbon black (82.7 m²g⁻¹) [50], Pd-Au NPs/PDDA-functionalized graphene $(58 \text{ m}^2 \text{g}^{-1})$ [56], Pd-Cu bimetallic NPs/graphene $(20.22 \text{ m}^2 \text{g}^{-1})$ [57], porous Pt-Pd nanospheres/graphene $(68.1 \text{ m}^2 \text{g}^{-1})$ [58], Pd-Ni-P NPs/carbon black $(62.9 \text{ m}^2 \text{g}^{-1})$ [59]. It should be noted that the Pd-g-C₃N₄ shows a low ECSA value of



Fig. 5. Charge transfer for a Pd atom on (a and b) graphene, (c and d) CNNF-G, and two Pd atoms on (e and f) CNNF-G. The big red, small grey and blue balls represent Pd, C and N atoms, respectively. The yellow and green isosurfaces correspond to the increase in the number of electrons and the depletion zone, respectively. The isosurfaces are 0.003 e A^{-3} .

6.9 m² g⁻¹ due to the poor electrical conductivity of the g-C₃N₄. In addition, the electrocatalytic activities of as-obtained catalysts were also evaluated in an alkaline medium. As illustrated in Fig. S11b, the potential limit of all CV curves is set at 1.40 V, associating with the completion of formation of the first monolayer of the Pd (II) oxide (Fig. S12), and a flat anodic (E \approx 1.3 V) along with a strong cathodic (E \approx 0.6 V) peak are distinctly recognized, corresponding to the formation and reduction of Pd (II) oxide, respectively [13,60,61] The ECSA values, calculated by the coulombic charge for reduction of Pd (II) oxide, follow an order of Pd-CNNF-G (89.4 m² g⁻¹) \approx Pd-g-C₃N₄-rGO (90.6 m² g⁻¹) > Pd-rGO (57.6 m² g⁻¹) > Pd-CNT (54.3 m² g⁻¹) > Pd-AC (39.6 m² g⁻¹) > Pd-g-C₃N₄ (8.8 m² g⁻¹), which is similar to that from CO stripping measurements in the acid medium.

The Pd electrocatalytic behaviors for all Pd catalysts were characterized by cyclic voltammogram measurement toward the formic acid oxidation reaction in acid medium and the methanol oxidation reaction in alkaline medium. Fig. 7a depicts the CV responses of the electrodes coated with the Pd-CNNF-G, Pd-g-C₃N₄-rGO, Pd-rGO, Pd-CNT, Pd-AC or Pd-g-C₃N₄ catalyst for the electrochemical oxidation in 0.5 M H₂SO₄ + 0.5 M HCOOH solution at 25 °C with a scan rate of 50 mV s⁻¹. All the curves were calibrated for iR losses (Fig. S13), and the ionic resistance (~20 Ω) from the solution was determined by the EIS technique. It is well known that the electrooxidation of HCOOH typically follows a dual-pathway mechanism [62,63]:

(1) Direct dehydrogenation pathway

Pd + HCOOH \rightarrow Pd + CO₂ + 2H⁺ + 2e⁻ (2) Indirect pathway

 $Pd + HCOOH \rightarrow Pd-CO + H_2O$

 $Pd + H_2O \rightarrow Pd-OH + H^+ + e^-$

 $Pd-CO + Pd-OH \rightarrow Pd + CO_2 + H^+ + e^-$

Therefore, the current peak at ~0.4V in the anodic scan may arise from the direct oxidation of formic acid to CO₂, while the shoulder at ${\sim}0.8\,V$ is related to the oxidation of both adsorbed CO and HCOOH. Clearly, the Pd-CNNF-G catalyst exhibits an impressively high mass current density of 1890 mA mg⁻¹, which is more than 2 times as high as that of Pd-rGO (970 mA mg⁻¹) or Pd-CNT (830 mA mg^{-1}) , and 3 times that of Pd-AC catalyst (515 mA mg^{-1}) . Also, the mass activity of Pd-CNNF-G is more competitive than those of recent state-of-the-art Pd-based nanostructures such as formic acid-reduced Pd/graphene (89.5 mA mg⁻¹) [12], Pd/DNAmodified graphene (228.1 mA mg⁻¹) [53], Pd/WC modified graphene (42.35 mA cm⁻²) [54], Pd/nitrogen-doped acetylene carbon black (1202 mA mg⁻¹) [50], Pd₃Au₁ NPs/PDDA-functionalized graphene (580 mA mg^{-1}) [56]. Pd/ITO-CNTs $(1356.4 \text{ mA mg}^{-1})$ [64], Ag₂S-hollow Pd nanocomposites (4.01 mA cm⁻²) [65]. Furthermore, at a given oxidation current density (e.g. as indicated by the dashed line in Fig. S14a), the Pd-CNNF-G catalyst shows an obviously lower oxidation potential than anyone of reference catalysts, implying that the formic acid electrooxidation occurred more easily on Pd-CNNF-G [66]. The effects of the g-C₃N₄ load on the catalysts were also considered. As shown in Fig. S15, the sample, obtained with the raw material's mass ratio of melamine to GO of 1:2, reveals the optimal electrochemical activity. This is attributed that suitable g-C₃N₄ nanoflakelets can influence the spin density and charge distribution of neighboring carbon atoms on the surface of graphene, which makes the CNNF-G support maintain acceptable conductivity and considerable active sites, while further increasing the amount of $g-C_3N_4$ in the composites may lead to a decrease in the electrocatalytic activity, which is due to the deteriorating electrical conductivity derived from the intrinsic porous microstructure of the $g-C_3N_4$.

In addition, Pd-CNNF-G also possesses a high catalytic activity in alkaline media (Fig. 7b). In the presence of 1 M NaOH and 1 M CH₃OH, two irreversible current peaks can be observed: one in the forward scan may be associated with the oxidation of freshly chemisorbed species coming from methanol adsorption, while the reverse scan peak may be assigned to the removal of the incompletely oxidized carbonaceous species formed during the forward scan. The generally accepted mechanism for the electrooxidation of methanol in alkaline medium, which involves the reaction of generation of formate ions, can be summarized as follows [67–69]:

$$CH_3OH + 5 OH^- \rightarrow HCOO^- + 4 H_2O + 4e^-$$

methanol adsorbed on the electrode surface can undergo successive dehydrogenation. However, the exact structure of the adsorbed intermediates is still unknown except for (CO)_{ads}. The magnitude of the peak current in the forward scan is directly proportional to electrocatalytic activity of Pd catalyst for methanol oxidation. As expected, Pd-CNNF-G exhibits the highest peak current density of 1770 mA mg⁻¹, which is much higher than those of Pd-g-C₃N₄-rGO (1550 mA mg⁻¹), Pd-rGO (835 mA mg⁻¹), Pd-CNT (725 mAmg^{-1}) , Pd-AC (535 mAmg^{-1}) , Pd-g-C₃N₄ (67 mAmg^{-1}) mg⁻¹), or recent reported Pd-based nanostructures such as Pd-Cu bimetallic NPs/graphene (392.6 mA mg⁻¹) [57], Porous Pt-Pd nanospheres/graphene (180 mA cm⁻²) [58], Pd-Ni-P NPs/carbon black (~360 mA mg⁻¹) [59], Pd-SnO₂/MWNTs (778.8 mA mg⁻¹) [70], Pd/graphene hydrogel on Ni foam (788 mA mg $^{-1}$) [71], Pd₁Ag₁ NPs/graphene (630 mA mg⁻¹) [72], Pd₁Pt₃/graphite nanoplatelets $(385.22 \text{ mA mg}^{-1})$ [73], Pd/CuO-TiO₂ (381 mA mg^{-1}) [74] (Table S7). Meanwhile, similar to that of the formic acid oxidation, the onset potential of Pd-CNNF-G in alkaline medium also suggests the significant enhancement in the kinetics of the methanol oxidation reaction [14] (Fig. S14b).

Long-term stability is another important factor that affects the practical application of electrocatalyst in fuel cell applications. It is known that some carboneous species, which come from redox reactions on the surface of Pd NPs, readily cause the inactivation of catalysts. Chronoamperometric measurement was used to



Fig. 6. CO_{ad} stripping voltammograms of different catalysts in 0.5 M H_2SO_4 solution with a scan rate of 50 mV s $^{-1}$ at 25 $^\circ C.$

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Compiled study comparing the CV results for different carbon based samples.

Electrode	ECSA $(m^2 g^{-1})$		Forward peak current (mA mg ⁻¹)	
	DMFC ^a	DMAFC ^b	DMFC	DFAFC
Pd-CNNF-G	89.4	91.2	1770	1890
Pd-g-C ₃ N ₄ -rGO	90.6	107.5	1550	1610
Pd-rGO	57.6	60.5	835	970
Pd-CNT	54.3	56.3	725	830
Pd-AC	39.6	39.8	535	515
Pd-g-C ₃ N ₄	8.8	6.9	67	40

^a The ECSA of the catalysts estimated by integration from the monolayer PdO reduction peak.

 $^{\rm b}$ The ECSA of the catalysts estimated by integration from the $\rm CO_{ad}$ stripping experiment.

appraise the electrochemical durability of Pd-based catalysts. As shown in Fig. 7c. the polarization current of all the catalysts decayed precipitously within the first 500s due to the chemisorbed carbonaceous species and then the hyperbolic decay slowly attained a pseudo-steady state [75]. This phenomenon is quite similar to that of the formic acid electrooxidation reaction on the Pt-based electrocatalysts, suggesting the same poisoning mechanism of the intermediate species coming from the formic acid oxidation on the electrocatalysts [76]. Upon the long-term operation, it can be seen from Fig. S16a that the Pd-CNNF-G electrode retained 34.6% of the initial current density after first 500 s, greatly surpassing the electrodes based on Pd-g-C₃N₄-rGO (30.4%), Pd-rGO (26.4%), Pd-CNT (17.2%), and Pd-AC (3%). The larger retention of Pd-CNNF-G indicates the relatively lower poisoning rate during the electrooxdiation reactions. Clearly, Pd-CNNF-G is able to maintain the highest current and slowest decay rate for the whole duration of the scan, exhibiting superior electrocatalytic activity and stability for formic acid oxidation of all the investigated catalysts. It is worth mentioning that the Pd-C₃N₄ exhibits only 21.7% decay after 500s and retains 78.2% for the whole time, suggesting that g-C₃N₄ is beneficial for improving the anti-poisoning property. Unfortunately, limited by the low electrical conductivity, the g-C₃N₄ materials cannot be used alone in the field of electrochemistry. Otherwise, the long-term stability for formic acid electrooxidation was also considered at 0.25 V, which is near the equilibrium potential (Fig. S17). As for methanol oxidation, the variation of currents with time has a similar tendency (Fig. 7d, Fig. S16b). Pd-CNNF-G shows the lowest current decay and retains the highest oxidation current density over the testing time, which is also in good agreement with the results of the CVs. Interestingly, when compared with the Pd-based catalyst supported on g-C₃N₄ modified graphene, Pd-CNNF-G exhibits a slight improvement of current density for both formic acid and methanol electrooxidation, but a great deal of enhancement of long-term stability. This is due to the stronger interactions between the Pd NPs and the support, which ensures the structure integrity maintenance during the harsh and long-term electrochemical process.

To gain further insight into the oxidation of formic acid on the Pd-CNNF-G catalyst, the kinetics of electron-transfer processes were studied by electrochemical impedance spectroscopy (EIS). As shown in Fig. S18a, the variation trend of Nyquist impedance polts at the Pd-CNNF-G electrode can be divided into three stages: (1) when potentials \leq 0.3 V, the impedance spectra are located within the first quadrant; (2) as the potentials are in the range of 0.4 V to 1.0 V, the negative impedance arcs can be observed in the second quadrant; (3) at higher potentials (>1.0 V), the impedance arcs return to the first quadrant. According to the previously study in formic acid oxidation on the Pd-based electrocatalysts [77,78], the



Fig. 7. CVs of different catalysts in (a) 0.5 M H₂SO₄+ 0.5 M HCOOH solution and (b) 1 M NaOH + 1 M CH₃OH with a scan rate of 50 mV s⁻¹ at 25 °C. Chronoamperometric curves of different catalysts in (c) 0.5 M H₂SO₄+ 0.5 M HCOOH solution at 0.4 V and (d) 1 M NaOH + 1 M CH₃OH at 0.7 V at 25 °C.

negative faradaic impedance suggests the presence of an inductive component. It can be considered that, as a co-catalyst, the $g-C_3N_4$ nanoflakelets in the Pd-CNNF-G hybrids may promote the reaction because the oxophilic nature of the N element can provide sites for the formation of chemisorbed hydroxyl species in this potential range, which speeds up the oxidative removal of the adsorbed intermediate poisoning species like CO_{ad} [26,27]. As compared to Pd-rGO (Fig. S18b), Pd-CNNF-G possesses more negative onset potential and smaller impedance arcs, indicating significantly facilitated for the removal of CO_{ad} and faster charge-transfer kinetics for formic acid oxidation, which are consistent with voltammetric and i-t response. To further investigate reaction process, linear sweep voltammetry (LSV) was conducted on the catalyst. When the scan rates varied from 2 to 200 mV s⁻¹, the peak current density (j_p) increased linearly with the square root of scan rate $(v^{1/2})$ (Fig. S19a), indicating a diffusion controlled behavior for electrooxidation of formic acid at the Pd-CNNF-G electrode [79]. A good linear dependence of the oxidation peak potential (E_p) versus $log(v^{1/2})$ can be observed in Fig. S19b, which demonstrates that the oxidation of formic acid was an irreversible electrode process. For a diffusion controlled and irreversible electrode process on the Pd-CNNF-G catalyst, the value of the diffusion coefficient was calculated to be $8.345 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [80].

Furthermore, the high-performance Pd-CNNF-G catalyst was used as anode material in a real direct formic acid fuel cell. The corresponding steady-state polarization and power-density curves of the studied catalysts are shown in Fig. 8a. Consistent with the results from electrochemical measurements, the Pd-CNNF-G catalyst exhibits a higher power density of 35 mW cm^{-2} , which is about 1.5 times of that of Pd-rGO. It is also noted from Fig. 8b that the discharge stability of the Pd-CNNF-G catalyst is largely improved compared with the Pd-rGO catalyst at 0.35 V, which is consistent with those results obtained from the CV and CA tests.

On the basis of the experimental results and theoretical analysis, the high catalytic activity and durability of Pd-CNNF-G can be attributed to the specific characteristics of the unique nanostructure of Pd-CNNF-G and the concerted effects of individual components. Firstly, the g-C₃N₄ nanoflakelets with much more exposed edge sites on the surface of rGO, especially pyridine-like N atoms, can be used as an excellent ligand for Pd²⁺ ions, promoting the formation of the highly dispersed Pd NPs. The bridging effect of g-C₃N₄ nanoflakelets facilitates the intimate interaction among individual components of Pd-CNNF-G, which may ensure the structure integrity maintenance, long-term electrochemical stability and durability. Secondly, the N atoms at the exposed edge sites are also capable of activating their neighboring carbon atoms and accelerating the formation of -OH by water dissociation, which can be a crucial factor for the oxidative removal of the absorbed intermediate poisoning species on the Pd sites during catalytic reactions [26]. Thirdly, the CNNF-G framework possesses abundant pore structures while maintaining 2D nanostructure of rGO with acceptable conductivity and accessible internal surface areas, providing a high rate of diffusion of the electrolyte and assisting the rapid removal of the carbonaceous intermediates from the Pd sites in the oxidation process. Finally, the small-sized and uniformly-dispersed Pd NPs



Fig. 8. (a) Steady-state polarization, power-density curves, (b) discharge curves at 0.35 V of the DFAFCs using Pd-CNNF-G and Pd-rGO as anodes with formic acid (3 M) at 60 °C. The flow rate of formic acid was 10 mL min⁻¹ and the flow rate of O_2 was 500 mL min⁻¹.

on the CNNF-G offer more triple-phase boundaries at per unit mass of Pd for the oxidation reaction of formic acid and methanol, improving the catalyst utilization.

4. Conclusions

In summary, we have demonstrated the successful fabrication of Pd NPs-decorated CNNF-G nanocatalyst by a facile two-step approach: CNNF-G was obtained from splitting decomposition of bulk g-C₃N₄ on rGO at higher temperatures, followed by the reaction of CNNF-G and Pd nitrate to form Pd/CNNF-G nanocatalyst. The as-prepared Pd-CNNF-G exhibits an unprecedented high and stable electrocatalytic activity for both formic acid and methanol oxidation reactions, far outperforming the Pd-rGO, Pd-CNT or commercial Pd-AC catalysts. The superior electrochemical performance of Pd-CNNF-G is attributed to the specific characteristics of its unique nanostructure and the concerted effects of Pd NPs and CNNF-G, including considerable edge sites and active nitrogen species for evenly dispersed decoration of Pd²⁺ ions, the strong adsorption energy of Pd adatoms on the CNNF-G resulting in a highly stable catalytic system, and the abundant pore structures providing a high rate of diffusion of the electrolyte and assisting the rapid removal of the carbonaceous intermediates from the Pd sites during the reaction. Overall, such a stable CNNF-G-based nanocatalyst may bring new design opportunities for highperformance fuel cells in the future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.03.169.

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