Graphitic C_3N_4 –Pt nanohybrids supported on a graphene network for highly efficient methanol oxidation

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Pt heterostructures can have distinctly different physical and chemical properties to their single-phase components. Herein, a smart approach was developed for the large-scale production of graphitic C_3N_4 –Pt (gC_3N_4 –Pt) heterostructures on three-dimensional (3D) graphene sheet networks for highly efficient methanol oxidation. Because the gC_3N_4 –Pt heterostructures on the conductive 3D graphene network support provide the methanol molecules good accessibility to the active sites, the obtained catalyst exhibits excellent electrocatalytic performance, including high catalytic activity, unusual CO tolerance, and good stability, and is superior to commercial Pt/C and Pt/graphene catalysts for methanol oxidation.

INTRODUCTION

Heterostructures of Pt-based nanomaterials, including metal–Pt [1–3], alloy–Pt [4], metal oxide–Pt [5], metal sulfide–Pt [6], and metal selenium–Pt [7], with coherent interfaces usually have distinctly different physical and chemical properties from their single-phase components. Pt-based heterostructures have attracted considerable attention because of their multifunctional capabilities and tunable properties in practical applications, especially as electrocatalysts [3–6]. Unfortunately, metal-containing species in Pt-based heterostructures are not stable under harsh chemical environments, such as strongly acid or alkali solutions, for long time testing. Although carbon-based substrates are chemically and mechanically stable, they commonly have low lattice match with Pt, which therefore could be a challenge for the development of nonmetal–Pt heterocomposites.

Graphitic carbon nitride (gC_3N_4) is a graphite-like layered material that is composed of ordered tri-*s*-triazine subunits connected by planar tertiary amino groups within layers and weak van der Waals forces between layers [8,9]. gC_3N_4 quantum dots with size of <3 nm contain a very high nitrogen content and abundant dangling bonds [10], and they have potential application as crystal seeds for the growth of Pt to form the gC_3N_4 –Pt heterocomposite.

Graphene is an attractive supporting material for catalyst loading owing to its fast two-dimensional (2D) electron-transfer kinetics, large surface area, and high mechanical, thermal, and chemical stability [11,12]. In particular, graphene with a three-dimensional (3D) self-supported structure is promising for catalyst loading to facilitate mass transfer and maximize the accessibility to the catalyst surfaces [13,14].

Herein, gC_3N_4 –Pt heterogeneous structures on 3D graphene networks (denoted as gC_3N_4 –Pt/3GN) were designed and prepared. Because the synergistic effect derived from heterostructured gC_3N_4 –Pt and a conductive 3D graphene network support offers good accessibility for active species to fuel molecules, gC_3N_4 –Pt/3GN can act as an excellent electrocatalyst for high-performance methanol oxidation. The catalyst has high catalytic activity, unusual CO tolerance, and remarkable stability that are superior to the properties of the well-established commercial catalysts Pt–Vulcan XC-72 (E-TEK 20% Pt/C) and Pt nanoparticles on 3D graphene networks (Pt/3GN).

RESULTS AND DISCUSSION

A procedure was devised to prepare the gC_3N_4 –Pt heterogeneous structure on 3D graphene networks. As illustrated in Fig. 1, few-layer graphene oxide (GO) sheets (Figs 1a and S1) were prepared from natural flake graphite according to a modified Hummers method [15], and bulk gC_3N_4 was obtained by sintering melamine [16]. After a solvothermal and further ultrasound processes, gC_3N_4 quantum dots were well-dispersed on graphene sheets (Figs 1b, 1c, S2 and S3). During this process, the functional groups on GO, such as carboxyl and hydroxyl groups, interconnected to give 3D architectures (Figs S2 and S3) [15], while gC_3N_4 tended to split into the form of quantum dots (Fig. S3) [16]. The gC_3N_4 –Pt nanohybrids were subsequently generated by reducing H_2PtCl_6 under UV light (Figs 1d and S4). The details of the experiments were presented in the Supple-

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Figure 1 Scheme for the preparation of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$. (a) Graphene oxide sheets; (b) gC_3N_4 adsorbed on graphene sheets; (c) well-dispersed gC_3N_4 quantum dots on graphene; (d) $\text{gC}_3\text{N}_4\text{-Pt}$ heterogeneous structure on graphene networks.

mentary information.

The morphologies and nanostructures of the $\text{gC}_3\text{N}_4\text{-Pt}$ nanohybrids on 3GN architectures were first examined by field-emission scanning electron microscopy (FE-SEM). Fig. 2a shows a well-defined and interconnected 3D network of graphene sheets with continuous pores ranging

from sub-micrometer to several micrometers in size. Close inspection of Fig. 2b reveals that numerous small particles are uniformly dispersed on the individual graphene sheets. Energy dispersive spectroscopy (EDS) (Fig. 2c) revealed that the sample was mainly composed of C, N and Pt, as well as O associated with the hydrothermally reduced GO [17]. According to X-ray photoelectron spectroscopy (XPS) analysis, the atomic ratio of Pt : N : C in the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ was ca. 0.024 : 0.031 : 1.0.

The XRD patterns of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ and Pt/3GN further verified their composition profiles (Fig. 2d). The broad peak located at $2\theta \approx 23^\circ$ is assigned to the (002) plane of stacked graphene sheets within 3GN [11]. For Pt/3GN, typical peaks of the face-centered cubic (fcc) structure of Pt are observed at ca. 40° , 47° , 68° , 82° and 86° , corresponding to the Pt (111), Pt (200), Pt (220), Pt (311) and Pt (222) planes, respectively, which are in agreement with those of standard Pt (JCPDS ICDD card No. 01-1194). Accordingly, the $\text{gC}_3\text{N}_4\text{-Pt}$ nanohybrids on 3GN show typical diffraction peaks of Pt, while the peaks of Pt shift to the transitive diffraction angles corresponding to those of the pure phase. The main peak (39.5°) corresponding to the (111) plane of Pt in $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ has a slightly negative shift value of 0.3° compared with the corresponding peak of Pt/3GN (39.8°). The calculated lattice spacing of $\text{gC}_3\text{N}_4\text{-Pt}$ was $2.28 \text{ \AA}$, which is slightly larger than that of the pure Pt ($2.26 \text{ \AA}$). The lattice expansion may arise from the tran-

Figure 2 FE-SEM images of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ at (a) $\times 2,000$ and (b) $\times 50,000$ magnification; (c) EDS spectrum of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$; (d) XRD patterns of $\text{gC}_3\text{N}_4\text{-Pt}$ and Pt on 3GN.

sition lattice of Pt and adjacent gC_3N_4 quantum dots, suggesting that Pt effectively interacts with gC_3N_4 .

The formation of gC_3N_4 -Pt nanohybrids was confirmed by transmission electron microscopy (TEM) (Figs 3a and 3b). Even after the use of ultrasonication for preparation of the TEM sample, the gC_3N_4 -Pt nanohybrids were still well-dispersed and firmly anchored to the graphene sheets (Fig. 3a). This might arise from the presence of a large number of nitrogen atoms surrounding activated carbon atoms in the 3GN architectures, which can substantially strengthen the interaction between the metal and the support [18,19].

To further confirm this point, we prepared Pt/3GN by the same synthesis approach used for gC_3N_4 -Pt/3GN but without gC_3N_4 quantum dots. As shown in Fig. S5, the Pt nanoparticles tended to form aggregates on the 3GN sheets owing to the relatively weak interactions. In this context, gC_3N_4 -Pt/3GN catalysts would provide more catalytic sites than Pt/3GN catalysts for the same Pt loading.

The Pt nanoparticles of gC_3N_4 -Pt/3GN have an average diameter of 3.5 nm and a narrow size distribution from 2.0 to 4.2 nm, and they were well-dispersed on the graphene sheets (based on the enlarged image in Fig. 3b). It has been demonstrated that the optimal particle size for Pt catalysts for methanol oxidation is in the range of 2.0–4.0 nm [20,21]. Therefore, the method used for the preparation of gC_3N_4 -Pt/3GN may be suitable for other Pt-based catalysts. Interestingly, each of the small Pt nanoparticles (white arrow and white outlines in Fig. 3b) is neighbored by a low contrast nanoparticle (red arrow and red outlines), which might be ascribed to gC_3N_4 with low crystallinity and low electron-density contrast. From the high-resolution TEM image in Fig. 3c, clearly defined lattice fringes can be identified on the neighboring nanoparticles, as highlighted by the red and white lines. These have spacings of 0.33 and 0.23 nm, which correspond to the (002) and (111) interplanar distances of the gC_3N_4 stacks and face-centered cubic (fcc) Pt, respectively, indicating that the Pt nanoparticles grow on the gC_3N_4 quantum dots. This suggests the formation of an intimate heterogeneous structure between Pt

nanoparticles and gC_3N_4 quantum dots. The electron-rich gC_3N_4 quantum dots with size <3 nm have very high nitrogen content and abundant dangling bonds, which means that they can potentially be used as crystal seeds for Pt nanoparticle growth at an early stage of the reaction to form uniform gC_3N_4 -Pt heterocomposites.

To further investigate the chemical composition of gC_3N_4 -Pt/3GN, XPS measurement was carried out. As shown in Fig. 4a, C, N, Pt, and O peaks are clearly observed. The high-resolution C1s XPS spectrum (Fig. 4b) shows that oxygen-containing groups have been removed. The C1s spectrum shows five types of carbon bond: C=C/C-C (ca. 284.7 eV), C-N (ca. 285.2 eV), C-O (hydroxyl and epoxy, ca. 286.4 eV), C=O (carbonyl, ca. 288.7 eV), and O-C=O (carboxyl, ca. 291.7 eV) [22,23]. However, the majority of oxygen functional groups have been removed and the C-C bonds are dominant (Figs 4b and S1), indicating the successful reduction of GO by hydrazine. The complex N1s spectrum (Fig. 4c) can be fitted to two main peaks located at binding energies of 398.5 and 399.9 eV, which correspond to sp^2 N atoms in triazine rings (N1) [24] and bridging N atoms in $\text{N}-(\text{C})_3$ (N2), respectively [25]. N1 species can form strong interactions with platinum [26,27]. Owing to the large percentage of N1 species in gC_3N_4 -Pt/3GN, it should be possible to enhance the adhesion between Pt and the 3D support, and effectively prevent agglomeration of Pt nanoparticles. Additionally, the high-resolution Pt4f scans show two states of Pt in the hybrids (Fig. 4c): the doublet binding energies of $\text{Pt}4f_{7/2}$ and $\text{Pt}4f_{5/2}$ at 71.4–74.8 eV, which are assigned to Pt^0 [28]. These results confirm the successful modification of Pt nanoparticles on 3D graphene.

The electrochemical behavior of gC_3N_4 -Pt/3GN was measured by cyclic voltammetry (CV) scan in 0.5 M H_2SO_4 solution, and compared with Pt/3GN and Pt/C catalysts (Fig. 5a). All of the catalysts have CV curves with peaks related to hydrogen adsorption/desorption and oxide formation/reduction in the regions of –0.2–0.15 V and 0.4–1.0 V, respectively. Both Pt/3GN and Pt/C catalysts show the characteristic peak of hydrogen adsorption/desorption in range 1 in Fig. 5a, while the corresponding peak of

Figure 3 TEM images of gC_3N_4 -Pt/3GN at different magnification.

Figure 4 (a) XPS survey of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$; (b–d) high-resolution XPS spectrum of C1s, N1s and Pt4f, respectively.

the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ catalyst shifts to a more positive value (range 2). The hydrogen adsorption/desorption ability of Pt in the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ catalyst could be altered by lattice expansion from the transition lattice of Pt and adjacent gC_3N_4 quantum dots. To determine the electrochemically active surface area (EASA), carbon monoxide (CO)-stripping voltammetry studies were performed (Fig. S6). The calculated EASA values were 68.3, 49.6, and $51.9 \text{ m}^2 \text{ g}^{-1}$ for the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$, Pt/3GN, and Pt/C catalysts, respectively. The larger EASA of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ can be attributed to the small well-dispersed Pt nanoparticles, which provide more catalytic sites for the electrooxidation of methanol molecules than the other two catalysts. Furthermore, the onset potential of CO-stripping on the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ electrode was more negative than the onset potentials on the Pt/3GN and Pt/C electrodes, indicating that the adsorption of CO is much weaker on the $\text{gC}_3\text{N}_4\text{-Pt}$ nanoparticles than on pure Pt nanoparticles and $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ is electrochemically more accessible.

To evaluate the catalytic activity of $\text{gC}_3\text{N}_4\text{-Pt}$ nanohybrids on 3GN, we investigated the electrooxidation reaction of methanol in acidic media. Fig. 5b shows the CV curves of methanol oxidation in a $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ solution at a scan rate of 50 mV s^{-1} on Pt/3GN (Pt loading: 0.062 mg cm^{-2}), $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ (Pt loading: 0.065 mg cm^{-2}), and 20% Pt/C (Pt loading: 0.067 mg cm^{-2}) elec-

trodes. The metal contents were evaluated by ICP-MS analysis. Methanol oxidation is characterized by well-separated anodic peaks in the forward and reverse scans. Thus, the magnitude of the anodic peak current density (J) in the forward scan is directly proportional to the amount of methanol oxidized at the catalyst electrodes [29,30]. As shown in Fig. 5b, $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ has the highest activity of the three catalysts when normalized to the total mass of available Pt. The peak current density was 0.72 A mg^{-1} for the reaction on the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ electrode, which is much higher than on the 20% Pt/C (0.48 A mg^{-1}) and Pt/3GN (0.51 A mg^{-1}) electrodes. The high anodic peak current for the methanol electrooxidation reaction on the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ electrode illustrates that the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ electrode has excellent electrocatalytic activity for direct methanol fuel cells, which highlights the important synergetic functions of the Pt and gC_3N_4 components in the system.

The ratio of the forward-scan peak current (I_F) to the reverse-scan peak current (I_R), i.e., I_F/I_R , is an important index to evaluate the catalyst's tolerance to the accumulation of intermediate carbonaceous species (mainly CO) [31,32]. A high ratio of I_F/I_R indicates effective removal of the poisoning species from the catalyst surface. The I_F/I_R values of $\text{gC}_3\text{N}_4\text{-Pt/3GN}$, Pt/3GN, and Pt/C were 1.22, 1.07, and 0.71, respectively. The relatively high value for $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ can be attributed to the high nitrogen con-

Figure 5 Cyclic voltammetry curves of gC₃N₄-Pt/3GN, Pt/3GN, and E-TEK 20% Pt/C catalysts in (a) 0.5 M H₂SO₄ aqueous solution and (b) 0.5 M H₂SO₄ + 0.5 M CH₃OH aqueous solution. The scan rate was 50 mV s⁻¹. (c) Chronoamperometric curves of gC₃N₄-Pt/3GN, Pt/3GN, and E-TEK 20% Pt/C electrodes in 0.5 M H₂SO₄ + 0.5 M CH₃OH aqueous solution at a given potential of 0.3 V vs. Ag/AgCl. (d) Schematic diagram of the electrocatalytic oxidation of methanol molecules on gC₃N₄-Pt/3GN.

tent in the architecture. This would activate a large number of neighboring carbon atoms and accelerate the formation of -OH by water dissociation, and thus promote oxidative removal of the adsorbed intermediate poisoning species [19,33].

The long-term stability of gC₃N₄-Pt nanohybrids, Pt nanoparticles on 3GN, and 20% Pt/C electrodes for methanol electrooxidation was investigated by chronoamperometric experiments at a given potential of 0.3 V in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution (Fig. 5c). The polarization current for the methanol electrooxidation reaction showed rapid decay in the initial period for all of the samples, probably because of the formation of CO-like species during the methanol electrooxidation reaction. Nevertheless, the gC₃N₄-Pt/3GN catalyst showed the lowest current decay and retained the highest oxidation current over the testing time, indicating the best electrocatalytic durability for methanol oxidation. At the end of a 6000-s test, the oxidation current on the gC₃N₄-Pt/3GN electrode was still nearly two times higher than that on Pt/3GN. Even at a high potential of 0.6 V, the gC₃N₄-Pt/3GN electrode showed better stability than the Pt/C electrode (Fig. S7). These results show that the gC₃N₄-Pt heterocomposite on 3GN has long-term high catalytic activity for the methanol electrooxidation reaction in acidic media. This result is also reflected

in the continuous CV tests, as shown in Fig. S8. The initial forward peak current density of the gC₃N₄-Pt/3GN catalyst decreased by only 7.5% after 150 CV cycles; whereas which of the Pt/C catalyst lost 20.9% of its initial current density.

Pt becomes unstable when exposed to hostile electrochemical environments, where Pt surface atoms migrate and agglomerate, resulting in aggregation of nanoparticles and loss of surface area and activity [34,35]. In particular, the instability of Pt at the anode side represents one of the main limitations for commercialization of this technology. The structure of the gC₃N₄-Pt hybrids showed negligible change in morphology after the long-time electrochemical test (Fig. S9). The gC₃N₄-Pt nanohybrids effectively prevented the aggregation of Pt and the catalyst retained high catalytic activity for methanol oxidation. To investigate the synergetic function between Pt and gC₃N₄ quantum dots, we prepared Pt nanoparticles on 3GN and gC₃N₄ support by mechanical mixing (Fig. S10). Both the catalytic activity and stability of gC₃N₄-Pt/3GN were much higher than the corresponding values of Pt/3GN+gC₃N₄ with a similar size (Fig. S11).

It is reasonable to conclude that the integration of gC₃N₄-Pt nanohybrids and graphene nanosheets into an interconnected 3D porous architecture is extremely beneficial for its use as an electrocatalyst for methanol oxidation.

A schematic diagram of the electrocatalytic oxidation of methanol molecules on $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ is shown in Fig. 5d. There are a number of reasons why $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ shows high catalytic activity for the methanol oxidation reaction. First, the 3D architecture not only provides large, accessible, multi-sized pores for fast transportation of reactants to the electroactive sites, but it is also conducive to maintaining the high electrical conductivity of the catalyst. Second, the homogeneous dispersion of $\text{gC}_3\text{N}_4\text{-Pt}$ nanoparticles on the novel 3D architecture can maximize the utilization of Pt. Third, the incorporation of gC_3N_4 quantum dots with high nitrogen content plays a critical role in stabilizing the noble metal nanoparticles, and simultaneously facilitates the elimination of CO-like intermediates adsorbed on the Pt sites during the reaction. Finally, 3GN acts as an ideal conducting substrate to provide sufficient electronic conductive channels, as demonstrated by the electrochemical impedance spectroscopy (EIS) analysis shown in Fig. S12, resulting in a higher population of triple-phase boundaries in the catalytic system [36].

CONCLUSION

In summary, a new complex catalyst system of graphitic $\text{gC}_3\text{N}_4\text{-Pt}$ nanohybrids on a graphene network has been designed via a facile and efficient approach. The resulting 3D architecture of graphene sheets not only provides large, accessible, multi-size pores for fast transportation of reactants to the electroactive sites, but it is also conducive to maintaining the high electrical conductivity of the catalyst. In addition, the significant synergetic effect of gC_3N_4 quantum dots and Pt, and the homogeneous dispersion of ultrafine $\text{gC}_3\text{N}_4\text{-Pt}$ nanoparticles, result in the $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ hybrids showing high electrocatalytic activity, unusually high poison tolerance, and high stability when they are used as anode electrocatalysts for methanol oxidation. Therefore, the newly designed $\text{gC}_3\text{N}_4\text{-Pt/3GN}$ catalyst shows great potential as an efficient electrocatalyst for methanol electrooxidation in direct methanol fuel cells. The unique heterostructure of the nonmetal-metal is not limited to gC_3N_4 and Pt, and a series of similar structures based on this concept could be developed for new applications.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supplementary data are available in the online version of the paper.

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中文摘要 Pt基异质结构具有与单一相材料不同的物理和化学性质. 本研究巧妙地设计了一种非金属gC₃N₄和Pt的异质结构, 并将其负载在三维石墨烯网状结构上作为甲醇氧化的催化剂. 由于Pt和gC₃N₄之间的协同作用, 结合三维多孔石墨烯作为导电载体, 为活性位点接触燃料分子提供了最大限度的可能, 使得到的催化剂表现出异常优越的性能, 包括高的催化活性、不同寻常的抗CO中毒能力, 以及良好的稳定性. 这些性能优于商业化的碳负载Pt催化剂以及三维石墨烯负载Pt催化剂.