Ternary Pd$_2$/PtFe networks supported by 3D graphene for efficient and durable electrooxidation of formic acid†

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A newly-designed network of ternary Pd$_2$/PtFe nanowires on a three-dimensional graphene framework has been fabricated via a dual solvothermal approach, which presents superior electrocatalytic activity towards the oxidation of formic acid.

Platinum (Pt) with foreign components$^1$ has been considered as an effective approach to overcome CO poisoning,$^2$ enhance the activity and decrease the usage of expensive Pt$^3$ in fuel cells. In particular, PtFe is one of the superior binary Pt-based nanomaterial electrocatalysts for formic acid oxidation,$^4$ which exhibits high resistance to CO poisoning and is a potential candidate for CO-tolerant alloyed catalysts.$^{1c,d,5}$

Graphene, with a 3D self-supported structure, is promising for catalyst loading to facilitate the mass transfer and maximize the accessibility. We have recently fabricated graphene-based cathodic catalysts for fuel cell applications,$^6$ and developed shape-defined ternary Pt/PdCu nanoboxes anchored onto a 3D graphene framework (3DGF) as an efficient anodic catalyst for ethanol oxidation.$^7$ Herein, we design a new complex catalyst system in which a network of ternary Pd$_2$/PtFe nanowires is supported by an open-pore 3DGF. The heterogeneous structure derived from Pd with PtFe under 3DGF support presents a significantly enhanced synergetic role for formic acid oxidation, remarkably outperforming the Pd or PtFe, and the well-established commercial Pt/C catalysts (E-TEK 20% Pt/C).

We first developed a facile solvothermal strategy to fabricate 3DGF with in situ formed PtFe nanowires. Ternary heterogeneous Pd$_2$/PtFe network is subsequently formed by reducing PdCl$_2$ through the second solvothermal process (See Experimental details in ESI†). This solvothermal approach works well for the formation of defined 3DGF$^5$ (Fig. 1a and Fig. S1, ESI†). PtFe nanowires, tens of nanometers in length and 2–5 nm in diameter, are anchored on the graphene sheets (Fig. 1b). The X-ray energy dispersive spectroscopy (EDS) reveals that the sample is mainly composed of C, Pt and Fe elements plus O associated with the solvothermally reduced GO (Fig. 1c). The atomic ratio of Pt and Fe is ca. 1/1.0, consistent with the stoichiometric proportion of initial reactants and the analysis of inductively coupled plasma-mass spectrometry (ICP-MS) (Table S1, ESI†). X-ray diffraction (XRD) pattern of PtFe/3DGF (Fig. 1d) shows the typical (111) diffraction peak of PtFe$^9$ at ca. 41°, apart from the broad peak at 2θ ≈ 23° assigned to the (002) plane of stacked graphene. The initial formation of PtFe nanowires is strongly dependent on the graphene planar structure within 3DGF as compared with commercial XC-72 carbon black (Fig. S2, ESI†).

Fig. 2a shows the SEM images of Pd$_2$/PtFe attached 3DGF. The 3D microstructures of graphene sheets maintained well after deposition of Pd. Fig. 2b shows the typical TEM image of Pd$_2$/PtFe network on graphene sheets, which has a nanowire diameter of ca. 5–10 nm slightly larger than that of initial PtFe nanowires due to the effective deposition of Pd. Fig. 2c exhibits a high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of a single Pd$_2$/PtFe wire. The elemental mappings reveal that Pd, Pt, and Fe are distributed along the nanowire (Fig. 2d–f), where Pt and Fe elements have relatively narrow spatial distributions along the nanowire. Since the deposition of single-phase Pd on 3DGF produces nanoparticles instead of nanowires (Fig. S3, ESI†),

Fig. 1 (a) SEM images of as-obtained PtFe/3DGF. The inset in (a) is the photo of a PtFe/3DGF sample. (b) TEM image of PtFe nanowires on 3D graphene sheets. (c,d) The corresponding EDS and XRD pattern of PtFe/3DGF.

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we speculate that the formation of the Pd2/PtFe network was mainly induced by the initial PtFe nanowires, which could act as the nucleation sites for Pd deposition. It was notable that the sequential addition of Pt, Fe precursor and PdCl2 is essential for the formation of a morphology-defined nanowire structure. Otherwise, random nanoparticles will be produced preferentially (Fig. S4, ESI†).

EDS analysis reveals that the sample contains C, Pd, Pt and Fe elements (Fig. 2g), and the atomic ratio of Pd, Pt and Fe is ca. 2.0/1.0/0.9, which is also close to the stoichiometric proportion of initial reactants and consistent with the ICP-MS analysis (Table S1, ESI†). The Pd:Fe atomic ratio in Pd2/PtFe nanowires is slightly higher than that of the initial PtFe wires (1/1.0), indicating that a partial displacement reaction might occur between Fe and Pd ions during the formation of ternary Pd2/PtFe nanowires. Besides the broad peak at ca. 20° for stacked graphene, the XRD pattern for Pd2/PtFe/3DGF (Fig. 2h) displays the feature peaks similar to those of both Pd12 and PtFe, indicating that the formation of ternary Pd2/PtFe (Fig. S5, ESI†). The XRD patterns of 3DGF and PtFe/3DGF before and after the second solvothermal treatment retain their initial feature (Fig. S6 and S7, ESI†), suggesting they are almost unchanged during this process.

The electrochemical behavior (Fig. 3) of Pd2/PtFe/3DGF was measured by CV scan in aqueous H2SO4 in comparison with Pd/3DGF, PtFe/3DGF (Fig. S8, ESI†), and Pt/C (Fig. S9, ESI†) catalysts. 3DGF maintained a porous structure on the working electrode (Fig. S10, ESI†). All of them exhibit the CV curves with peaks related to hydrogen adsorption/desorption and oxide formation/reduction, as revealed in the regions of ca. 0.2–0.15 V and 0.4–1.0 V, respectively. Both Pd2/PtFe/3DGF and Pd/3DGF catalysts present the stronger peaks of hydrogen adsorption/desorption at more negative potentials than those of PtFe/3DGF and Pt/C catalysts, most likely due to the existence of Pd.13 Importantly, the hydrogen adsorption/desorption area on Pd2/PtFe/3DGF is even smaller than that of Pd/3DGF catalyst, indicating that more active sites will be free for the oxidation of formic acid. From the surface oxide reduction process in the region between 0.4 and 1.0 V, the reduction peak of Pd2/PtFe/3DGF was 0.52 V, showing a positive shift compared with 0.48 V for Pd on 3DGF catalyst. These results suggest the relatively weak adsorption strength of the intermediate oxides on Pd2/PtFe surfaces,14 which will be conducive to the oxidation of intermediates, effectively reducing the possibility of catalyst poisoning, and favoring the active durability of Pd2/PtFe/3DGF. An additional peak observed on PtFe/3DGF located at 0.49 V with respect to that of Pd/3DGF and E-TEK 20% Pt/C (Fig. S11, ESI†) indicates that the ability to form oxides on the PtFe is stronger than that of pure Pd and Pt.15 Therefore, the PtFe has a specific advantage as seeds for the formation of ternary Pd2/PtFe nanowires.

To evaluate the electrocatalytic activities of Pd2/PtFe/3DGF catalyst towards the electrooxidation of formic acid, we carried out the CV experiments of Pd2/PtFe/3DGF (Pd: 0.04 mg cm−2, Pt: 0.056 mg cm−2) in the electrolyte containing 1 M HCOOH and 0.5 M H2SO4 in comparison with Pd/3DGF (Pd: 0.074 mg cm−2, PtFe/3DGF (Pt: 0.057 mg cm−2) and E-TEK 20% Pt/C catalysts. The current was normalized to the total mass of the active metals such as Pd and/or Pt.7 As shown in Fig. 4a, the two main oxidation peaks of formic acid on the Pd/3DGF catalyst were located at ca. 0.2 V in both the positive and negative directions, which is...
attributed to the direct oxidation pathway of formic acid oxidation.\(^{16}\) For the Pt/C catalyst, the forward and backward oxidation current peaks occur at \(ca.\) 0.78 V and 0.38 V, respectively, characteristic of the oxidation of formic acid on Pt sites. The low forward peak current is caused by its indirect oxidation pathway associated with Pt poisoning by CO at lower potential. Different from the Pt/3DG and Pt/C, the forward and backward peaks on PtFe/3DG were downshifted to \(ca.\) 0.62 V, and the current was largely enhanced, indicating that the PtFe alloy was more effective than the single Pt phase during the oxidation process.

Two peaks at 0.08 V and 0.65 V in the positive direction and two peaks at 0.51 V and 0.18 V in negative direction appear for the Pd\(_2\)/PtFe/3DG, which forms the combinatorial oxidation characteristics of both PtFe and Pt. It is notable that the current on Pd\(_2\)/PtFe/3DG maintained the higher value than those of others almost along the entire CV cycle, indicating the favorably synergetic function between Pt and PtFe. The mass activity of the catalysts for formic acid oxidation can be represented by the magnitude of the forward anodic current. As shown in Fig. 4a and Fig. S12 (ESI\(^+\)), the first forward peak current at 0.2 V of the Pd\(_2\)/PtFe/3DG catalyst is \(ca.\) 0.74 A mg\(^{-1}\), higher than that of Pd/3DG (0.43 A mg\(^{-1}\)) and PtFe/3DG (0.25 A mg\(^{-1}\)), and more than ten times that of Pt/C (0.06 A mg\(^{-1}\)). This value is also much higher than those previously reported for Pd (0.27 A mg\(^{-1}\))\(^{17}\) and PdPt (0.28 A mg\(^{-1}\)).\(^{18}\) Furthermore, the onset potential of formic acid oxidation is \(ca.\) –0.10 V for Pd\(_2\)/PtFe/3DG, lower than –0.05 V for Pd/3DG, 0.21 V for PtFe/3DG and 0.61 V for Pt/C. The higher current and the lower onset potential of formic acid oxidation on Pd\(_2\)/PtFe/3DG exhibit a significantly enhanced electrode kinetics and oxidation activity. It is also found that Pd\(_2\)/PtFe has the optimal Pd:Pt atomic ratio of 2:1 to achieve the highest activity (Fig. S13, ESI\(^+\)). The electrochemically active surface area (EAS) was determined by CO-stripping measurements (Fig. S14, ESI\(^+\)), and the current normalized to the EAS was provided in Fig. S15 (ESI\(^+\)). The EAS-specific activity of Pd\(_2\)/PtFe/3DG was clearly superior to others, consistent with the results of mass activity evaluation. On the other hand, Pd\(_2\)/PtFe with the nanowire network has an obvious advantage over random particles in catalytic activity (Fig. S4 and S16, ESI\(^+\)).

Pd\(_2\)/PtFe on 3DGF has higher activity than that on XC-72 carbon (Fig. S17, ESI\(^+\)). Similarly, Pt on 3DGF is more active than Pt/C catalyst (Fig. S18, ESI\(^+\)). In combination with the observation in Fig. 4a, it can be concluded that both the Pd\(_2\)/PtFe heterostructures and 3DGF have positive impact on the activity toward the electrooxidation of formic acid.

As can be seen in Fig. 4b for stability comparison, the pure Pd on 3DGF and 20% Pt/C electrodes have an unfavorable catalytic performance. In contrast, PtFe catalyst can maintain a relatively high catalytic activity during a certain period, but the anodic current decreased gradually to the low level. Remarkably, the Pd\(_2\)/PtFe/3DG catalyst has much higher current and slower degradation. The anodic current density after running 3000 s is still several times higher than all the others, indicating a high catalytic activity and good stability of Pd\(_2\)/PtFe/3DG for formic acid oxidation.

In summary, a new complex catalyst system consisting of the network of Pd\(_2\)/PtFe supported on 3D graphenes has been synthesized via a dual solvothermal process. The unique combination of the ternary Pd\(_2\)/PtFe with 3D graphene support facilitates a maximum accessibility for active species to the catalyst, and hence creates superior electrocatalytic activity and stability towards the oxidation of formic acid.

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Notes and references