Electronic Supplementary Information

Ternary Pd_2/PtFe networks supported by 3D graphene for efficient and durable electrooxidation of formic acid

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Experiments

Synthesis of Graphene Oxide (GO): GO was prepared from natural graphite powder *via* acid-oxidation according to a modified Hummers method as reported in our previous papers.[s1–s3]

Synthesis of PtFe nanowires and Pd_2/PtFe nanowire network on 3D graphene framework (3DGF): The aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ (8.0 mg/mL, 1.5 mL), GO (8 mg/mL, 3.2 mL), 6.5 mg of $FeSO_4 \cdot 7H_2O$, and 50 mg of glutamate were mixed with 40 mL of ethylene glycol (EG). Having been ultrasonicated and stirred for 2 h to obtain a homogeneous suspension, its pH value was adjusted to *ca.* 13 by the dropwise addition of 8 wt% KOH/EG solution under vigorous stirring. Subsequently, the suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave, followed by thermal treatment at 185°C for 6 h. After cooled to room temperature, a columnar hydrogel of 3DGF loaded with PtFe nanowires was obtained. If the H_2PtCl_6, $FeSO_4$ and glutamate were absent during this process, a 3D pure graphene structure was generated (Fig. S1). The PtFe/3DGF hydrogel was then exposed to the EG solution containing appropriate amounts of $PdCl_2$ (6.7 mg/mL, 1 mL) and 20 mg of glutamate at a given pH of *ca.* 12. The second solvothermal treatment was carried out at 140°C for another 3 h under the same Teflon-lined stainless-steel autoclave. The resulting product was collected after washing with dilute hydrochloric acid and deionized water several times, which was then freeze-dried to prevent the aggregation of graphene sheets. The resulting samples produced by this two step process are denoted as Pd_2/PtFe/3DGF according to the stoichiometric ratio. For comparison of catalytic activity, the PtFe/3DGF sample was further subjected to the second solvothermal treatment at 140°C for 3 h.

Synthesis of Pd nanoparticles on 3DGF: The Pd nanoparticle anchored 3DGF was prepared by following the similar procedure to that for formation Pd_2/PtFe/3DGF but without the preformed PtFe/3DGF. Briefly, an aqueous solution of $PdCl_2$ (6.7 mg/mL, 1.5 mL), GO (8 mg/mL, 3.2 mL) and 20 mg of glutamate were mixed with 40 mL of ethylene glycol (EG), which was ultrasonicated and stirred to obtain a homogeneous suspension. Under a pH of 12, the suspension was heated at 140°C for 9 h by use of the same Teflon-lined stainless-steel autoclave. After cooled to room temperature, a columnar hydrogel of 3DGF loaded with Pd nanoparticles (Pd/3DGF) similar to the above-mentioned Pd_2/PtFe/3DGF was obtained.

Synthesis of Pd_2PtFe alloy particles on 3DGF: The aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ (8.0 mg/mL, 1.5 mL), GO (8 mg/mL, 3.2 mL), 6.5 mg of $FeSO_4 \cdot 7H_2O$, $PdCl_2$ (6.7 mg/mL, 1.5 mL), and 50 mg of glutamate were simultaneously mixed with 40 mL of ethylene glycol (EG). Then, the formed solution undergoes the same procedure as the synthesis of Pd_2/PtFe/3DGF. The final collected sample is denoted as Pd_2PtFe/3DGF distinguishing from Pd_2/PtFe/3DGF.

Synthesis of Pt nanoparticles on 3DGF: The Pt nanoparticle supported on 3DGF was prepared by the similar procedure to that for the formation of PtFe/3DGF in the absence of $FeSO_4$.

Synthesis of PtFe nanostructure on XC-72: The synthetic procedure of PtFe/XC-72 was same as that of the PtFe/3DGF, except the commercialized XC-72 carbon black was used as support.

Synthesis of Pd_2/PtFe nanostructure on carbon XC-72: The synthetic procedure of Pd2/PtFe/XC-72 was same to that of the Pd_2/PtFe/3DGF, except the commercialized XC-72 was used as support.

Electrochemical investigation

The electrochemical measurements were conducted in a three-electrode cell by using a CHI760D electrochemical workstation. A glassy carbon disk coated with catalyst was used as the working electrode. An Ag/AgCl electrode and a platinum foil (1 cm^2) were used as the reference and counter electrodes, respectively. The glassy carbon disk was rinsed with double distilled water and dried at room temperature before the catalyst layer was applied to the disk. The electrode was prepared as follows: 2 mg of the catalyst was added into 0.4 mL of ethanol and 50 μL of 5 wt% perfluorosulfonic acid (PFSA), which was treated by ultrasonication for approximately 30 min to obtain a homogeneous dispersion. Next, 5 μL of the sample was uniformly dropped onto a freshly polished glassy carbon electrode (3 mm in diameter) and was dried under ambient conditions.

Electrochemical CO-stripping voltammograms were obtained by oxidizing pre-adsorbed CO (CO_{ad}) in 0.5M H_2SO_4 at a scan rate of 50 mV s^{-1}. CO was purged through 0.5M H_2SO_4 for 3000 s to allow complete adsorption of CO onto the catalyst. The working electrode was maintained at 0.15V (vs. Ag/AgCl), and excess CO in the electrolyte was removed by purging with high-purity nitrogen for 30min. The amount of adsorbed CO was evaluated by integrating the CO_{ad} stripping peak and correcting for the capacitance of the electric double-layer. The activity evaluation of electrocatalysts for the formic acid oxidation reaction was carried out in a nitrogen-saturated 0.5 M H_2SO_4 electrolyte containing 1 M HCOOH. Cyclic voltammetry (CV) curves were recorded by applying a linear potential scan at a sweep rate of 50 mV s^{-1}. The cycling was repeated until a reproducible CV curve was obtained before the measurements were recorded. All electrochemical experiments were performed at 20 ± 1°C.

Characterization

The morphology of the samples was determined by JEM-2010 high resolution transmission electron microscopy (HR-TEM) at an acceleration voltage of 200 kV. Scanning electron microscope (SEM) images and EDS data of the samples were taken on JSM-7001F SEM unit. The elemental mappings were carried out on a scanning transmission electron microscope (STEM) unit with high-angle annular dark-field (HAADF) detector (HITACHI S-5500) operating at 30 kV. X-ray diffraction (XRD) patterns were obtained by using a Netherlands 1,710 diffractometer with a Cu Kα irradiation source (λ = 1.54 Å), and a self-calibration process was performed with a SiO_2 internal standard sample prior to target measurements. Raman spectra were recorded using a RM 2000 Microscopic Confocal Raman Spectrometer (Renishaw PLC, England) with an Ar laser at a wavelength of 514.5 nm. The composition of the catalysts was evaluated by inductively coupled plasma-mass spectrometry (ICP-MS) analysis from Perkin Elmer instrument using flow injection on-line preconcentration.

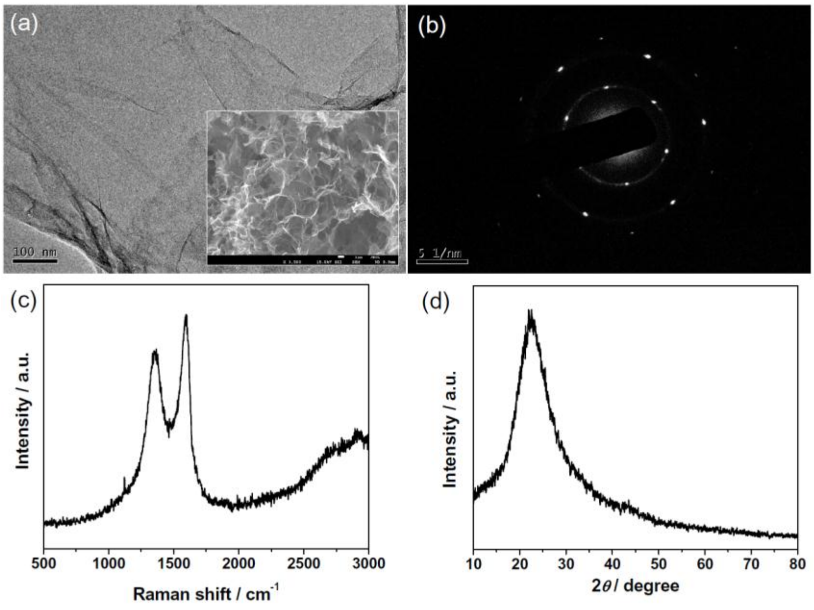

Fig. S1 TEM image of the graphene sheets within 3DGF (a), the electron diffraction of graphene sheet (b), the corresponding Raman spectrum (c) and XRD pattern (d). The inset in (a) is the SEM image of as-obtained 3DGF with a scale bar of 1 μm.

The 3D graphene framework was obtained *via* a one-step solvothermal method without metal-containing precursors. All the TEM, electron diffraction, Raman, and XRD results (Fig. S1) confirm the formation 3D graphene structures by the solvothermal method.

Table S1. A composition comparison of the preformed PtFe and Pd_2/PtFe determined by ICP-Ms.

Sample	**Atomic ratio (Pd/Pt/Fe)**
PtFe	0/1.0/1.04
Pd2/PtFe	2.04/1.0/0.92

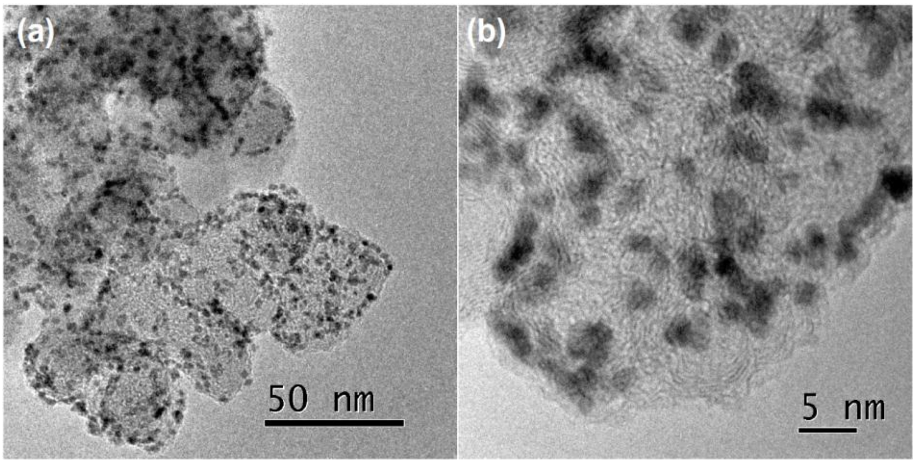

Fig. S2 TEM images of PtFe nanoparticles on XC-72 at different magnifications.

To understand the impact of graphene on the morphology of PtFe, we prepared the PtFe on the commercial XC-72 carbon black (Fig. S2). Unlike the graphene sheets beneficial for the formation of nanowires (Fig. 1b), it was found that most of PtFe produced on the XC-72 are agglomerated particles. We speculate that the 2D planar structure of graphene sheets may play role for the formation of PtFe nanowires. The firstly obtained PtFe nuclei with high surface energies would preferentially connect with the neighbor nanoparticles on the surface of graphene sheets, this trend would finally lead to the formation of wire and even network structures as we observed. In the case of disordered carbon (XC-72), the effective connection between nanoparticles for wire structure was prohibited by the irregular carbon particles.

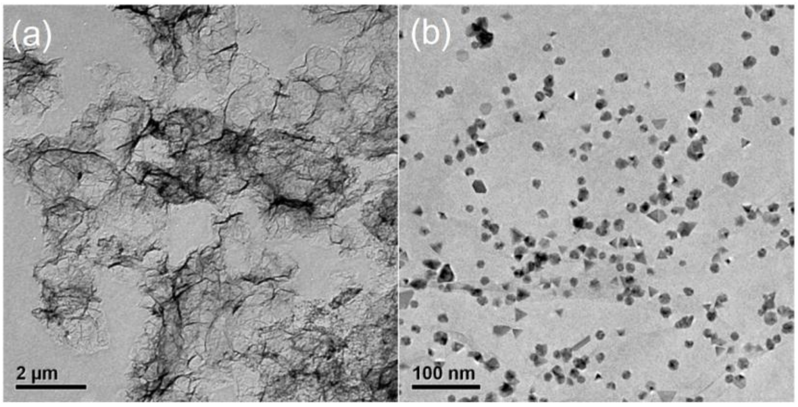

Fig. S3 TEM images (a, b) of Pd nanoparticles on 3DGF at different magnifications.

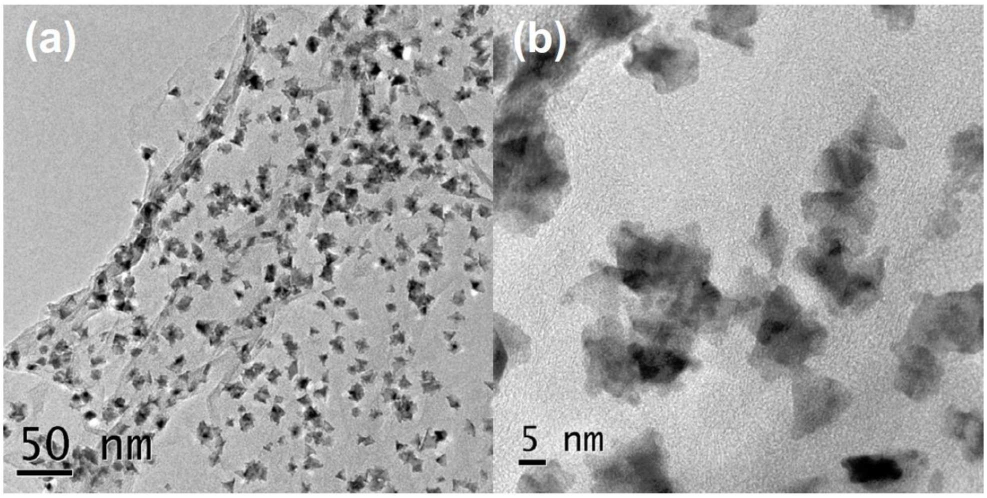

Fig. S4 TEM images (a, b) of Pd_2PtFe nanoparticles on 3DGF obtained by mixing H_2PdCl_4 with H_2PtCI_6 and $FeSO_4$ simultaneously.

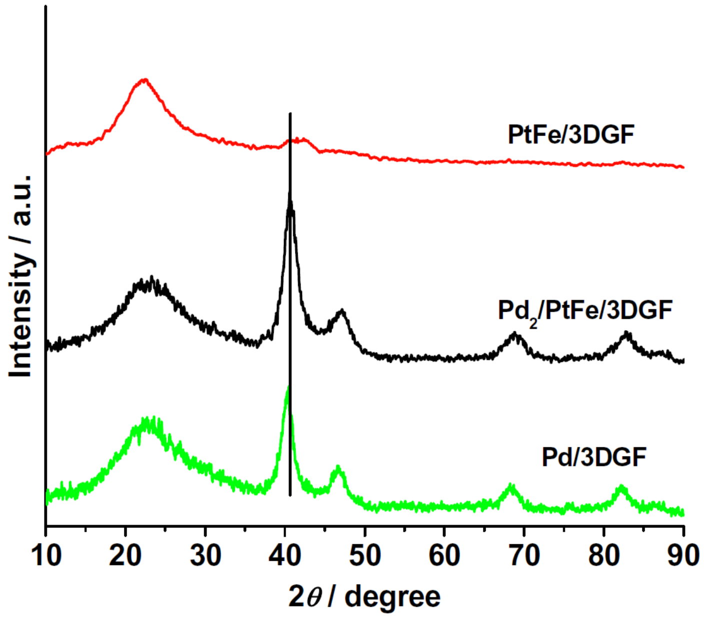

Fig. S5 XRD patterns of Pd, PtFe and Pd_2/PtFe nanostrucrures on 3DGFs. Besides the broad peak at $2\theta \approx 23^o$ related to stacked graphene sheets, XRD pattern for Pd_2/PtFe/3DGF displays the feature peaks similar to that of both Pd and PtFe, indicating the formation of ternary Pd_2/PtFe.

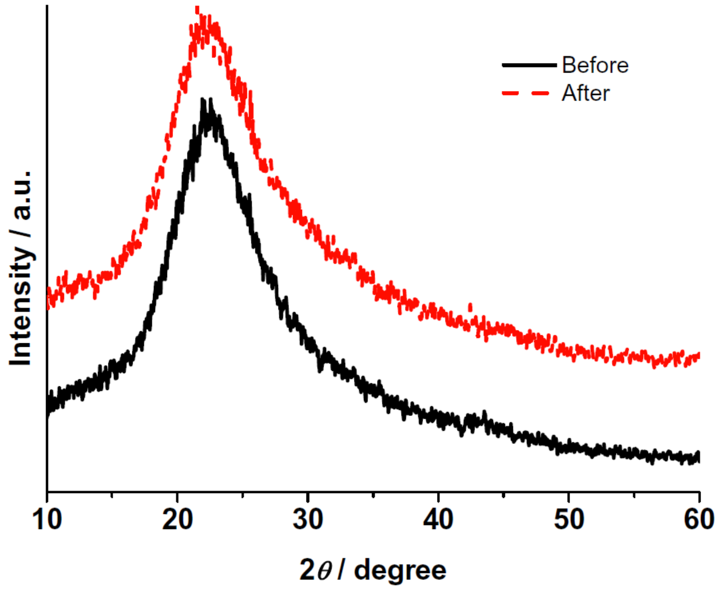

Fig. S6 XRD pattern 3DGF before and after the 140°C solvothermal treatment for 3h without any metal precursors.

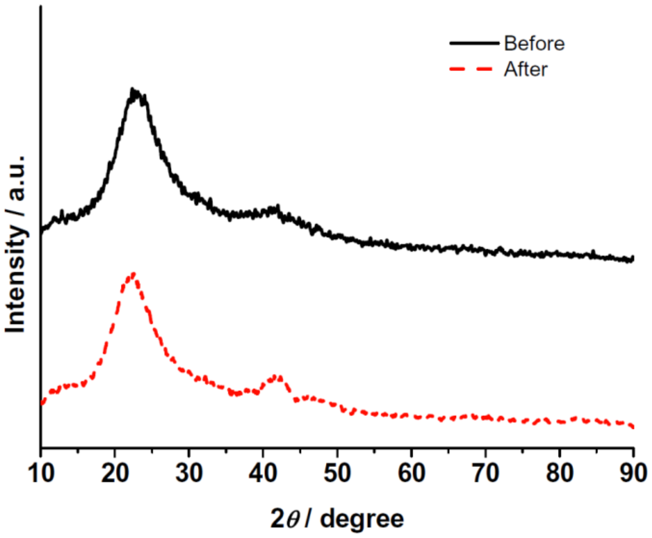

Fig. S7 XRD pattern of PtFe/3DGF before and after the 140°C solvothermal treatment for 3h.

The XRD patterns of 3DGF and PtFe/3DGF before and after the second solvothermal treatment almost remain unchanged (Fig. S6 and S7). Therefore, it can be proposed that the change of support itself and PtFe, if any, is negligible.

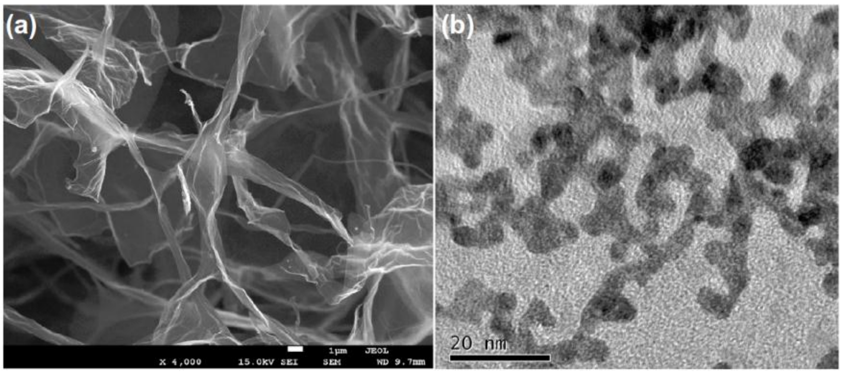

Fig. S8 SEM (a) and TEM (b) images of PtFe/3DGF after the second solvothermal treatment.

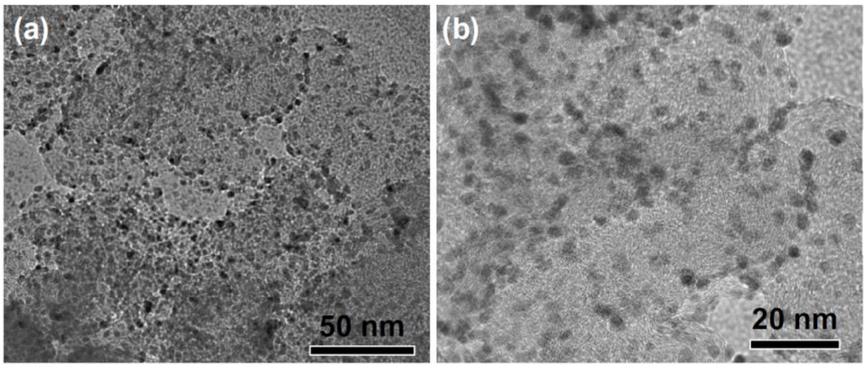

Fig. S9 TEM images (a, b) of E-TEK Pt/C catalyat at different magnifications. The mean particle size of the Pt is ca. 3 nm.

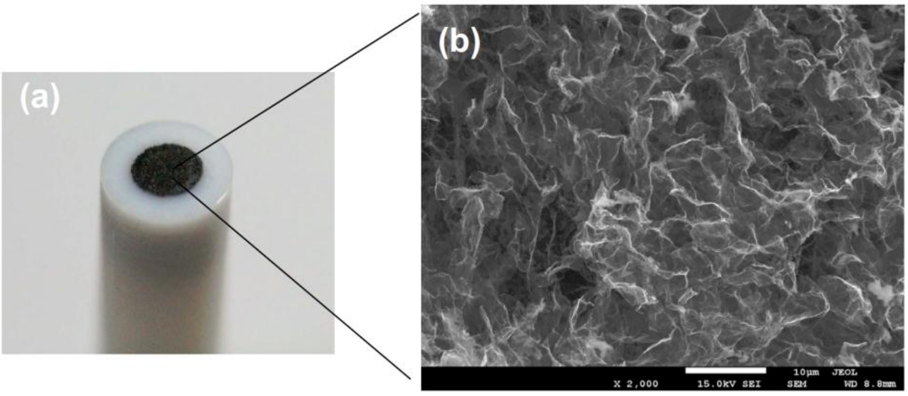

Fig. S10 (a) A photo of the sonicated Pd_2/PtFe/3DGF dropped on the glassy carbon electrode, and (b) the corresponding SEM image of the dispersed Pd_2/PtFe/3DGF.

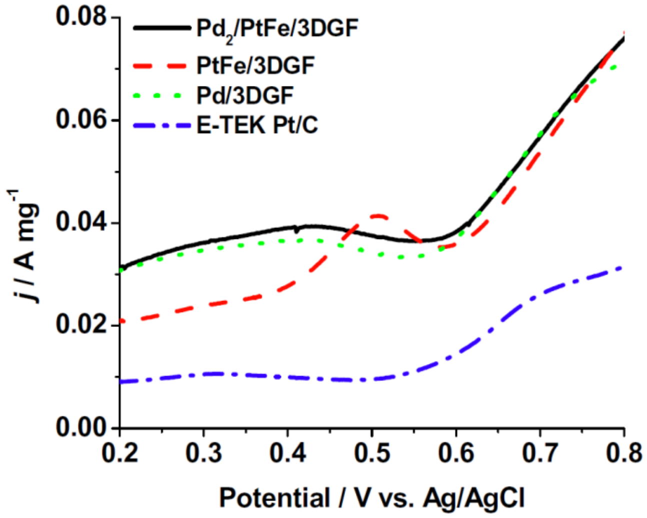

Fig. S11 The enlarged view of the positive scan of the CV curves within potential region of 0.2–0.8V in Fig. 3.

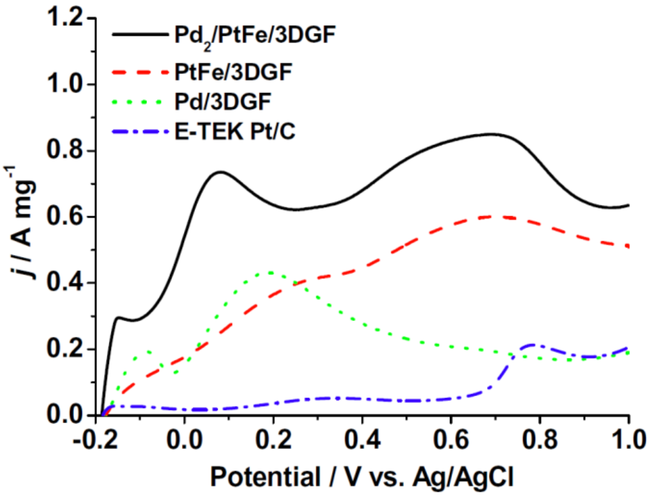

Fig. S12 CV curves of the Pd_2/PtFe, Pd, PtFe on 3DGFs, and E-TEK 20% Pt/C catalysts in the positive direction in 1M H_2SO_4 and 1M HCOOH aqueous solution. The scan rate is 50 mV s^{-1}.

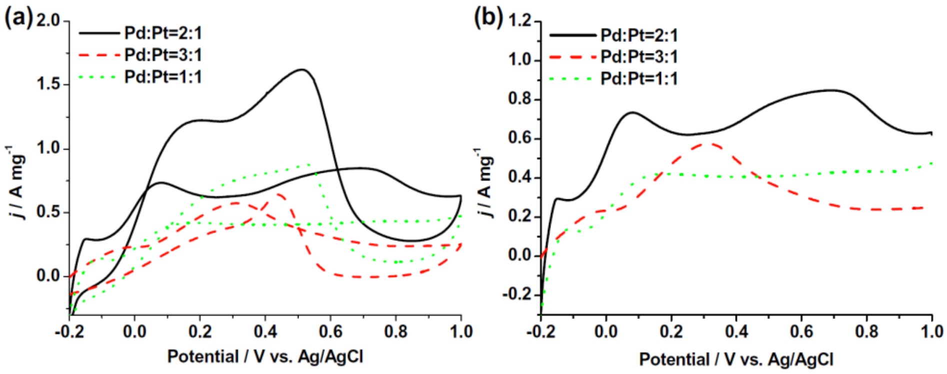

Fig. S13 CVs of the Pd/PtFe catalysts supported on 3DGF with the nominal atomic ratio Pd:Pt=3:1, 2:1 and 1:1. The electrolyte solution: 0.5 M H_2SO_4 and 0.5 M HCOOH. The scan rate: 50 mV s^{-1}.

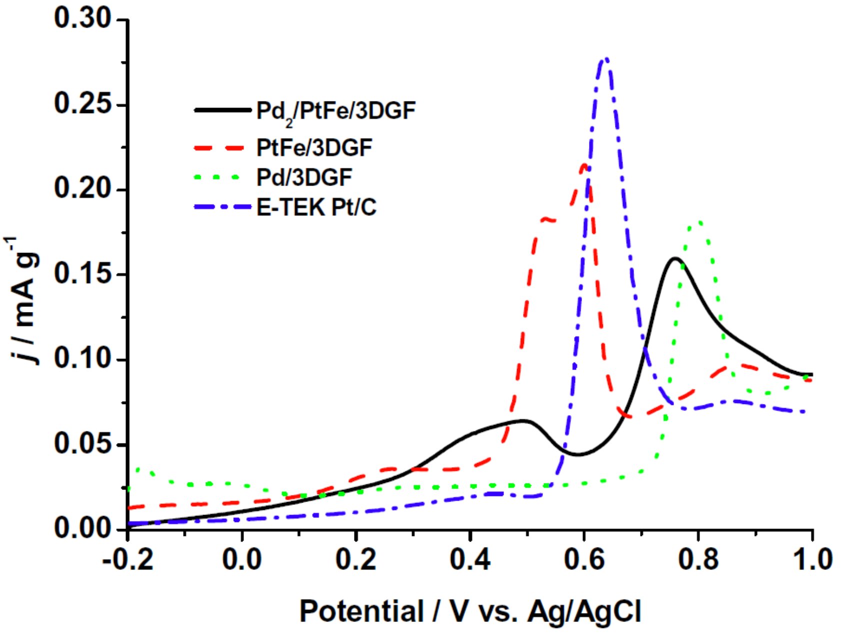

Fig. S14 CO-stripping voltammograms of Pd_2/PtFe, PtFe, Pd on 3DGFs, and E-TEK 20% Pt/C catalysts in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

Science the bulk Pd can absorb hydrogen, the electrochemically active surface area (EAS) of the catalysts was determined by CO-strippingmeasurements^{s4}. Fig. S14 shows the CVs obtained with CO adsorbed onto the catalysts, conducted in a solution of 0.5M H_2SO_4. The corresponding EAS of the catalyst was obtained from Eq. (1)^{s5,6}:

$$\mathrm{EAS} = \frac{Q}{G \times 420} \tag{1}$$

where Q is the charge of CO desorption-electrooxidation in microcoulomb (μC), G represents the total amount of Pd (μg) on the electrode, and 420 is the charge required to oxidize a monolayer of CO on the catalyst in μC·cm^{-2}. The calculated EAS was 54.4, 55.7, 39.6 and 51.4 $m^2\cdot g^{-1}$ for Pd_2/PtFe/3DGF, PtFe/3DGF, Pd/3DGFs, E-TEK 20% Pt/C catalysts, respectively.

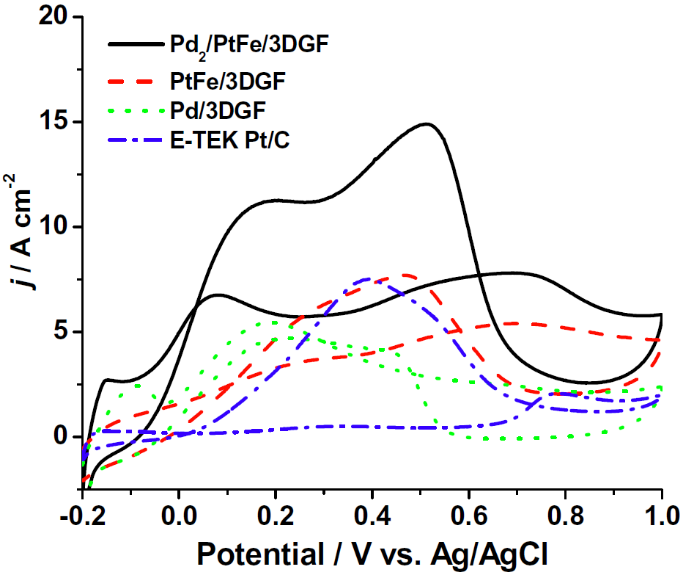

Fig. S15 CV curves of the Pd_2/PtFe, PtFe, Pd on 3DGFs, and E-TEK 20% Pt/C catalysts in 1 M H_2SO_4 and 1 M HCOOH aqueous solution. The current is normalized to the EAS of active metals such as Pd + Pt for Pd_2/PtFe/3DGF, Pd for Pd/3DGF, Pt for PtFe/3DGF and Pt/C catalysts.

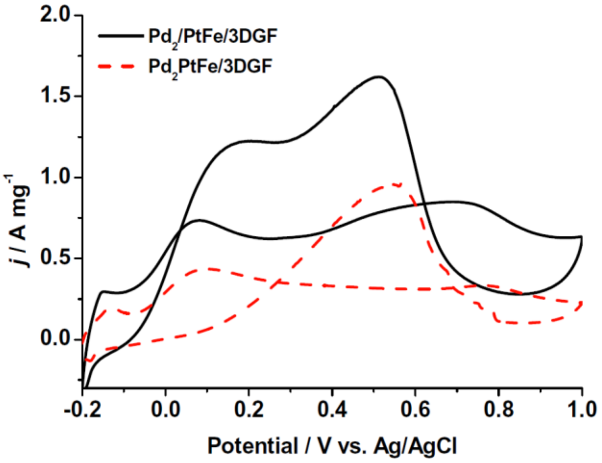

Fig. S16 The CV curves of the Pd_2/PtFe/3DGFs, and Pd_2PtFe/3DGF catalysts in 1 M H_2SO_4 and 1 M HCOOH aqueous solution. The scan rate is 50 mV s^{-1}.

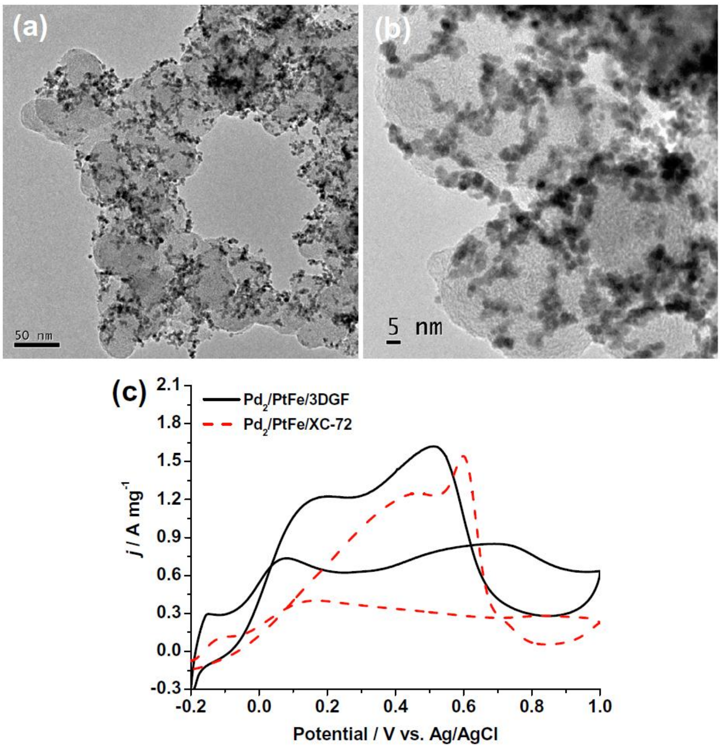

Fig. S17 (a, b) are TEM images of Pd_2/PtFe nanoparticles on XC-72 carbon at different magnifications. (c) is the CV curves of the Pd_2/PtFe/3DGFs, and Pd_2/PtFe/XC-72 catalysts in 1 M H_2SO_4 and 1 M HCOOH aqueous solution. The scan rate is 50mV s^{-1}.

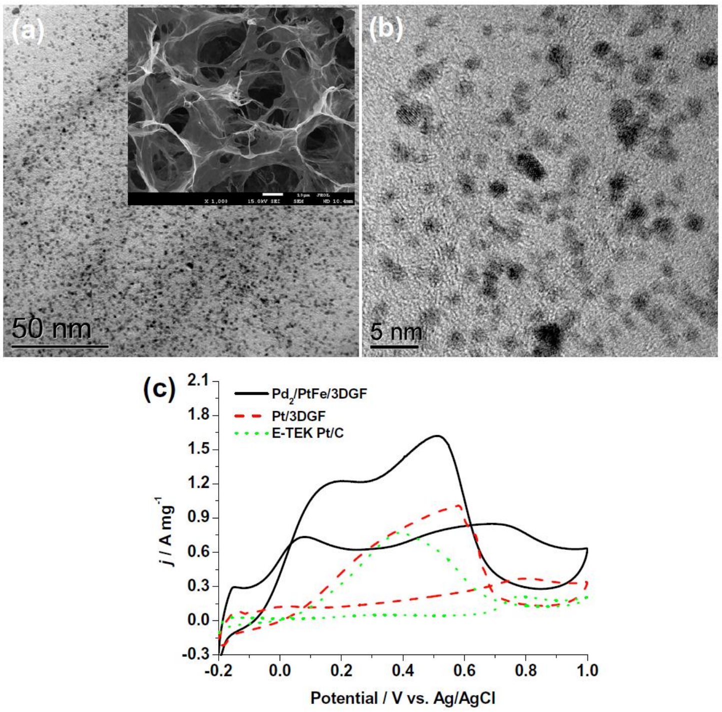

Fig. S18 (a, b) TEM images of Pt nanoparticles on 3DGF at different magnifications. (c) CV curves of the Pd_2/PtFe, Pt on 3DGFs, and E-TEK 20% Pt/C catalysts in 1 M H_2SO_4 and 1 M HCOOH aqueous solution. The scan rate is 50 mV s^{-1}. The inset in (a) is the SEM image of Pt/3DGF.

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