Supplementary Information

Facile one-pot surfactant-free synthesis of uniform Pd_6Co nanocrystals on 3D graphene as an efficient electrocatalyst toward formic acid oxidation

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Experimental Section

Synthesis of 3D graphene (3DG)

Firstly, the graphene oxide was synthesized using a modified Hummers method.[1,2] The prepared graphene oxide was dried at 60°C for 10h and then put into a sealed glass bottle under high vacuum level at 70°C overnight, followed by heating to 230°C quickly. The obtained highly loose black powder was denoted as three-dimensional graphene.

Synthesis of 3DG supported Pd_6Co electrocatalyst

To synthesize electrocatalysts, 15mg 3DG, $Pd(acac)_2$ and $Co(ac)_2$ were added in 25 mL of ethylene glycol. The mixture was treated in an ultrasonic bath for one hour, and then continuous stirred overnight. The mixed solution was placed in a 50 mL Teflon-sealed autoclave and maintained at 260°C for 10 h under high-purity argon protection, followed by centrifugation and washing for three cycles. After oven-dried at 70°C for more than 6 h, the obtained sample was denoted as Pd_6Co/3DG, Pd_3Co/3DG, PdCo/3DG and Pd/3DG, respectively. The Pd and Co atomic ratio can be tuned by controlling the amount of Pd and Co precursors. Pd/C was also prepared under the same approach except using XC-72 carbon instead of 3DG.

Synthesis of reduced graphene oxide (RGO) sheets supported Pd_6Co catalyst

Typically, 25 ml graphene oxide (4mg/ml) aqueous dispersion was transferred into 50 ml Teflon-sealed autoclave and maintained at 180°C for 12 h. After the autoclave was naturally cooled to room temperature, the RGO was obtained by a freeze-drying method. Then the Pd_6Co/RGO and Pd/RGO were prepared with the same procedure of Pd_6Co/3DG except using reduced graphene oxide instead of 3DG.

Physicochemical Characterization

The morphology and nanostructure of prepared samples were obtained on scanning electron microscope (SEM, JSM-7800F) and transmission electron microscope (TEM, JEOL JEM2100). Elements distribution of synthesized nanoparticle was detected by highly sensitive Super-X energy dispersive X-ray (EDX) detector system with high angle annular dark field scanning transmission electron microscope (HAADF-STEM, Titan G2 60-300). The crystal structure was characterized by powder X-ray diffraction (XRD, XRD-7000). The weight and composition of simples were carried out using thermogravimetric analysis (TGA-Q50) and inductively coupled plasma atomic emission spectrometric (ICP-AES, iCAP 6300 Duo). Nitrogen adsorption-desorption experiments were carried out at 77.3K by using an automated gas sorption system (Quantachrome Instruments, 2QDS-MP-30). Contact angle was studied on JC2000D drop meter and X-ray photoelectron spectroscopy (XPS) measurements were performed with Thermo Scientific ESCALAB 250Xi X-Ray Photoelectron Spectrometer.

Electrochemical Measurements

Electrochemical characterizations were carried out in a three-electrode electrochemical cell using a saturated calomel electrode (SCE) and a platinum foil as the reference and counter electrode, respectively. Catalyst ink was prepared by ultrasonically mixing catalysts (4 mg), ethanol (1 ml) and Nafion solutions (50 μl, 5 wt %), then 6μl ink was pipetted and spreaded onto a pre-polished glass carbon (GC) disk electrode (4 mm diameter, 0.126 cm^2) followed by drying for 15 min as the working electrode for measurements.

Cyclic voltammetry (CV) curves were measured in N_2-saturated 0.5 M H_2SO_4 and/or 0.5 M H_2SO_4 + 0.5 M HCOOH at 50 mV s^{-1}. Chronopotentiometry curves were obtained in 0.5 M H_2SO_4 + 0.5 M HCOOH. All electrochemical experiments were performed at 25±1°C.

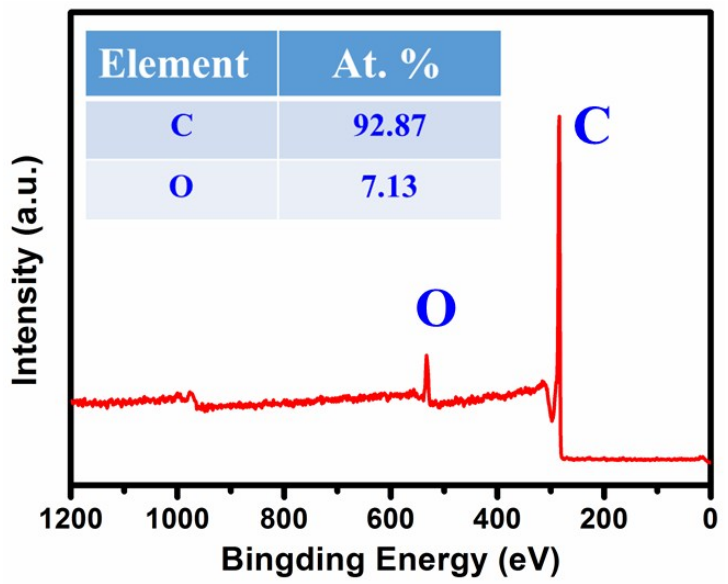

Figure S1. XPS spectrum of prepared 3DG materials.

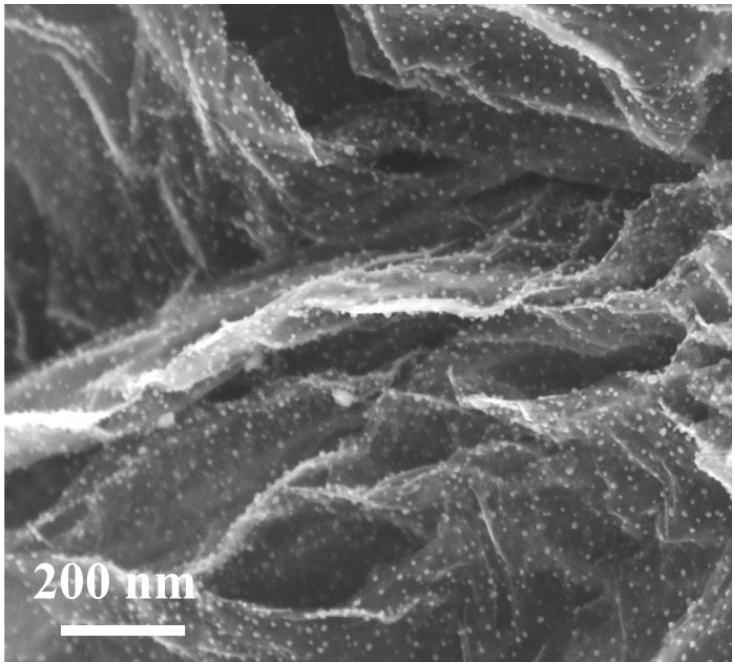

Figure S2. SEM image of prepared Pd/3DG materials.

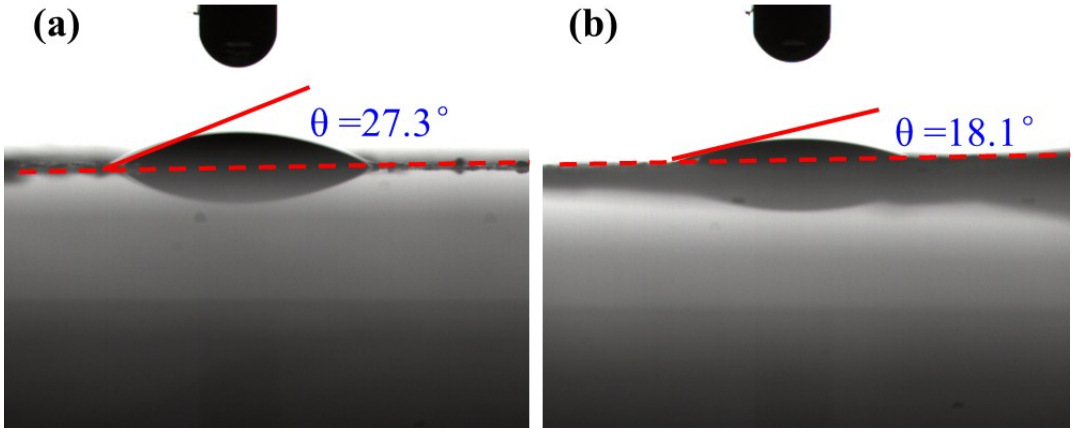

Figure S3. Ethylene glycol contact angle of XC-72 Carbon (a) and 3D graphene (b), respectively.

Obviously, 3D graphene materials exhibit smaller ethylene glycol contact angle than that of XC-72 Carbon, indicating its better ethylene glycol-philicity.

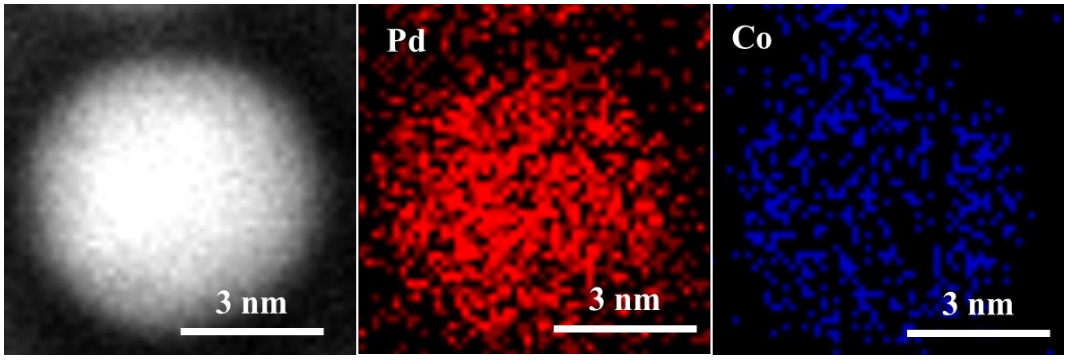

Figure S4. EDAX mapping images of Pd and Co elements distribution of a Pd_6Co nanoparticle.

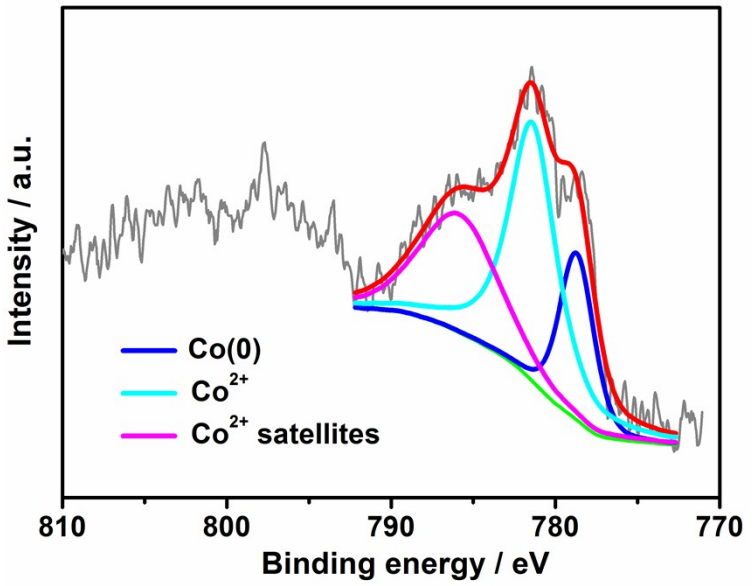

Figure S5. The high-resolution XPS spectrum of Co2p of Pd_6Co/3DG.

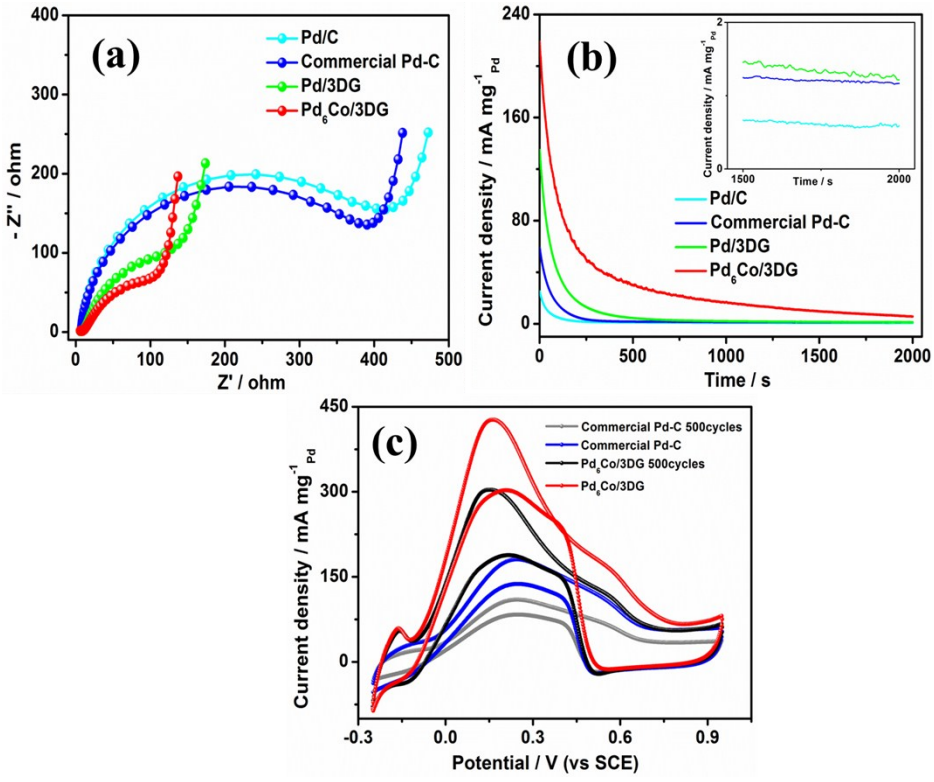

Figure S6. (a) Nyquist plots of various Pd-based catalysts. (b) chronoamperometric (CA) curves of various Pd-based catalysts in 0.5 M H_2SO_4 + 0.5 M HCOOH at 0.1 V. (c) CV curves of Pd_6Co/3DG and commercial Pd-C catalysts before and after repeated cycling (500 cycles, from -0.25V to 0.95V at 50 mV s^{-1})

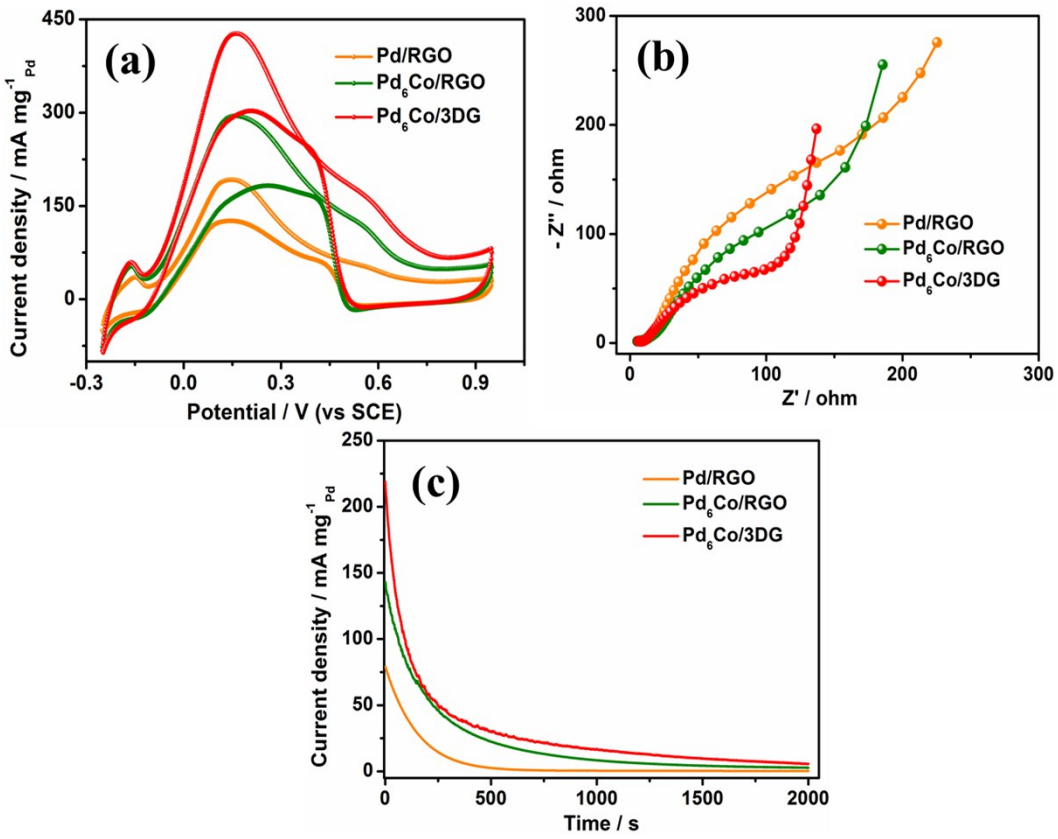

Figure S7. (a) CV curves of formic acid oxidation for Pd_6Co/3DG, Pd_6Co/RGO and Pd/RGO catalysts in 0.5 M H_2SO_4 + 0.5 M HCOOH at 50 mV s^{-1}. (b) Nyquist plots of Pd_6Co/3DG, Pd_6Co/RGO and Pd/RGO catalysts. (c) CA curves of Pd_6Co/3DG, Pd_6Co/RGO and Pd/RGO catalysts in 0.5 M H_2SO_4 + 0.5 M HCOOH at 0.1 V.

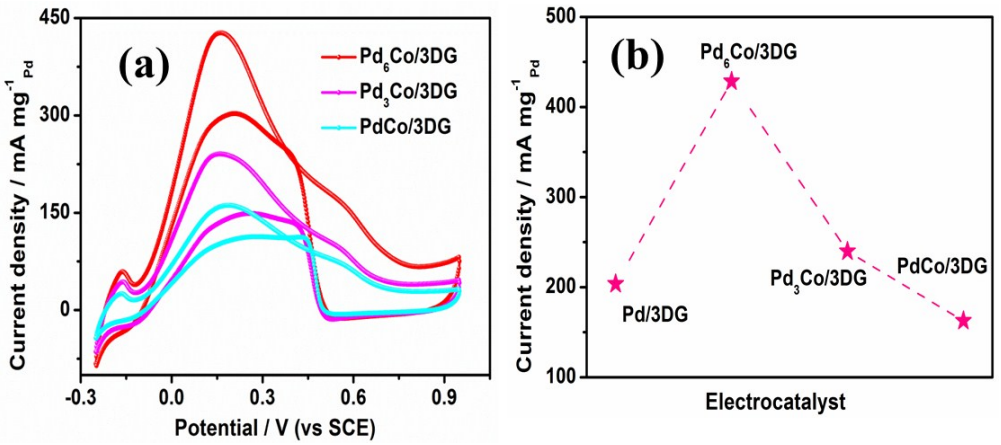

Figure S8. (a) CV curves of formic acid oxidation for Pd_6Co/3DG, Pd_3Co/3DG and PdCo/3DG catalysts in 0.5 M H_2SO_4 + 0.5 M HCOOH at 50 mV s^{-1}. (b) The catalytic peak current density of various Pd-based catalyst including Pd_6Co/3DG, Pd_3Co/3DG, PdCo/3DG and Pd/3DG.

References

1 W. S. Hummers Jr, R. E. Offeman, *J. Am. Chem. Soc.,* 1958, **80**, 1339-1339.

2 J. Zhang, Z. Xiong, X. Zhao, *J. Mater. Chem.,* 2011, **21**, 3634-3640.