

Supporting Information

A general green strategy for fabricating metal nanoparticles/polyoxometalate/graphene tri-component nano hybrids: enhanced electrocatalytic properties

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Experimental Section

1. Materials

PW12, K₂PtCl₄ and K₂PdCl₄ were purchased from Aldrich Chemical Company. Isopropanol was purchased from Beijing Chemical Reagents Corporation (Analytic grade) and was used as received. All other reagents were of analytical grade. Ultrapure water purified with Milli-Q (MQ) plus system (Millipore Co.) with resistivity of 18.2 MΩcm was exclusively used in all aqueous solutions and rinsing procedures.

2. Synthesis of nano hybrids of Pt and Pd NPs@POM-GNSs

GO was oxidized from NG flakes by a modified Hummers method^{S1} using H₂SO₄, NaNO₃ and KMnO₄ in an ice bath as reported in great detail elsewhere.^{S2} The resulting homogeneous brown GO dispersion was tested to be stable for several months and used for reduction. For preparation of Pt and Pd NPs@POM-GNSs nano hybrids, the PW12 was firstly reduced photochemically. A 500 W Hg lamp was used as a ultra-violet (UV) light source. In a typical synthesis, PW12 (2mL, 2 mM) was added in a spectrophotometer cell (1 cm pathlength) and mixed with excessive isopropanol (220 μL). 19 μL GO (8 mg ml⁻¹) was then added into the mixed solution followed by deaeration with Ar for 15 min. Then the mixed solution was irradiated under the UV light for 30 min. The concentration of the reduced PW12 can be controlled by varying the irradiation time. Then the blue-black solution of reduced PW12 and GNSs hybrids was mixed with aqueous solution of K₂PtCl₄ (5 μL, 50 mM) or K₂PdCl₄ (10 μL, 50 mM), respectively, at room temperature by soft shaking with hand. After several minutes of reaction, the tri-component nano hybrids were prepared. The samples were then centrifuged at 13 500 rpm for 60 min and washed three times with pure water. At last, the samples were re-dispersed in 2 ml pure water. The hybrids Pt and Pd NPs@POM-CB were prepared with the same method by substituting GO with 19 μL CB (8 mg ml⁻¹). Then the

initial designed Pt and Pd loading amount in the hybrids (both for GNSs and CB support) were 24.5 and 26.1 wt%, respectively.

3. Characterization

Transmission electron microscopy (TEM) images were obtained using a JEM-2010 transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed in ultrahigh vacuum (UHV) with Krato, AXIS-HS monochromatized Al K α cathode source, at 75–150 W, using low energy electron gun for charge neutralization. X-ray diffraction (XRD) studies were recorded on a Bruker AXS D advance powder diffractometer with a Cu K α (λ = 0.15418 nm). Raman spectra were obtained with a Renishaw Raman system model 1000 spectrometer. The 532-nm radiation from a 20-mW air-cooled argon ion laser was used as the exciting source. The laser diameter was 1 μ m, and the laser power at the sample position was 4.0 mW. The data acquisition time was 10 s. The composition of catalysts was determined by inductively coupled plasma-mass spectroscopy (ICP-MS, X Series 2, Thermo Scientific USA).

4. Electrochemistry experiment

The mother solution was centrifuged at 13 500 rpm for 60 min and about 80 μ L of the black catalyst paste was left in the bottom of the centrifuge tube. Then, 5 μ L of the prepared catalyst ink (actual Pt and Pd loading mass were $\sim 3.05 \times 10^{-3}$ and 3.33×10^{-3} mg for Pt and Pd hybrids, respectively) was dropped onto the surface of a pre-polished glassy carbon (GC) disk electrode (3 mm in diameter), followed by dropping 5 μ L of the Nafion solution (0.5%) in isopropanol as a binder after 12 hours.

CV measurements were performed on a ZAHNER ZENNIUM electrochemical workstation (ZAHNER Instrument, Inc., Germany). A standard three-electrode cell was used and was controlled at room temperature. A platinum foil (3.0 cm²) and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The prepared thin film GC electrode was used as the working electrode. The electrolyte, consisting of a solution of 0.5 M H₂SO₄, was saturated with ultrahigh-purity Ar for 15 min before CV measurements and a Ar atmosphere was kept over the solution in the cell during CV measurements. The CV and current-time curves were recorded after 20 CV cycles until a constant background current had been established.

Supplementary Results

1. TEM image of the photochemically reduced bare GNSs

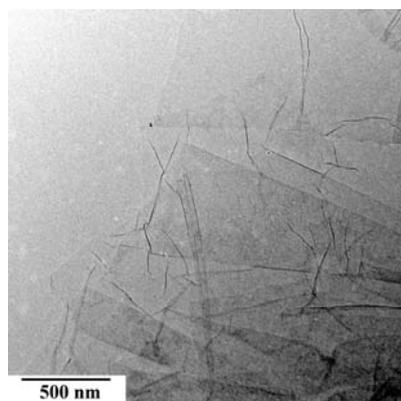


Fig. S1 TEM image of the photochemically reduced GNS before the addition of the metallic salt.

2. Characterizations of Pt and Pd NPs@POM-GNSs

(1) EDX

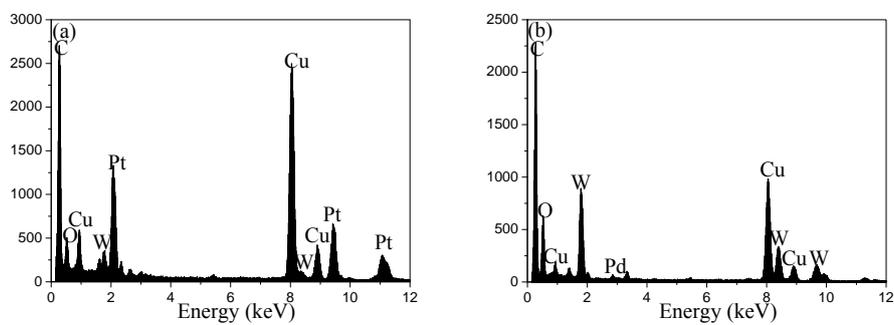


Fig. S2 EDX analysis of Pt NPs@POM-GNSs (a) and Pd NPs@POM-GNSs (b).

(2) XPS

The oxidation state of Pt or Pd in the NPs attached on GNSs and the presence of W were determined by XPS as shown in Fig. S3. The XPS spectrum of the as-prepared Pt NPs@POM-GNSs nano hybrid shows the Pt $4f$ 7/2 and $4f$ 5/2 doublet (Fig. S3a). With the charge effect corrected by fixing the photoelectric peak $1s$ of carbon at 284.8 eV, the $4f$ 7/2 level is located at 71.9 ± 0.3 eV and the $4f$ 5/2 level at 75.1 ± 0.3 eV. These values suggest unambiguously that platinum is present only in the metallic form, indicating the formation of Pt NPs on the surface of GNSs. The XPS spectrum of the as-prepared Pd NPs@POM-GNSs nano hybrid shows the Pd $3d$ 5/2 and $3d$ 3/2 doublet (Fig. S3b). It is different from Pt $4f$, take the peak of Pd $3d$ 5/2 for example, besides the main metallic palladium (Pd^0) peak which is located at 335.3 ± 0.3 eV, there are also two other peaks located at 336.4 ± 0.3 and 338.2 ± 0.3 eV, respectively, which are attributed to palladium in the valence state II and palladium in the valence state IV, respectively.^{S3} The presence of metallic palladium is then confirmed in association with two other valence states. The presence of tungsten was also detected, despite the thorough washing of the samples. As shown in Fig. S3c, there is $W4f$ 5/2 and $W4f$ 7/2 doublet with the binding energies of 36.13 and 38.23eV, respectively, for both Pt and Pd NPs@POM-GNSs, which indicates that tungsten is in its full oxidation form in the POM.

Table S1 Fitting of the C 1s peak binding energy (eV) (relative atomic percentage %)

Samples	graphite-like C	C-O	C=O	O-C=O
GO	284.8 (38.6%)	286.8 (60.2%)	287.8 (0.77%)	288.8 (0.43%)
Pt NPs@POM-GNSs	284.8 (69.1%)	286.8 (30.6%)	287.8 (0)	288.6 (0.3%)
Pd NPs@POM-GNSs	284.8 (80.2%)	286.8 (19.8%)	287.8 (0)	289 (0)

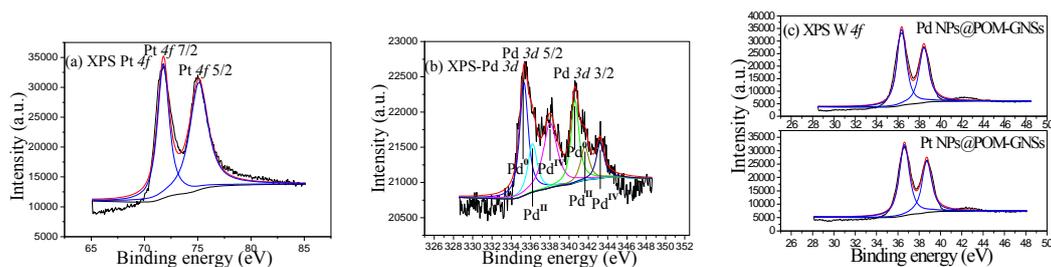


Fig. S3 XPS spectra of the as-prepared Pt and Pd NPs@POM-GNSs nano hybrids. (a) Pt $4f$, (b) Pd $3d$ and (c) W $4f$.

(3) XRD

An XRD pattern of PW12, NG, GO, Pt and Pd NPs@POM-GNSs nanohybrids is displayed in Fig. S4a. It can be seen that NG showed a sharp diffraction peak at 26.5° corresponding to (002) plane with d-spacing of 0.336 nm. Compared with NG, the feature diffraction peak of GO appeared at 11.2° corresponding to the C (002) interlayer spacing of 0.790 nm.^{S4} The increase in d value of GO can be due to the evolution of 0.336 nm spacing between typical graphene sheets in NG to integrate the water molecules trapped between oxygen containing functional groups in GO sheets. The absence of any peak at a 2θ value of 26.5° reveals the complete oxidation of NG.^{S5} After the exfoliation of GO by photoreduction, the sharp peak of NG at 26.5° almost disappeared and became a broader peak at around $20\text{-}30^\circ$, meaning the layers of NG along c-axis were exfoliated and the carbon sp^2 bond were restored. In addition, the as-prepared nanohybrids also showed the diffraction peaks for both the POM and metal NPs (the observed characteristic peaks at 39.8° for Pt NPs@POM-GNSs and 39.9° for Pd NPs@POM-GNSs (Fig. S4b) are assigned to the (111) planes of Pt and Pd crystals of face-centered cubic structure, respectively), which confirmed the formation of tri-component nanohybrids of Pt and Pd NPs@POM-GNSs.

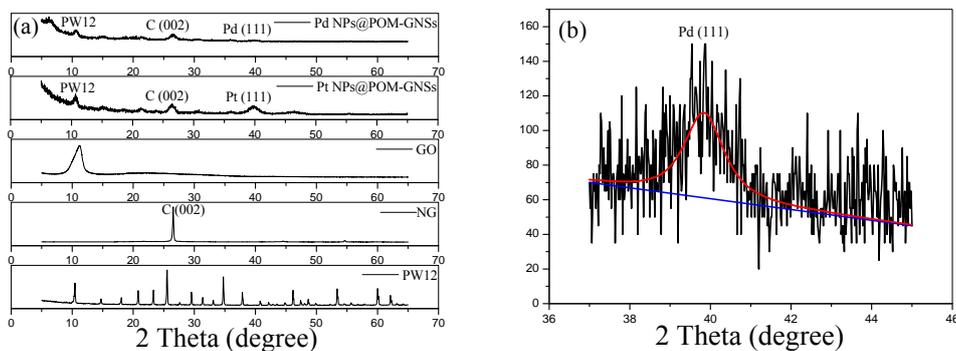


Fig. S4 XRD patterns of (a) raw PW12, NG, GO and the as-prepared Pt and Pd NPs@POM-GNSs and (b) the local part of Pd NPs@POM-GNSs.

3. Characterizations of Pt and Pd NPs@POM-CB

The as-prepared Pt and Pd NPs@POM-CB were analyzed by TEM and EDX, and these results were shown in Fig. S5. It can be seen that the Pt NPs with the diameter of about 5 ± 1 nm aggregated seriously to CB (Fig. S5a), while the Pd NPs with the diameter of about 10 ± 2 nm have a better dispersion on the CB (Fig. S5c). It is similar to the result of dispersion of Pt and Pd NPs on GNSs as reported in the text. In situ EDX analysis showed that W peaks exist as well as the Pt (Fig. S5b) or Pd peaks (Fig. S5d), confirming the existence of the POM in the hybrids. The strong peaks of Cu are from the copper grid.

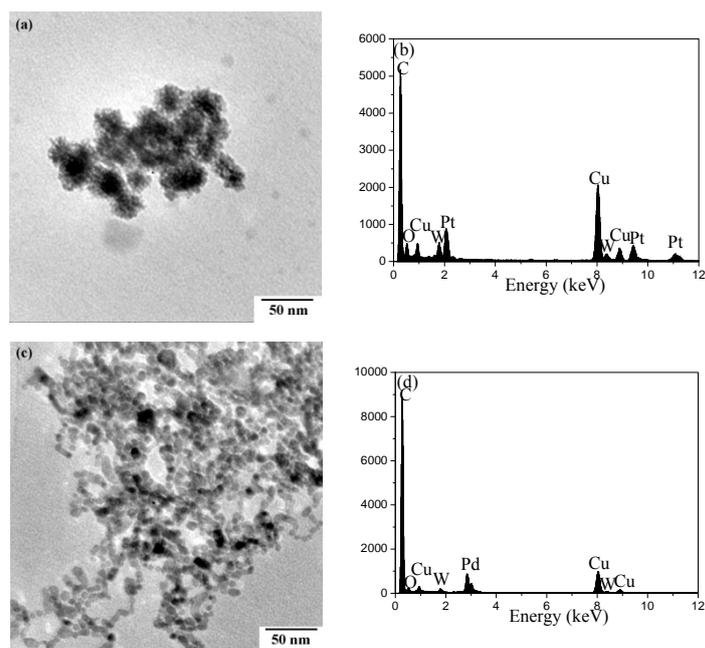


Fig. S5 TEM images of (a) Pt NPs@POM-CB and (c) Pd NPs@POM-CB; EDX analysis of (b) Pt NPs@POM-CB and (d) Pd NPs@POM-CB.

4. Electrochemistry measurement

(1) Bare GC electrode for methanol and formic acid oxidation

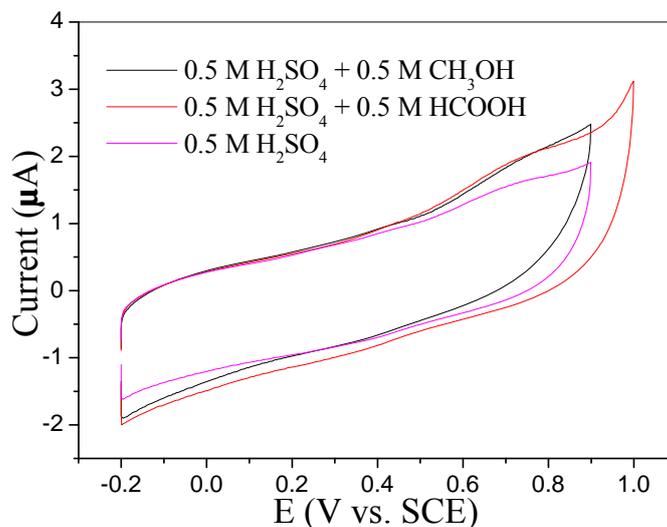


Fig. S6 CV curves of bare GC electrode for methanol and formic acid oxidation in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

(2) Measurement of ECSAs of different catalysts

In order to calculate the ECSAs of catalysts, we have measured the CV curves of different electrodes modified with Pt NPs@POM-GNSs, Pt NPs@POM-CB, Pd NPs@POM-GNSs and Pd NPs@POM-CB in 0.5 M H₂SO₄ solution respectively at a scan rate of 50 mV s⁻¹. The CV curves were recorded after 20 CV cycles until a constant background current had been established. We calculated the ECSA values of the above catalysts, according to the formula: $ECSA = Q_H / Q_H^0$. Where Q_H ($\mu\text{C mg}^{-1}$) is the electric charge of hydrogen desorption in the hydrogen region of the CV curves as shown in Fig. S7 (shown as integration of shaded areas),^{S6} and the assumption of $Q_H^0 = 210 \mu\text{C cm}^{-2}$ is the electrical charge associated with monolayer adsorption of hydrogen on Pt or Pd. According to this, the ECSAs of Pt NPs@POM-GNSs and Pd NPs@POM-GNSs are about 2.9-fold and 1.4-fold higher than that of Pt NPs@POM-CB and Pd NPs@POM-CB, respectively.

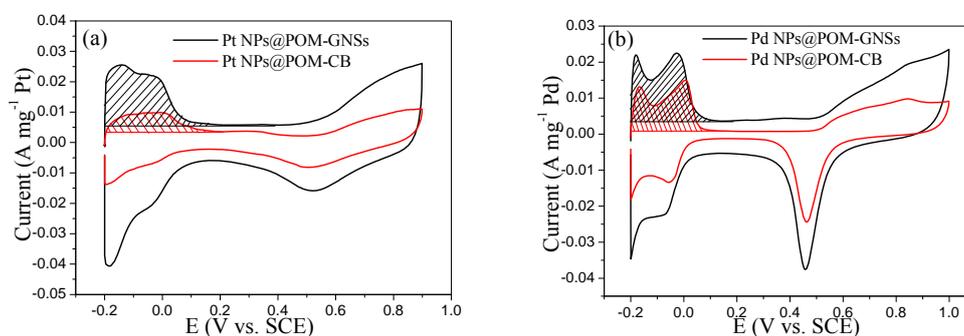


Fig. S7 CV curves of (a) Pt NPs@POM-GNSs (—) and Pt NPs@POM-CB (—) catalysts in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹; (b) Pd NPs@POM-GNSs (—) and Pd NPs@POM-CB (—) catalysts in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹.

(3) Pt NPs@POM-GNSs and Pd NPs@POM-GNSs in the second reaction for formic acid and methanol oxidation

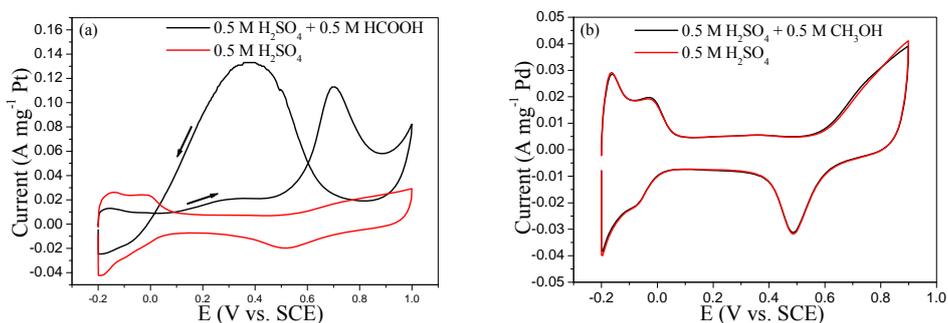


Fig. S8 CV curves of Pt NPs@POM-GNSs modified electrode for formic acid oxidation in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹ (a) and Pd NPs@POM-GNSs modified electrode for methanol oxidation in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹ (b).

References:

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