

Electronic Supplementary Information

Green synthesis of PdCu supported on graphene/polyoxometalate LBL films for high-performance formic acid oxidation

Ai Ma ^a, Xiaofeng Zhang ^a, Xiaoying Wang ^a, Zhongshui Li ^a, and Shen Lin^{*ab}

^a College of Chemistry & Chemical Engineering, Fujian Normal University, Fuzhou 350007, China.

E-mail: shenlin@fjnu.edu.cn; Fax: +86-591-22867399; Tel: +86-591-22867399

^b Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, Fujian, China.

E-mail: shenlin@fjnu.edu.cn; Fax: +86-591-22867399; Tel: +86-591-22867399

Experimental Details

1. Chemicals

All chemicals are analytical grade and used as received without further purification.

2. Preparation of PDDA-GN/*PMo*₁₂ composite films

Graphene oxide (GO) was carried out by the modification of Hummers' methods in which a very long oxidation period was combined with a high purity purification process [1]. The preparation of PDDA-GN is according to ref [2]. Prior to modification, a glass carbon electrode (GCE) was carefully polished and sonicated. After cleaning, it was dipped into 1 mg·mL⁻¹ PDDA-GN solution for 30 min, rinsed with distilled water, and dried with nitrogen stream. Again, it was immersed in 0.1

mM PMo_{12} (containing 0.5 M H_2SO_4) for 30 min. The pre-coated substrates were alternately immersed in PDDA-GN and PMo_{12} solutions, respectively. This process was repeated two times. After each immersion, the substrates were rinsed with distilled water and dried with nitrogen. An indium tin oxide (ITO) glass was ultrasonically cleaned and dried over N_2 . Then, the assembly of composite films on ITO followed the same procedure as that for the GCE.

3. Preparation of PdCu@PDDA-GN/ PMo_{12} composite films

PdCu particles were deposited on the surface of the PDDA-GN/ PMo_{12} composite films modified GCE or ITO electrode in situ PDDA-GN/ PMo_{12} by potentiostatic electrodeposition in a 0.5 M H_2SO_4 solution containing 2 mM PdCl_2 and 2 mM CuCl_2 at -0.15 V for 1200 s. For comparison, PdCu/GCE and PdCu@PDDA-GN/ PMo_{12} /GCE were also prepared under same conditions. Commercial Pd/C modified electrode was prepared by pipetting 10 μL of a well-dispersed mixture (2 mg, Aldrich 10% Pd/C catalyst dispersed in 1 mL ethanol with 50 μL 5% nafion) on the polished GCE.

In summary, the method is that the LBL electrostatic assembly technique was used to fabricate composite films constructed from PDDA functionalized graphene and PMo_{12} on electrode surfaces, which were used as a novel catalyst support for the electrodeposition of PdCu particles in situ (Scheme S1).

4. Characterization

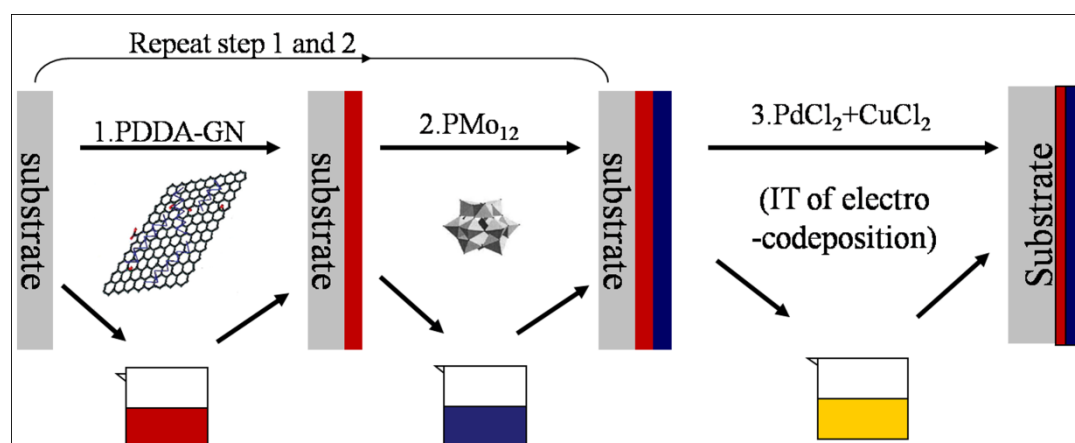
X-ray diffraction (XRD) patterns were obtained on an X'pert Pro diffractometer (Philips, USA), using $\text{Cu K}\alpha$ radiation. Transmission electron microscopic (TEM)

images and selected area electron diffraction (SAED) patterns were obtained with a TECNAI G2 high-resolution transmission electron microscope (FEI, USA) operating at 200 k. Field emission scanning electron microscopy (FESEM) images were obtained on a JSM-7500F field emission scanning electron microanalyzer (JEOL, Japan), equipped with an energy dispersive X-ray (EDS) spectrometer. The surface roughness of multilayer films on silicon wafer was studied using a 5500 atomic force microscopy (AFM, Agilent, USA). X-ray photoelectron spectroscopy (XPS) was performed at room temperature with monochromatic Al K α radiation (1486.6 eV) using a Quantum 2000 system (PHI, USA). The actual amounts of Pd and Cu loadings of the catalysts were determined by inductively coupled atomic emission spectroscopy (ICP-AES, ICAP6300, Thermo Scientific USA).

5. Electrochemical Measurements

Electrochemical experiments were carried out at the CHI 660C electrochemical work station (Shanghai, China). A conventional three-electrode system was used, with a composite film coated GCE or ITO electrode as a working electrode, a platinum wire as a counter electrode, and an Ag/AgCl (3 M KCl) electrode as a reference electrode. The electrolyte used in this work was 0.5 M H₂SO₄ solution with or without 1.0 M HCOOH. Before each measurement, high purity N₂ gas was bubbled through the electrolyte to remove oxygen. CV experiments were performed in 0.5 M H₂SO₄ solution containing 1.0 M HCOOH from -0.2 V to 1.0 V with a scan rate of 50 mV s⁻¹. The chronoamperometric experiments were performed in the same solution at a potential of 0.2 V for 3600 s. For CO stripping, high-purity N₂ was bubbled into 0.5

M H₂SO₄ for 30 min, then high-purity CO was bubbled into solution for 15 min while keeping the electrode potential at 0.1 V vs. Ag/AgCl. Dissolved CO was then purged out of the electrolyte by bubbling N₂ for 10 min. Two consecutive CVs were recorded for the catalysts between -0.2 and 1.2 V at 50 mV s⁻¹. The electrochemical active surface areas (ECSA) of the PdCu thin films were calculated based on the charge of the CO_{ads} stripping peak and the mass of Pd was used to normalize the current densities [3,4]. For electrochemical impedance spectra (EIS): the EIS were recorded at the frequency range from 100 kHz to 1 Hz with the three-electrode system. All measurements were carried out at room temperature.



Scheme S1 Schematic representation of the synthesis of the PdCu@PDDA-GN/PMo₁₂ catalyst.

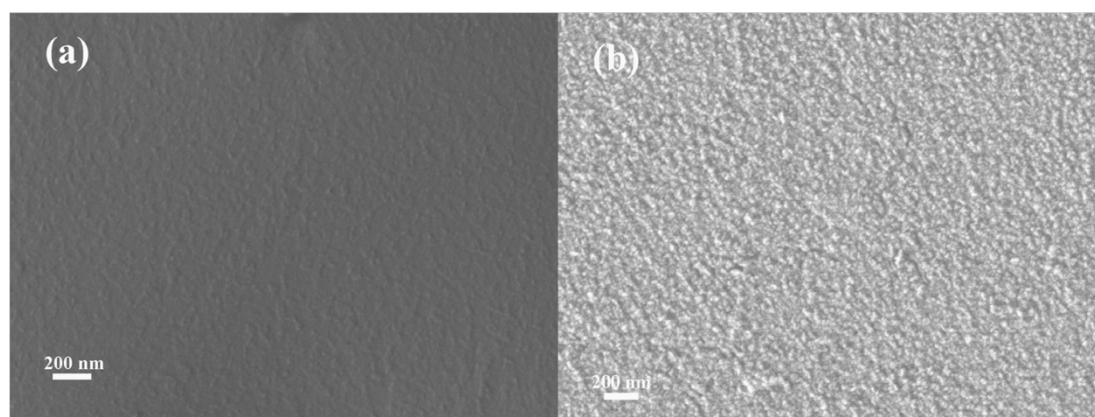


Fig. S1 FE-SEM images of the composite films of PDDA-GN/PMo₁₂/ITO (a) and PdCu@PDDA-GN/PMo₁₂/ITO (b).

The surface morphologies of PDDA-GN/PMo₁₂ and PdCu@PDDA-GN/PMo₁₂ on ITO were characterized with FE-SEM. As shown in Fig. S1a, the surface morphologies of PDDA-GN/PMo₁₂ with PMo₁₂ as the outmost layer is very smooth and uniform. As seen in Fig. 4B, the PdCu alloy nanoparticles are very small, with average diameter of about 10 nm, and a few nanoparticles aggregate.

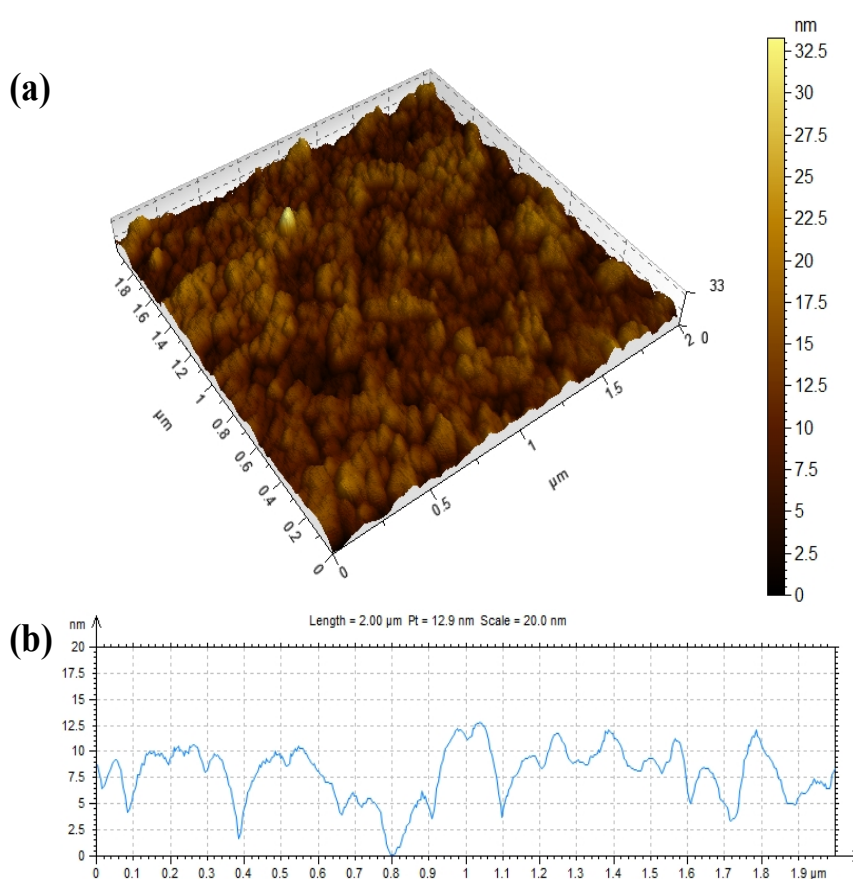


Fig. S2 AFM 3D image (a) and height profile (b) of the composite film PDDA-GN/PMo₁₂/ITO

The AFM images of the PDDA-GN/PMo₁₂ composite film was taken to obtain detailed information about the surface morphology and homogeneity of the deposited film. As seen in Fig. S2a, the PdCu-free film presents a granular texture surface, with a root-mean-square roughness of 3.54 nm calculated over an area of 2.0 μm×2.0 μm.

AFM 3D topographical image shows multilayer films have relatively smooth surfaces, which is consistent with SEM. In Fig. S2b, the average the thickness of PDDA-GN/PMo₁₂ composite film is about 10 nm.

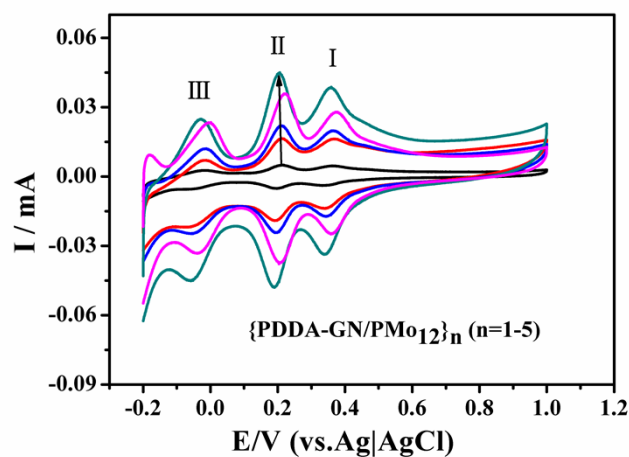


Fig. S3 CV of the composite films of $\{\text{PDDA-GN/PMo}_{12}\}_n$ ($n=1-5$) /GCE.

Fig. S3 depicts the cyclic voltammogram of the composite film PDDA-GN/PMo₁₂ with PMo₁₂ as the outermost layer in 0.5M H₂SO₄ solution in the potential region of -0.2 – 1.0 V. Three redox peaks are observed, and these are assigned to three 2-electron transfer process of Mo, respectively [5]. When the cycle number increases, the peak currents of three redox peaks increase gradually, suggesting that PMo₁₂ were deposited onto the composite films.

Table S1 The ECSA of different modified electrodes

Sample	Pd/C	PdCu@PDDA-GN/PMo ₁₂	Pd@PDDA-GN/PMo ₁₂	PdCu
Pd/mg	0.0200	0.0158	0.0162	0.0192
Pd/cm ²	2.0666	3.7441	2.6316	2.9516
ECSA(m ² /g)	10.33	23.62	16.22	15.40

Table. S2 Binding energy of the Pd3d and Cu2p XPS spectra of
the PdCu@ PDDA-GN/PMo₁₂

	Pd 3d _{5/2}	Pd 3d _{3/2}	Cu 2p _{3/2}	Cu 2p _{1/2}
PdCu B.E (eV)	335.1	340.4	933.1	952.9
Simple substance B.E (eV)	335.4	340.8	932.5	952.6
Shift (eV)	-0.3	-0.4	+0.6	+0.3

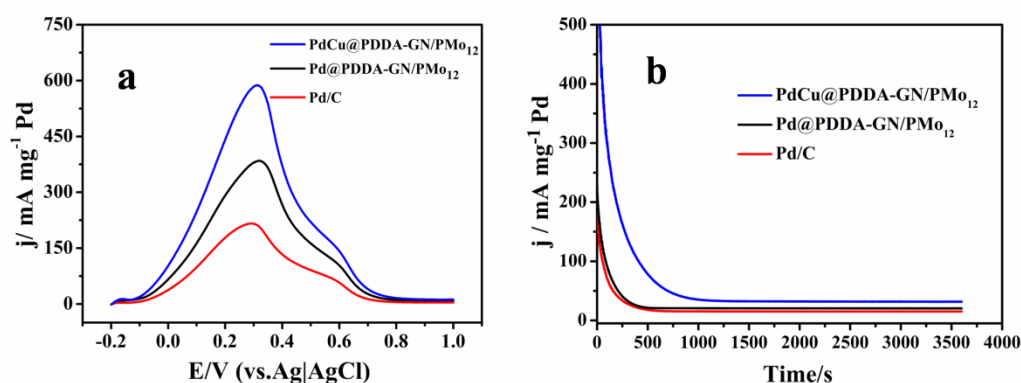


Fig. S4 (a) CV of the different modified composite films in 0.5 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹ and (b) chronoamperometric curves of the different modified composite films in 0.5 M H₂SO₄ solution containing 1 M HCOOH at 0.2 V for 3600 s.

References

- [1] Hummers WS, Offeman RE, Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 80 (1958) 1339-1339.
- [2] J.-J. Shi, G.-H. Yang, J.-J. Zhu, Sonoelectrochemical fabrication of PDDA-RGO-PdPt nanocomposites as electrocatalyst for DAFCs, *J. Mater. Chem.*, 21 (2011) 7343-7349.
- [3] Q. L. Zhang, J. N. Zheng, T. Q. Xu, A. J. Wang, J. Wei, J. R. Chen and J. J. Feng, Simple one-pot preparation of Pd-on-Cu nanocrystals supported on reduced graphene oxide for enhanced ethanol electrooxidation, *Electrochim. Acta*, 132 (2014) 551-560.
- [4] S.Z. Hu, L. Scudiero, S. Ha, Electronic effect on oxidation of formic acid on supported Pd-Cu bimetallic surface, *Electrochim. Acta*, 83 (2012) 354-358.
- [5] Y. Wu, J. Zheng, L. Xu, Z. Wang and D. Wen, *Journal of Electroanalytical Chemistry*, 589 (2006) 232-236.