Supporting Information

Polyoxometalate-assisted fabrication of Pd nanoparticles/reduced graphene oxide nanocomposite with enhanced methanol-tolerance for the oxygen reduction reaction

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Experimental Sections

Materials

All reagents were analytical grade and used without further purification. All solutions used in electrochemical experiments were prepared with Millipore water (≥18 MΩ).

Synthesis of GO. GO was synthesized by a modified method of the Hummers.1 In a typical process, 2 g of graphite was put into an solution of concentrated H₂SO₄ (10 mL), K₂S₂O₈ (1 g), and P₂O₅ (1 g). And then, The solution was heated to 80 °C and stirred for 6 h in an oil bath. The mixture was diluted with deionized water, and the product was obtained by filtration through a 0.2 μm Nylon film and dried under ambient conditions. Thereafter, the product was reoxidized by adding KMnO₄ (0.6 g) to concentrated H₂SO₄ (10 mL) containing of the preoxidized products (0.2 g). After the resulting solution was stirred for 2h at 35 °C, deionized water (9.2 mL) was added followed by additional deionized water (28 mL) and H₂O₂ (0.5 mL) with continuous stirring for 15 min. During the above process, a light yellow hydrosol was obtained. The light yellow hydrosol was washed with concentrated hydrochloric acid (10 mL) and deionized water (100 mL). After centrifugation and ultrasonic dispersion, the final product was dried under vacuum.

Synthesis of Pd/PMo12/rGO.

60 mg of GO was dispersed in 20 mL double-distilled H₂O to form a homogeneous suspension by ultrasonication. And then, 20 mL Pd(NO₃)₂ solution (3 mg L⁻¹) was added into the above solution followed by ultrasonication for 30 min. During the process, the brown-colored product appeared. Subsequently, 20 mL PMo12 solution (5 mM) and 20 mL double-distilled H₂O were added into above solution followed by ultrasonication for 30 min at 30 - 40 °C. Hydrazine hydrate (1 mL, 80 wt%) was added into the mixture. The solution became black immediately. After 2 h, large particles or solids floating on the liquid surface were obtained, and PMo12 was converted into heteropoly blue (HPB). And then, all solids were centrifuged and washed with water and ethanol to remove byproducts, and dried in vacuum at 40 °C for 12 h (denoted as Pd/HPB/rGO). The obtained composite was dispersed in 40 mL double-distilled H₂O, further added 13 mL solution (10 mL H₂O + 3 mL H₂O₂) and vigorous stirring for 2 h, followed by keeping quiescent for another 12 h. The sample was collected by the above procedures which are similar to that for HPB/rGO (defined as Pd/PMo12/rGO).

For comparison, the PMo12/rGO or Pd/rGO was prepared by the above procedures similar to that
for Pd/PMo12/rGO, but without addition of Pd(NO$_3$)$_2$ or PMo12.

For Pd/PMo12/rGO (30) and Pd/PMo12/rGO (100), the synthetic processes were similar to that for Pd/PMo12/rGO, but the addition of different contents of Pd(NO$_3$)$_2$.

**Characterizations**

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL-2100F apparatus at an accelerating voltage of 200 kV. The powder X-Ray diffraction (XRD) patterns were recorded on a D/max 2500VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation ($\lambda =$ 1.54060 Å). Corresponding work voltage and current is 40 kV and 100 mA, respectively. Fourier transform infrared (FTIR) spectra were acquired in the range of 400-4000 cm$^{-1}$ on Tensor 27 (Bruker, Germany) at room temperature. The Raman spectra of dried samples were obtained on Lab-RAM HR800 with excitation by an argon ion laser (514.5 nm). The nitrogen adsorption-desorption experiments were operated at 77 K on a Micromeritics ASAP 2050 system. The pore distributions were measured by Barret-Joyner-Halenda (BJH) method. Prior to the measurement, the samples were degassed at 150 °C for 10 h.

**Electrode preparation**

All electrochemical experiments were conducted on a CHI 760D electrochemical station (Shanghai Chenhua Co., China) in a standard three electrode cell at room temperature. An Ag/AgCl with saturated KCl, and a Pt wire were used as reference and counter electrode, respectively.

The procedures of glass carbon electrodes (5.0 mm in diameter from Gamry Instruments, USA) preparation were as follows: prior to use, the electrodes were polished mechanically with aluminitie power under an chamois, successively washed with ethanol and de-ionized water by sonication for 5 minutes, and dried in a desiccator. 4 mg of the catalysts were dispersed in 2 mL of solvent of Nafion (5%) and de-ionized water (1:9) by sonication, respectively. Typically, 10 μL (2 mg/mL) well-dispersed catalysts suspensions were pipetted onto the glassy carbon electrode surface and allowed to dry at room temperature for 30 minutes. For comparison, a commercially available Pt-C (20 wt%, Johnson Matthey) catalyst was prepared in the same way.

Cyclic voltammetry experiments (CVs) were performed at room temperature in 0.1 M HClO$_4$
solutions which were purged with N\textsubscript{2} or O\textsubscript{2} for at least 30 minutes before measuring oxygen reduction reaction (ORR) activity from 0.2 to 1.0 V at a scan rate of 50 mV s\textsuperscript{-1}.

In the rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) tests, the linear sweep voltammograms (LSVs) were measured in O\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} solution and the potential was varied from 1.0 to -0.2 V with a scan rate of 10 mV s\textsuperscript{-1} at various rotating speeds from 100 to 2500 rpm.

To examine the ORR performance, the number of electron (n) was conducted according to Koutecky-Levich (K-L) equation:

\begin{equation}
(1) \ j^{-1} = j_{L}^{-1} + j_{k}^{-1} = (B \omega^{1/2})^{-1} + j_{k}^{-1}
\end{equation}

\begin{equation}
(2) \ B = 0.62 \ n \ F \ C_{O2} (D_{O2})^{2/3} \nu^{-1/6}
\end{equation}

\begin{equation}
(3) \ j_{k} = n \ F \ k \ C_{O2}
\end{equation}

Where \( j \) is the measured current density, \( j_{k} \) and \( j_{L} \) are the kinetic and diffusion-limiting current density, respectively. \( B \) is Levich slope which is given by (2). \( n \) is the number of electrons transferred for ORR. \( \omega \) is the rotation rate (\( \omega = 2 \pi N \), \( N \) is the linear rotation speed), \( F \) is the Faraday constant (\( F = 96485 \text{ C mol}^{-1} \)), \( \nu \) is the kinetic viscosity, and \( C_{O2} \) is the concentration of O\textsubscript{2} (1.2*10\textsuperscript{-3} \text{ mol L}^{-1}), and \( D_{O2} \) is the diffusion coefficient of O\textsubscript{2} in 0.1 M HClO\textsubscript{4} (1.9*10\textsuperscript{-5} cm s\textsuperscript{-1}).

The electron transfer numbers (n) were also estimated by the RRDE technique, which was calculated as follows,

\[ n = 4 \frac{I_{D}}{I_{D} + I_{R} / N} \]

where \( I_{D} \) and \( I_{R} \) are the disk current and ring current, respectively, \( N = 0.37 \) is the current collection efficiency.

\textbf{Reference}

Fig. S1 (a) XRD pattern of Pd/PMo12/rGO; (b) N$_2$ adsorption-desorption isotherms of Pd/PMo12/rGO, and PMo12/rGO; (c) FTIR, and (d) Raman spectra of different samples.

Fig. S2 FTIR spectrum of Pd/PMo12/rGO.
**Fig. S3** RRDE voltammograms of Pd/PMo12/rGO (a) and Pt-C (b) in an O$_2$-saturated 0.1 M HClO$_4$ solution at a scan rate of 10 mV s$^{-1}$ and a rotating rate of 1600 rpm, and the ring potential is kept constant at 1.0 V versus Ag/AgCl.

**Fig. S4** LSVs of Pd/PMo12/rGO (30), Pd/PMo12/rGO, and Pd/PMo12/rGO (100) in O$_2$-saturated 0.1 M HClO$_4$ solution at a rotation rate of 1600 rpm, respectively.
Fig. S5 (a-b) TEM images of Pd/PMo12/rGO (30), and Pd/PMo12/rGO (100), respectively.

Fig. S6 LSVs for the ORR at the commercial Pt-C electrode in an O$_2$-saturated 0.1 M HClO$_4$ solution or an O$_2$-saturated 0.1 M HClO$_4$ solution upon addition of methanol.
**Table S1** FTIR spectra of PMo12, PMo12/rGO, and Pd/PMo12/rGO.

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