

## Electronic Supplementary Information

Efficient synergism of V<sub>2</sub>O<sub>5</sub> and Pd for alkaline methanol electrooxidation

Jiixin Li<sup>a,c</sup>, Yajun Chang<sup>b</sup>, Dongze Li<sup>c</sup>, Ligang Feng<sup>\*c</sup> and Baogang Zhang<sup>\*a</sup>

<sup>a</sup> School of Water Resources and Environment, MOE Key Laboratory of Groundwater Circulation and Environmental Evolution, China University of Geosciences (Beijing), Beijing 100083, P. R.

China. E-mail: baogangzhang@cugb.edu.cn

<sup>b</sup> Coray Power Co. Ltd, Shanghai, 201100, China.

<sup>c</sup> School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China.

E-mail: ligang.feng@yzu.edu.cn; fenglg11@gmail.com

## Experiments

### Materials and chemicals

Vulcan XC-72 carbon black was purchased from the Cabot Corporation. Sodium metavanadate, ammonium chloride, palladium (II) chloride, and potassium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol, ethylene glycol, and concentrated hydrochloric acid were bought from Beijing Chemical Works. Pure methanol was bought from Fisher Scientific Worldwide Co., Ltd. 5 wt.% Nafion solution was purchased from Shanghai Hesen Co., Ltd. Commercial Pd/C (20 wt.% Pd) catalyst was bought from Alfa Aesar (Tianjin) Chemical Co., Ltd. All these chemical reagents were of analytical grade and used as received unless extra noted. The ultra-pure water (18.2 M $\Omega$ ) was produced by Thermo Scientific Barnstead GenPure Pro.

### Preparation of V<sub>2</sub>O<sub>5</sub>/C composites and Pd-V<sub>2</sub>O<sub>5</sub>/C catalysts

V<sub>2</sub>O<sub>5</sub>/C composite fabrication: The weight percentage of V<sub>2</sub>O<sub>5</sub> in the catalyst was set to be 10%, 20%, and 30%, respectively (abbreviated as Pd-V<sub>2</sub>O<sub>5</sub>/C-10%, Pd-V<sub>2</sub>O<sub>5</sub>/C-20%, and Pd-V<sub>2</sub>O<sub>5</sub>/C-30%). Firstly, aqueous solution with different concentration of NaVO<sub>3</sub> was prepared, and a given amount of Vulcan XC-72 carbon black was ultrasonically dispersed into the above solution, then the mixed solution was kept at room temperature under vigorous agitation for 6 hours. Secondly, certain amount of NH<sub>4</sub>Cl according to the stoichiometric relationship was added to the solution respectively. Then, the generated NH<sub>4</sub>VO<sub>3</sub> was precipitated on the surface of carbon black uniformly under stirring. Finally, the suspension was filtered, and the resulting solid was transferred into a tubular oven at 550 °C under the protection of nitrogen for 3 hours to obtain the stable V<sub>2</sub>O<sub>5</sub>/C composites.

Pd-V<sub>2</sub>O<sub>5</sub>/C catalysts with 20 wt.% Pd were synthesized by a microwave-assisted ethylene glycol reduction process. 40 mg of V<sub>2</sub>O<sub>5</sub>/C produced in the above step was dispersed in 50 mL ethylene glycol ultrasonically and then mixed round intensely to form a uniform suspension. And then the calculated amount of H<sub>2</sub>PdCl<sub>4</sub> with Pd amount of 10 mg was added into the above suspension and agitated vigorously continuously for 2 hour and ultrasonic treatment for 30 minutes. The resultant mixture was placed in the middle of a microwave oven operating at 700 W for 60 s on and 15 s off in turn for three times repeatedly and then cooled down to room temperature under stirring for 6 hours. The mixture was finally filtered, washed, and dried overnight at 60 °C in a

vacuum oven to obtain Pd-V<sub>2</sub>O<sub>5</sub>/C catalysts. To confirm the effect of vanadium incorporation, a homemade Pd/C (20 wt.% Pd) was also fabricated and compared that was obtained via the same method (Pd/C).

### **Physical characterization**

The composition of catalysts was analyzed by energy dispersive X-ray spectroscopy (EDX) on a JEOL JAX-840 scanning electron microscope (SEM) operating at 20 kV. X-ray diffraction (XRD) measurements were performed using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with a Cu K $\alpha$  ( $\lambda=1.5405\text{\AA}$ ) as radiation source operating at 40 kV and 200 mA. The transmission electron microscope (TEM) images were obtained on a JEOL TEM system operating at 200 kV, and the distribution histograms of catalysts were analyzed by Nanomeasurer software. X-ray photoelectron spectroscopy (XPS) measurements were carried on an ECSALAB250Xi spectrometer with an Al K $\alpha$  radiation source and the XPS spectra were analyzed by XPSPEAK software.

### **Electrochemical measurements**

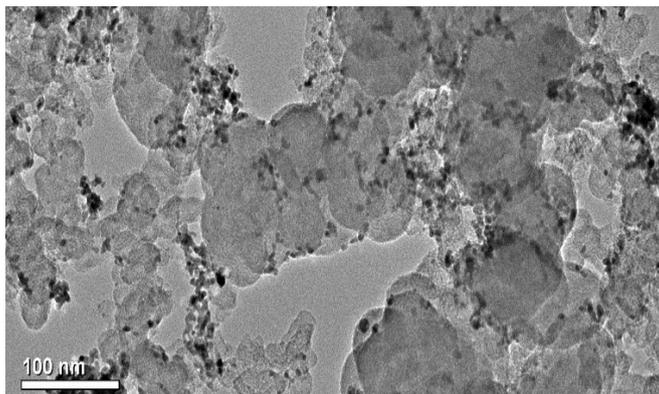
All the electrochemical measurements were carried out with an electrochemical workstation (VMP3, Bio-Logic, French) and a conventional three-electrode test cell. A graphite rod and a saturated calomel electrode (SCE, Hg/Hg<sub>2</sub>Cl<sub>2</sub>) were used as counter and reference electrodes, respectively. The working electrode was prepared as follows. Firstly, 5 mg catalyst was dispersed in 950  $\mu\text{L}$  ethanol along with 50  $\mu\text{L}$  of 5 wt.% Nafion solution and then an ultrasonic treatment was performed at least 30 minutes to ensure uniform mixing. Subsequently, 10  $\mu\text{L}$  of the above catalyst ink was pipetted and spread on a mirror-treated glassy carbon electrode with 3 mm inner diameter and 4 mm outer diameter. Finally, it was dried at room temperature. The glassy carbon electrode was polished with alumina slurry of 0.5 and 0.03  $\mu\text{m}$  successively and washed ultrasonically in ultra-pure water prior to use.

Cyclic voltammetry was conducted at room temperature in 1 M KOH with/without 1 M CH<sub>3</sub>OH solution from -1 to 0.2 V at different scan rates of 5, 20, 50, 75, 100, and 150 mV s<sup>-1</sup>. CA experiments were performed in 1 M KOH containing 1 M CH<sub>3</sub>OH solution at -0.25 V for 7200 s. The current density was calculated by normalizing the raw current to the geometrical surface area of the working electrode (0.07 cm<sup>2</sup>).

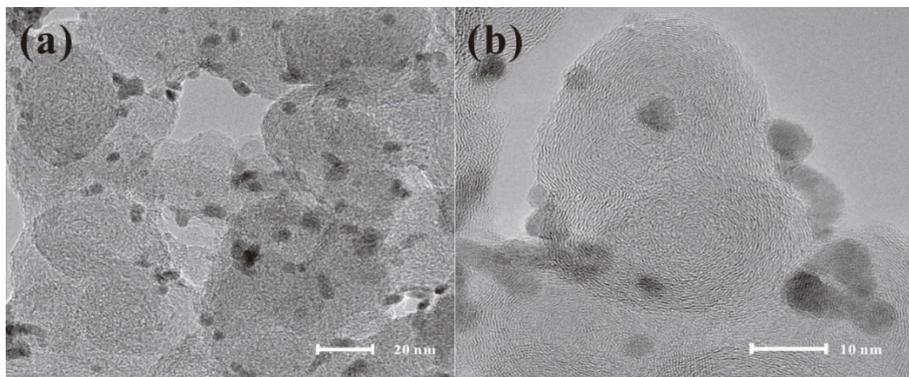
The electrochemical impedance spectra (EIS) were recorded at the frequency range from

1000 kHz to 15 mHz with 12 points per decade. The sinus amplitude potential signal was 5 mV.

CO<sub>ads</sub> stripping voltammetry was measured in 1 M KOH solution. CO was purged into the KOH solution for 15 min to allow the complete adsorption of CO onto the catalyst surface when the working electrode was kept at -0.8 V, and the excess CO in the electrolyte was purged out with N<sub>2</sub> for 15 min. The ECSA was calculated by the integration of the CO<sub>ads</sub> stripping peak, presuming a monolayer CO was adsorbed on the palladium active sites surface.<sup>1, 2</sup> The calculation formula was as follows:  $ECSA = Q_{CO} / ([Pd] \times 0.42)$ , where  $Q_{CO}$  (mC) is the charge of CO<sub>ads</sub> oxidation, [Pd] is the mass loading of Pd, 0.42 (mC cm<sup>-2</sup>) is the coulombic charge required for the oxidation of CO monolayer.<sup>3, 4</sup> All electrolyte solutions were deaerated by high-purity nitrogen for at least 15 minutes prior to any measurement.



**Fig. S1.** TEM image of Pd/C catalyst.



**Fig. S2.** (a-b) TEM images of Pd-V<sub>2</sub>O<sub>5</sub>/C at different magnifications.

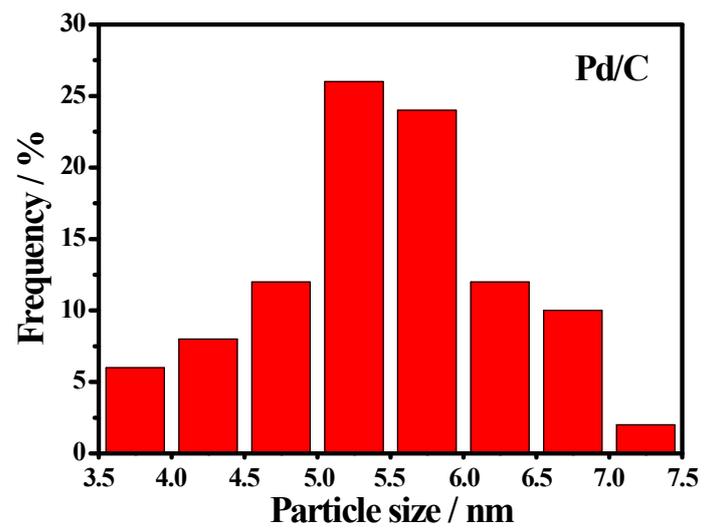


Fig. S3. Histogram of the particle size distribution for Pd/C catalyst.

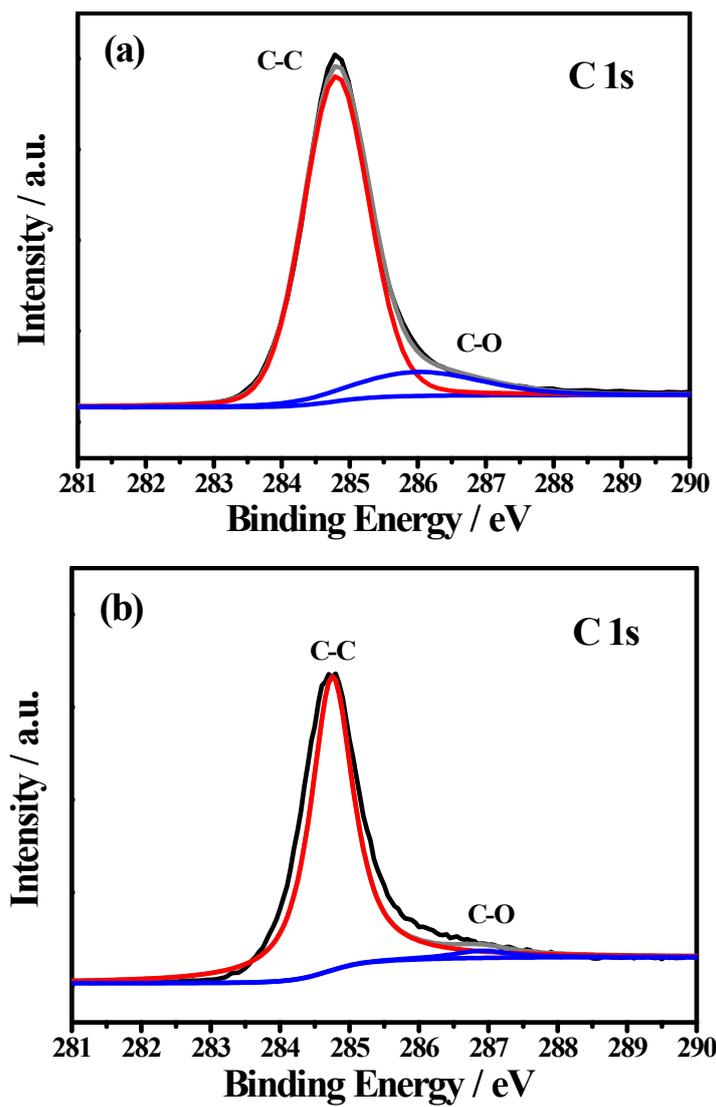


Fig. S4. XPS spectra of C 1s region for Pd-V<sub>2</sub>O<sub>5</sub>/C catalyst (a) and Pd/C catalyst (b).

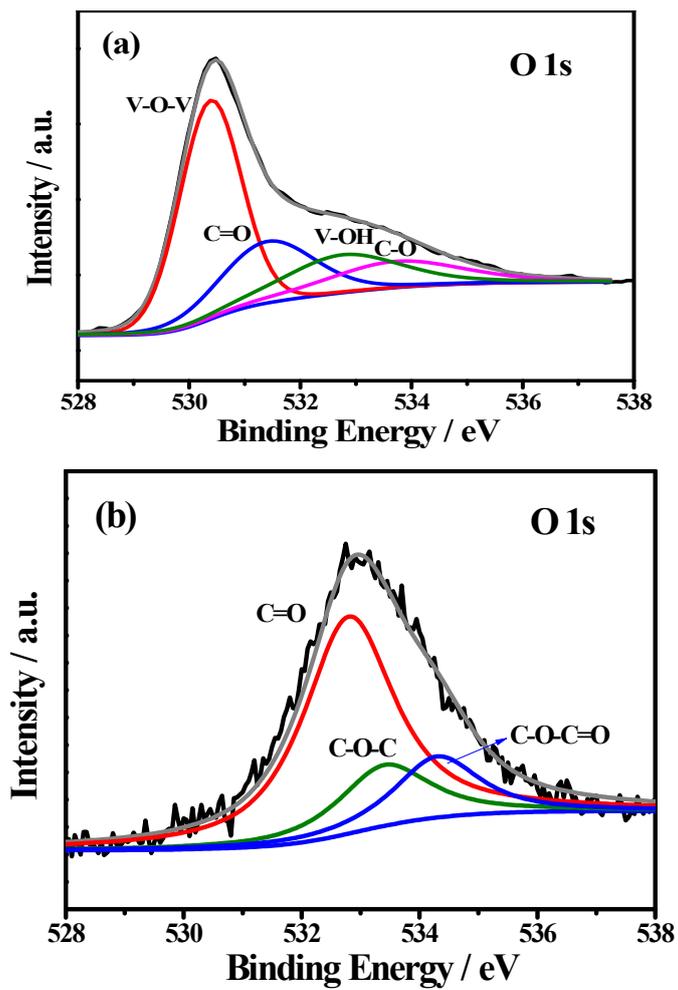
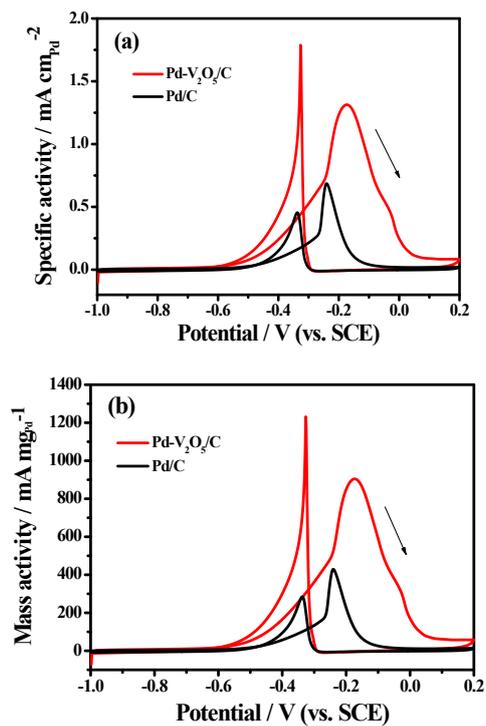
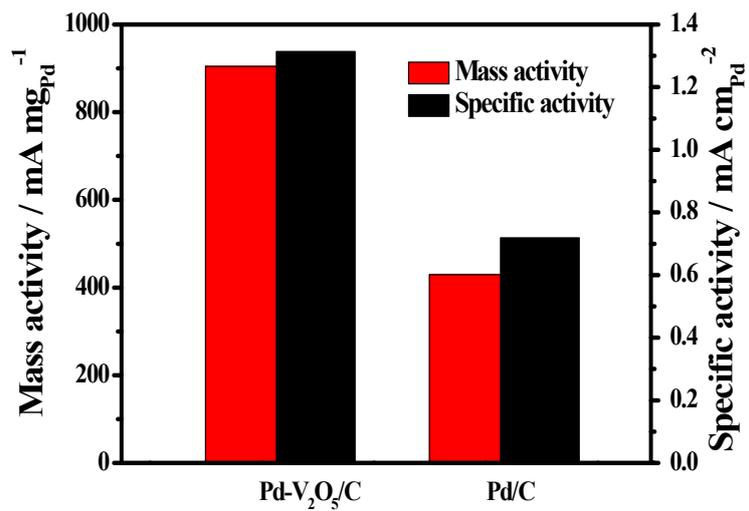


Fig. S5. XPS spectra of O 1s region for Pd-V<sub>2</sub>O<sub>5</sub>/C catalyst (a) and Pd/C catalyst (b).



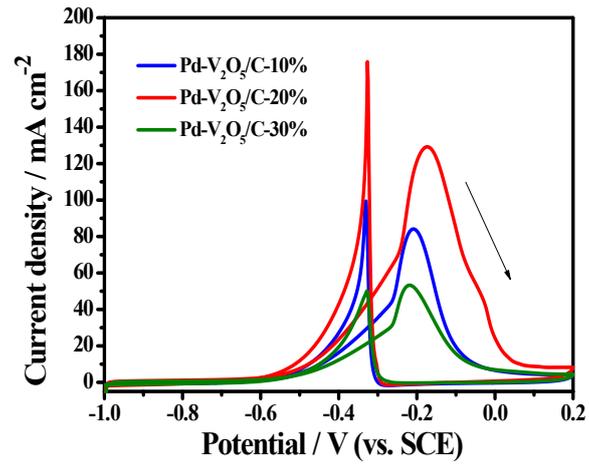
**Fig. S6.** (a) Specific activity (b) and mass activity of Pd-V<sub>2</sub>O<sub>5</sub>/C and Pd/C catalysts in 1 M KOH

with 1 M CH<sub>3</sub>OH at scan rate of 50 mV s<sup>-1</sup>.

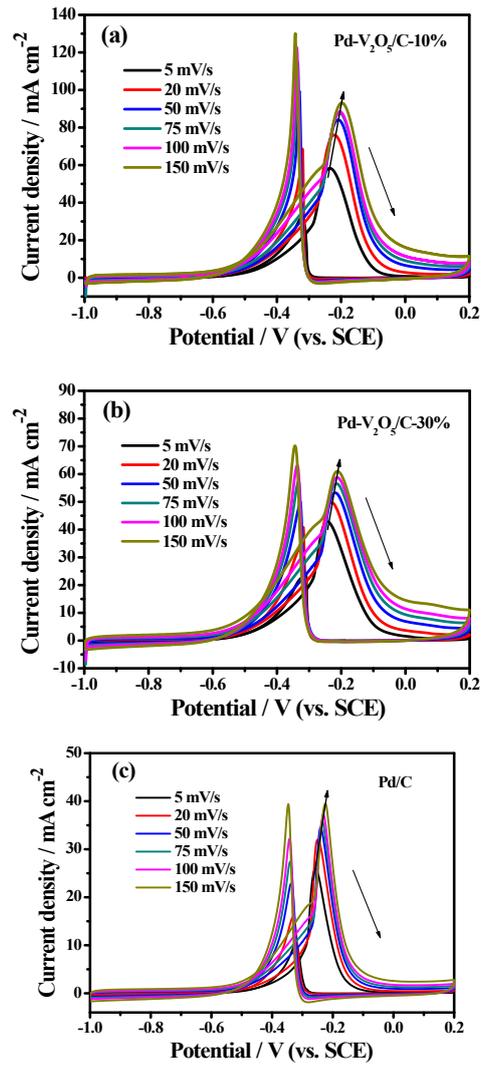


**Fig. S7.** Mass activity and specific activity of Pd-V<sub>2</sub>O<sub>5</sub>/C and Pd/C catalysts at peak potential in 1

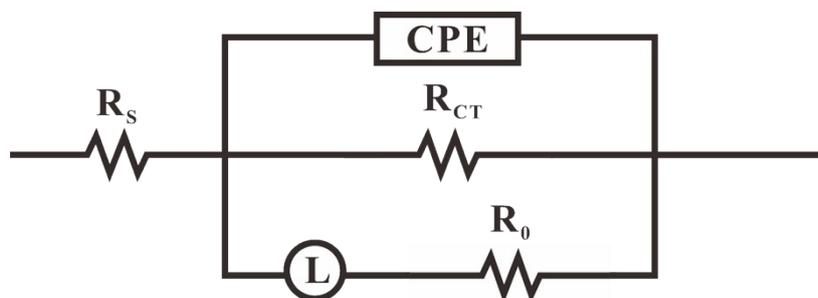
M KOH with 1 M CH<sub>3</sub>OH at scan rate of 50 mV s<sup>-1</sup>.



**Fig. S8.** Cyclic voltammograms of different Pd-V<sub>2</sub>O<sub>5</sub>/C catalysts for methanol oxidation in 1 M KOH with 1 M CH<sub>3</sub>OH at scan rate of 50 mV s<sup>-1</sup>.



**Fig. S9.** Cyclic voltammetry curves in 1 M KOH solution with 1 M CH<sub>3</sub>OH at different scan rates of 5, 20, 50, 75, 100 and 150 mV s<sup>-1</sup> for (a) Pd-V<sub>2</sub>O<sub>5</sub>/C-10%, (b) Pd-V<sub>2</sub>O<sub>5</sub>/C-30%, and (c) Pd/C catalysts.



**Fig. S10.** The equivalent circuit used in EIS fitting

The  $R_s$  corresponds to the solution resistance, the constant phase element of CPE composition represents the double-layer capacitance,  $R_{CT}$  is for the charge transfer resistance caused by methanol oxidation,  $L$  usually refers to the external circuit inductance and does not include electrochemical process,  $R_0$  is relevant to the contact resistance between the catalyst and the glass carbon electrode.

**Table S1.** XPS fitting of Pd 3d and its contents for Pd-V<sub>2</sub>O<sub>5</sub>/C and Pd/C catalysts.

| Catalysts                           | Assignment | Binding energy / eV | Relative intensity / % |
|-------------------------------------|------------|---------------------|------------------------|
| Pd-V <sub>2</sub> O <sub>5</sub> /C | Pd(0)      | 335.53              | 47                     |
|                                     |            | 340.78              |                        |
|                                     | Pd(II)     | 336.40              | 29                     |
|                                     |            | 341.65              |                        |
|                                     | Pd(IV)     | 337.76              | 24                     |
|                                     |            | 343.01              |                        |
| Pd/C                                | Pd(0)      | 335.71              | 77                     |
|                                     |            | 340.96              |                        |
|                                     | Pd(II)     | 336.60              | 13                     |
|                                     |            | 341.85              |                        |
|                                     | Pd(IV)     | 338.10              | 10                     |
|                                     |            | 343.35              |                        |

**Table S2.** XPS fitting of V 2p and its contents in Pd-V<sub>2</sub>O<sub>5</sub>/C catalyst.

| <b>Catalyst</b>                     | <b>Assignment</b> | <b>Binding energy / eV</b> | <b>Relative intensity / %</b> |
|-------------------------------------|-------------------|----------------------------|-------------------------------|
| Pd-V <sub>2</sub> O <sub>5</sub> /C | V(V)              | 517.57                     | 76                            |
|                                     |                   | 525.07                     |                               |
|                                     | V(IV)             | 516.29                     | 24                            |
|                                     |                   | 523.79                     |                               |

**Table S3.** Onset potential and CO oxidation peak potential for CO stripping voltammograms and the estimated ECSA for Pd-V<sub>2</sub>O<sub>5</sub>/C and Pd/C catalysts.

| Samples                             | Onset potential<br>(V vs. SCE) | Oxidation peak potential<br>(V vs. SCE) | ECSA (m <sup>2</sup> g <sup>-1</sup> ) |
|-------------------------------------|--------------------------------|---|--|
| Pd-V <sub>2</sub> O <sub>5</sub> /C | -0.34                          | -0.28                                   | 68.80                                  |
| Pd /C                               | -0.31                          | -0.22                                   | 59.79                                  |

**Table S4.** Comparison of the specific activity and mass activity of Pd-V<sub>2</sub>O<sub>5</sub>/C and Pd /C catalysts

| Samples                             | Specific activity<br>(mA cm <sup>-2</sup> <sub>Pd</sub> ) | Mass activity<br>(mA mg <sup>-1</sup> <sub>Pd</sub> ) |
|-------------------------------------|---|---|
| Pd-V <sub>2</sub> O <sub>5</sub> /C | 1.31  | 904.43  |
| Pd/C                                | 0.72  | 429.33  |

**Table S5.** EIS fitting parameters from equivalent circuit catalyzed by the catalysts for methanol oxidation.

| Catalysts                               | $R_s / \Omega$ | CPE / S s <sup>-n</sup> | n / 0<n<1 | $R_{ct} / \Omega$ | L      | $R_o / \Omega$ |
|---|----------------|-------------------------|-----------|-------------------|--------|----------------|
| Pd-V <sub>2</sub> O <sub>5</sub> /C-10% | 7.14           | 1.465E-003              | 0.78      | 55.16             | 59.92  | 43.97          |
| Pd-V <sub>2</sub> O <sub>5</sub> /C-20% | 7.01           | 2.395E-003              | 0.80      | 36.08             | 108.00 | 27.64          |
| Pd-V <sub>2</sub> O <sub>5</sub> /C-30% | 7.75           | 7.039E-004              | 0.77      | 101.1             | 193.1  | 90.50          |
| Pd/C                                    | 7.33           | 4.664E-004              | 0.86      | 144.2             | 78.05  | 73.31          |

## References

1. G. H. L. Savithra, R. H. Bowker, B. A. Carrillo, M. E. Bussell and S. L. Brock, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5403-5407.
2. T. Kawaguchi, W. Sugimoto, Y. Murakami and Y. Takasu, *Electrochem. Commun.*, 2004, **6**, 480-483.
3. D. Chen, Q. Tao, L. W. Liao, S. X. Liu, Y. X. Chen and S. Ye, *Electrocatalysis*, 2011, **2**, 207-219.
4. W. Qiao, X. Yang, M. Li and L. Feng, *Nanoscale*, 2021, DOI: 10.1039/d1nr01005k.