Niobium Dioxide Prepared by a Novel La-reduced Route as Promising Catalyst Support for Pd towards Oxygen Reduction Reaction

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Experimental section

Synthesis of Nb_2O_5 nanoparticles

All reagents were highly pure and used without further purification. Nb_2O_5 nanoparticles were prepared by hydrothermal method. Initially, 4 g ammonium niobite oxalate hydrate and 12 g urea were dissolved in 155 mL pure water with 5 mL acetic acid and then stirred for 2 h. Secondly, the mixed solution was transferred into a 200 mL Teflon-lined autoclave, which was subsequently sealed and placed in an oven at 160 °C for 12 h. The white precipitate was collected by washing and filtering, and then

dried at 60 □ in air. Finally, the precipitate was annealed at 500 °C for 4 h and Nb_2O_5 nanoparticles were obtained.

Synthesis of NbO_2 nanoparticles

As-prepared Nb_2O_5 nanoparticles were mixed with lanthanum powders prior to being sealed in a quartz tube and calcined at 500 ºC for 6 h. The specific procedure was as follows: 0.25 g Nb_2O_5 nanoparticles and 1 g La powders were mixed and homogenized by grinding. Next, the powder mixture was transferred into a quartz tube which was subsequently sealed and kept in an oven at 500 ºC for 6 h. After cooling, the product was immersed in diluted hydrochloric acid solution to remove La_2O_3 and unreacted La. Lastly, the sediments were obtained by filtration and washed with de-ionized water for several times. After dried in an oven at 60 °C for 6 h, the NbO_2 nanoparticles were synthesized eventually.

Synthesis of Pd/NbO_x composite

In a typical synthesis, 50 mg as-obtained NbO_x nanoparticles and 5 mg PVP were distributed in 40 mL deionized water. Then, 2.10 mL 0.0564 M $PdCl_2$ aqueous solution was added into the above solution. After stirring overnight, 10 mL 0.05 M $NaBH_4$ was added into the solution in order to reduce the Pd^{2+} into Pd. Subsequently, the solution was filtered and the black precipitate was washed several times with deionized water and ethanol so as to remove the residual $NaBH_4$ and byproducts (e.g. NaCl, H_3BO_3). Ultimately, the Pd/NbO_x composite was obtained after the precipitate was dried at 60 □ in air.

Material Characterization

Powder X-ray diffraction data of all these samples were collected by using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation (λ = 1.5405 Å). Morphologies of samples were observed on a JEOL-2100F Transmission electron microscopy (TEM) operated at an acceleration voltage of 200 kV. Raman spectra were collected on a LabRAM HR Evolution spectrometer using a laser with an excitation wavelength of 532 nm at laser power of 10 mW. X-ray photoelectron spectroscopy (XPS) experiments was carried out on the RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Mg K α radiation ($h\nu$ = 1253.6 eV). Resistivity of the as-prepared NbO_2 at room temperature was measured on a Physical Properties Measurement System (PPMS, Quantum Design). Resistivity of the pristine Nb_2O_5 was estimated by current-voltage (I-V) measurements which was performed by sweeping the voltage from the positive maximum to the negative minimum using a semiconductor characterization system (Keithley 4200).

Electrochemical measurements

ORR catalytic activity of samples was carried out with a conventional three-electrode configuration using rotating disk electrode (RDE) coating with a film of catalyst as the working electrode, saturated calomel electrode (SCE) as the reference electrode and carbon electrode as the counter electrode, 0.1 M KOH solution as the electrolyte. As for the preparation of the working electrode, 5 mg of catalyst and 1 mg of acetylene black were dispersed in 1 mL of Nafion/alcohol solution (0.5 wt. %) by sonication for 60 min to form 5.0 mg mL^{-1} slurry. Then, 10 μL of slurry was pipetted onto the polished

RDE in order to obtain a film of catalyst (loading mass of 250 μg cm^{-2}). All the data were recorded by a CHI660E Electrochemical Workstation (Chenhua, Shanghai).

Oxygen reduction performances of the samples were detected in 0.1 M KOH solution de-aerated by oxygen through cyclic voltammetry at scan rate of 100 mV s^{-1} and linear sweep voltammetry at scan rate of 10 mV s^{-1} under various rotating speeds. The reference electrode was calibrated for the reversible hydrogen potential. The current density was the ratio of current to geometric surface area of rotating disk electrode (0.19635 cm^2). The presented LSV curves were corrected for the ohmic potential drop losses. Onset potential was determined to be the potential value corresponding to 5% of the diffusion-limited current in this work.[1, 2] Kouteckey-Levich plots showing the linear relation between J^{-1} and $\omega^{-1/2}$ were obtained based on the following equations:

$$\frac{1}{J}=\frac{1}{J_k}+\frac{1}{B\omega^{1/2}}$$

$$B=0.62nFC_0(D_0)^{2/3}v^{-1/6}$$

where J is the current density, J_k is the kinetic current density, ω is the rotating rate of the working electrode, F is the Faraday constant (96485 C mol^{-1}), n is the electron transfer number, C_0 is the solubility of oxygen in the electrolyte (1.2×10^{-3} mol L^{-1}), D_0 is the diffusion coefficient (O_2, 1.9×10^{-5} cm^2 s^{-1}), and v is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}) for the case of 0.1 M KOH solution.[3]

In addition, the electron transfer numbers (n) and the peroxide yields (H_2O_2 %) of Pd/NbO_2 were further precisely determined by the rotating ring-disk electrode (RRDE) measurements. And the detailed values for n and H_2O_2 % were calculated from the following equations:

$$n=4\times\frac{I_d}{I_d+\frac{I_r}{N}}$$

$$H_2O_2(\%)=200\times\frac{\frac{I_r}{N}}{I_d+\frac{I_r}{N}}$$

where I_r and I_d are the ring and disk current, respectively. N (0.37) is the current collection efficiency of the Pt ring in RRDE.[4]

To investigate the long-term stability of Pd/NbO_2, the test was carried out by taking continuous potential cycling in the potential window of 0.21 V to ~ 1.21 V (*vs.* RHE) at a scan rate of 100 mV s^{-1}. After potential cycling, the LSV curve was recorded at a scan rate of 10 mV s^{-1}. Moreover, the chronoamperometric test (current *versus* time) for Pd/NbO_2 and Pd/C was executed under 0.37 V (*vs.* RHE).

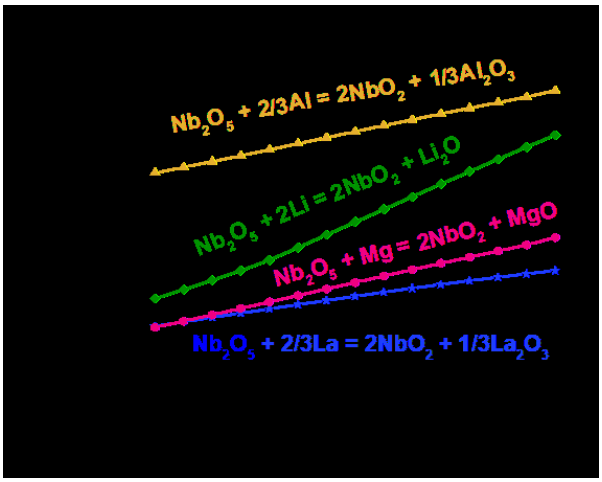

Figure S1. ΔG^0-Ellingham diagram of reduction reaction for different metals and Nb_2O_5 (data from the HSC chemistry).

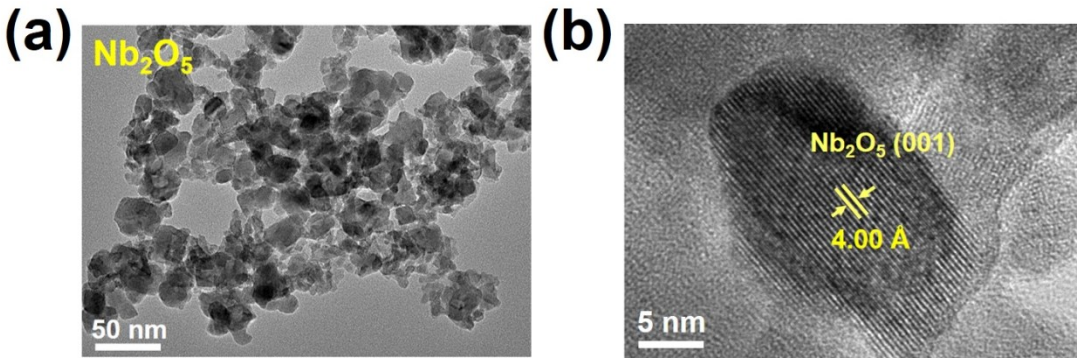

Figure S2. (a) TEM image and (b) HRTEM image of pristine Nb_2O_5.

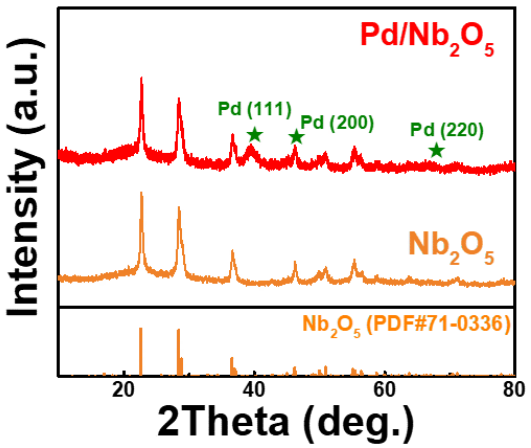

Figure S3. XRD patterns of Pd/Nb_2O_5 composite.

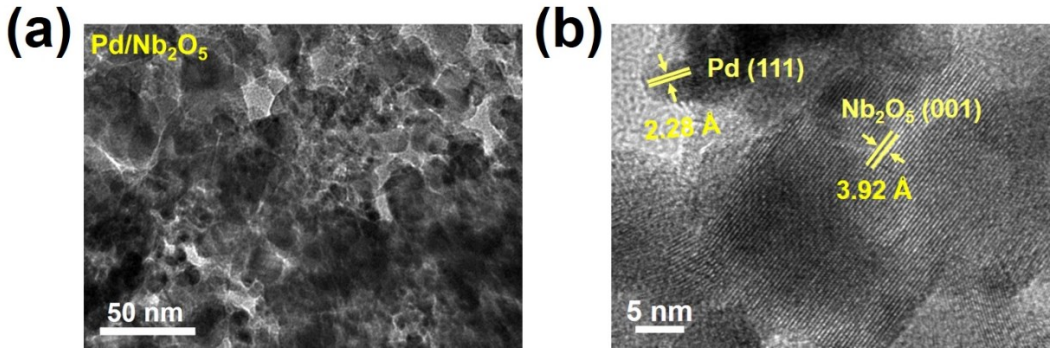

Figure S4. (a) TEM image and (b) HRTEM image of Pd/Nb_2O_5.

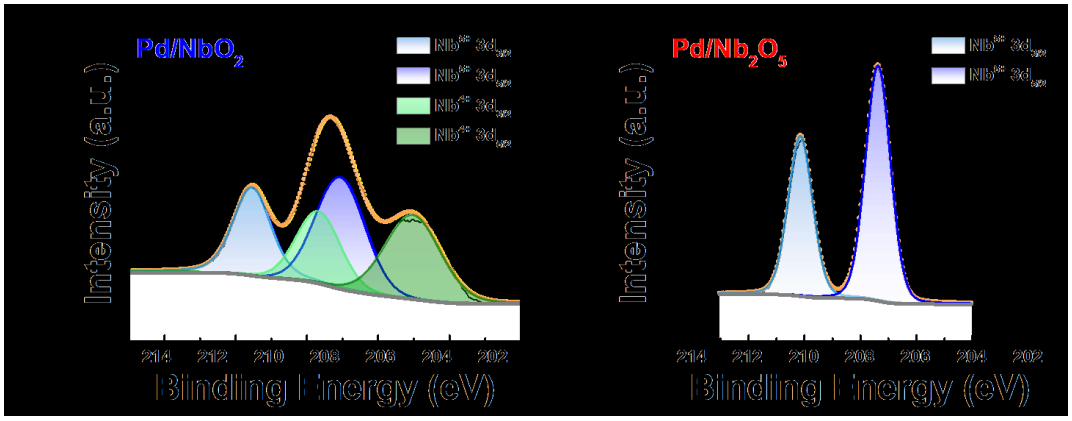

Figure S5. X-ray photoelectron spectrum of Nb 3d region in (a) Pd/NbO_2 and (b) Pd/Nb_2O_5.

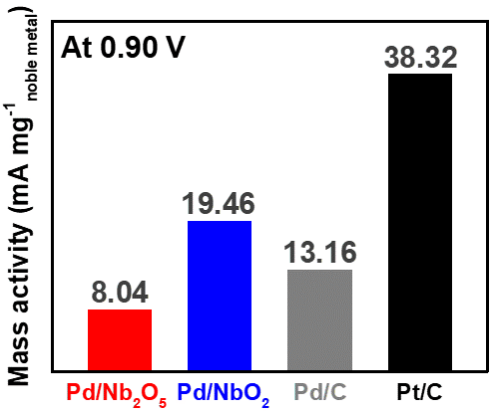

Figure S6. Corresponding mass activities of all the catalysts at 0.90 V (vs. RHE).

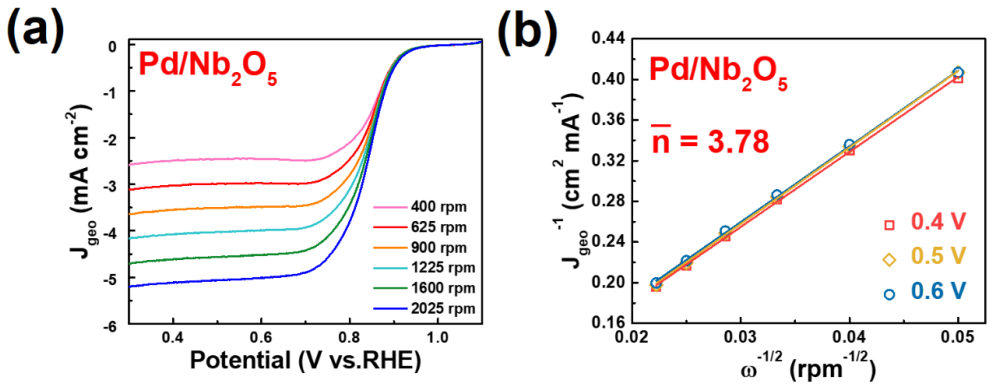

Figure S7. (a) LSV curves of Pd/NbO_2 at different rotation speeds; (b) K-L plots for Pd/NbO_2 derived from (a).

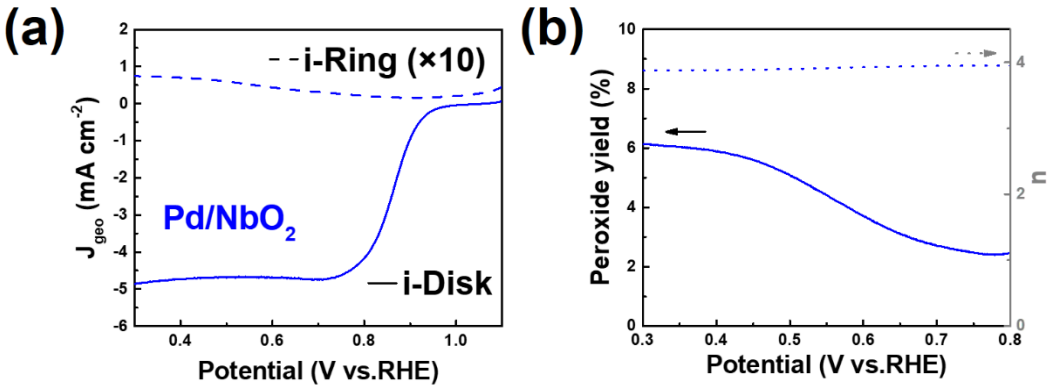

Figure S8. (a) RRDE voltammograms of Pd/NbO_2; (b) Peroxide yield of Pd/NbO_2 during the ORR process (solid line) and the calculated electron transfer number (dot line) derived from (a).

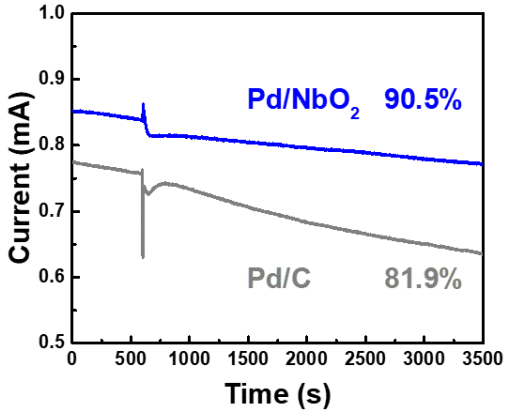

Figure S9. Chronoamperometric curves of Pd/NbO_2 and Pd/C catalysts at 0.37 V (vs. RHE) with addition of CH_3OH after 600 s.

Table S1. Electrical conductivity of NbO_2 and Nb_2O_5 at room temperature.

Sample	Electric conductivity (S/m)
NbO_2	2.95×10^{-3}
Nb_2O_5	8.89×10^{-7}

Table S2. Comparison of ORR catalytic activity between Pd/NbO_2 and Pd-based catalysts in the alkaline electrolytes.

Catalyst	Half-wave potential (V *vs.*RHE)	Reference
Pd/NbO_2	0.872	This work
Pd/TiO_{2-x}:N	0.81	[3]
$Ni@Pd_3/C$	0.86	[5]
$Au_{10}Pd_{40}Co_{50}$	0.83	[6]
PdFS-CSNS	0.892	[7]
Ni@Pd-rGO	0.8138	[8]
Pd-Ru@NG	0.8	[9]
Pd_3Pb SNP	0.887	[10]
Ordered PaCuCo NPs/C	0.872	[11]
Ordered PaCuNi NPs/C	0.862	[11]
$Pd/W_{18}O_{49}$	0.875	[12]
Icosahedral Pd_6Ni/C	0.89	[13]

Table S3. Noble metal content in Pd/NbO_2, Pd/Nb_2O_5, commercial Pd/C and Pt/C obtained from ICP-OES.

Sample	Noble metal content (wt %)
Pd/NbO_2	21.39
Pd/Nb_2O_5	21.95
Commercial Pd/C	17.08
Commercial Pt/C	17.86

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