Pd supported N-doped CeO_2 as an efficient hydrogen oxidation reaction catalyst in PEMFC

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Experimental

Chemicals

All chemicals were of analytical grade and used as such without any further purification. $Ce(NO_3)_3.6H_2O$ (99.99 %), Urea (99.00 %), H_2PdCl_4 (98 %), CTAB (99 %) and CTAC (98 %) were purchased from Sigma Aldrich. Trisodium citrate hydrate ($C_6H_5Na_3O_7.2H_2O$, 98 %) were supplied by Showa Chemicals.

Synthesis of N-CeO_2

Firstly, 1.5 g $Ce(NO_3)_3.6H_2O$ was added to 40 mL of 1 M urea aqueous solution (**Fig. S1**). The mixture was magnetically stirred for 30 min and transferred into a 50 mL teflon-lined stainless steel autoclave. The autoclave was heated to 180°C and maintained for 24 h. Next, the precipitate was separated by centrifugation at 10,000 RPM for 5 min. The obtained material was washed several times with distilled water and absolute ethanol to wholly remove redundant components and then dried at 80°C in air for 1 h, successively. Finally, the powder was calcined at 500°C in air for 2 h to obtain N-CeO_2 nanoparticles. CeO_2 material was also prepared using same procedure and NaOH instead of urea.

Synthesis of N-CeO_2@Pd

As shown in **Fig. S1**, 50 mg of pure N-CeO_2 was firstly dispersed in 50 mL aqueous solution containing 15 mM CTAB and 1.5 mM CTAC and sonicated for 10 min. Next, 6.25 mL of 10 mM H_2PdCl_4 was slowly added to the solution. Then, 2.5 mL of 100 mM Na_3-citrate was dropped and stirred for 20 min. The uniform solution was transferred to 100 mL glass vessel and tightly sealed. Finally, the reaction was taken place at 80°C for 10 h in oven. After the completion of synthesis, the solution was centrifuged at 15,000 RPM for 20 min to separate the precipitate. The collected precipitate was washed with distilled water and ethanol several times to wholly remove the superfluous CTAB and CTAC components. The powders were calcined 300°C in Ar for 2 h for achieving N-CeO_2@Pd nanocatalysts. CeO_2@Pd catalyst was also prepared using same procedure and CeO_2

instead of N-CeO_2. Pd loading in these two samples measured by ICP analysis was found to be around 9.5 %. The pure Pd catalyst was also prepared using the same route without adding N-CeO_2 precursor.

Physical characterizations

The loading of the Pt catalyst was measured by inductively coupled plasma (ICP) spectrometry (ICPS-7500, Shimadzu), after the as-prepared catalyst electrodes were completely treated with aqua regia at 100°C for 10 h. Then, the obtained solutions were filtered carefully to clear solid components before the ICP measurements. The microstructures of prepared catalysts were observed by high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2010), with an accelerating voltage of 200 kV. For HRTEM analysis, the samples were dropped onto a carbon-coated copper grid, then dried at 80 °C for overnight. The crystal structure of materials deposited on working electrodes was analyzed by X-ray diffractometry (XRD, D/Max 2005, Rigaku), using CuK_α radiation (λ=1.54178 Å). Surface areas were investigated by nitrogen gas-adsorption using the Barrett–Emmett–Teller (BET) technique (Micromeritics Tristar 3000 analyzer). X-ray photoelectron spectroscopy (XPS; Multilab 2000, Thermo Fisher Scientific, USA) was carried out by using monochromated Al Kα X-ray photon (hν = 1,486.6 eV) sources to investigate the surface chemical states of the elements existing in the prepared catalysts. The binding energies of the adventitious carbon (C 1s) peak located at around 285 eV were used for calibration of the other peaks. The cross-sectional images and energy dispersive spectroscopy (EDS) of the working catalyst electrodes and MEAs were all observed by field emission scanning electron microscopy (FESEM, S-4800, Hitachi).

CeO_2@Pd/C (Pd ~20 wt.%) and Pd/C (Pd ~20 wt.%) electrocatalyst preparation

Initially, 5 mg N-CeO_2@Pd was mixed with 2.5 mg active carbon black. Next, the distilled water, 2-propanol and Nafion were added to the obtained mixture. Later, the catalyst mixture was sonicated at room temperature for 1 h to achieve uniform slurry. Then, the as-prepared catalyst slurry was uniformly sprayed on the surface of the MPL of carbon cloth to obtain CeO_2@Pd/C electrocatalyst. Finally, the obtained electrode was dried at 60°C for 12 h to wholly evaporate the solvents. The working area of electrode was kept with 1 × 1 cm^2 for cyclic voltammetry (CV) tests and 2.5 × 2.5 cm^2 for single cell tests, as presented in **Fig. S2**. The Pd loading in the anode CeO_2@Pd/C electrocatalyst was found to be 0.1 mg cm^{-2} measured by ICP analysis. The Pd/C electrocatalyst was prepared in the same procedure with Pd loading of 0.1 mg cm^{-2}.

Pt/C electrocatalyst slurry preparation

5 mg of Pt/C catalyst (Pt 20 wt.%) was mixed the distilled water, 2-propanol and Nafion solutions. Then, the catalyst mixtures were sonicated at room temperature for 1 h to obtain uniform slurries. Then, the as-prepared catalyst slurry was evenly sprayed on the surface of the MPL of carbon cloth to obtain Pt/C electrocatalysts. Finally, the obtained electrode was dried at 60°C for 12 h to wholly evaporate the solvents. The working area of electrode was kept with 1 × 1 cm^2 for CV tests and 2.5 × 2.5 cm^2 for single cell tests. The Pt loading in the anode side was found to be 0.1 mg cm^{-2}, and in the cathode side: 0.2 mg cm^{-2}, which were measured by ICP analysis.

Preparation of MEAs

First, a Nafion 212 membrane (DuPont, USA) was utilized as a proton exchange membrane (PEM) electrolyte without any pretreatment. Then, four kinds of the MEAs are prepared with the difference of materials on anode side such as N-CeO_2@Pd/C, CeO_2@Pd/C, Pd/C and Pt/C, while the Pt/C electrodes is constantly used for cathodic side activity. Thereby, the obtained devices are hereafter called as N-CeO_2@Pd/C, CeO_2@Pd/C, Pd/C and Pt/C MEAs, respectively. To handle the MEAs, two prepared electrodes were symmetrically attached to both sides of the Nafion 212 membrane, and the active geometric areas of the prepared MEAs were set to 5.0 cm^2 (**Fig. S2**). After that, the platinum-catalyzed MEAs were hot-pressed at 100°C with the pressure of 60 kg/cm^2 for 3 min. The obtained MEAs are placed between two gasket layers, then center between two graphite plates with the fuel transfer channels. Finally, the stack fuel cell is carefully tightened using the bolts.

Electrocatalytic measurements

Cyclic voltammetry (CV) curves were performed on a potentiostat (Gamry instruments, Reference 3000 Potentiostat/Galvanostat/ZRA) for the electrochemical surface area (ECSA) evaluation of the prepared catalyst electrodes. An area of 1.0 cm × 1.0 cm electrode was used as working electrode. The CV tests were performed in a 500 mL glass beaker containing freshly prepared 0.1 M H_2SO_4 electrolyte with the sweep rate of 50 mV/s at room temperature. Notably, the electrolyte solutions were saturated with pure N_2 by purging during the electrochemical tests, to prevent attack from the oxygen. The ECSA value of each catalyst electrode was quantitatively calculated by the following equation;

$\mathrm{ECSA} = Q_\mathrm{H}/(0.21 \times m_\mathrm{metal})$

where, Q_H (mC/cm^2) is determined by the integration of the hydrogen desorption region, and then divided by the sweep rate, and 0.21 (mC/cm^2) is the required charge to oxidize a monolayer of hydrogen on the Pd surface, and m_metal (mg/cm^2) is the total Pd or Pt loading weight into the anodic working catalyst electrode measured by ICP spectrometry.

The CO stripping voltammetry was also performed in 0.1 M H_2SO_4 electrolyte at 25 °C to determine ECSA values for all electrodes. Firstly, the electrolyte was purged with pure N_2 gas for 30 min, then pure CO gas was bubbled into the electrolyte for 20 min at a potential of 0.05 V (vs. SCE) for adsorbing on the surface of the catalysts. Lastly, the dissolved CO gas in the electrolyte was removed with pure N_2 by purging for 20 min. The CO stripping voltammetry was recorded at a sweep rate of 50 mV/s.

Electrochemical impedance spectroscopy and single cell tests

The prepared fuel cell devices were tested using a fuel cell test station (SMART-II, WonAtech Com.). The humidified hydrogen and air fuels were supplied to the MEA through the serpentine flow channels on the graphite plates with the flow rate of 100 and 260 cm^3/min, respectively. Prior to the experiments, the inside of the fuel cell devices was totally cleaned by the purge of pure nitrogen for 30 min. The back pressure and temperature were constantly controlled at 1.5 atm and 80°C for both sides during the PEMFC operation. The PEMFC system was humidified at 100 % during the cell operation.

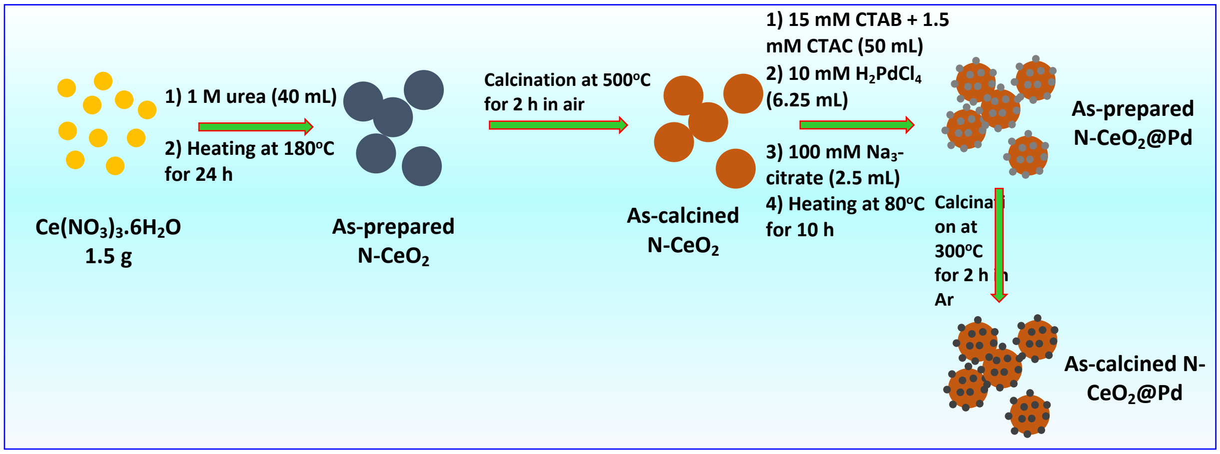

Fig. S1 Hydrothermal synthesis of $N-CeO_2$@Pd catalyst.

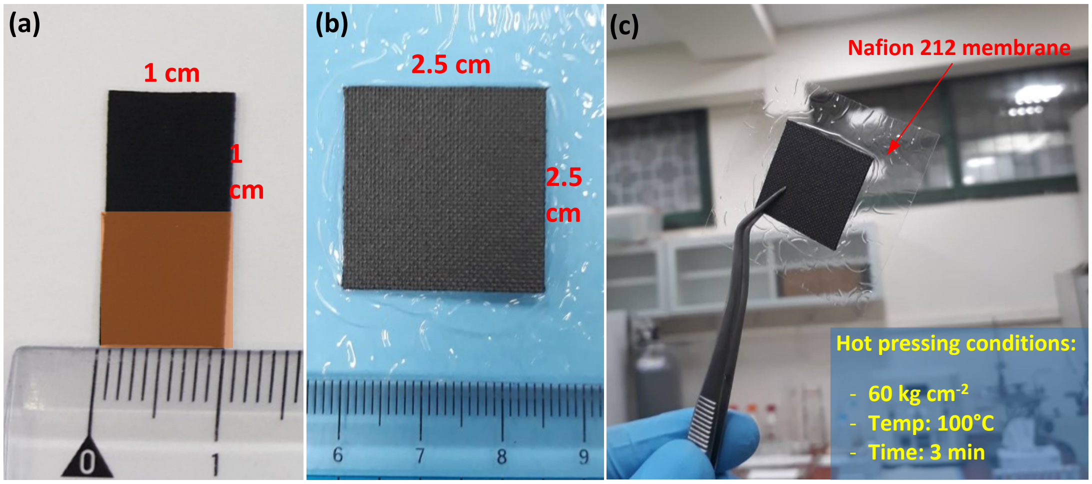

Fig. S2 Working area of electrodes for (a) CV and (b) single cell tests. (c) Prepared MEA consisting $N-CeO_2$@Pd/C as anode and Pt/C as cathode.

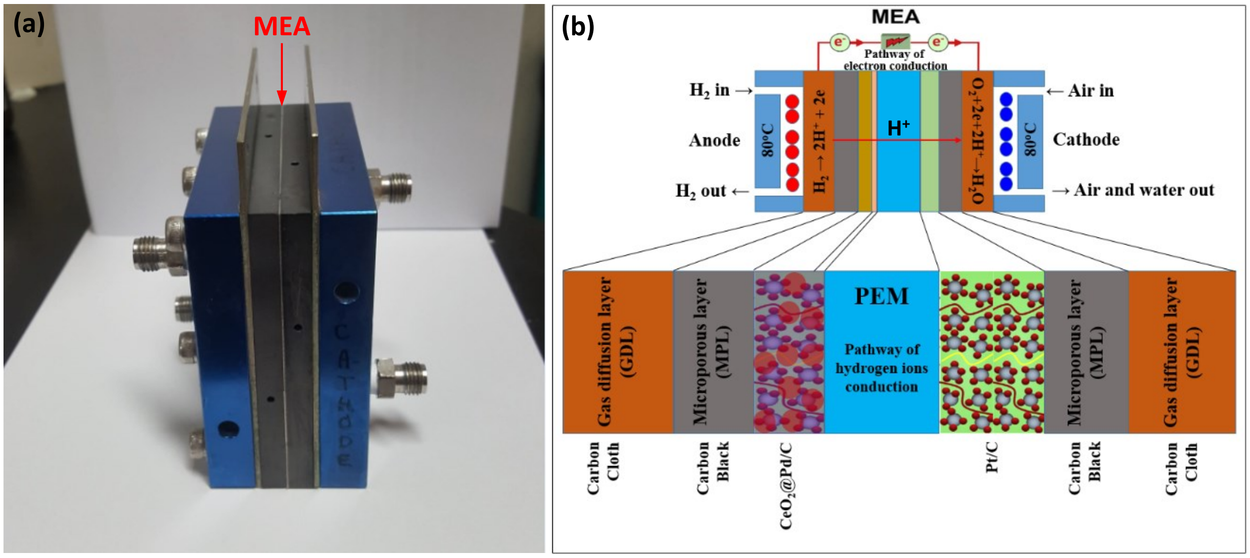

Fig. S3 (a) Prepared device for single cell test and (b) device simulation for layer-by-layer.

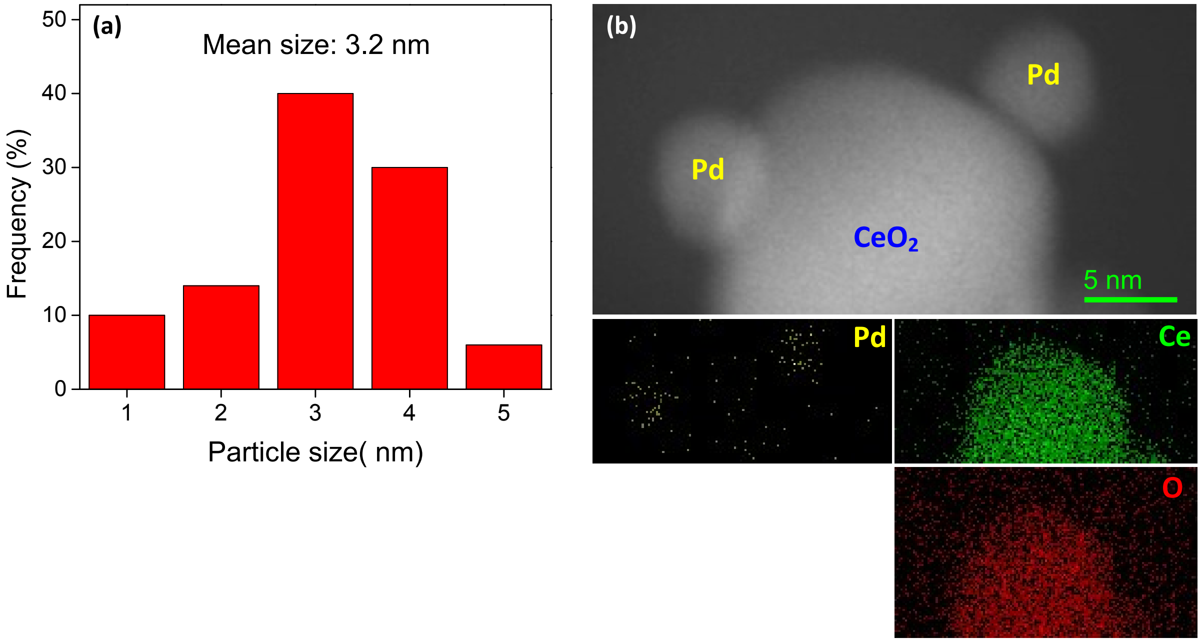

Fig. S4 (a) Particle size distribution of Pd loaded on N-CeO_2 and (b) HRTEM mapping elements of N-CeO_2@Pd nanocatalyst.

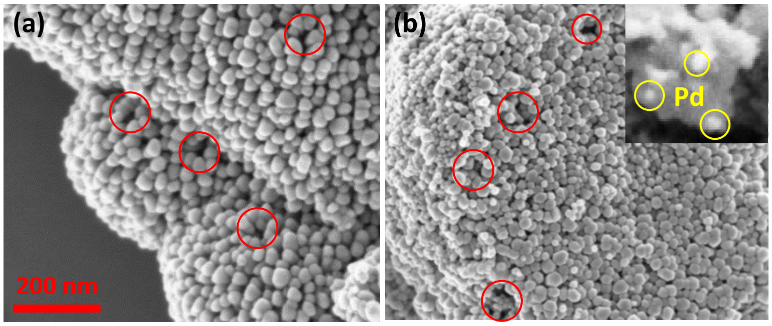

Fig. S5 FEM analysis of (a) N-CeO$_2$ and (b) N-CeO$_2$@Pd nanocatalyst.

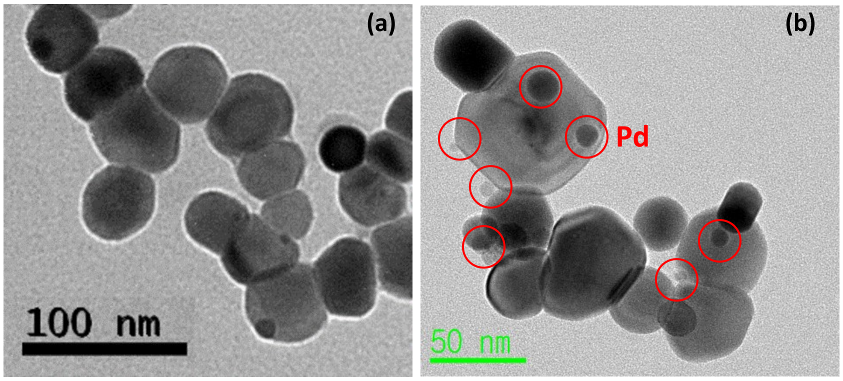

Fig. S6 TEM analysis of as-calcined CeO$_2$ support and as-calcined CeO$_2$@Pd.

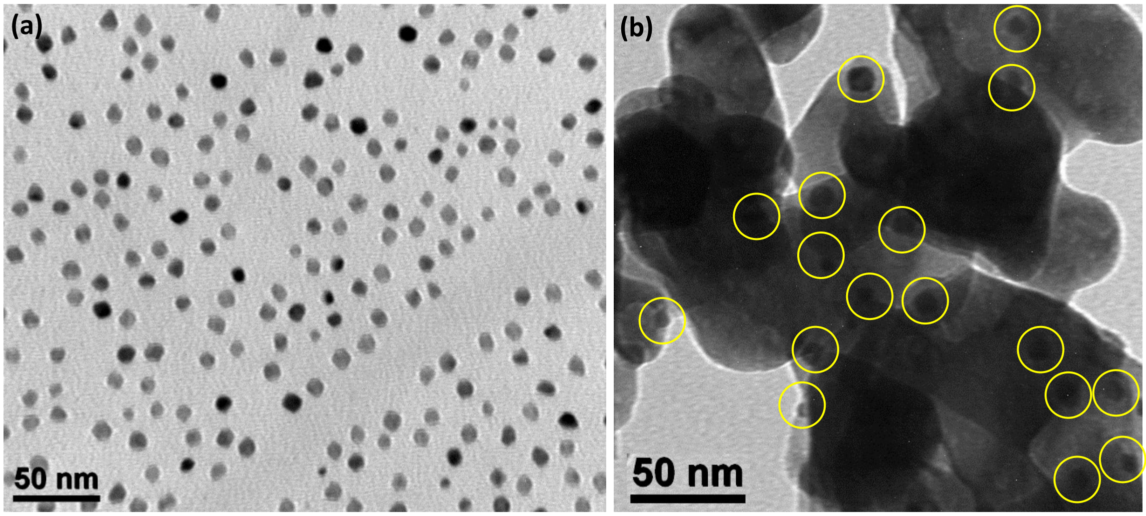

Fig. S7 HRTEM image of (a) the synthesized Pd and (b) Pd/C (~20 wt.% Pd) nanocatalyst.

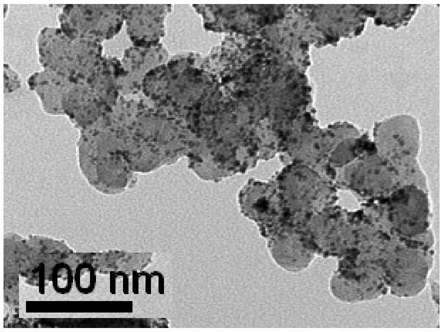

Fig. S8 HRTEM image of Pt/C (~20 wt.% Pt) nanocatalyst.

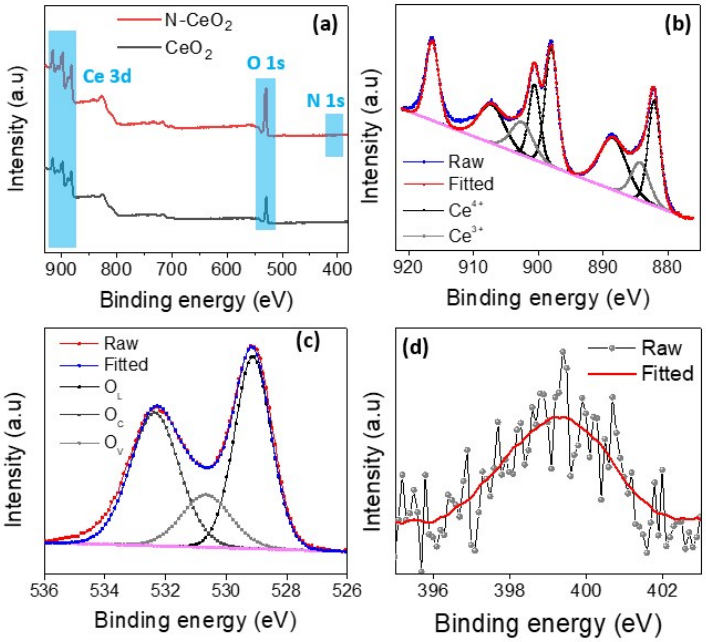

Fig. S9 Full survey XPS analysis for (a) CeO_2 and N-CeO_2 catalysts. XPS analysis for (b) Ce 3d, (c) O 1s, and (d) N 1s present in N-CeO_2 catalyst.

Table S1. XPS comparison for CeO_2 and N-CeO_2 catalysts.

Catalysts	**Ce^{3+}**		**Oxygen**		
	Binding energy (eV)	Relative percentage (%)	Species	Binding energy (eV)	Relative percentage (%)
CeO_2	884.00 902.30	12.60	O_L (Ce-O)	529.05	58.30
			O_V (vacancy)	530.40	11.40
			O_C (chemisorbed)	532.10	30.30
N-CeO_2	**884.20** **902.70**	**20.50**	**O_L (Ce-O)**	**529.10**	**55.60**
			O_V (vacancy)	**530.60**	**18.50**
			O_C (chemisorbed)	**532.40**	**25.90**

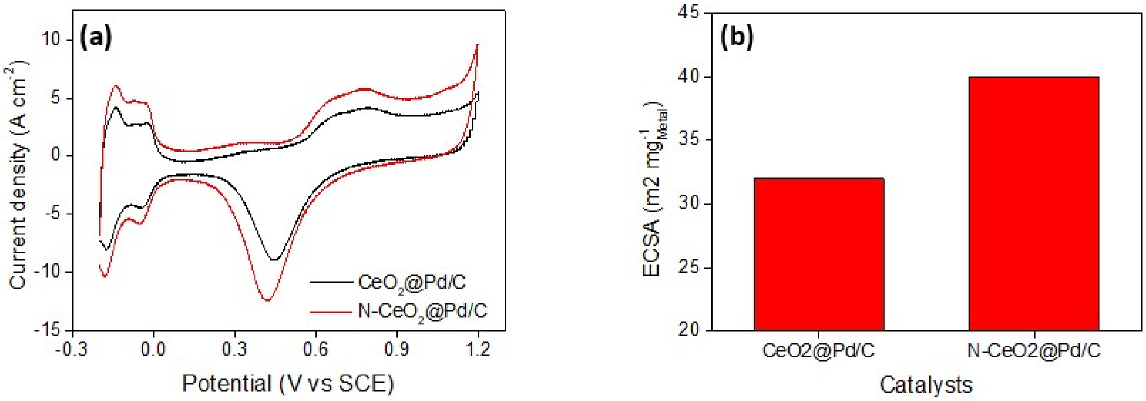

Fig. S10 (a) CV curves of hydrogen oxidation reaction and (b) ECSA results in the N_2-saturated solution of 0.1 M H_2SO_4 for CeO_2@Pd/C and N-CeO_2@Pd/C electrodes.

Table S2. ECSA comparison for Pd- and CeO_2-related materials determining from integrating hydrogen desorption peaks.

Catalysts	ECSA (m^2 g^{-1})	Electrolyte	Scan speed (mV s^{-1})	Refs.
Pd/C	25	0.1 M H_2SO_4	50	This work
PdAg/C	33	1 M KOH	50	1
Pd_2Ni_3/C	32.9	1 M NaOH	50	2
PdPt/C	31.59	0.5 M H_2SO_4	50	3
PdAu-P/C	39.56	0.1 M KOH	50	4
Pd(6%)/C-CeO_2	22	0.1 M KOH	10	5
Pt/C	44	0.25 M H_2SO_4	50	6
Pt-CeO_2/C	66.29	0.5 M H_2SO_4	50	7
N-CeO_2@Pd/C	40	0.1 M H_2SO_4	50	This work

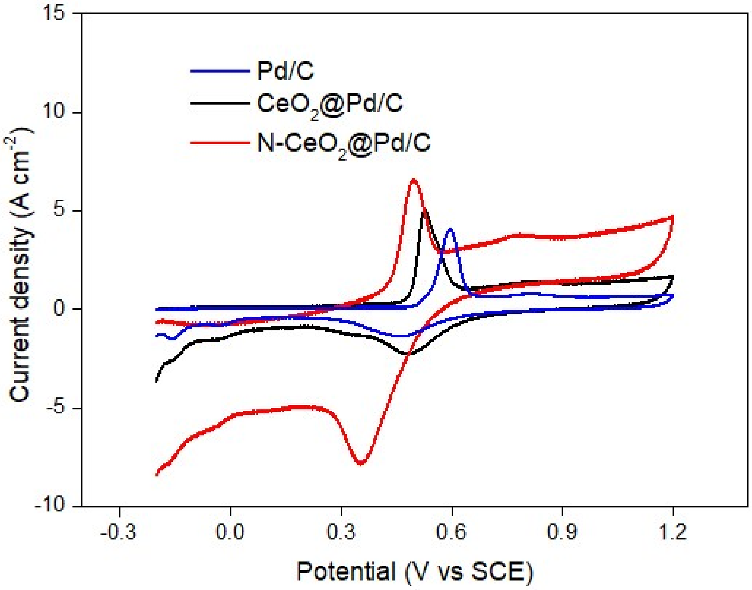

Fig. S11 CO stripping measurements recorded in N_2-saturated solution of 0.1 M H_2SO_4 electrolyte at scan rate of 50 mV s1 and 25 C for Pd/C, CeO$_2$@Pd/C and N-CeO$_2$@Pd/C catalysts.

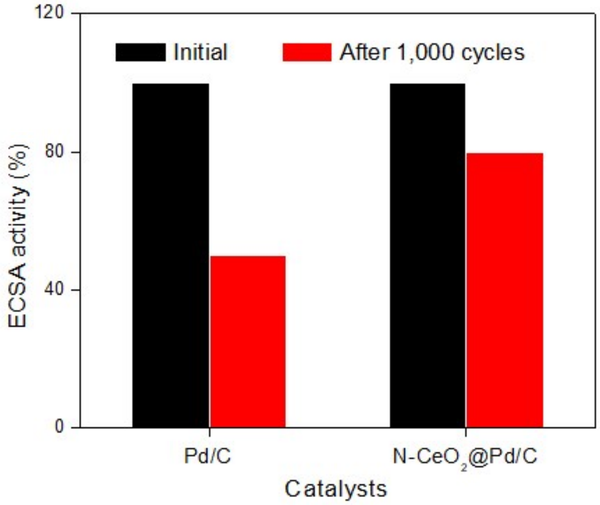

Fig. S12 ECSA stability tests for Pd/C and N-CeO$_2$@Pd/C catalysts in the N_2-saturated solution of 0.1 M H_2SO_4 at a sweep rate of 50 mV s^{-1} at room temperature.

References

1 R. Carrera-Cerritos, C. Salazar-Hernandez, I. Galindo-Esquivel and R. Fuentes-Ramirez, *J. Nanomater.*, 2018, **2018**.

2 Z. Zhang, L. Xin, K. Sun and W. Li, *I. J. Hydrogen Energy*, 2011, **36**, 12686-12697.

3 Y. Yang, Y. Cao, L. Yang, Z. Huang and N. Å. V. Long, *Nanomaterials*, 2018, **8**.

4 T. Li, Y. Wang, Y. Tang, L. Xu, L. Si, G. Fu, D. Sun and Y. Tang, *Catal. Sci. Technol.*, 2017, **7**, 3355-3360.

5 H. A. Miller, F. Vizza, M. Marelli, A. Zadick, L. Dubau, M. Chatenet, S. Geiger, S. Cherevko, H. Doan, R. K. Pavlicek, S. Mukerjee and D. R. Dekel, *Nano Energy*, 2017, **33**, 293-305.

6 D. V. Dao, T. D. Le, G. Adilbish, I.-H. Lee and Y.-T. Yu, *J. Mater. Chem. A*, 2019, **7**, 26996-27006.

7 S. Dai, J. Zhang, Y. Fu and W. Li, *New J. Chem.*, 2018, **42**, 18159-18165.