Supplementary Information (SI) for Chemical Communications.

Electronic Supporting Information

Pd-CeO_2/C nanocomposite derived from MIL-101(Al) for enhanced glycerol electrooxidation

1. Experimental Section

1.1 Chemicals

2-aminoterephthalic acid (NH_2-BDC), aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), palladium(II) chloride ($PdCl_2$), glycerol, potassium hydroxide (KOH) and sodium hydroxide (NaOH) were provided by Macklin. Commercial Pd/C (10 wt%) was provided by Bide Pharmaceutical Co., Ltd. Nafion solution (5 wt%) was purchased from DuPont Corporation (United States). Methanol and N, N-Dimethylformamide (DMF) were provided by XiLong Scientific. Sodium borohydride ($NaBH_4$) was provided by Tianjin Kemio Chemical Reagent Co., Ltd. Ultra-pure water (18.2 MΩ) has been purified by an ultra-pure water machine. All chemicals were used without any further purifications.

1.2 Preparation of CeO_2/MDC

The synthesis of NH_2-MIL-101(Al, Ce) including different methodologies. The 2-aminoterephthalic acid (2.77 g, 15 mmol) was dissolved in N, N-dimethylformamide (DMF, 600 mL) in a 1000 mL of round-bottom flask and heated to 110°C in an oil bath. Subsequently, $AlCl_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were introduced in seven equal portions, with an interval of 15 minutes between each addition. Following the final addition, the solution should be stirred at 110 °C for three hours, after which stirring should cease and the solution should be left to stand at 110 °C for 16 hours. Following a period of cooling to room temperature, the solid was subjected to centrifugation, washed on three occasions with methanol, and treated with solvent exchange for a period of three days in order to remove residual DMF from the pores. Subsequently, the solid residue should be collected and subjected to vacuum drying at a temperature of 60°C for a period of 12 hours. The total quantity of metal salts introduced is 30 mmol, and the molar ratios of $AlCl_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ introduced are 2:1, 1:1, and 1:2, respectively. These products were designated as $CeO_2/MDC_{0.5}$, CeO_2/MDC_1, and CeO_2/MDC_2, respectively. The product prepared without adding $Ce(NO_3)_3 \cdot 6H_2O$ was designated as MDC.

1.3 Preparation of Pd-CeO_2/MDC

To synthesize Pd-CeO_2/MDC, 20 mg of CeO_2/MDC, 1 mL of NaOH (7.5 mg mL^{-1}), and 0.375 mL of H_2PdCl_4 (0.1 mol L^{-1}) were mixed in 15 mL deionized water. 4 mL of $NaBH_4$ aqueous solution (2 mg mL^{-1}) was slowly added to the above mixture, and reacted for 30 minutes. Pd-CeO_2/MDC catalysts with different CeO_2/MDC ratios were synthesized similarly with the above procedures. Finally, the products were centrifuged and washed, the products were denoted as Pd-CeO_2/MDC_2, Pd-CeO_2/MDC_1 and Pd-$CeO_2/MDC_{0.5}$, respectively. The MDC with CeO_2 doping was also used to support the Pd NPs similarly, the corresponding catalyst was denoted as Pd/MDC. The Pd loading in the synthesized catalyst was analyzed by the inductively coupled plasma emission spectroscopy (ICP-OES).

1.4 Characterizations

The crystallographic profiles of the samples were recorded in a systematic manner using a Bruker D8Advance X-ray diffractometer, which was furnished with Cu K_a radiation sources operating at 40 kV and 40 mA, sourced from the United

States. The morphological features were examined in detail through scanning electron microscopy (XL30 ESEM-FEG, USA) at a standardized voltage of 10.0 kV, and subsequently analyzed by transmission electron microscopy (ARM200F, Japan). An X-ray photoelectron spectroscopy (XPS) analysis was conducted on the ESCALAB 250 Xi instrument (Thermo Fisher, China) to determine the elemental surface composition. The excitation source employed was Al K_a. Throughout the course of this process, the experimental chamber was maintained at an ultra-high vacuum level of 1.7×10^{-10} mbar to ensure the precision. The quantitative determination of the palladium content was conducted using inductively coupled plasma optical emission spectrometry (ICP-OES), specifically the ICAP 7000 model from Thermo Scientific. Furthermore, the textural properties of the catalysts, including their specific surface area and pore size distribution, were rigorously examined through Brunner-Emmet-Teller (BET) measurements conducted on an HD88 instrument (USA) and the Barrett-Joyner-Halenda (BJH) methodology, respectively. This comprehensive suite of characterization techniques ensures an accurate and reliable assessment of the catalysts' physicochemical properties.

1.5 Electrochemical measurements

The catalyst ink formulations were prepared in a systematic manner, with varying amounts (20 mg for Pd-CeO_2/MDC and Pd/MDC, 40 mg for commercial Pd/C with 10% Pd content) dissolved in deionized water. The catalyst was subjected to sonication for a period of 30 minutes, with the objective of achieving a uniform suspension. Subsequently, a precise volume (5 μL) of the ink was dispensed onto the surface of a glassy carbon electrode (GCE, 3 mm diameter), resulting in a uniform catalyst loading density of 14.2 μg cm^{-2} upon ambient drying. In order to enhance ionic conductivity and durability, the dried catalyst layer was subjected to a further coating process, comprising the addition of 5 μL of a 0.02% Nafion solution dispersed in ethanol, followed by a second drying step. The electrochemical evaluations were conducted in accordance with a rigorous framework utilizing a standard three-electrode configuration on the CHI760E electrochemical workstation from Shanghai Chenhua Instrument Co. The experimental setup comprised a glassy carbon electrode (GCE) acting as the working electrode, modified with distinct catalysts (Pd-CeO_2/MDC, Pd/MDC, or commercial Pd/C), a potassium chloride-saturated silver/silver chloride electrode (Ag/AgCl) serving as the reference electrode, and a platinum wire as the counter electrode. Throughout the course of the experiments, a consistent electrolyte composition was employed, comprising 0.1 mol L^{-1} glycerol and 1 mol L^{-1} KOH, in order to facilitate the electrochemical reactions under investigation.

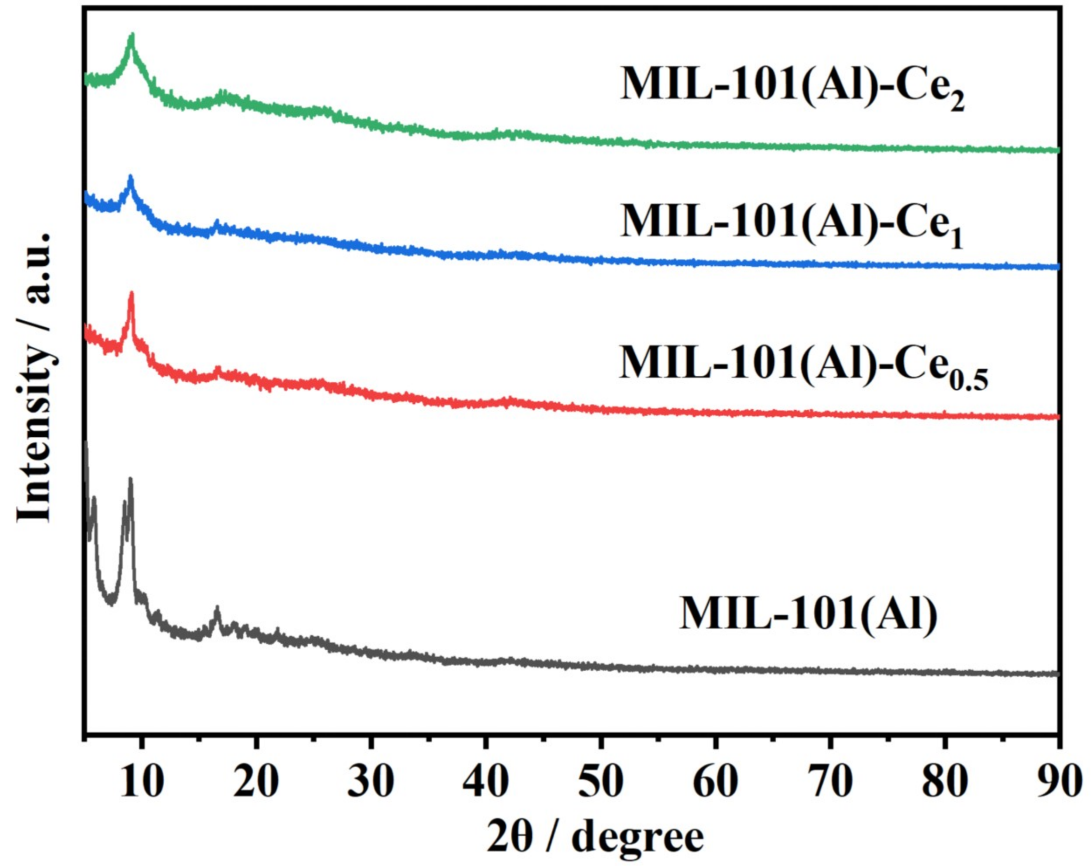

Fig. S1 (a) XRD patterns of MIL-101(Al) and Ce^{3+}-doped MIL-101(Al) with different Al^{3+}/Ce^{3+} ratios.

Table S1. The ICP-OES results of different Pd-CeO_2/MDC electrocatalysts.

Sample	**Element**	**Wt/%**
Pd-CeO_2/$MDC_{0.5}$	Pd	19.86
Pd-CeO_2/MDC_1	Pd	19.77
Pd-CeO_2/MDC_2	Pd	19.91
Pd/MDC	Pd	20.24
Pd/C	Pd	10.02

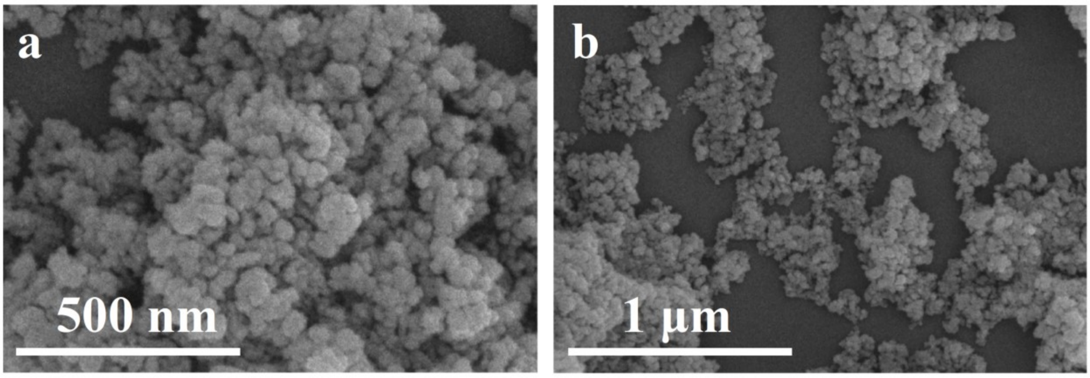

Fig. S2 Typical SEM images of the Pd-CeO_2/MDC_1.

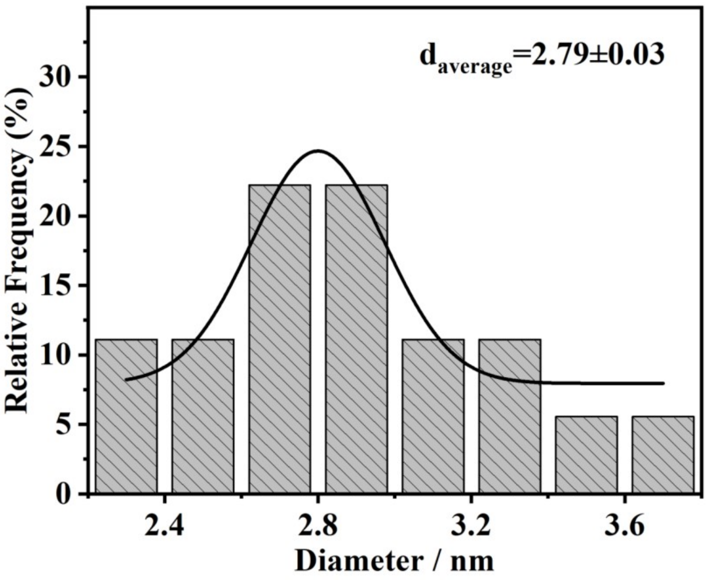

Fig. S3 Size distribution of the Pd NPs in Pd-CeO_2/MDC_1.

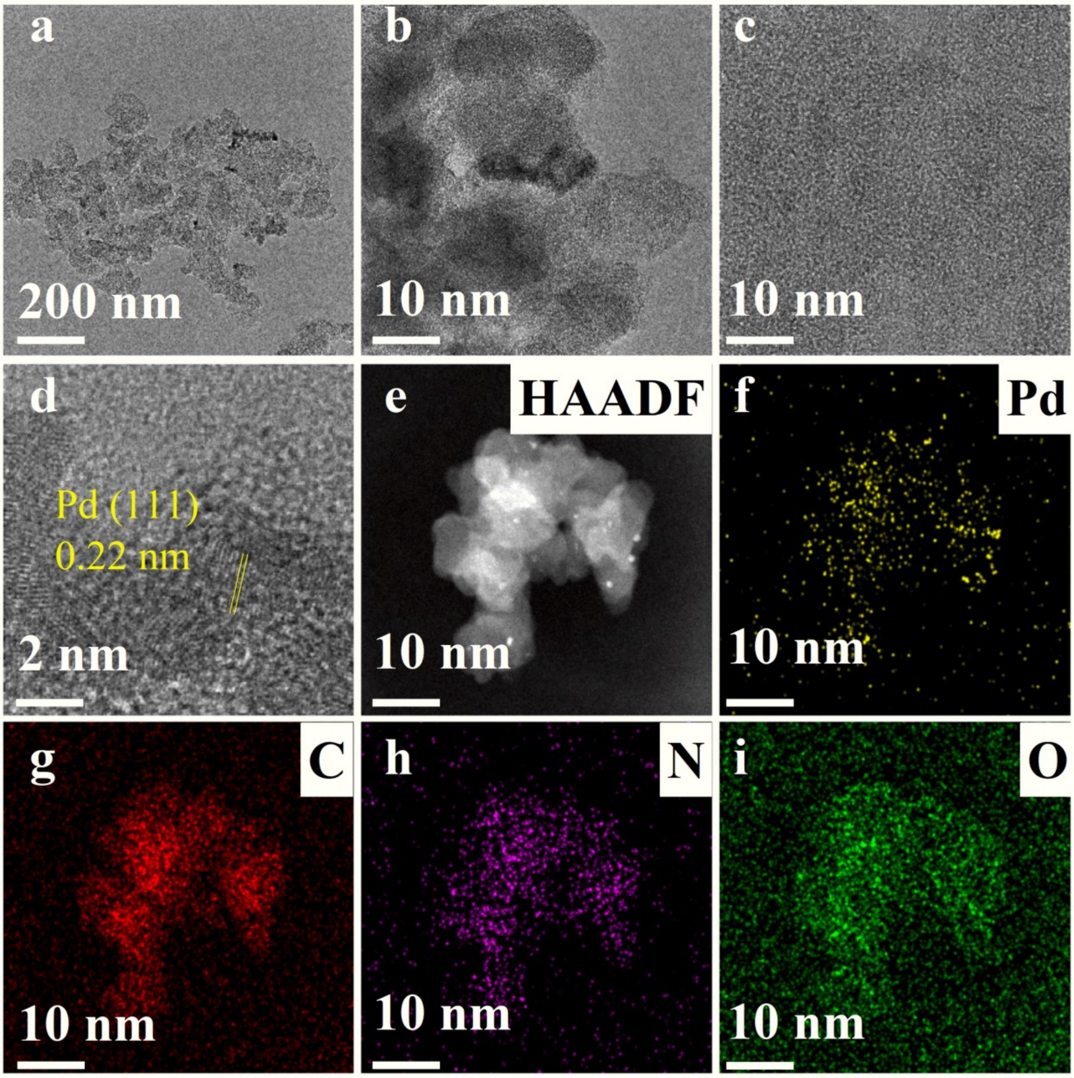

Fig. S4 (a-d) TEM images of Pd/MDC, and elemental mapping images for Pd/MDC (f) Pd (g) C (h) N (i) O.

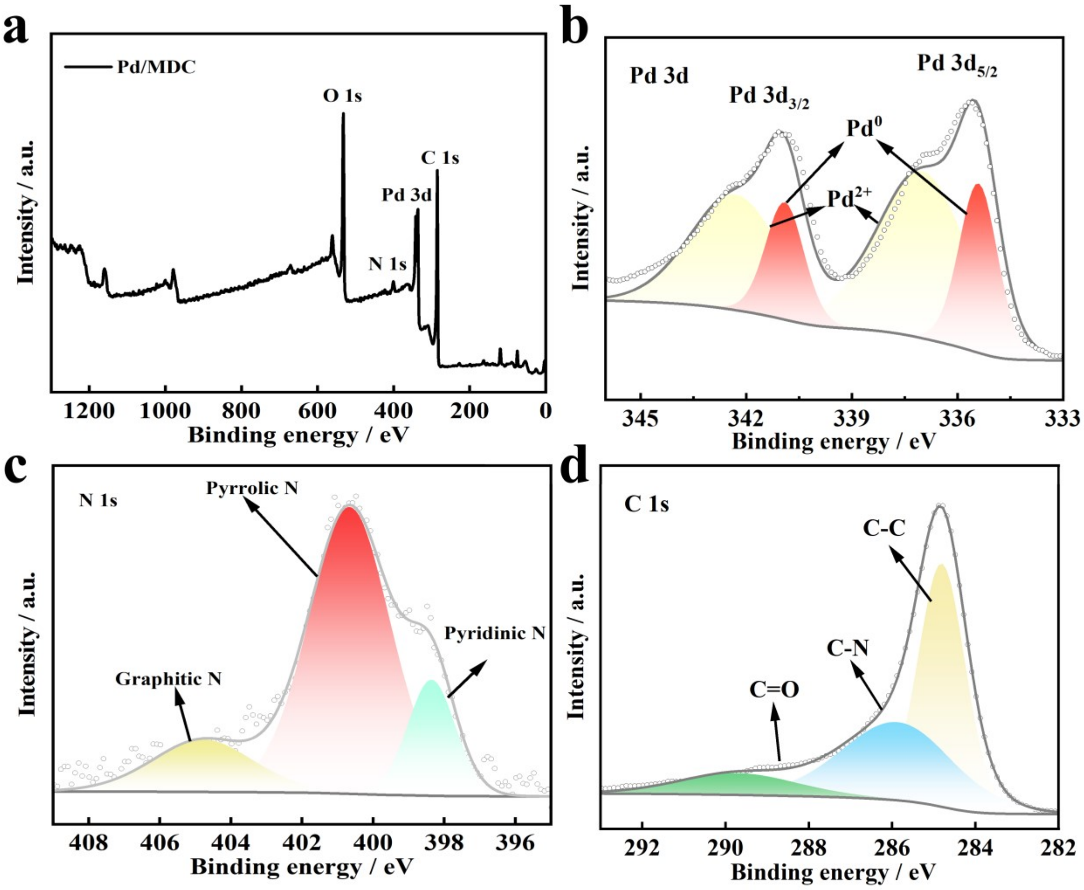

Fig. S5 (a) XPS survey spectrum of Pd/MDC; XPS spectra of (b) Pd 3d (c) N 1s (d) C 1s of Pd/MDC.

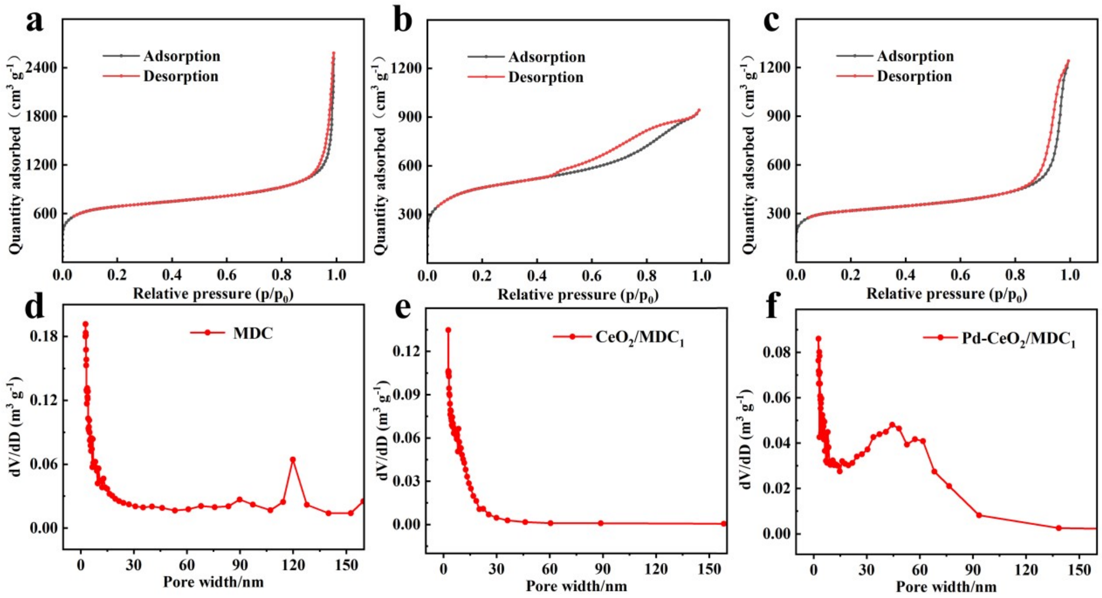

Fig. S6 N_2 adsorption/desorption plots of (a) MDC, (b) CeO_2/MDC_1, (c) Pd-CeO_2/MDC_1 and pore distribution of (d) MDC, (e) CeO_2/MDC_1, (f) Pd-CeO_2/MDC_1.

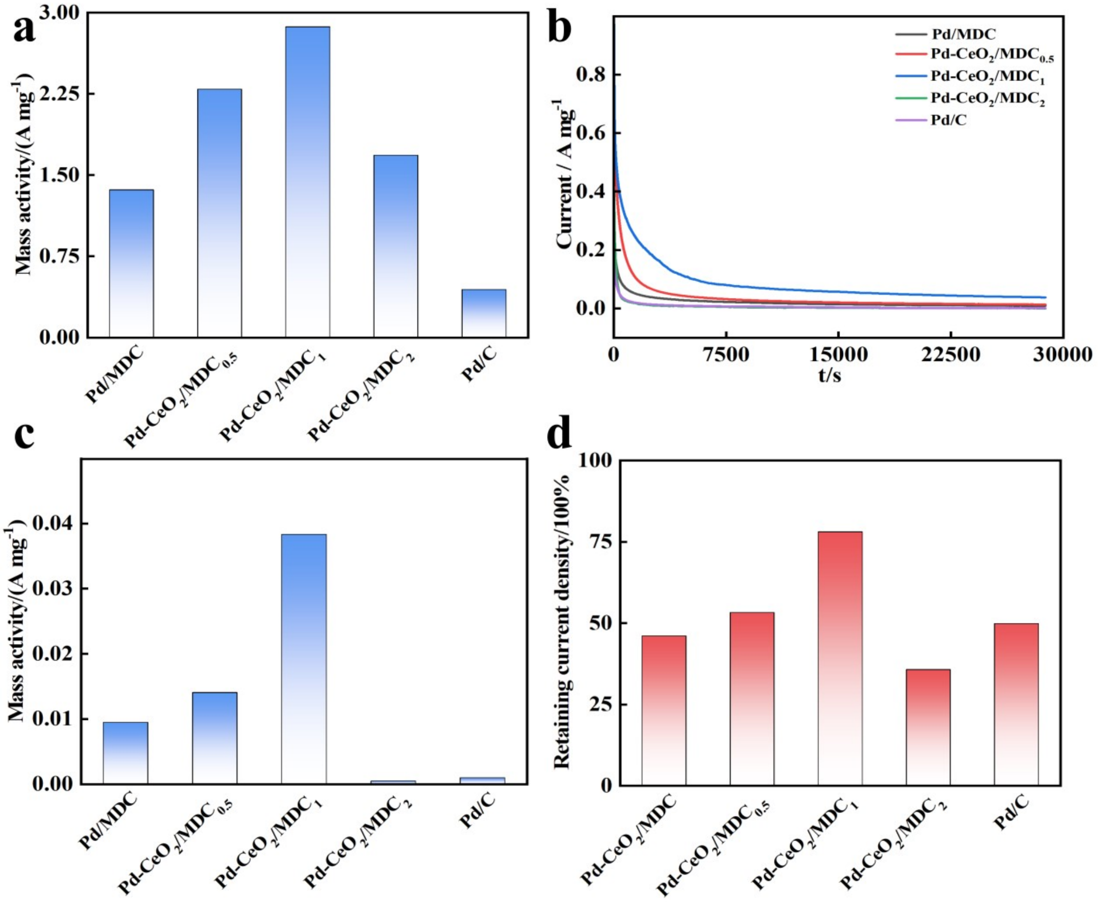

Fig S7 (a) Mass activities of these studied electrodes, (b) CA plots, (c) the remaining mass activity after CA test, and (d) the retaining current density after 8 hours of cycling of different catalysts.

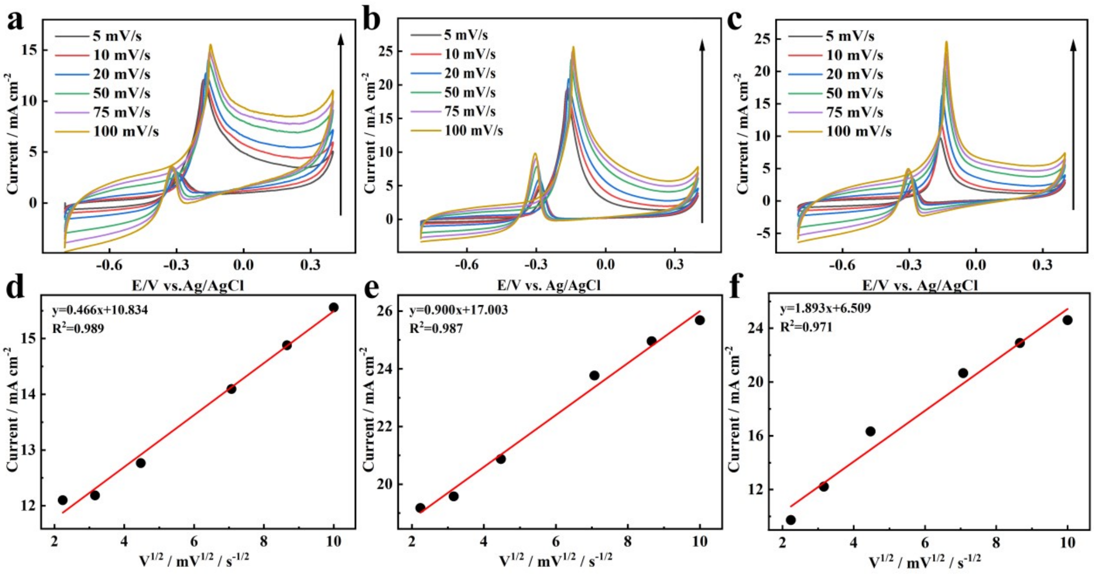

Fig. S8 CV plots of GER by (a) Pd/MDC (b) Pd-CeO$_2$/MDC$_{0.5}$, (c) Pd-CeO$_2$/MDC$_2$ at different scan rates and (b, c, d) the corresponding plot of j_p versus $v^{1/2}$.

Table S2. Comparison for electrocatalytic activity of Pd-CeO_2/MDC_1 catalysts with other previously-reported catalysts for Glycerol oxidation.

Catalysts	Electrolytes	Mass activities	Ref.
$Ag_{99.5}Pt_{0.5}$	0.1 M NaOH + 1M GC	4.58 A mg^{-1}_{pd}	[1]
Pd-Co-EGF	0.5 M KOH + 1 M GC	3.41 A mg^{-1}_{pd}	[2]
Pd-CeO_2/MDC_1	1 M KOH + 0.1 M GC	2.87 A mg^{-1}_{pd}	**our work**
Pd/Bi_2Te_3-20%	1 M KOH + 1 M GC	2.64 A mg^{-1}_{pd}	[3]
$Pt_{0.85}Cu_{0.15}$-CuO(3)/C	0.1 M NaOH + 0.1M GC	1.68 A mg^{-1}_{Pt}	[4]
Pd-CN_x/G	0.5 M NaOH + 0.5 M GC	1.1 A mg^{-1}_{pd}	[5]
Pd_4Bi	1 M KOH + 0.1 M GC	0.7 A mg^{-1}_{pd}	[6]
Pd-NiO_x-P/C	1 M KOH + 1 M GC	0.36 A mg^{-1}_{pd}	[7]
$Pt_{0.95}$-$Bi_{0.05}$/TiN HNWs/CC	1 M KOH + 0.05 M GC	0.31 A mg^{-1}_{Pt}	[8]
$Pd_{50}Ag_{50}$/C	0.1 M NaOH + 0.1 M GC	0.26 A mg^{-1}_{pd}	[9]
$Pd_{50}Ni_{50}$/C	0.1 M NaOH + 0.1 M GC	0.19 A mg^{-1}_{pd}	[9]
Pd_3Sn/phen-C	0.1 M KOH + 0.5 M GC	0.18 A mg^{-1}_{pd}	[10]

References

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