Electronic Supporting Information

Design of hollow PdO-Co_3O_4 nano-dodecahedrons with moderate catalytic activity for Li-O_2 batteries

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Experimental section

Materials

Cobal(II) nitrate hexahydrate and palladium acetate were purchased from Aladdin, 2-methylimidazole was purchased Sinopharm Chemical Reagent Corp. Other solvents were purchased from Beijing Tongguang fine chemical. All chemicals used as received without further purification.

Experimental Procedures

Synthesis of ZIF-67:

In a typical synthesis, Cobal(II) nitrate hexahydrate (3.49 g, 12 mmol) and 2-methylimidazole (5.91 g, 72 mmol) were dissolved in 120 mL methanol, respectively. Then, under magnetic stirring for 30 min to form two clear solutions. After that, the solution of 2-methylimidazole was poured in to the solution of Cobal(II) nitrate hexahydrate. Thereafter, stirring at room temperature for 24 h, the purple solid was centrifuged and washed with methanol for several times, and finally dried at 60 ^oC.

Synthesis of Pd@ZIF-67:

In a typical synthesis, 50 mg of palladium acetate was dissolved in 3 mL of acetone and stirred to form a clear solution. Then, 50 mg of ZIF-67 with 2 mL acetone were added into the solution refluxing for 1 h at 70 ^oC. Then, collecting the solid and washing with acetone several times, finally dried at 60 ^oC.

Synthesis of PdO-Co_3O_4:

The as-synthesized Pd@ZIF-67 was placed in a tube furnace and heated to 250 ^{o}C with a ramp rate of 3 ^{o}C min^{-1} and kept for 30 min in flowing Ar, then cooled to room temperature. Thereafter, the carbonized materials were further heated to 600 ^{o}C with a ramp rate of 3 ^{o}C min^{-1} and also kept for 30 min in flowing Air to yield PdO-Co_3O_4.

Synthesis of Pd/PdO-Co_3O_4 and Co_3O_4:

The preparation processes of Pd/PdO-Co_3O_4 are similar to that for PdO-Co_3O_4, except for the temperature of pyrolysis. Pd@ZIF-67 was placed in a tube furnace and heated to 350 ^{o}C with a ramp rate of 3 ^{o}C min^{-1} and kept for 30 min in flowing Ar, then continued to keep for 60min in Air to yield Pd/PdO-Co_3O_4. Co_3O_4 was obtained by pyrolyzing ZIF-67 directly.

Characterization

Powder X-ray diffraction patterns of the obtained products were carried out with a Rigaku RU-200b X-ray powder diffractometer (XRD) with Cu Kα radiation，λ =1.5418 Å. Transmission electron microscopy (TEM) was operated by a Hitachi-7700 working at 100 kV. The high-resolution TEM (HRTEM), high angle annular dark field scanning TEM (HAADF-STEM) images and elemental mapping were carried out by a JEOL-2100F FETEM with electron acceleration energy of 200 kV. The scanning electron microscope (SEM) was carried out by a S-4800 Hitachi SEM working at 5kV. X-ray photoelectron spectroscopy (XPS) analyses were conducted on ESCALAB 250 Xi X-ray photoelectron spectrometer with Al Kα radiation.

Electrochemical Characterization

The air cathodes were prepared by painting a slurry of material onto carbon papers. The slurry consisted of 60 wt% synthesized catalysts, 30 wt% carbon black(KB) and 10 wt% polyvinylidene fluoride(PVDF) dispersed in N-methyl-2-phrrolidone(NMP). Then cathodes were dried at 100 ^{o}C in a vacuum oven for 12 h. The CR2032 coin-type cell was assembled in an argon-filled glove box, which consisted of a lithium foil anode, glass fiber filter separator, air electrode and an electrolyte which was 1 M lithium bis(trifluoromethane sulfonimide) dissolved in a tetra(ethylene) glycol dimethyl ether(LiTFSI-TEGDME). Galvanostatic discharge/charge performance of the batteries was tested in the voltage range of 2.0-4.5 V on a Neware battery test system. All the battery performance compare were based on the weight of KB. Electrochemical impedance spectroscopy (EIS) are measured on a Zennium IM6 electrochemical workstation. Cyclic voltammetry(CV) and linear sweep voltammetry(LSV) were measured on an Chen-hua electrochemical workstation.

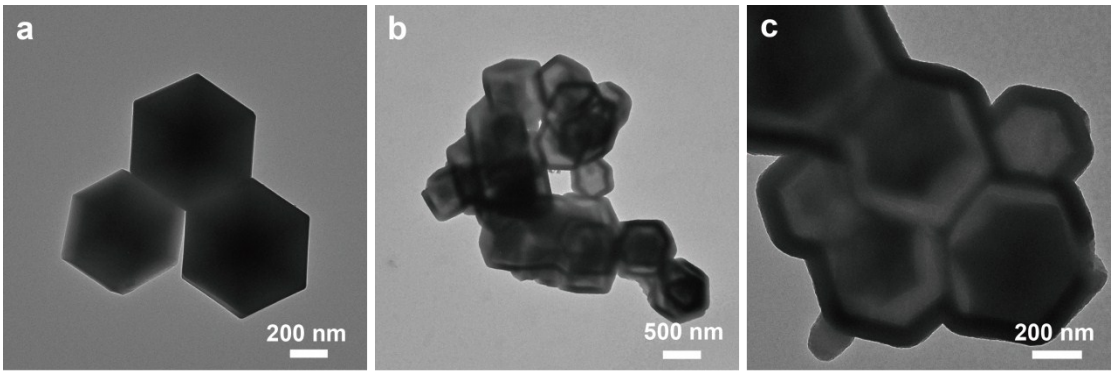

Fig. S1 The TEM images of (a) ZIF-67 and (b-c) Pd@ZIF-67.

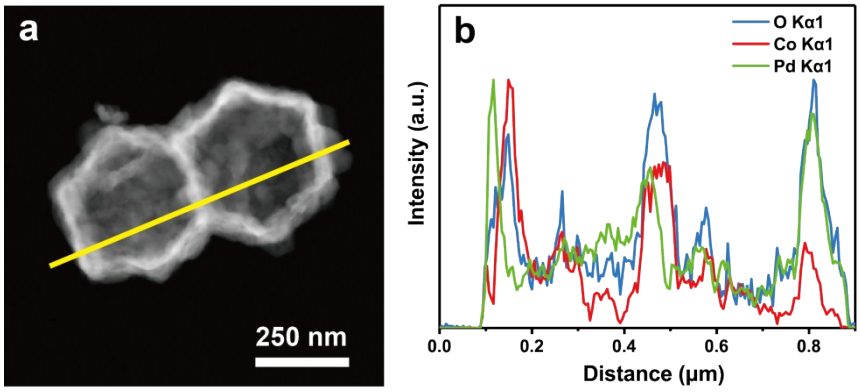

Fig. S2 Line scan pattern of PdO-Co_3O_4.

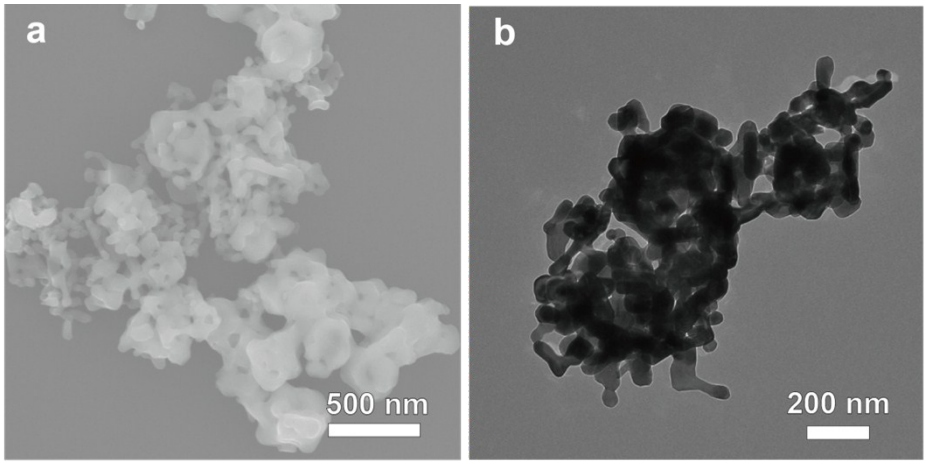

Fig. S3 (a) SEM and (b) TEM images of Co_3O_4.

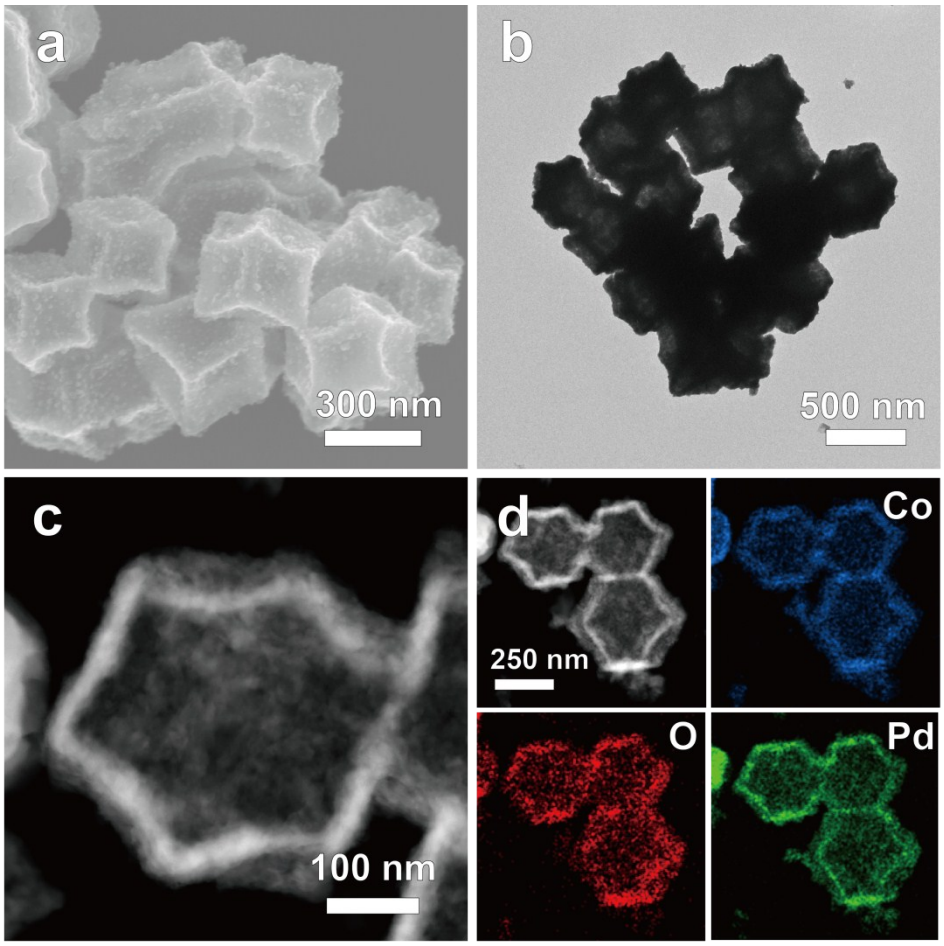

Fig. S4 (a) SEM, (b) TEM, (c-d) HAADF-STEM elemental mapping for Co (blue), O (red) and Pd (green) of the Pd/PdO-Co_3O_4.

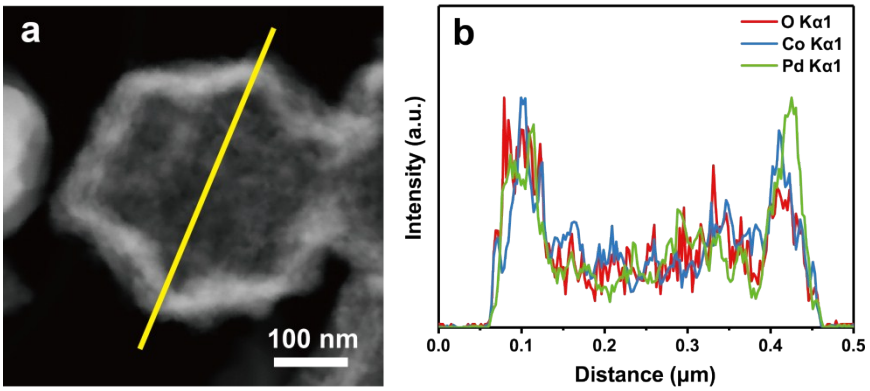

Fig. S5 Line scan pattern of Pd/PdO-Co_3O_4.

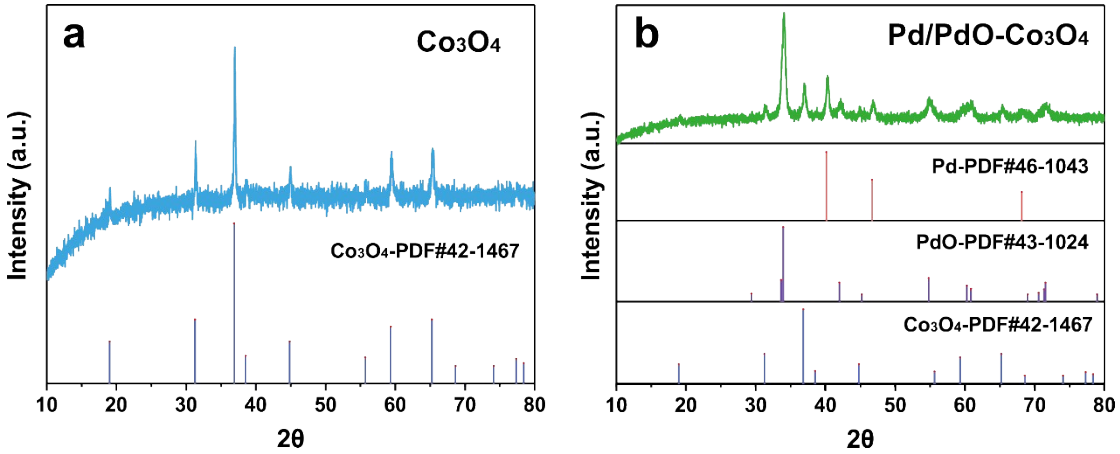

Fig. S6 XRD patterns of the (a) Co_3O_4 and (b) Pd/PdO-Co_3O_4.

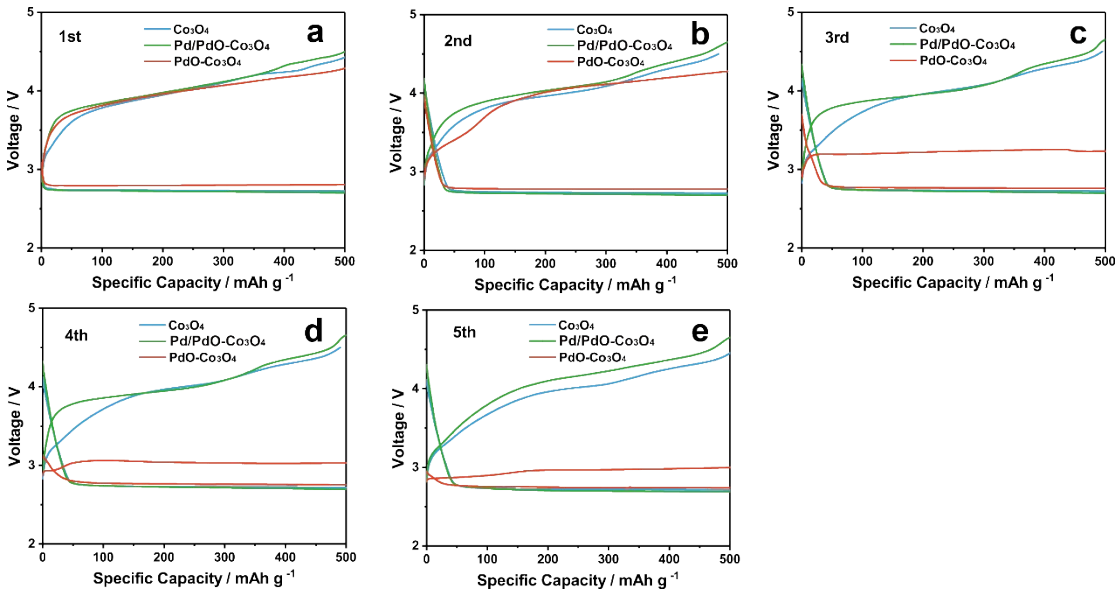

Fig. S7 Comparison of the first five cycles of discharge and charge curves of Co_3O_4, Pd/PdO-Co_3O_4 and PdO-Co_3O_4.

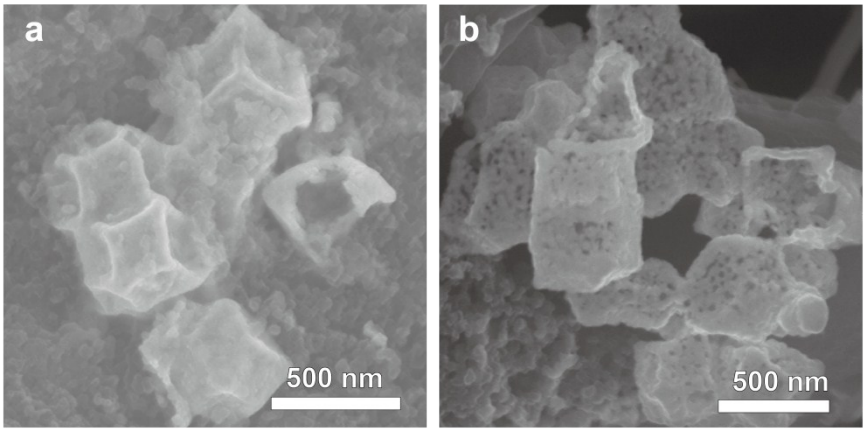

Fig. S8 SEM images of (a)PdO-Co_3O_4 nano-dodecahedron on carbon paper and (b)after the 2nd cycle.

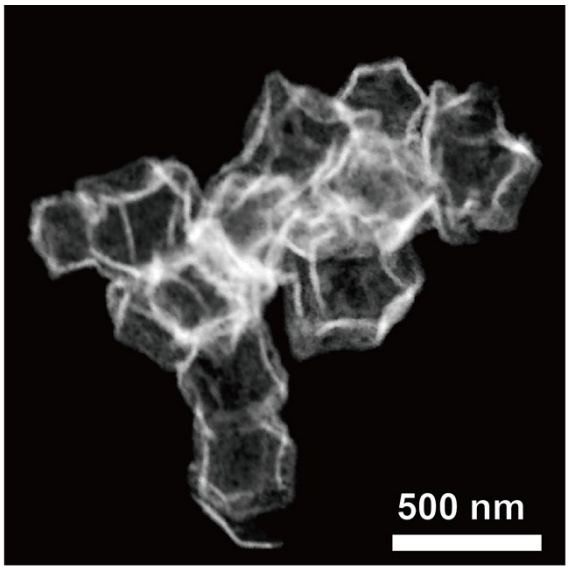

Fig. S9 TEM image of PdO-Co_3O_4 nano-dodecahedron after the 2nd cycle.

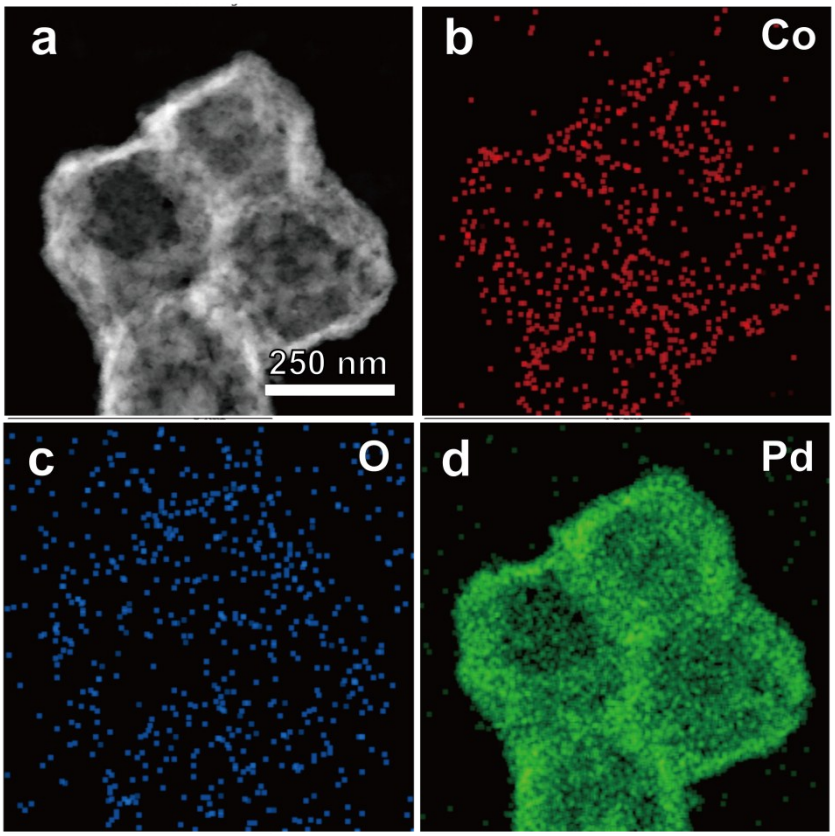

Fig. S10 HAADF-STEM elemental mapping for Co (red), O (blue) and Pd (green), of PdO-Co_3O_4 nano-dodecahedron after the 2nd cycle.

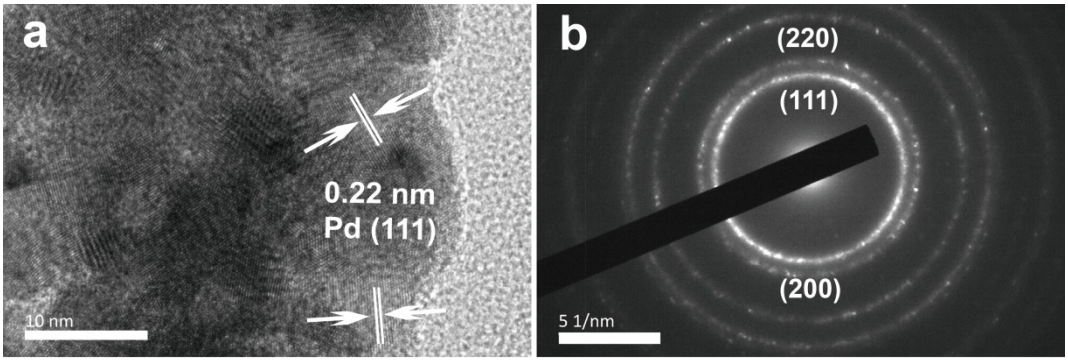

Fig. S11 (a)HRTEM and (b)the SAED pattern of PdO-Co_3O_4 nano-dodecahedron after the 2nd cycle.

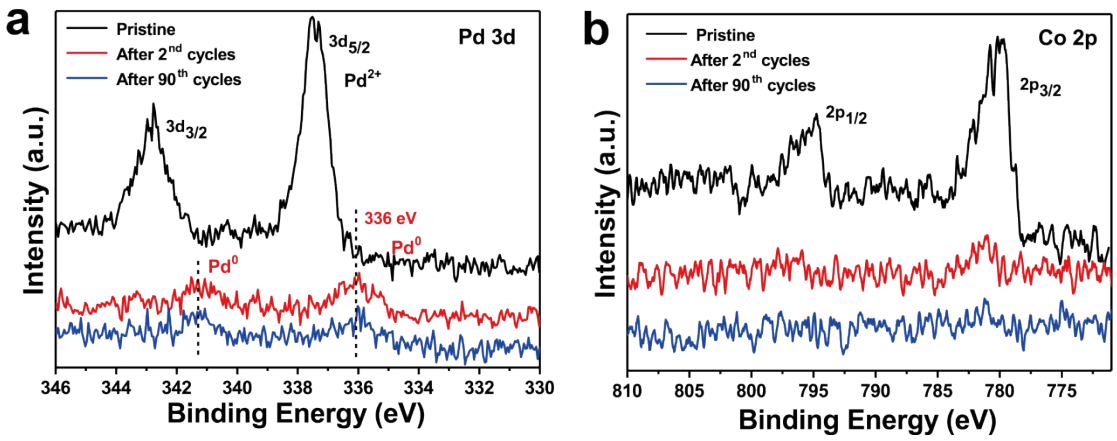

Fig. S12 XPS spectrum of PdO-Co_3O_4 nano-dodecahedrons after the 2nd cycle and 90th cycle: (a) Pd 3d and (b)Co 2p.

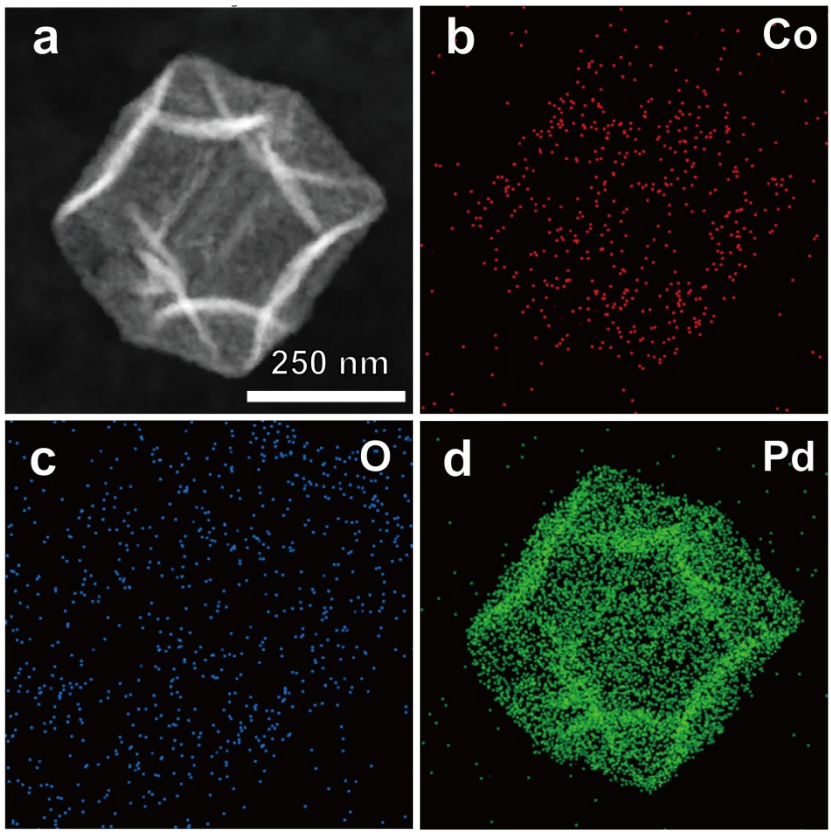

Fig. S13 HAADF-STEM elemental mapping for Co (red), O (blue) and Pd (green), of PdO-Co_3O_4 nano-dodecahedron after the 90th cycle.

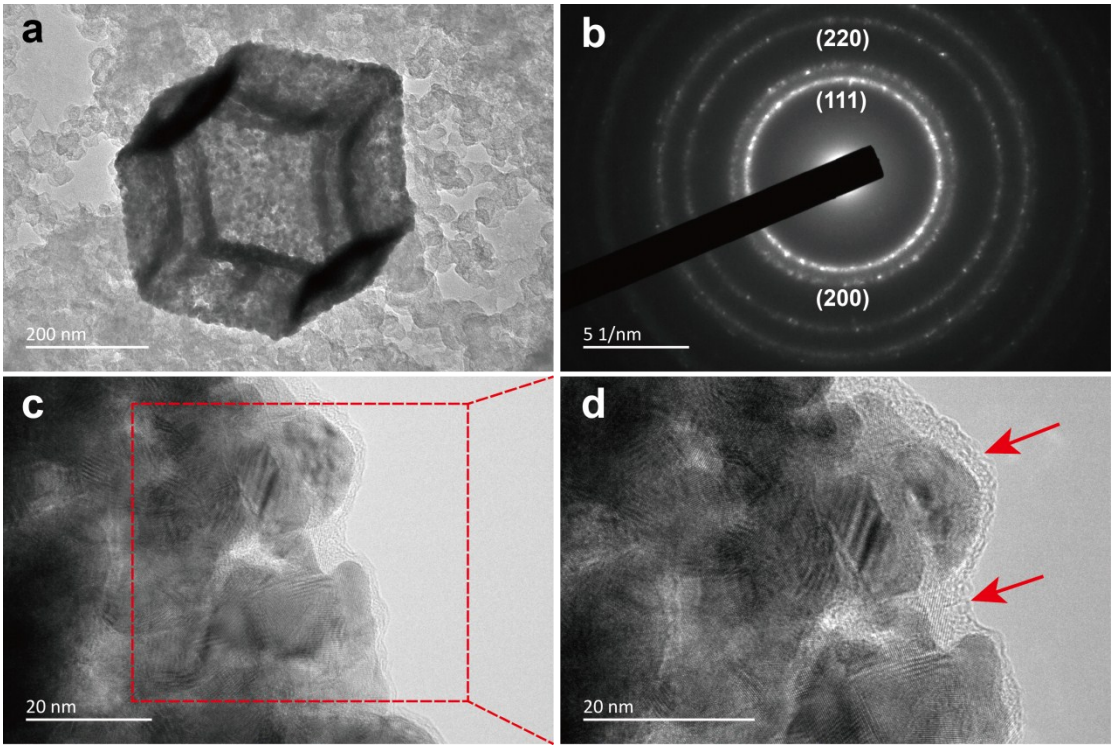

Fig. S14 (a)STEM, (b) the SAED pattern, (c) and (d) HR-TEM of PdO-Co_3O_4 nano-dodecahedron after the 90th cycle.

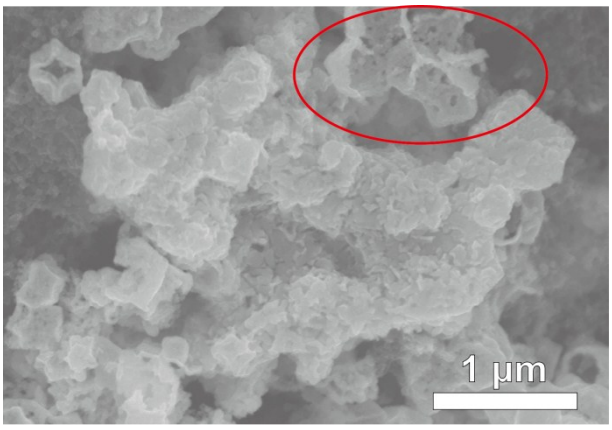

Fig. S15 SEM image of PdO-Co_3O_4 nano-dodecahedron after the 90th cycle.

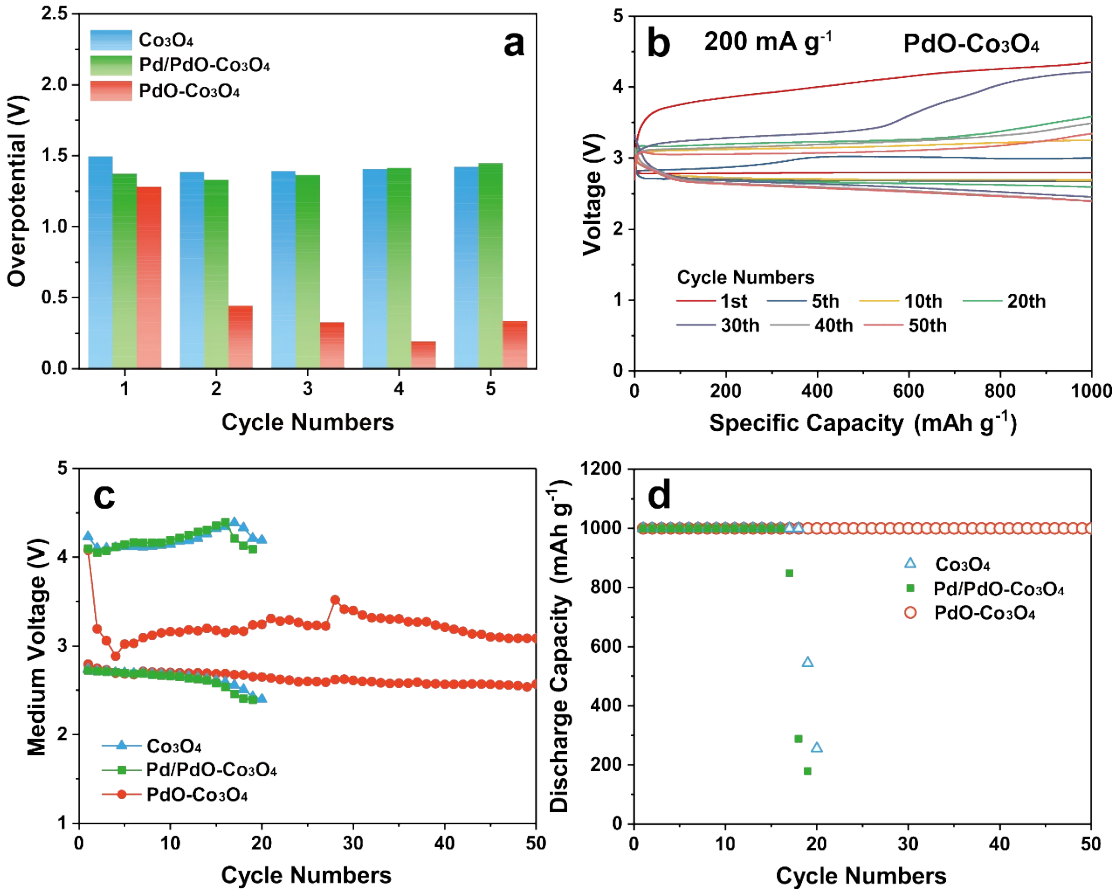

Fig. S16 (a) The value of overpotential. (b) Discharge-charge curves of PdO-Co_3O_4 nano-dodecahedrons at a current density of 200 mA/g with a cut-off capacity of 1,000 mA h/g. The corresponding curves of (c) medium voltage and (d) discharge specific capacity against cycle number.

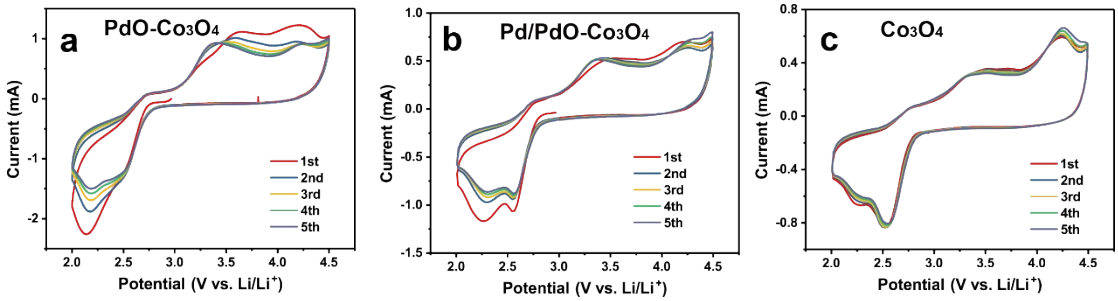

Fig. S17 CV curves of PdO-Co_3O_4, Pd/PdO-Co_3O_4 and Co_3O_4 at a sweeping rate of 5 mV/s.

Table S1 Comparison of minimum overpotential with reported catalysts.

Catalysts	Current density ($mA\ g^{-1}$)	Minimum Overpotential (V)	References
$PdO\text{-}Co_3O_4$	**200**	**0.22**	**This work**
PdCu NPs	200	0.67	[1] Energy Environ. Sci., 7, 1362 (2014)
$Pd/MnO_x/Pd$	200	0.55	[2] Adv. Sci., 2, 1500113 (2015)
$Pd/MnO_x/Pd$	70	0.29	[2] Adv. Sci., 2, 1500113 (2015)
Pd/NiO	70	0.47	[3] Nano Energy, 30, 69 (2016)
Pd/NiO	200	0.75	[3] Nano Energy, 30, 69 (2016)
Ru@MWCNTPs	500	1.04	[4] Energy Environ. Sci., 7, 1648 (2014)
$CNT@RuO_2$	385	0.72	[5] Angew. Chem. Int. Ed., 53, 442 (2014)
Ru-CNT	500	0.74	[6] Nano Lett., 15, 8084 (2015)
Pt/Co_3O_4	100	1.12	[7] ACS Cata., 5, 241 (2015)
Pt/CNTs-NF	160	1.1	[8] ACS Appl. Mater. Interfaces, 6, 12479 (2014)

References

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