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Interface Engineering of Ru-Co_3O_4 nanocomposites for Enhancing CO Oxidation

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Experimental

Synthesis of Co-MOFs

The rodlike Co-MOFs was synthesized according to the method described in the related literatures with some modifications[1]. The synthetic experiments were as follows. Solution A: 360 mg 1,3,5-Benzenetricarboxylic acid was also dissolved in an ethanol/water (20/20 ml) system under stirring to give a transparent solution. 200 mg cobalt acetate and 1.2g PVP (K-30, 0.3 g) were dissolved in an ethanol/water (20/20 ml) system under stirring to give a transparent solution. Then solution A was poured into solution B with a constant speed by using an injector (10 ml). The whole reaction process was kept at room temperature with stirring until the precipitation formed. Then the resulting solution was incubated at room temperature without interruption for 24 h. Finally, the product was centrifuged and washed three times by ethanol before drying in the vacuum drying oven.

Synthesis of Ru-Co_3O_4 interfacial structure

The Ru-doped Co-MOFs precursor was obtained via an ion-exchange reaction in the liquid phase. The as-prepared Co-MOFs nanoparticles (50 mg) were dispersed in a a ethanol/water (20/20 ml) system under agitated stirring to get an absolutely homogeneous mixed solution, followed by the addition of 1ml $RuCl_3$ solution (0.01 g/ ml $^{-1}$). After agitated stirring for 24 h in dark, the product was collected and rinsed several times by ethanol, and then dried in the vacuum drying oven. Finally, the product was pyrolyzed at 600 ° C for 2 h with a heating rate of 5 °C/min under continuous nitrogen flow and then cooled to room temperature. The gas flow was switched from N_2 to air, and the furnace was heated at a rate of 5 °C/min to 250 °C, which was maintained for 1 h in air.

Synthesis of Co_3O_4

Co_3O_4 was obtained by the thermal decomposition of Co-MOFs at 600 °C for 2 h with a temperature ramp of 5 °C / min in air.

Commercial Ru powder was Aladdin Industrial Co.

Material characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Japan Rigaku D/MAX-A X-ray diffractometer using monochromated Cu K radiation. Field emission scanning electron microscopy (FESEM) images were collected on a JEOL JSM-6700 M scanning electron microscope. Transmission electron microscopy (TEM) images recorded with a Hitachi H-800 transmission electron microscope using an accelerating voltage of 200kV, and the high resolution transmission electron microscope (HRTEM) (JEOL-2011) was operated at an acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K (Micromeritics ASAP 2020) using the Brunauer–Emmett –Teller (BET) method, while the pore volume and pore size were calculated according to the Barrett–Joyner–Halenda (BJH) formula applied to the adsorption branch. Thermogravimetric analysis (TGA) was carried out using a Shimadzu-50 thermoanalyser under air flow. X-ray photoelectron spectroscopy (XPS) studies were carried out on a VGESCALAB MKII X-ray photoelectron spectrometer using an Al Kα excitation source.

Catalytic performance measurements

The catalytic activity of Ru-Co_3O_4 interfacial structure for the oxidation of CO was carried out using a fixed-bed flow reactor. For a typical measurement, 50 mg of catalyst was loaded into the reactor. And the reaction gas consisting of 1% CO and 99% dry air was fed at a rate of 30 mL/min. The catalyst was heated to the desired reaction temperature at a rate of 2 °C/min and then kept there for 30 min until the catalytic reaction reached a steady state. Then the composition of effluent gas was analyzed with an online GC-14B gas chromatograph. The conversion of CO was calculated from the change in CO concentration of the inlet and outlet gases.

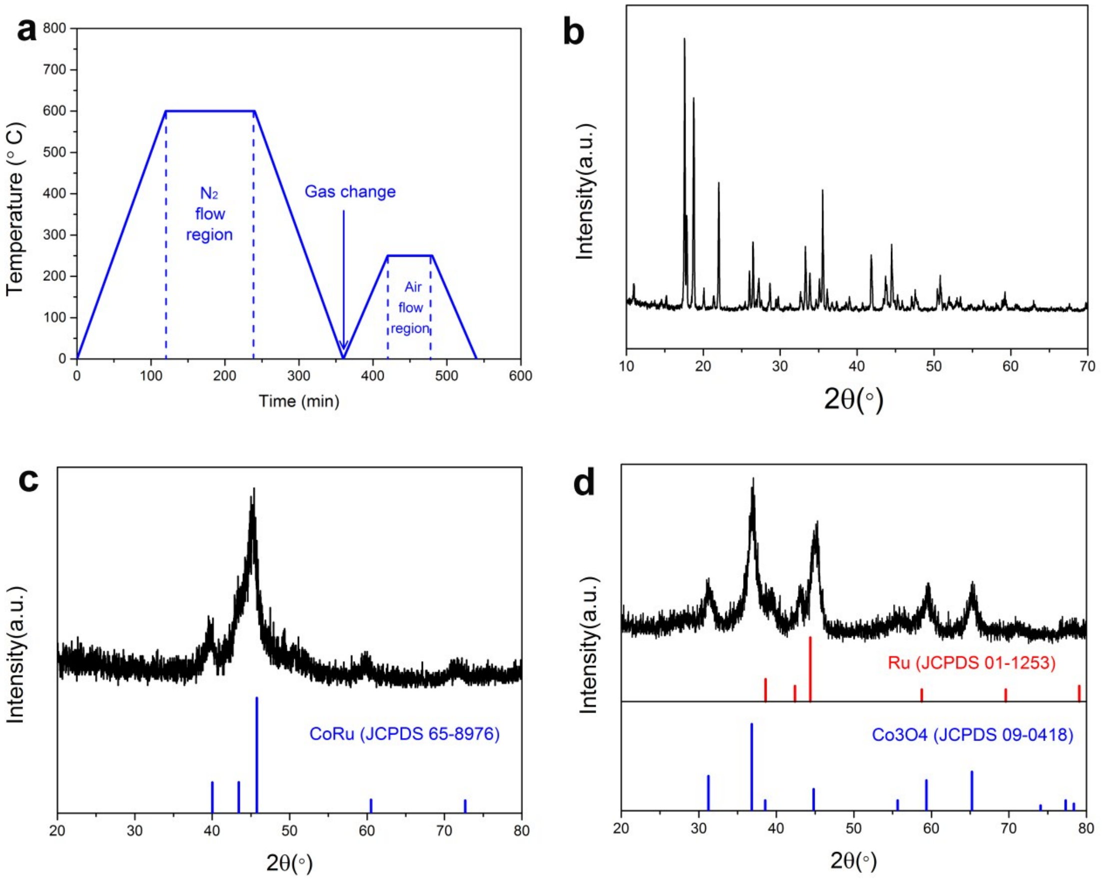

Figure S1 (a) The synthesis procedure of the Ru-Co_3O_4 interfacial structure derived from the Co-MOFs via a thermal transformation process, (b) XRD patterns of Co-MOFs, (c) XRD patterns of CoRu alloy, (d) XRD patterns of Ru-Co_3O_4 interfacial structure.

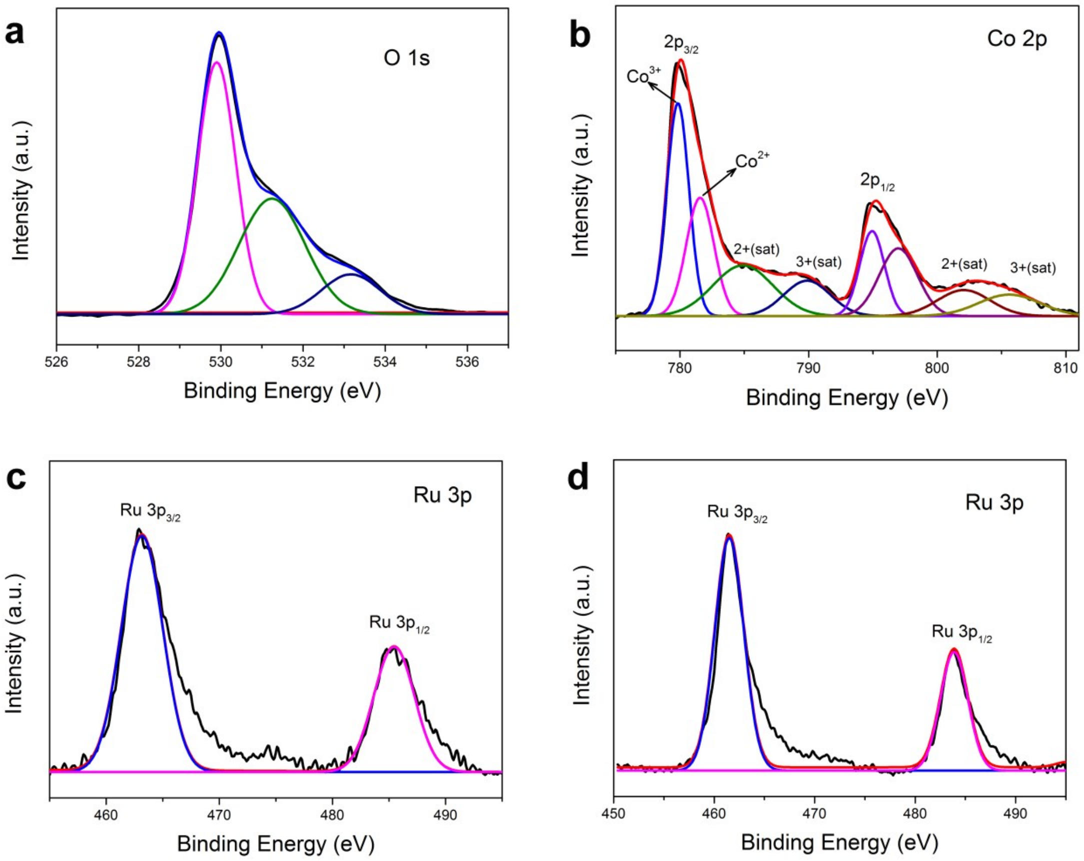

Figure S2 XPS spectra (a,b,c) of the as-prepared Ru-Co_3O_4 interfacial structure: (a) O 1s binding energy spectrum, (b) Co 2p binding energy spectrum, (c) Ru 3p binding energy spectrum.(d) XPS spectra of pure ruthenium.

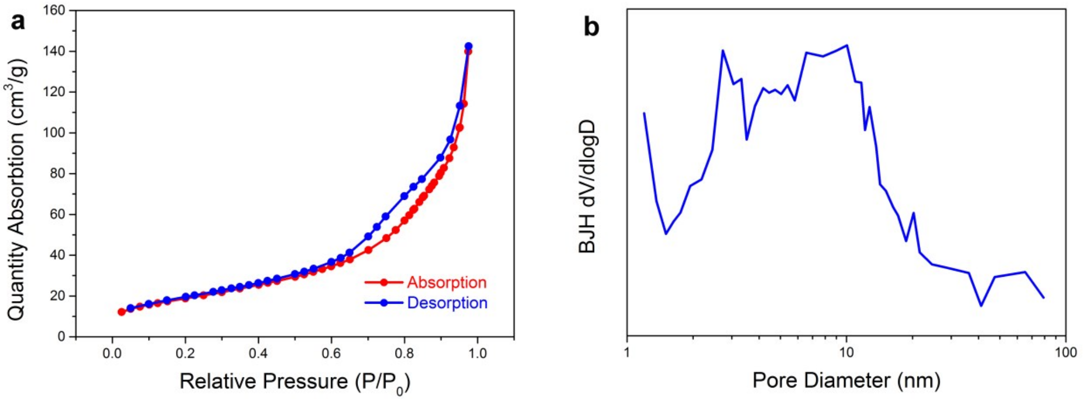

Figure S3 (a) Nitrogen adsorption/desorption isotherm of the Ru-Co_3O_4 interfacial structure, (b) Barrett–Joyner–Halenda (BJH) pore size distribution plot of the Ru-Co_3O_4 interfacial structure.

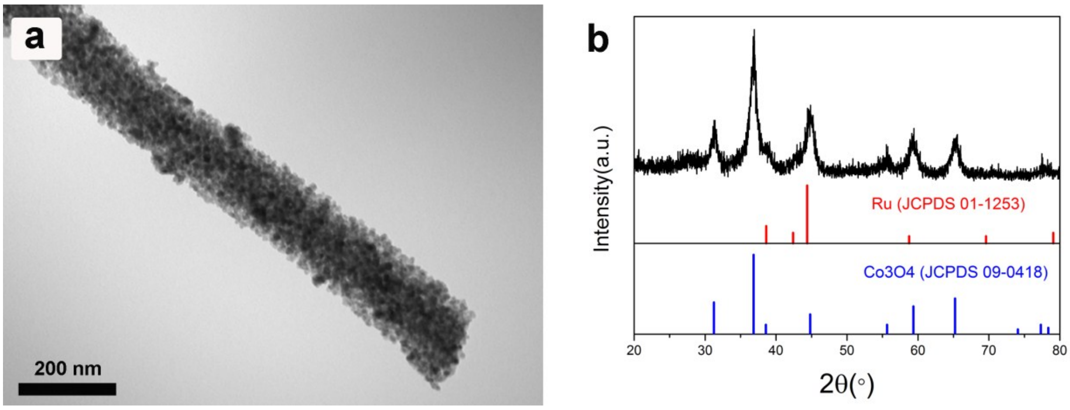

Figure S4 (a) The TEM image and (b) the XRD pattern of of the Ru-Co_3O_4 interfacial structure after the CO oxidation stability test for 60h.

Calculation method

All theoretical calculations were based on density functional theory by using the Vienna Ab-initio Simulation Package (VASP)[2]. The exchange-correlation potential was described by the generalized-gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional[3]. To ensure the accuracy of the calculated results, the cutoff energy was set to 400 eV for the plane-wave expansion of the electronic wave function. All structures were optimized with a convergence criterion of 1×10^{-4} eV for the energy and 0.05 eV/Å for the forces. Brillouin-zone integration was performed with 3 × 3 × 1 Monkhorst-Pack grid. The reaction pathway and activation barriers were calculated using the nudged elastic band (NEB) method. The charge density difference, ρ_{diff}, on the Co_3O_4 surface before and after Ru deposition was calculated following Equation 1.

$$\rho_{diff} = \rho(\text{Ru}/Co_3O_4) - \rho(Co_3O_4) - \rho(\text{Ru}) \qquad \text{Eq. 1}$$

The adsorption energy (E_{ads}) was calculated using Equation 2.

$$E_{ads} = E_{total} - E_{substrate} - E_{gas\ phase\ adsorbate} \qquad \text{Eq. 2}$$

where E_{total} is the calculated total energy of the adsorption system, $E_{substrate}$ is the energy of the clean substrate and $E_{gas\text{-}phase\ adsorbate}$ is the energy of the gas-phase molecule.

Table S1 The comparison of the catalytic properties for CO oxidation of some related catalysts and our Ru-Co_3O_4 interfacial structure.

Catalysts	T_{100}/°C	Reference
Ru-Co_3O_4	75	This work
Pt@C/SiO_2	138	Carbon, 2016, 101, 324-330.
Pd/ZnO	160	Nano Res. 2011, 4(1): 83-91
Ag-CuO	>150	J. Am. Chem. Soc. 2014, 136, 14650-14653
Pd/ZrO_2-SiO_2	205	Angew. Chem. Int. Ed. 2015, 54, 13263-13267

Table S2 Bader charge analysis of Ru-Co_3O_4

Atom	Charge	Atom	Charge
Co1	8.2730	O15	6.8973
Co2	7.9739	O16	6.9429
Co3	7.8269	O17	6.8981
Co4	7.8582	O18	6.9154
Co5	7.8255	O19	6.8246
Co6	7.8513	O20	6.8564
Co7	7.8768	O21	6.9833
Co8	7.6895	O22	6.8936
Co9	7.6865	O23	6.9835
Co10	8.2760	O24	6.8960
Co11	7.9816	O25	6.8626
Co12	7.8224	O26	6.8948
Co13	7.8535	O27	6.9026
Co14	7.9179	O28	6.8109
Co15	7.8506	O29	6.9024
Co16	7.8979	O30	6.8097
Co17	7.6894	O31	6.8267
Co18	7.6841	O32	6.8381
Co19	8.2755	O33	6.9860
Co20	7.7934	O34	6.8172
Co21	7.8269	O35	6.9870
Co22	7.8524	O36	6.8480
Co23	7.9486	O37	6.8696
Co24	7.8510	O38	6.8891
Co25	7.8649	O39	6.9024
Co26	7.6853	O40	6.8090
Co27	7.6856	O41	6.9021
Co28	8.2756	O42	6.8167
Co29	7.7928	O43	6.8259
Co30	7.8310	O44	6.8426
Co31	7.8534	O45	6.9848
Co32	7.8631	O46	6.8343
Co33	7.8498	O47	6.9846
Co34	7.8303	O48	6.8624
Co35	7.6851	Ru1	8.0038
Co36	7.6860	Ru2	8.0372
O1	6.8640	Ru3	8.0639
O2	6.8826	Ru4	7.7091
O3	6.8989	Ru5	7.7130
O4	6.9391	Ru6	8.0211
O5	6.8987	Ru7	7.7849
O6	6.9076	Ru8	7.7164
O7	6.8340	Ru9	7.6845

O8	6.8477	Ru10	8.0955
O9	6.9782	Ru11	8.0461
O10	6.9081	Ru12	7.7491
O11	6.9754	Ru13	7.9923
O12	6.8746	Ru14	7.4448
O13	6.8573	Ru15	8.0054
O14	6.8804		

Table S3 Bader charge analysis of O_2 molecule adsorbed on Ru-Co_3O_4

Atom	Charge	Atom	Charge
Co1	8.2739	O16	6.9605
Co2	7.9776	O17	6.8935
Co3	7.8211	O18	6.8981
Co4	7.8615	O19	6.8288
Co5	7.9486	O20	6.8478
Co6	7.8540	O21	6.9814
Co7	7.9059	O22	6.8744
Co8	7.6840	O23	6.9838
Co9	7.6905	O24	6.9079
Co10	8.2729	O25	6.8705
Co11	8.0516	O26	6.9170
Co12	7.8215	O27	6.9019
Co13	7.8532	O28	6.7985
Co14	7.9686	O29	6.9000
Co15	7.8414	O30	6.7515
Co16	7.9092	O31	6.8154
Co17	7.6909	O32	6.833
Co18	7.6793	O33	6.9862
Co19	8.2742	O34	6.8467
Co20	7.8057	O35	6.9904
Co21	7.8254	O36	6.8310
Co22	7.8491	O37	6.8674
Co23	7.8855	O38	6.9163
Co24	7.8518	O39	6.9035
Co25	7.7943	O40	6.8115
Co26	7.7042	O41	6.9017
Co27	7.6838	O42	6.8171
Co28	8.2727	O43	6.8252
Co29	7.7835	O44	6.8420
Co30	7.8208	O45	6.9837
Co31	7.8543	O46	6.7860
Co32	7.7042	O47	6.9851
Co33	7.8508	O48	6.8251
Co34	7.7889	O49	6.4388

Co35	7.6872	O50	6.3659
Co36	7.6801	Ru1	8.0255
O1	6.8579	Ru2	8.0097
O2	6.9182	Ru3	7.8940
O3	6.8999	Ru4	7.5415
O4	6.9173	Ru5	7.8696
O5	6.9009	Ru6	7.9792
O6	6.8975	Ru7	7.7031
O7	6.8316	Ru8	7.6942
O8	6.8610	Ru9	7.5449
O9	6.9740	Ru10	8.1473
O10	6.8813	Ru11	7.9531
O11	6.9784	Ru12	7.6058
O12	6.9107	Ru13	7.9672
O13	6.8565	Ru14	7.4729
O14	6.8813	Ru15	8.0230
O15	6.8925		

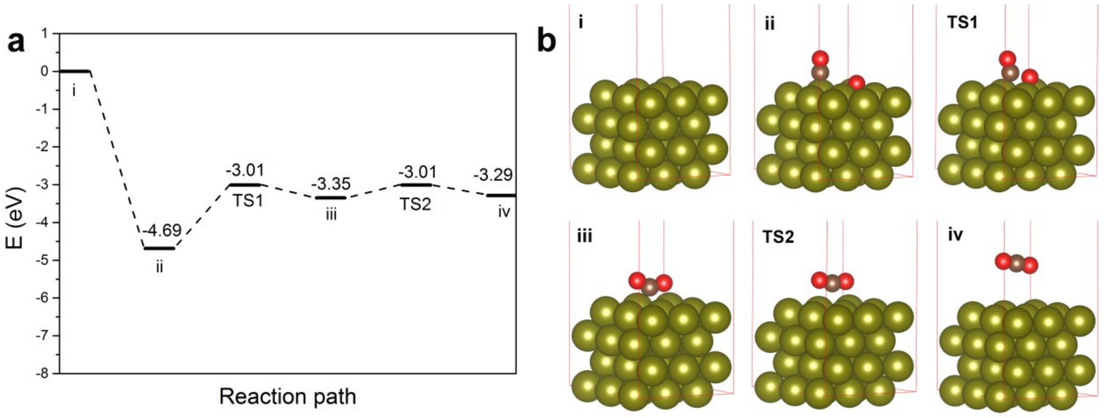

Figure S5 Reaction mechanism for CO oxidation on pure Ru. (a) Reaction pathways, (b) configurations of reactants, intermediates and products. The catalytic processes proceed as the following steps: (1) i–ii, O and CO co-adsorb at the Ru(001) surface, (2) ii-TS1-iii, CO is oxidized by co-adsorbed O, forming a bent intermediate, (3) iii-TS2-iv, CO2 desorbs into the gas phase.

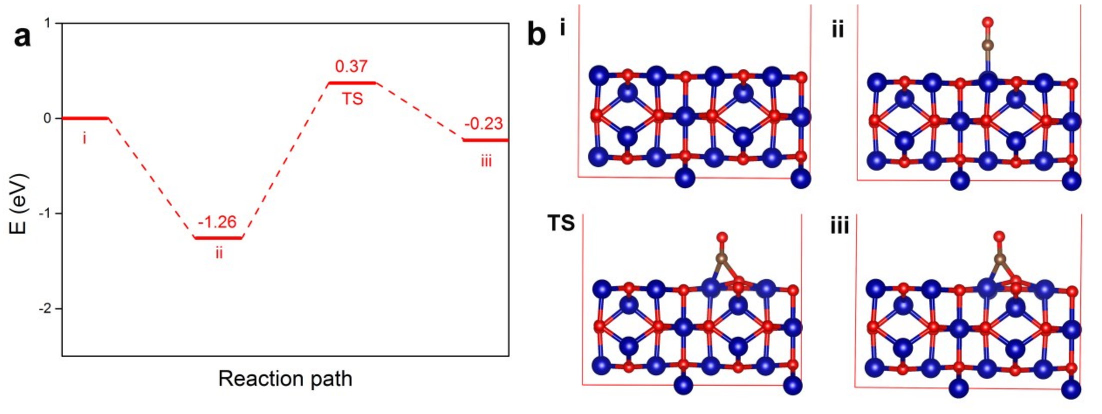

Figure S6 Reaction mechanism for CO oxidation on Co_3O_4. (a) Reaction pathways, (b) configurations of reactants, intermediates and products. The catalytic processes proceed as the following steps: (1) i–ii, CO adsorb at the Co_3O_4 (110) surface, (2) ii-TS-iii, CO is oxidized by a lattice oxygen atom of Co_3O_4.

Reference

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3. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865-3868.