Supporting Information

Surface Differences of Oxide Nanocrystals Determined by Geometry and Exogenously Coordinated Water Molecules

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Supporting References

Section A: Supporting methods

Characterization

Synchrotron X-ray diffraction measurements were conducted at Beamline BL14B1 of Shanghai Synchrotron Radiation Facility (SSRF) in China with a medium energy (18 keV, k = 0.6887 Å) X-ray beam (200 μm × 200 μm). The aberration-corrected (*C*s) field emission Scanning Transmission Electron Microscope (STEM) (Hitachi HF5000, 200 kV) was utilized to acquire the bright field (BF) imaging with a collection angle of β < 4.9 mrad, and the secondary electron (SE) images of surface morphology were recorded simultaneously. Conventional high-resolution transmission electron microscopy (HRTEM) experiments were carried out on a JEOL JEM-2010 instrument with an acceleration voltage of 200 kV. Brunauer-Emmett-Teller (BET) surface area data was recorded on a Micromeritics ASAP 2020 system based on N_2 adsorption isotherms. X-ray Photoelectron Spectra (XPS) were collected on a Thermo ESCALAB 250 X instrument using monochromatic Al Kα radiation (1486.6 eV) as the excitation source. The binding energies were referenced to C 1s at 284.8 eV. The amount of Na cations was checked on an Optima 5300DV inductively coupled plasma mass spectrometer (ICP-MS). The amount of species containing N was determined on a Heraeus CHN-0-Rapid elemental analyzer. The N content was determined with a Heraeus CHN-0-Rapid analyzer.

Dynamic nuclear polarization (DNP) NMR spectroscopy

^{17}O DNP NMR experiments were conducted on a 14.1 T Bruker Avance III HD 600 spectrometer equipped with a 395 GHz gyrotron microwave source. Radical solution (16 mM TEKPol[1] in dried tetrachloroethane, TCE) was mixed with ^{17}O-labeled ceria NRs700 and NRs300 in an Ar glove box. ^{17}O chemical shift is referenced to bulk ceria at 875 ppm.

^{1}H Solid-state NMR spectroscopy

^{1}H magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were measured on a 9.4 T Bruker Avance III 400 spectrometer. The Larmor frequency for ^{1}H is 400 MHz. Every sample was packed into a ZrO_2 rotor in a N_2-filled glove box. ^{1}H shift was referenced to adamantane at 1.92 ppm.

DFT Calculations

Spin-polarized DFT calculations were conducted via the *Vienna Ab initio Simulation Package* (*VASP*),[2] utilizing the Perdew-Burke-Ernzerhof (PBE) functional[3] with a Hubbard *U* correction (PBE + *U*).[4] The effective *U* value to the localized Ce 4*f* orbitals was 5.0 eV.[5,6] The core interacts with valence electrons was described with the projector augmented wave (PAW) methodology.[7] The plane-wave kinetic energy cutoff was 500 eV. Geometry optimizations were terminated by the Hellman−Feynman force on each relaxed ion reached 0.02 eV·Å^{-1}. 10^{-5} eV of the convergence criterion for electronic minimization was applied for geometry optimizations and 10^{-8} eV for chemical shift and electric field gradient (EFG) calculations.[8] The lattice parameter of ceria was optimized to 5.448 Å, consisting with the experimental values of ~ 5.410 Å.

The ceria (110) surfaces were simulated by 12-oxygen-layer surface slabs (six O-Ce-O tri-layers) with a (2 × 2) surface cell, using the DFT-D3 method[9] to connect the water molecules with the ceria surfaces.

The experimental quadrupole moment (Q) of -0.02558 barns[10] for ^{17}O was used to calculate the ^{17}O quadrupolar parameters (C_Q and η). The isotropic chemical shifts (δ_{iso}) were simulated by the following equation

$$\delta_{iso} = \delta_{cal} + \delta_{ref}$$

where δ_{cal} is the unaligned DFT chemical shift and δ_{ref} represents the reference chemical shift.

Section B: Characterization of the ceria NRs700 and NRs300 (XRD, XPS, surface area and composition)

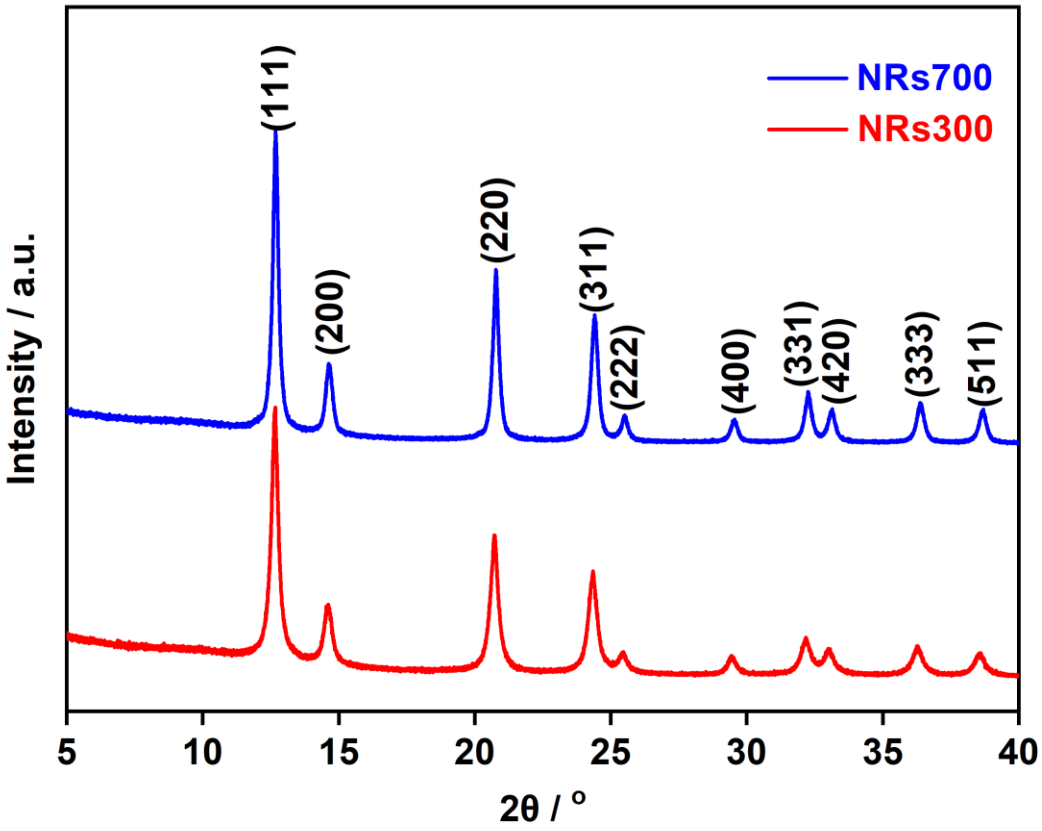

Fig. S1 Synchrotron powder XRD patterns of ceria NRs700 and NRs300.

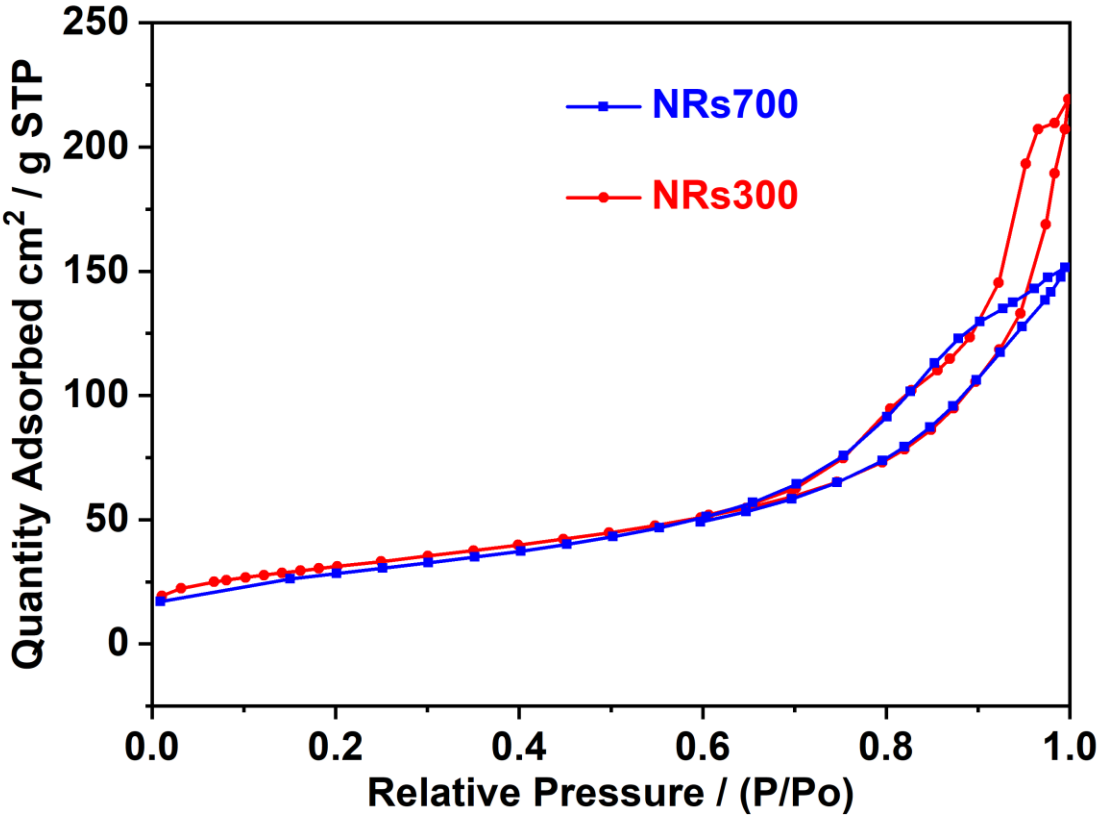

Fig. S2 N_2 sorption isotherms of ceria NRs700 and NRs300.

Table S1 Some properties of ceria NRs700 and NRs300.

Sample	Na Content[a] / wt %	N Content[b] / wt %	S_{BET}[c] / $m^2 \cdot g^{-1}$
NRs700	< 0.1	< 0.1	110.9
NRs300	< 0.1	< 0.1	132.7

[a] Na contents were determined with an inductively coupled plasma mass spectrometry (ICP-MS);

[b] N contents were recorded at a CHN-0-Rapid elemental analyzer;

[c] The surface area (S_{BET}) data is obtained from the N_2 sorption isotherms shown in Fig. S3.

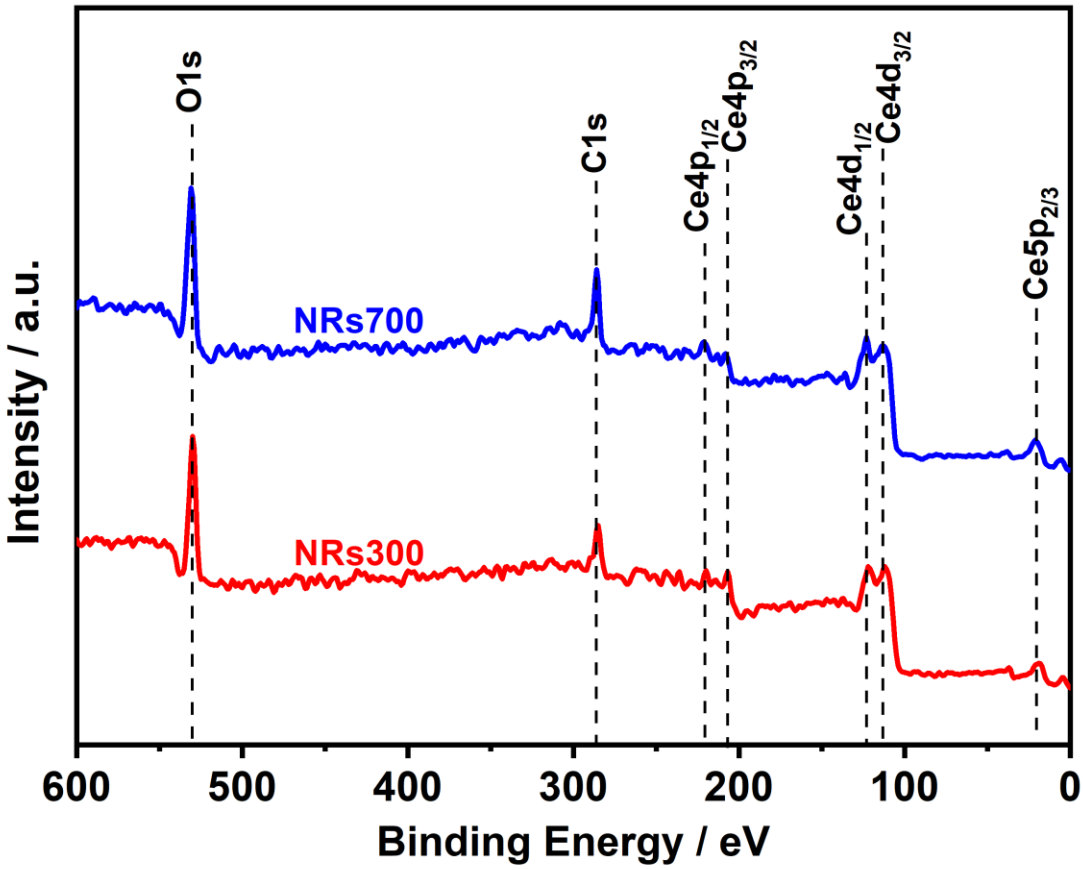

Fig. S3 Full XPS spectra of ceria NRs700 and NRs300.

Section C: ^{17}O NMR spectra of ceria NRs700 and NRs300 isotopically labeled with $^{17}O_2$.

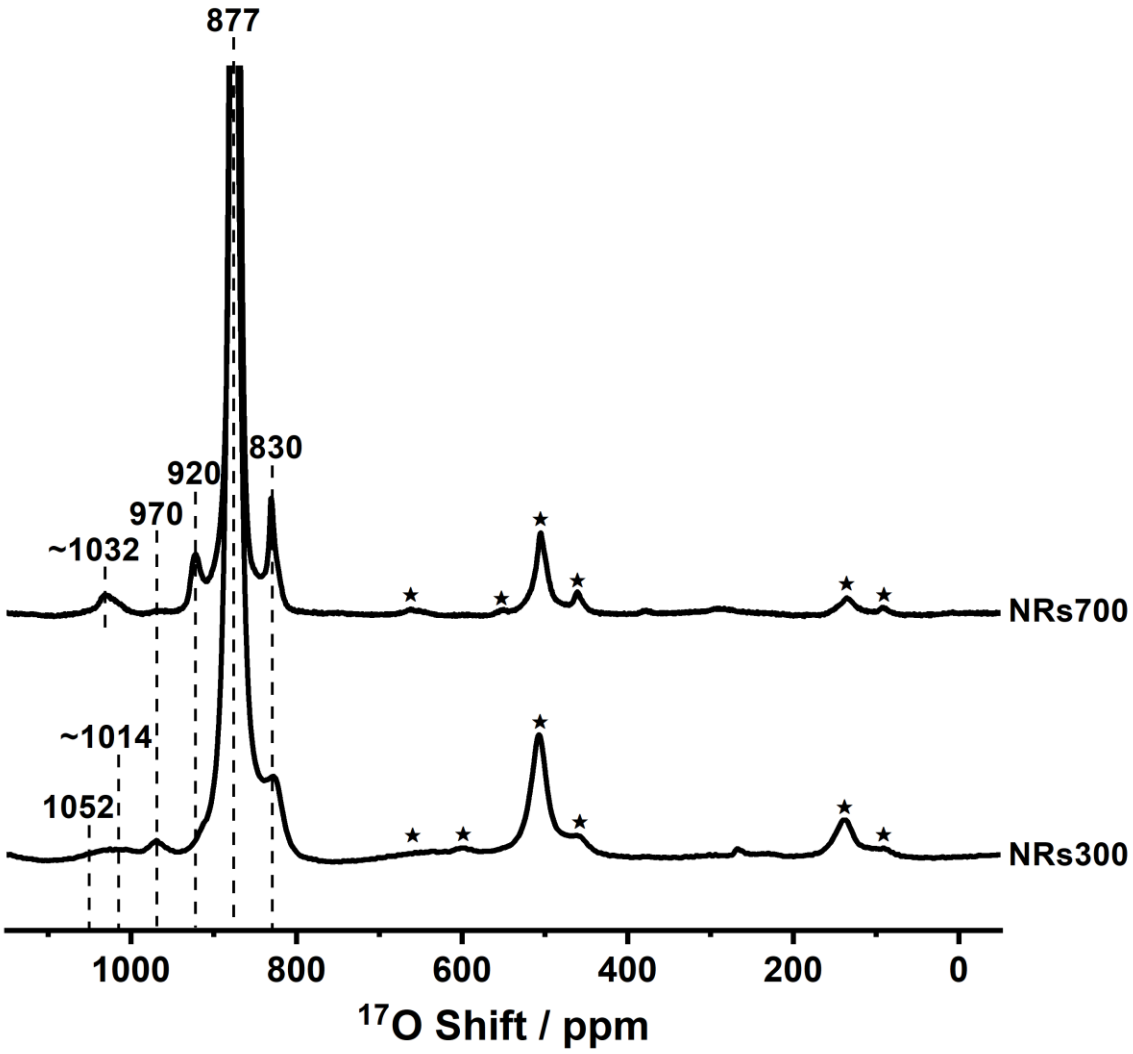

Fig. S4 Untruncated ^{17}O solid-state NMR spectra of the highly ^{17}O-labeled ceria NRs700 and NRs300. Asterisks represent spinning sidebands.

Section D: DFT calculations of ^{17}O NMR parameters on pristine ceria (110) O-t surfaces (pristine and reconstructed)

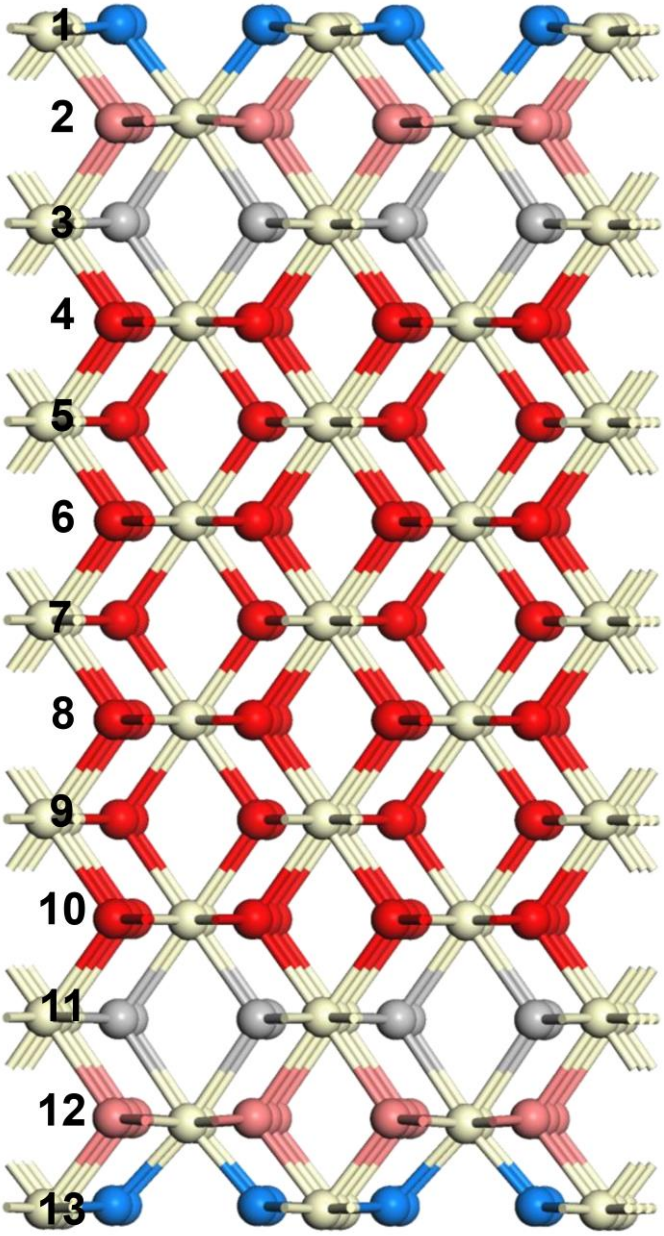

Fig. S5 Calculated structure of clean pristine ceria (110) O-t surface. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

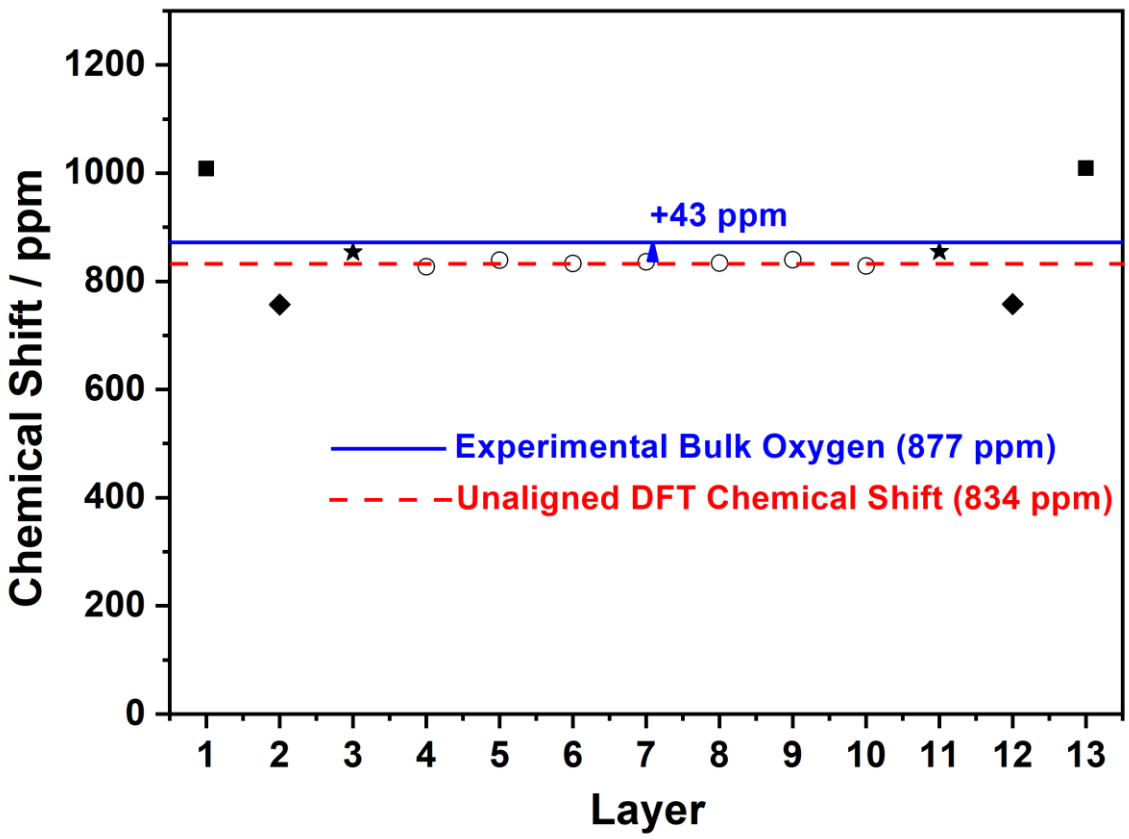

Fig. S6 The determination of the ^{17}O reference chemical shift (δ_{ref}) from clean pristine ceria (110) O-t surface. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S2 Simulated ^{17}O NMR parameters for oxygen ions in clean pristine ceria (110) O-t surface. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and calculated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. δ_{CG} is simulated according to Lippmaa[11] at 9.4 T including the second order quadrupolar shift. The corresponding structure has been shown in Fig. S5.

O_{ion} No.	**δ_{iso} / ppm**	**C_Q / MHz**	**η**	**δ_{CG} / ppm**	**Assignment**
1	1052	0.64	0.19	1052	1st Layer O_{3C}
2	800	0.26	0.39	800	2nd Layer O_{4C}
3	897	0.18	0.84	897	3rd Layer O_{4C}
4	870	0.07	0.15	870	Bulk Like
5	882	0.07	0.94	882	Bulk Like
6	876	0.05	0.16	876	Bulk Like
7	879	0.06	0.80	879	Bulk Like
8	877	0.05	0.13	877	Bulk Like
9	883	0.08	0.94	883	Bulk Like
10	871	0.07	0.22	871	Bulk Like
11	898	0.18	0.88	898	11th Layer O_{4C}
12	801	0.26	0.40	801	12th Layer O_{4C}
13	1053	0.63	0.19	1053	13th Layer O_{3C}

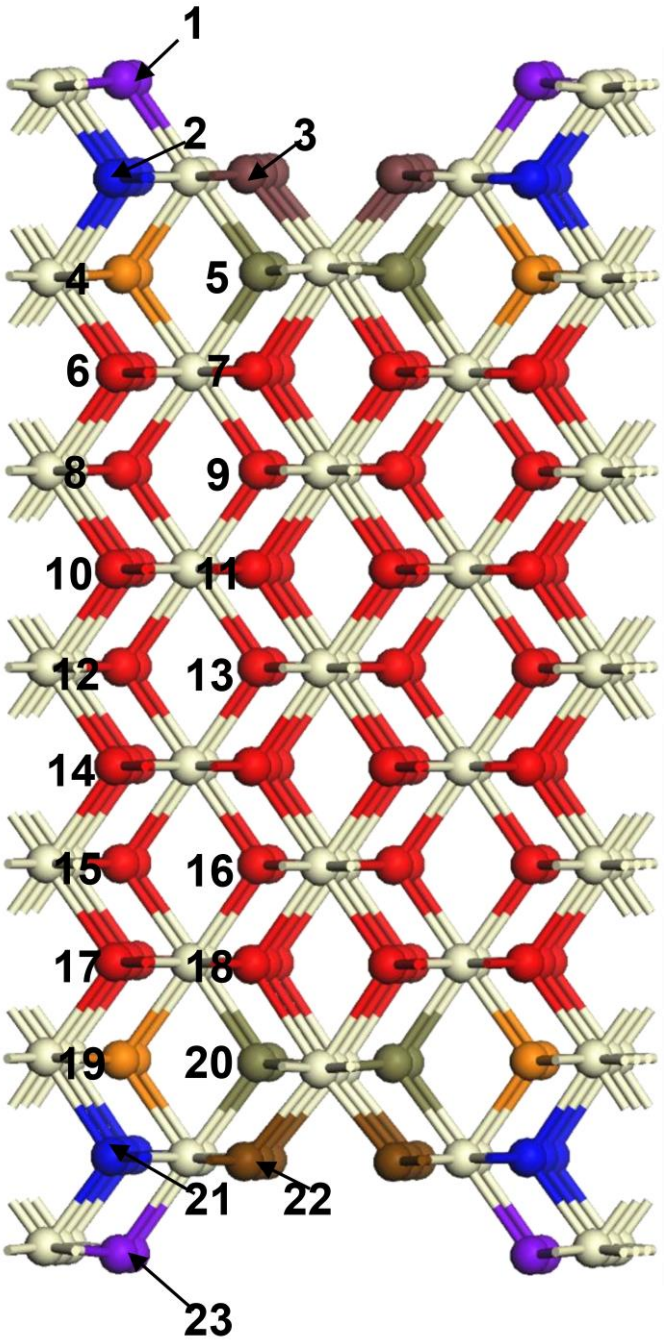

Fig. S7 Calculated structure of clean reconstructed ceria (110) O-t surface. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

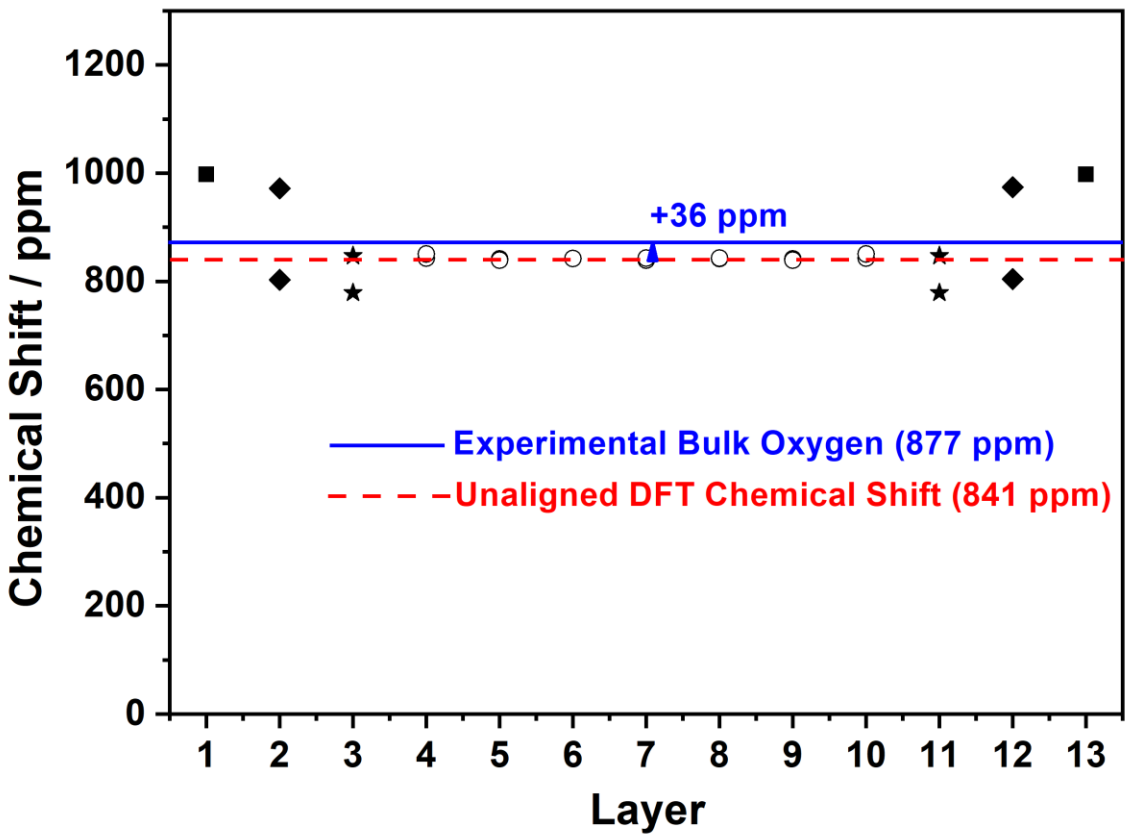

Fig. S8 The determination of the ^{17}O reference chemical shift (δ_{ref}) from clean reconstructed ceria (110) O-t surface. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S3 Simulated ^{17}O NMR parameters for oxygen ions in clean reconstructed ceria (110) O-t surface. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and simulated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. The corresponding structure has been showed in Fig. S7.

O_{ion} No.	δ_{iso} / ppm	C_Q / MHz	η	δ_{CG} / ppm	Assignment
1	1033	0.61	0.48	1033	1st Layer O_{3C}
2	838	0.12	0.76	838	2nd Layer O_{4C}
3	1009	0.15	0.76	1008	2nd Layer O_{4C}
4	813	0.17	0.79	813	3rd Layer O_{4C}
5	881	0.12	0.99	881	3rd Layer O_{4C}
6	878	0.15	0.95	878	Bulk Like
7	885	0.10	0.66	884	Bulk Like
8	876	0.11	0.31	876	Bulk Like
9	873	0.11	0.62	873	Bulk Like
10	876	0.10	0.35	876	Bulk Like
11	877	0.13	0.12	877	Bulk Like
12	873	0.13	0.11	873	Bulk Like
13	878	0.14	0.49	878	Bulk Like
14	877	0.13	0.41	877	Bulk Like
15	875	0.13	0.12	875	Bulk Like
16	873	0.11	0.65	873	Bulk Like
17	877	0.11	0.38	877	Bulk Like
18	884	0.10	0.70	884	Bulk Like
19	814	0.11	0.44	814	11th Layer O_{4C}
20	881	0.17	0.75	881	11th Layer O_{4C}
21	838	0.12	0.54	838	12th Layer O_{4C}
22	1009	0.12	0.70	1008	12th Layer O_{3C}
23	1033	0.20	0.44	1033	13th Layer O_{3C}

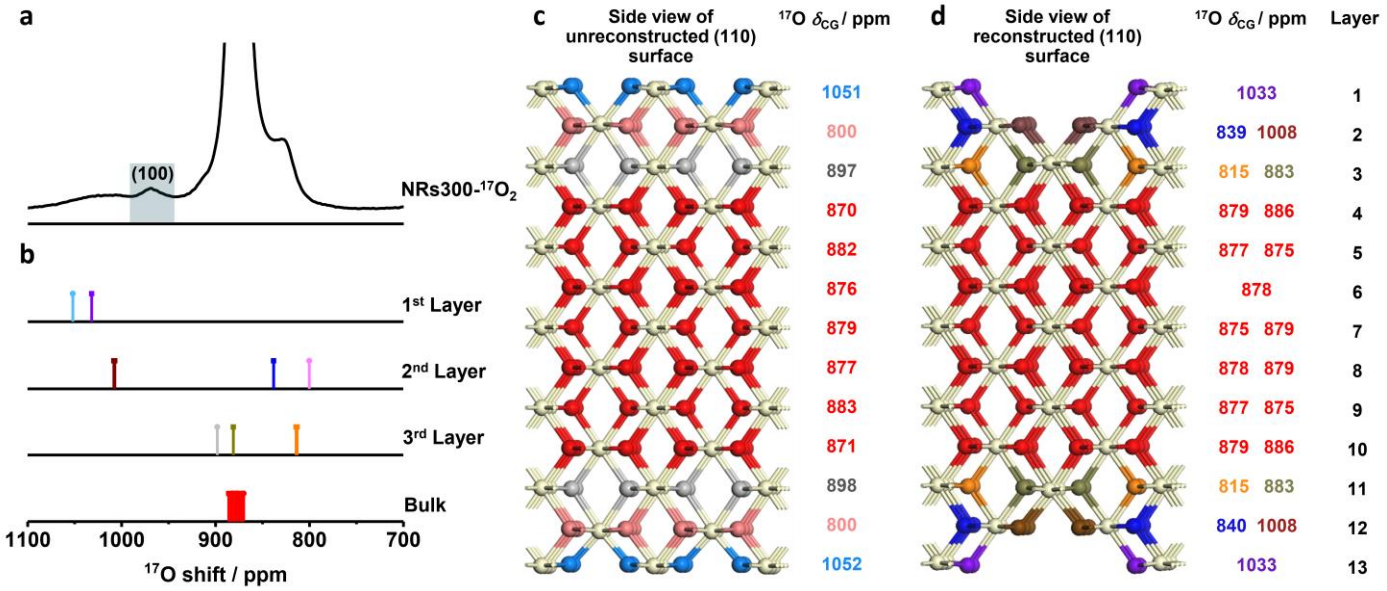

Fig. S9 ^{17}O NMR spectra, calculated ^{17}O NMR shifts and the clean O-t structure model of ceria. (a) ^{17}O solid-state NMR spectra of ceria NRs300-$^{17}O_2$. (b) The summarized ^{17}O NMR shifts (δ_{CGS}) predicted with DFT simulations for clean pristine and reconstructed ceria models with (110) O-t surfaces presented in (c) and (d), respectively. (c,d) Pristine and reconstructed models employed in DFT simulations with calculated shifts (δ_{CGS}) for oxygen ions and the layer numbers displayed on the right. The spheres representing bulk oxygen, cerium and hydrogen ions consist with the color in Fig. S5 and S7. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Tables S2 and S3.

Section E: Direct DNP ^{17}O and conventional ^{1}H NMR data of ceria NRs700 and NRs300.

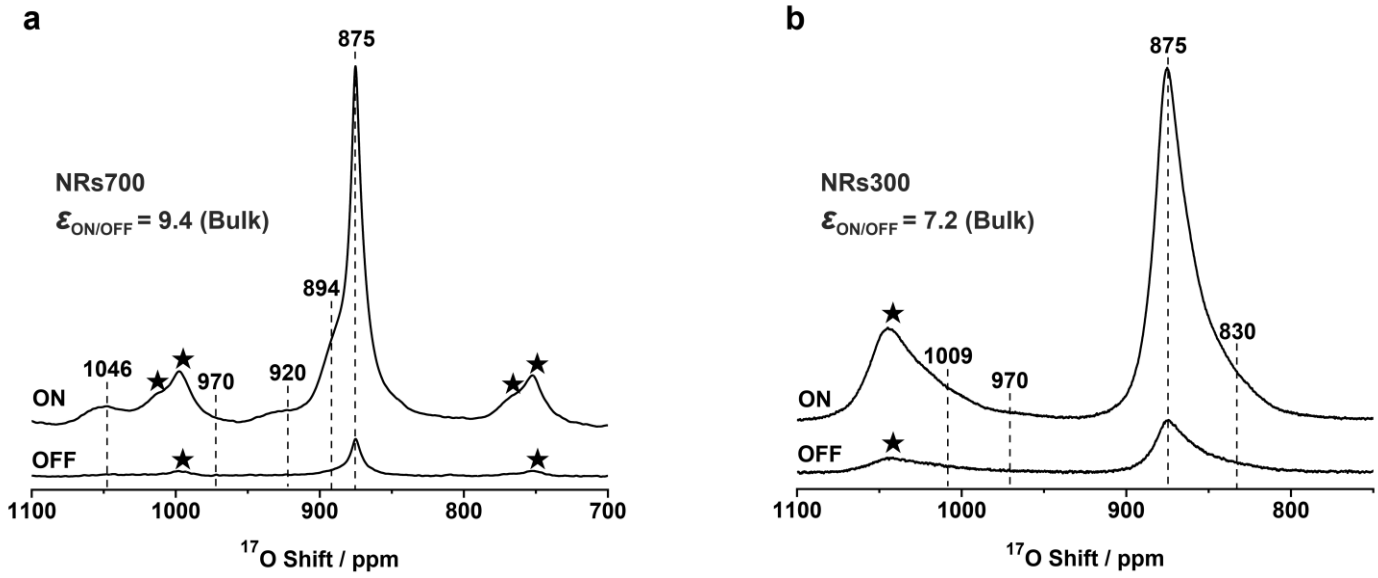

Fig. S10 Direct DNP spectra of ^{17}O-labeled ceria (a) NRs700 and (b) NRs300 with and without microwave irradiation. The spectra were recorded at spinning speeds of 13.9 kHz and a recycle delay of 60 s using a pre-saturated rotor synchronized Hahn-echo pulse sequence (π/2-τ-π-τ-acquisition). Asterisks represent spinning sidebands.

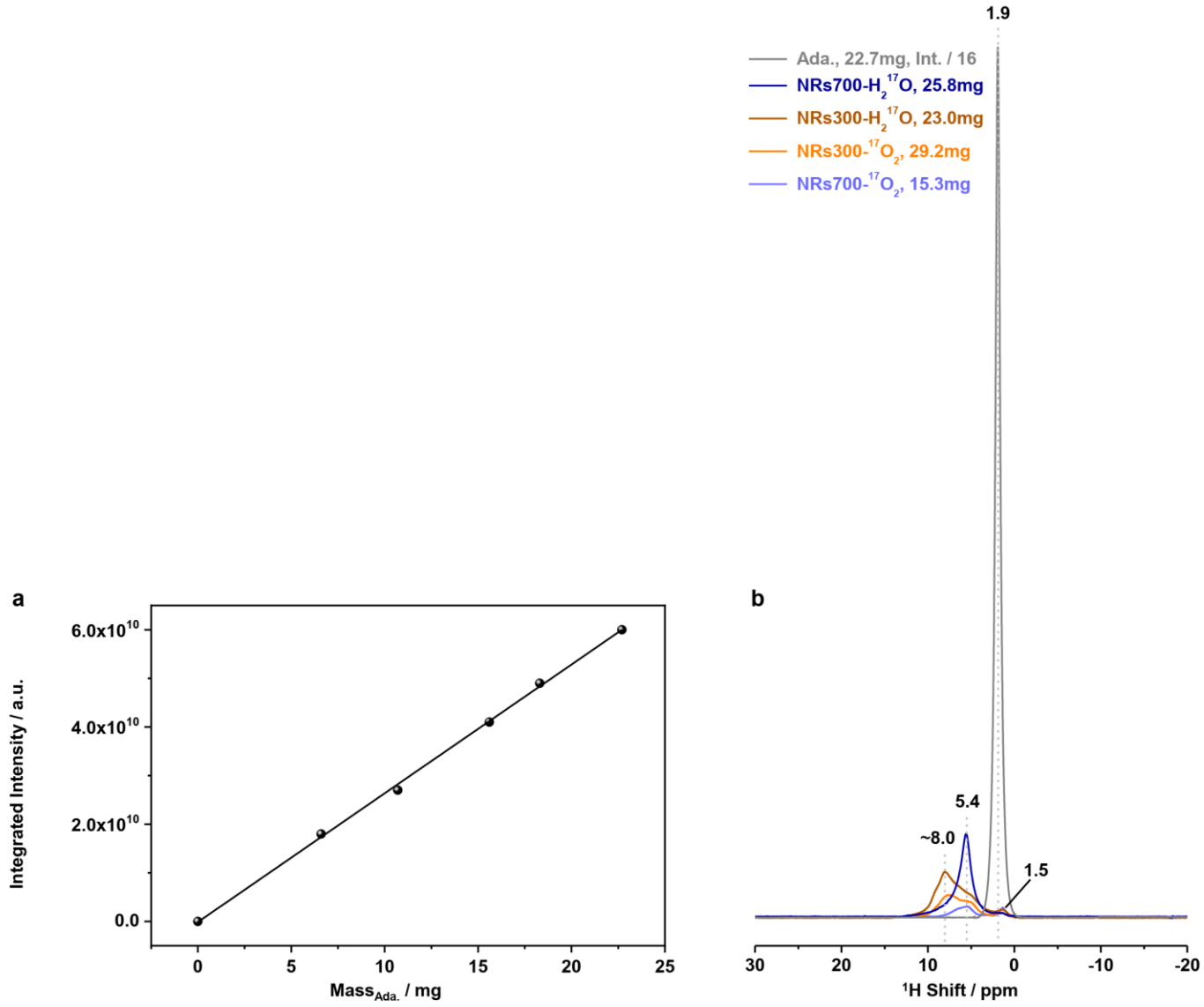

Fig. S11 Interpolation approach for measuring the content of hydrogen on ceria NRs700 and NRs300 from quantitative ^{1}H NMR, employing adamantane as the reference material.[12,13] (a) The integrated intensity of ^{1}H NMR peaks as a function of the mass of center-packed adamantine. The integral range of 30 ~ -20 ppm is shown. The number of scans recorded for each spectrum was 1024 with a spinning speed of 20 kHz. A saturated recycle delay of 16 s was used to satisfy quantitative measurement. The linear correlation between peak intensity (y / a.u.) of the spectra and the content of hydrogen atoms (x / mg) is $y = -1.2 \times 10^{8} + 2.6 \times 10^{9}$ x. (b) ^{1}H NMR spectra of adamantine, the ceria NRs700 and NRs300 enriched with $^{17}O_2$ and $H_2{}^{17}O$, respectively. The identical integral range, spinning frequency, and number of scans were utilized with a saturated recycle delay of 4 s.

Table S4 The coverage of hydrogen on the surfaces of ceria NRs700 and NRs300 respectively enriched with $^{17}O_2$ and $H_2{}^{17}O$.[a]

Sample	Mass / mg	Intensity of 1024 Scans / a.u.	Total Content of Hydrogen / mol·g^{-1}	Concentration of H_2O[b] / surface unit^{-1}
Adamantane	22.7	6.0×10^{10}	1.2×10^{-1}	—
NRs700-$^{17}O_2$	15.3	8.4×10^{7}	2.5×10^{-4}	0.3
NRs300-$^{17}O_2$	29.2	5.4×10^{8}	8.4×10^{-4}	1.4
NRs700-$H_2{}^{17}O$	25.8	1.6×10^{9}	2.9×10^{-3}	4.0
NRs300-$H_2{}^{17}O$	23.0	8.1×10^{8}	1.6×10^{-3}	2.6

[a] The concentrations of hydrogen are quantified with the interpolation method employing adamantane as the reference material;[12,13]

[b] The coverage of Hydrogen is acquired from the following formula:

The concentration of H_2O (surface unit^{-1}) = Total Content of Hydrogen (mol·g^{-1}) × N_A / S_{BET} (m^2·g^{-1}) × S_{Unit} (m^2) / 2, where N_A represents the Avogadro constant (6.02×10^{23} mol^{-1}), S_{BET} is the sample surface area from BET (see Table S1), and S_{Unit} denotes the surface area of one surface unit. Note that the surface units of ceria (111), (110), and (100) surfaces are 51.3, 83.9, and 59.3 Å^2, respectively. 51.3 Å^2 is used for NRs700, for (111) surfaces are dominating the surface of NRs700; while 71.6 Å^2 is used for NRs300 assuming it consists of about 50 % (110) and 50 % (100) surfaces, see the model of NRs300 displayed in Fig. 2.

Notes S1

In Table S4, the concentration of H_2O for $H_2{}^{17}O$ labeled NRs300 is 2.6 per surface unit. The $H_2{}^{17}O$ labeled ceria (100) surface contains 3.7 dissociated H_2O molecules per surface unit according to our previous study,[12] and assuming NRs300 consists of 50 % (110) and 50 % (100) surfaces (Fig. 1), the $H_2{}^{17}O$ labeled ceria (110) surfaces in NRs300 is therefore estimated to contain 1.5 H_2O per surface unit.

Section F: DFT calculations of ^{17}O NMR parameters on ceria (110) O-t surfaces (pristine and reconstructed) with one water molecule on per surface unit (dissociatively or molecularly adsorption)

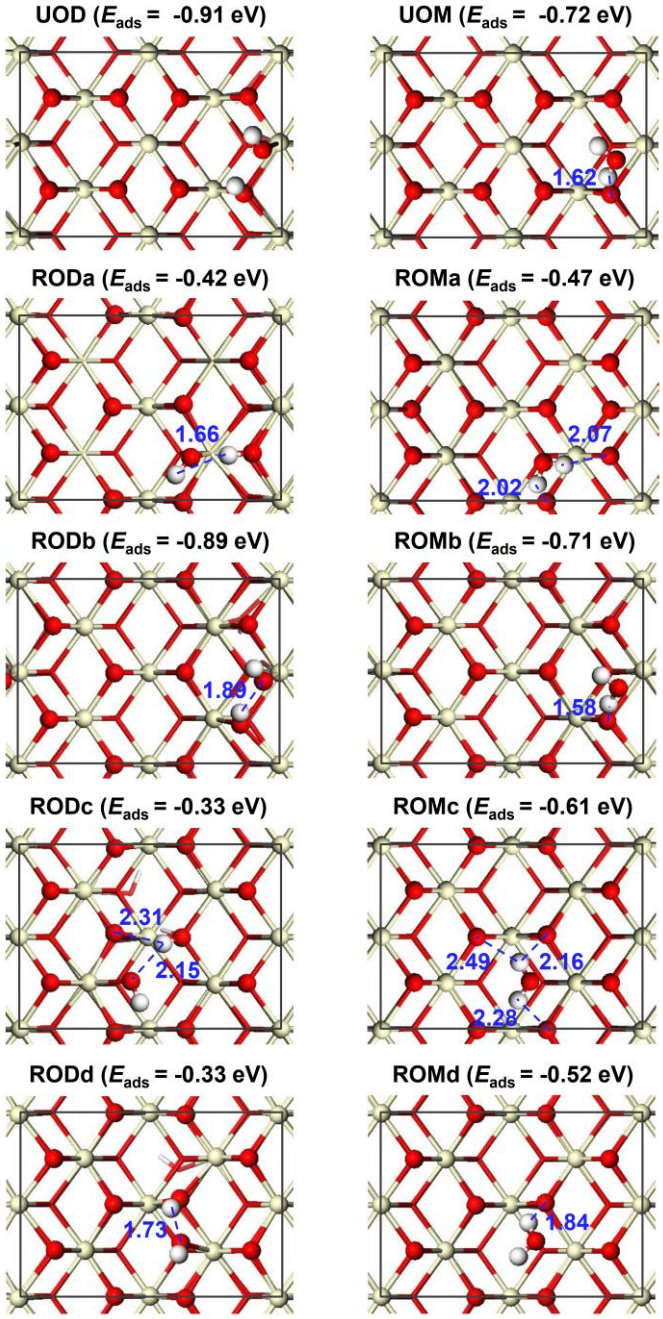

Fig. S12 Top views of calculated ceria (110) hydrated surfaces at the water coverages of one water molecule per surface unit. The unreconstructed ceria (110) O-t surfaces with one dissociated and molecular water molecule on per sure unit are marked as UOD and UOM, respectively; the reconstructed surfaces with one dissociated and molecular water molecule on per surface unit are RODa–d and ROMa–d, respectively. Red, off-white and white spheres represent oxygen, hydrogen and cerium ions, respectively. Blue dashed lines denote hydrogen bonds, for which the hydrogen bond distances are also given.

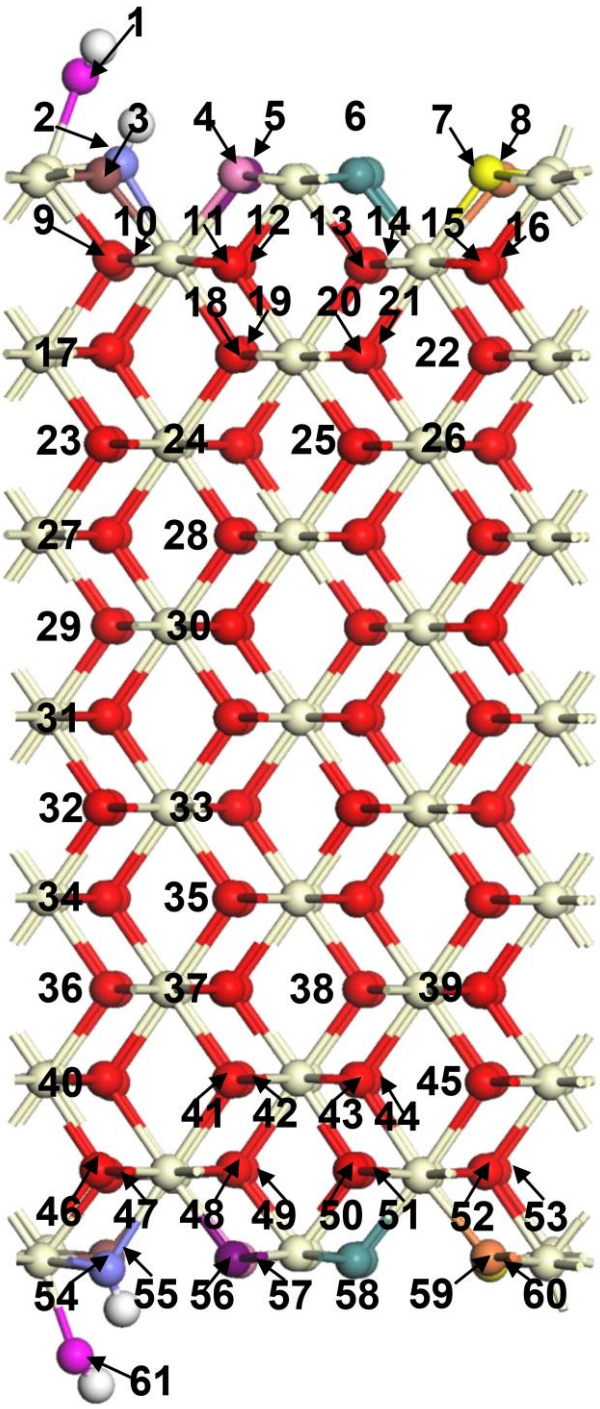

Fig. S13 Calculated structure of UOD. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

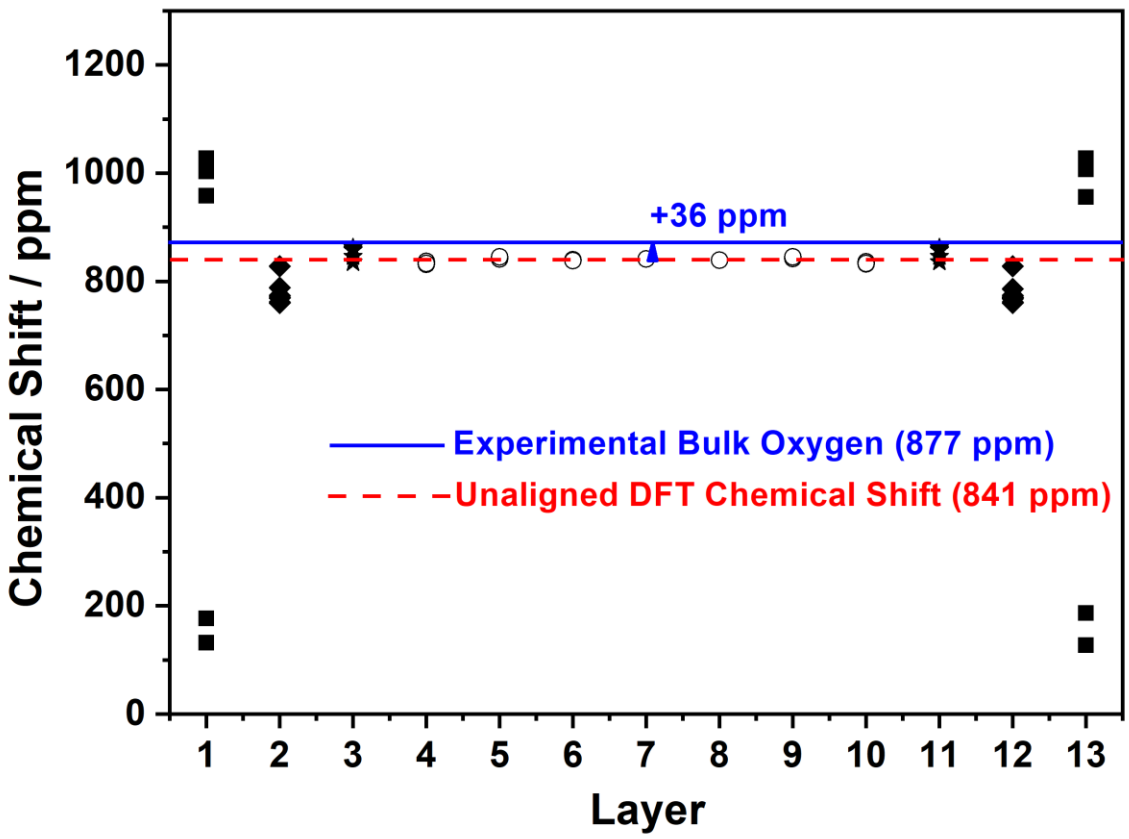

Fig. S14 The determination of the ^{17}O reference chemical shift (δ_{ref}) from UOD. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S5 Simulated ^{17}O NMR parameters for oxygen ions in UOD. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and simulated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. The corresponding structure has been showed in Fig. S13.

O_{ion} No.	**δ_{iso} / ppm**	**C_Q / MHz**	**η**	**δ_{CG} / ppm**	**Assignment**
1	286	7.61	0.03	168	Surface -OH
2	303	6.58	0.24	213	Surface -OH
3	1053	0.40	0.36	1053	1st Layer O_{3C}
4	1065	0.80	0.07	1063	1st Layer O_{3C}
5	1041	0.86	0.30	1039	1st Layer O_{3C}
6	1058	0.87	0.06	1057	1st Layer O_{3C}
7	995	0.61	0.97	994	1st Layer O_{3C}
8	1057	0.68	0.89	1056	1st Layer O_{3C}
9	824	0.22	0.76	824	2nd Layer O_{4C}
10	808	0.24	0.58	807	2nd Layer O_{4C}
11	810	0.18	0.81	810	2nd Layer O_{4C}
12	805	0.18	0.50	805	2nd Layer O_{4C}
13	798	0.20	0.82	798	2nd Layer O_{4C}
14	807	0.19	0.54	807	2nd Layer O_{4C}
15	796	0.30	0.69	796	2nd Layer O_{4C}
16	864	0.34	0.90	864	2nd Layer O_{4C}
17	895	0.25	0.62	895	3rd Layer O_{4C}
18	898	0.23	0.96	898	3rd Layer O_{4C}
19	871	0.22	0.51	871	3rd Layer O_{4C}
20	882	0.22	0.58	882	3rd Layer O_{4C}
21	895	0.24	0.50	895	3rd Layer O_{4C}
22	894	0.21	0.86	893	3rd Layer O_{4C}
23	868	0.18	0.45	867	Bulk Like
24	873	0.11	0.68	873	Bulk Like
25	868	0.12	0.34	868	Bulk Like
26	869	0.15	0.67	869	Bulk Like
27	877	0.18	0.35	877	Bulk Like
28	881	0.15	0.58	881	Bulk Like
29	876	0.15	0.27	876	Bulk Like
30	874	0.13	0.12	874	Bulk Like
31	877	0.15	0.52	877	Bulk Like
32	875	0.15	0.18	875	Bulk Like
33	875	0.13	0.15	875	Bulk Like
34	878	0.17	0.40	878	Bulk Like
35	881	0.15	0.53	881	Bulk Like
36	868	0.17	0.42	868	Bulk Like
37	872	0.11	0.65	872	Bulk Like
38	868	0.12	0.36	868	Bulk Like
39	869	0.15	0.61	869	Bulk Like

40	895	0.25	0.61	895	11th Layer O_{4C}
41	872	0.22	0.52	872	11th Layer O_{4C}
42	898	0.23	0.98	898	11th Layer O_{4C}
43	895	0.24	0.50	895	11th Layer O_{4C}
44	882	0.22	0.55	882	11th Layer O_{4C}
45	893	0.21	0.88	893	11th Layer O_{4C}
46	807	0.24	0.59	807	12th Layer O_{4C}
47	822	0.21	0.81	822	12th Layer O_{4C}
48	805	0.18	0.50	804	12th Layer O_{4C}
49	810	0.17	0.84	810	12th Layer O_{4C}
50	806	0.19	0.53	806	12th Layer O_{4C}
51	798	0.20	0.84	798	12th Layer O_{4C}
52	865	0.34	0.86	864	12th Layer O_{4C}
53	796	0.30	0.70	796	12th Layer O_{4C}
54	1052	0.41	0.33	1052	13th Layer O_{3C}
55	1044	0.86	0.29	1043	13th Layer O_{3C}
56	1064	0.80	0.07	1063	13th Layer O_{3C}
57	1059	0.81	0.04	1057	13th Layer O_{3C}
58	1056	0.69	0.87	1055	13th Layer O_{3C}
59	994	0.62	0.94	994	13th Layer O_{3C}
60	310	6.47	0.25	223	Surface -OH
61	281	7.60	0.03	163	Surface -OH

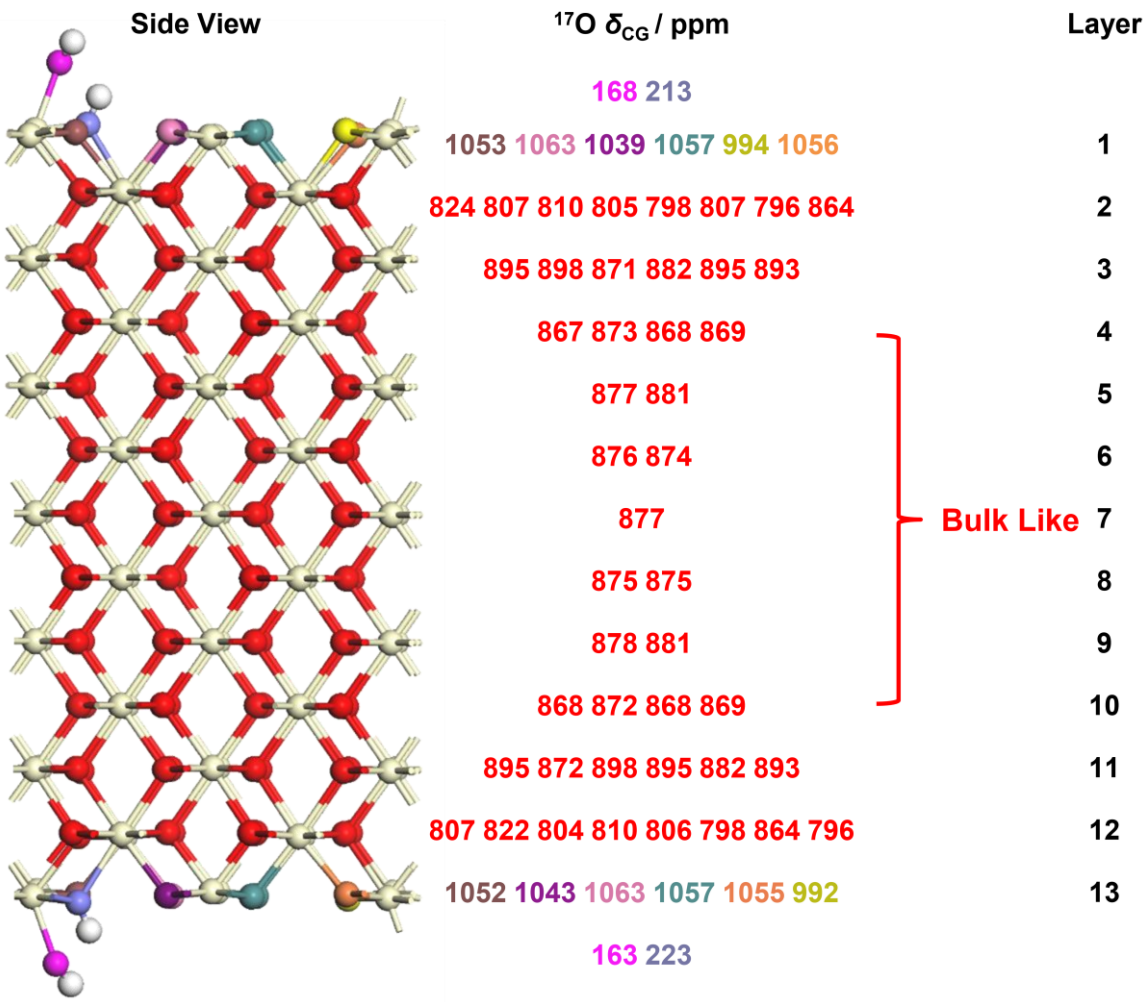

Fig. S15 The UOD structure model of ceria employed in DFT simulations with calculated shifts (δ_{CGS}) for oxygen ions and the layer numbers displayed on the right. The spheres representing bulk oxygen, cerium and hydrogen ions consist with the color in Fig. S13. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Table S5.

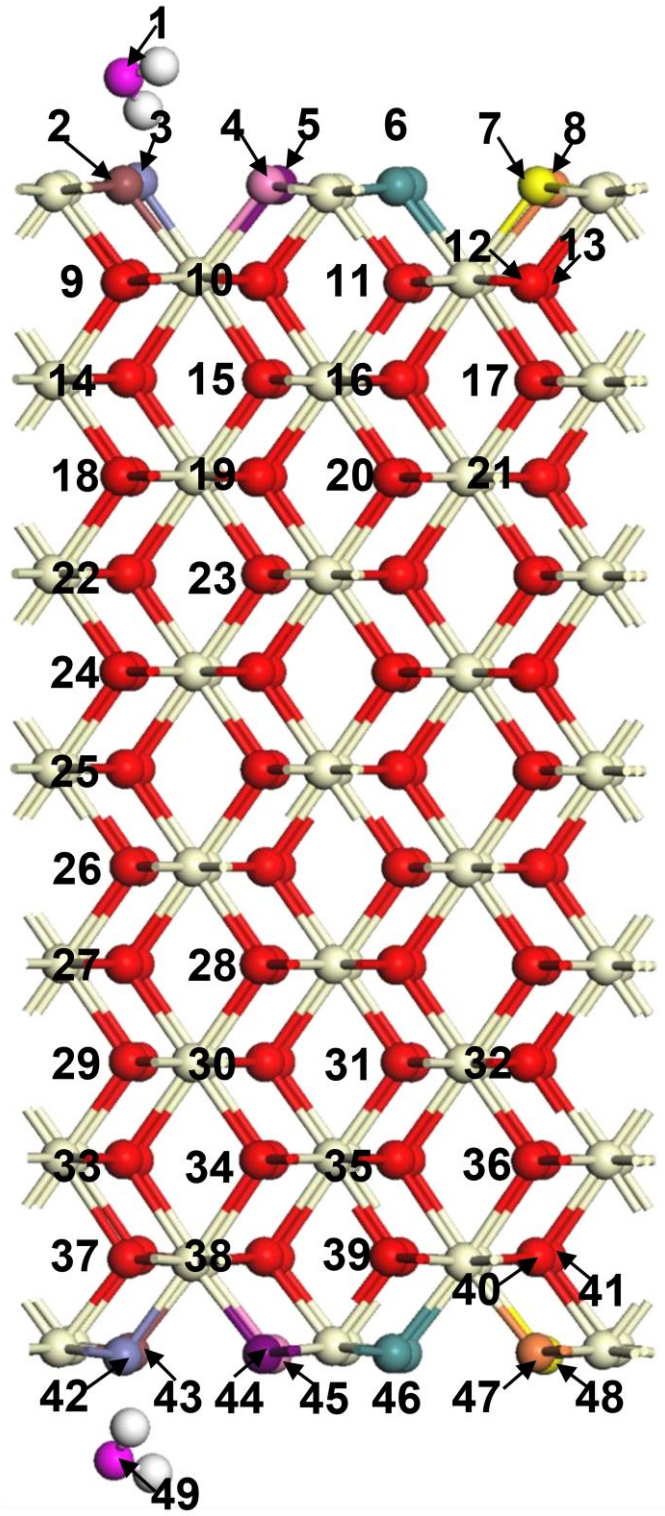

Fig. S16 Calculated structure of UOM. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

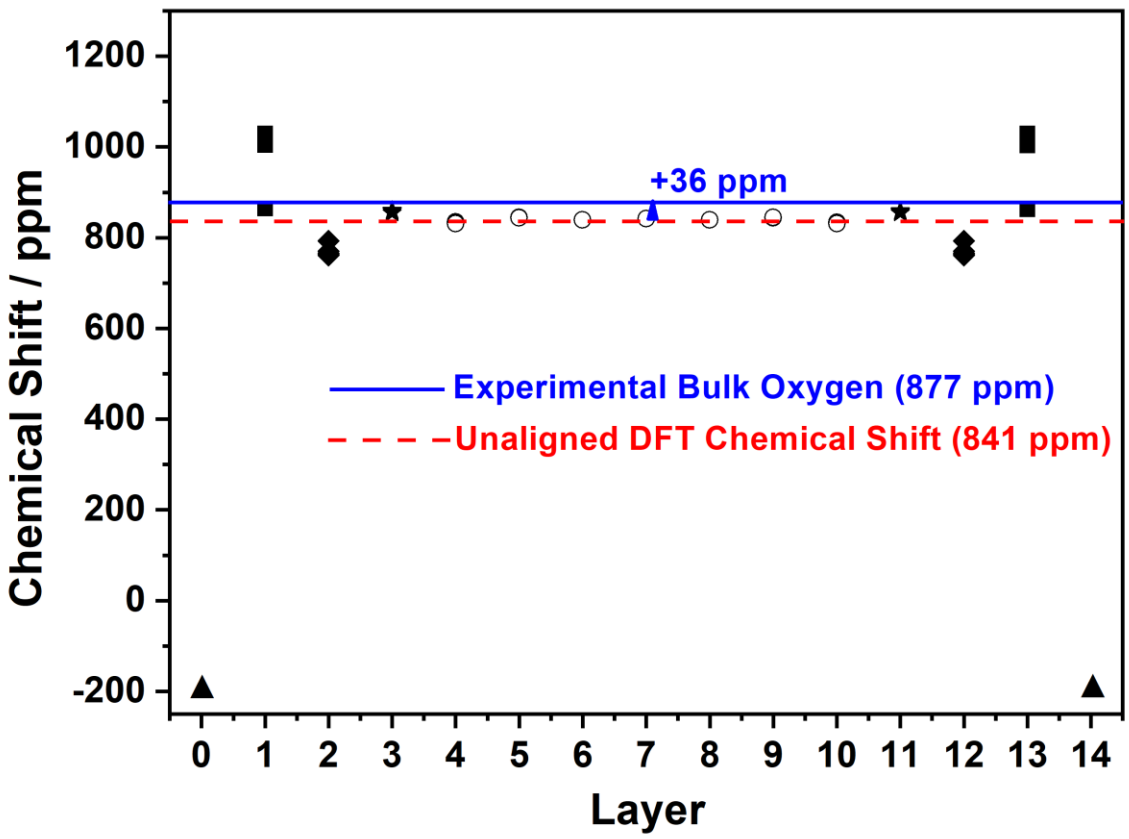

Fig. S17 The determination of the ^{17}O reference chemical shift (δ_{ref}) from UOM. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S6 Simulated ^{17}O NMR parameters for oxygen ions in UOM. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and simulated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. The corresponding structure has been showed in Fig. S16.

O_{ion} No.	**δ_{iso} / ppm**	**C_Q / MHz**	**η**	**δ_{CG} / ppm**	**Assignment**
1	-11	7.78	0.94	-171	Surface H_2O
2	1055	0.72	0.04	1054	1st Layer O_{3C}
3	903	1.05	0.45	900	1st Layer O_{3C}
4	1053	0.87	0.22	1052	1st Layer O_{3C}
5	1047	0.89	0.30	1045	1st Layer O_{3C}
6	1057	0.86	0.10	1056	1st Layer O_{3C}
7	1041	0.77	0.35	1040	1st Layer O_{3C}
8	1066	0.80	0.24	1065	1st Layer O_{3C}
9	806	0.18	0.25	806	2nd Layer O_{4C}
10	802	0.22	0.56	802	2nd Layer O_{4C}
11	799	0.22	0.60	799	2nd Layer O_{4C}
12	797	0.24	0.58	797	2nd Layer O_{4C}
13	829	0.27	0.70	829	2nd Layer O_{4C}
14	895	0.27	0.93	895	3rd Layer O_{4C}
15	896	0.26	0.80	896	3rd Layer O_{4C}
16	891	0.24	0.61	891	3rd Layer O_{4C}
17	894	0.23	0.76	894	3rd Layer O_{4C}
18	867	0.15	0.25	867	Bulk Like
19	871	0.12	0.41	871	Bulk Like
20	868	0.12	0.20	868	Bulk Like
21	867	0.13	0.14	867	Bulk Like
22	881	0.16	0.52	881	Bulk Like
23	880	0.16	0.55	880	Bulk Like
24	875	0.14	0.15	875	Bulk Like
25	878	0.15	0.38	878	Bulk Like
26	875	0.14	0.20	875	Bulk Like
27	880	0.17	0.55	880	Bulk Like
28	881	0.16	0.56	881	Bulk Like
29	867	0.15	0.25	867	Bulk Like
30	870	0.12	0.37	870	Bulk Like
31	869	0.11	0.22	869	Bulk Like
32	867	0.13	0.15	867	Bulk Like
33	895	0.26	0.73	895	11th Layer O_{4C}
34	894	0.25	0.84	894	11th Layer O_{4C}
35	891	0.24	0.61	891	11th Layer O_{4C}
36	893	0.25	0.91	893	11th Layer O_{4C}
37	806	0.19	0.49	806	12th Layer O_{4C}
38	802	0.19	0.87	802	12th Layer O_{4C}
39	799	0.22	0.60	799	12th Layer O_{4C}

40	829	0.27	0.70	829	12th Layer O_{4C}
41	797	0.24	0.60	797	12th Layer O_{4C}
42	900	1.07	0.45	898	13th Layer O_{3C}
43	1055	0.72	0.03	1054	13th Layer O_{3C}
44	1048	0.90	0.31	1046	13th Layer O_{3C}
45	1054	0.88	0.22	1052	13th Layer O_{3C}
46	1057	0.86	0.09	1056	13th Layer O_{3C}
47	1066	0.80	0.25	1065	13th Layer O_{3C}
48	1040	0.77	0.36	1039	13th Layer O_{3C}
49	-11	7.79	0.94	-171	Surface H_2O

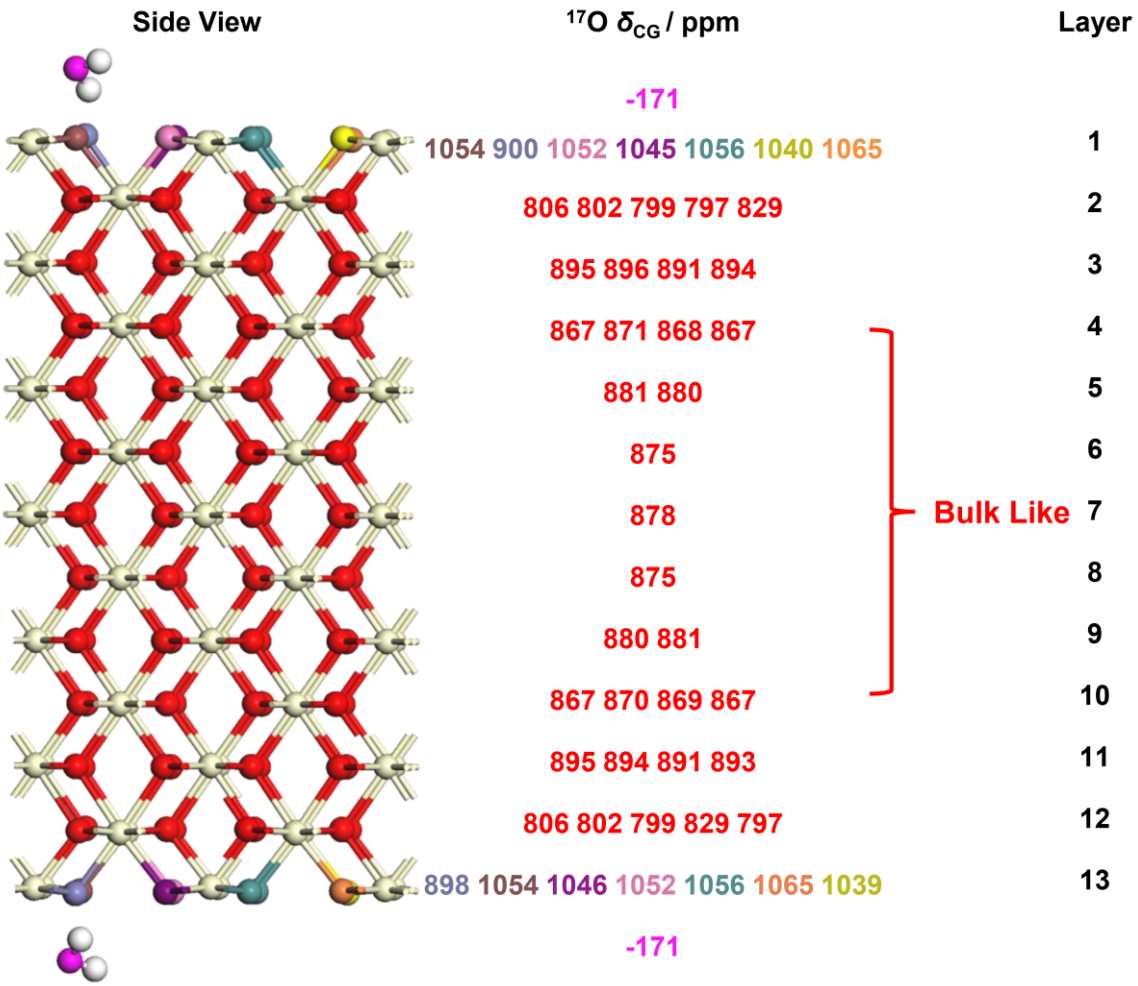

Fig. S18 The UOM structure model of ceria employed in DFT simulations with calculated shifts (δ_{CGS}) for oxygen ions and the layer numbers displayed on the right. The spheres representing bulk oxygen, cerium and hydrogen ions consist with the color in Fig. S16. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Table S6.

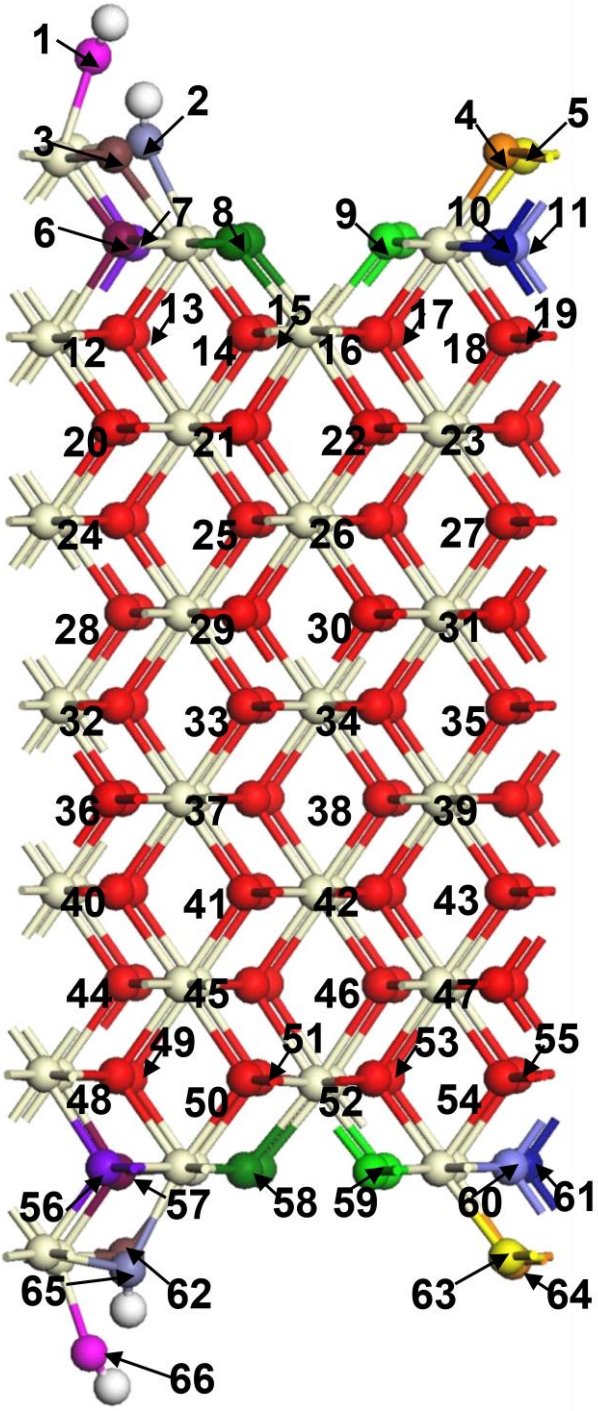

Fig. S19 Calculated structure of RODb. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

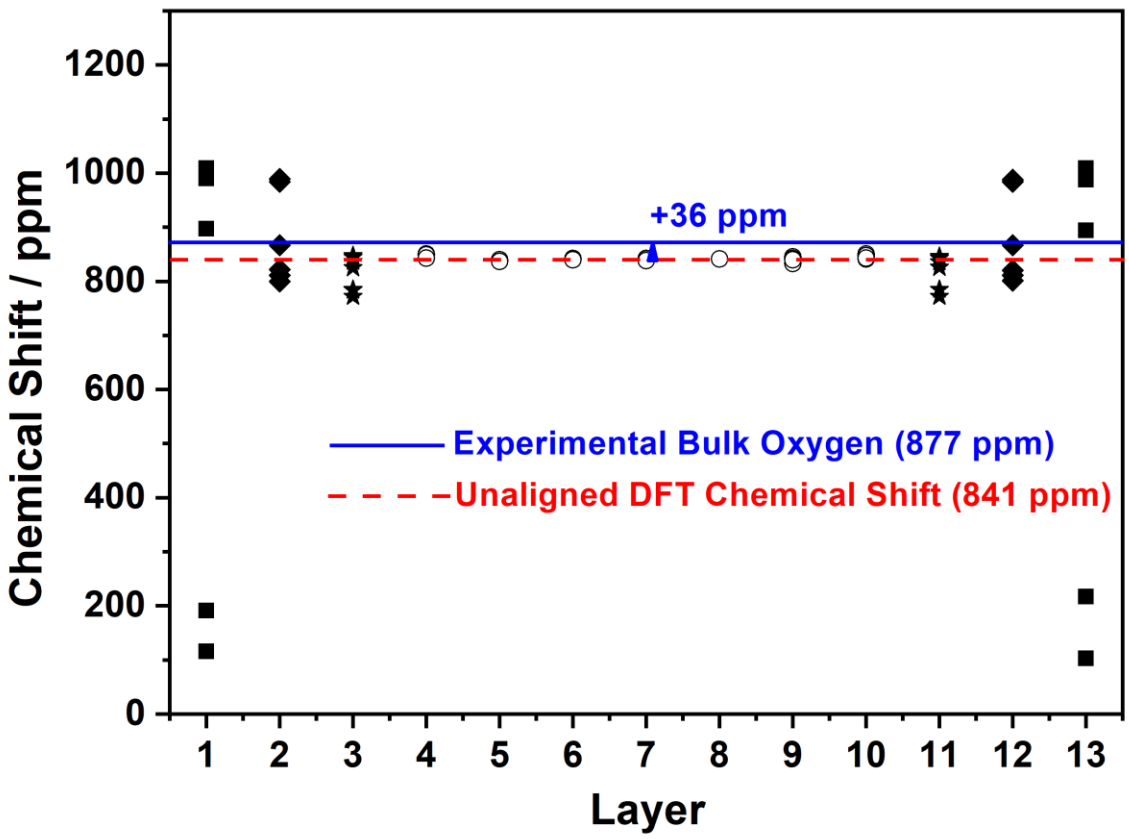

Fig. S20 The determination of the ^{17}O reference chemical shift (δ_{ref}) from RODb. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S7 Simulated ^{17}O NMR parameters for oxygen ions in RODb. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and simulated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. The corresponding structure has been showed in Fig. S19.

O_{ion} No.	δ_{iso} / ppm	C_Q / MHz	η	δ_{CG} / ppm	Assignment
1	268	7.54	0.06	152	Surface-OH
2	297	5.84	0.09	227	Surface-OH
3	1045	0.29	0.35	1045	1st Layer O_{3C}
4	934	0.48	0.32	933	1st Layer O_{3C}
5	1026	0.40	0.84	1026	1st Layer O_{3C}
6	858	0.34	0.88	858	2nd Layer O_{4C}
7	847	0.46	0.78	847	2nd Layer O_{4C}
8	1025	0.56	0.43	1025	2nd Layer O_{3C}
9	1021	0.58	0.14	1020	2nd Layer O_{3C}
10	836	0.26	0.47	836	2nd Layer O_{4C}
11	904	0.35	0.63	903	2nd Layer O_{4C}
12	808	0.17	0.41	808	3rd Layer O_{4C}
13	822	0.22	0.72	821	3rd Layer O_{4C}
14	883	0.25	0.36	883	3rd Layer O_{4C}
15	861	0.34	0.58	861	3rd Layer O_{4C}
16	873	0.28	0.39	873	3rd Layer O_{4C}
17	880	0.20	0.18	880	3rd Layer O_{4C}
18	821	0.17	0.80	820	3rd Layer O_{4C}
19	808	0.14	0.42	808	3rd Layer O_{4C}
20	885	0.10	0.89	885	Bulk Like
21	886	0.27	0.97	886	Bulk Like
22	886	0.27	0.89	885	Bulk Like
23	879	0.09	0.65	879	Bulk Like
24	873	0.12	0.25	873	Bulk Like
25	876	0.18	0.22	876	Bulk Like
26	876	0.17	0.16	876	Bulk Like
27	873	0.11	0.51	873	Bulk Like
28	877	0.14	0.14	877	Bulk Like
29	878	0.17	0.55	878	Bulk Like
30	877	0.17	0.67	877	Bulk Like
31	876	0.13	0.21	876	Bulk Like
32	874	0.14	0.42	874	Bulk Like
33	878	0.16	0.26	878	Bulk Like
34	877	0.15	0.22	877	Bulk Like
35	874	0.13	0.34	874	Bulk Like
36	877	0.13	0.14	877	Bulk Like
37	879	0.18	0.57	879	Bulk Like
38	878	0.17	0.64	878	Bulk Like

39	876	0.13	0.21	876	Bulk Like
40	879	0.11	0.48	879	Bulk Like
41	876	0.18	0.22	876	Bulk Like
42	871	0.19	0.12	871	Bulk Like
43	878	0.10	0.24	878	Bulk Like
44	878	0.14	0.72	877	Bulk Like
45	886	0.27	0.99	886	Bulk Like
46	883	0.27	0.98	883	Bulk Like
47	879	0.10	0.75	879	Bulk Like
48	821	0.22	0.69	821	11^{th} Layer O_{4C}
49	808	0.18	0.35	808	11^{th} Layer O_{4C}
50	862	0.34	0.56	862	11^{th} Layer O_{4C}
51	882	0.25	0.39	882	11^{th} Layer O_{4C}
52	879	0.20	0.19	879	11^{th} Layer O_{4C}
53	872	0.28	0.40	872	11^{th} Layer O_{4C}
54	808	0.14	0.42	808	11^{th} Layer O_{4C}
55	821	0.17	0.79	821	11^{th} Layer O_{4C}
56	847	0.47	0.75	847	12^{th} Layer O_{4C}
57	856	0.34	0.91	856	12^{th} Layer O_{4C}
58	1025	0.56	0.40	1024	12^{th} Layer O_{3C}
59	1021	0.59	0.15	1020	12^{th} Layer O_{3C}
60	903	0.36	0.68	903	12^{th} Layer O_{4C}
61	837	0.26	0.44	837	12^{th} Layer O_{4C}
62	1045	0.30	0.37	1045	13^{th} Layer O_{3C}
63	1025	0.39	0.88	1024	13^{th} Layer O_{3C}
64	931	0.49	0.38	930	13^{th} Layer O_{3C}
65	316	5.56	0.08	253	Surface-OH
66	255	7.54	0.07	139	Surface-OH

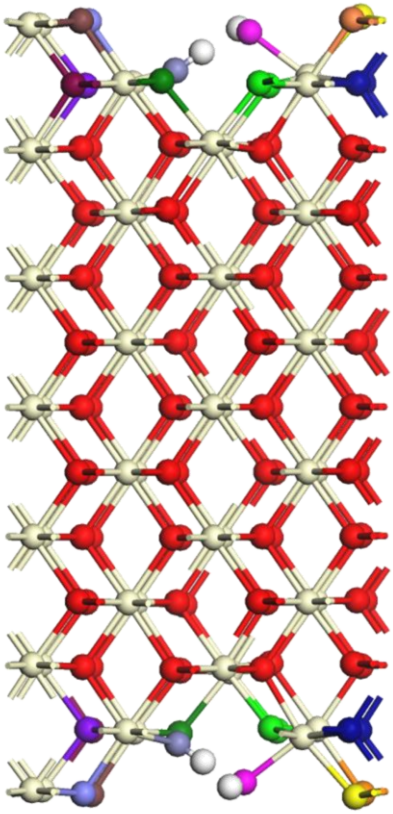

Fig. S21 The RODb structure model of ceria employed in DFT simulations with calculated shifts (δ_{CGS}) for oxygen ions and the layer numbers displayed on the right. The spheres representing bulk oxygen, cerium and hydrogen ions consist with the color in Fig. S19. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Table S7.

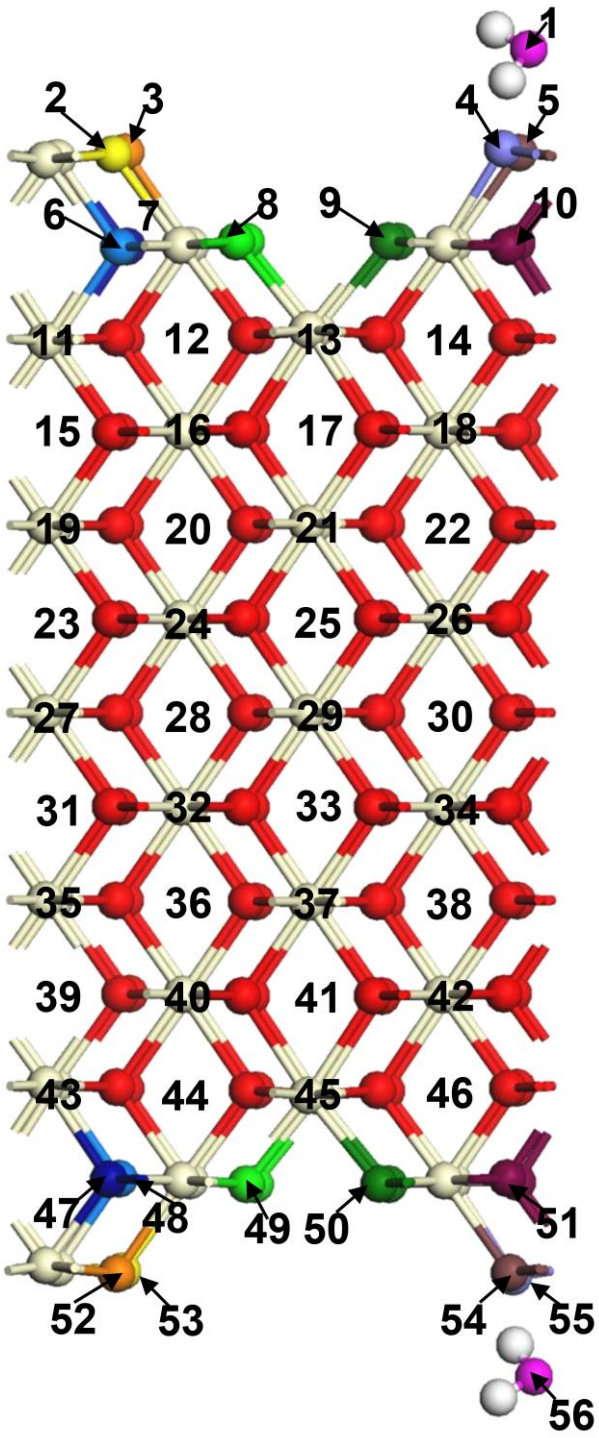

Fig. S22 Calculated structure of ROMb. Oxygen ions with the same chemical environment (thus the same NMR parameters) are marked with identical number. Red, off-white and white spheres denote bulk oxygen, hydrogen and cerium ions, respectively. Surface oxygen groups with variable chemical shifts are marked in different colors.

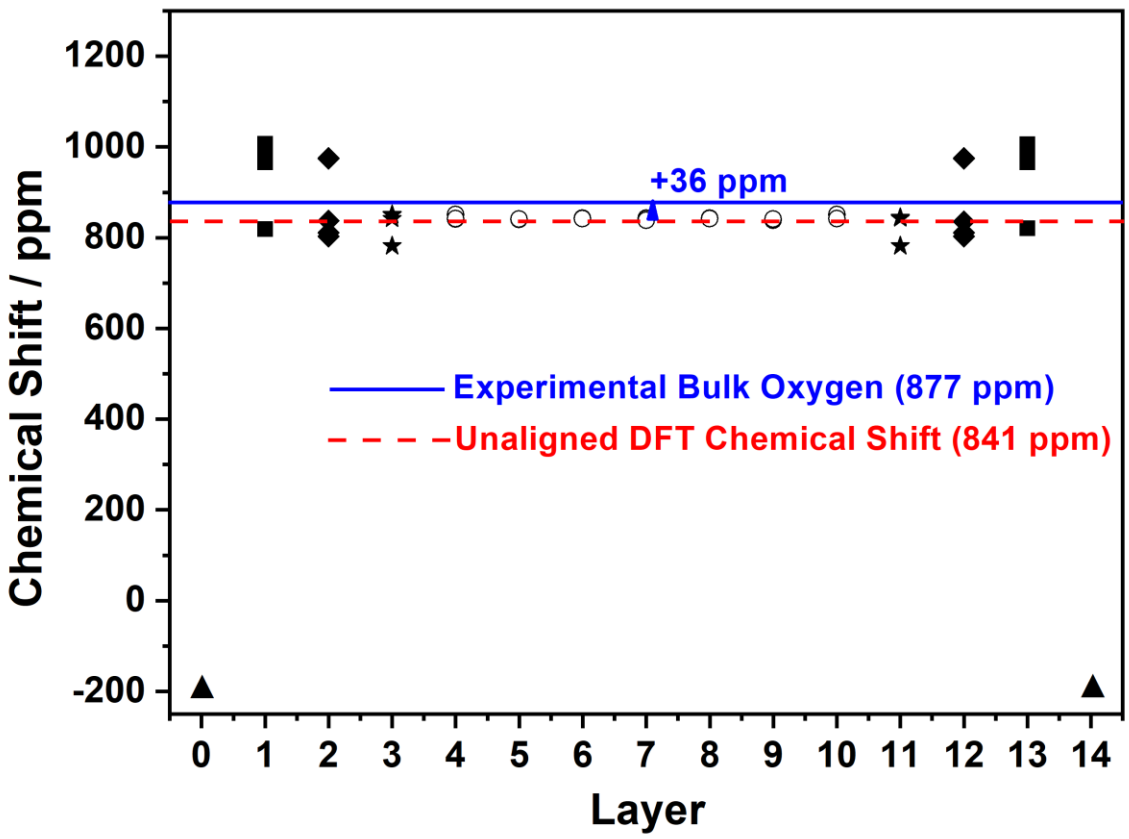

Fig. S23 The determination of the ^{17}O reference chemical shift (δ_{ref}) from ROMb. Squares, diamonds, stars and circles denote the unaligned DFT chemical shifts of oxygen ions at the top/bottom 1st, 2nd, 3rd surface layers and the "bulk". The red dashed line show the average value of the unaligned ^{17}O chemical shifts of the oxygen ions in the "bulk".

Table S8 Simulated ^{17}O NMR parameters for oxygen ions in ROMb. Isotropic chemical shifts (δ_{iso}), quadrupolar parameters (C_Q and η) and simulated NMR shift (center of gravity, δ_{CG}) for each ^{17}O resonance are displayed. The corresponding structure has been showed in Fig. S22.

O_{ion} No.	**δ_{iso} / ppm**	**C_Q / MHz**	**η**	**δ_{CG} / ppm**	**Assignment**
1	-6	7.80	0.93	-166	Surface H_2O
2	1043	0.46	0.26	1043	1^{st} Layer O_{3C}
3	1002	0.48	0.93	1002	1^{st} Layer O_{3C}
4	856	0.77	0.88	855	1^{st} Layer O_{3C}
5	1036	0.37	0.98	1036	1^{st} Layer O_{3C}
6	873	0.25	0.83	873	2^{nd} Layer O_{4C}
7	839	0.17	0.86	839	2^{nd} Layer O_{4C}
8	1011	0.57	0.22	1010	2^{nd} Layer O_{3C}
9	1011	0.52	0.23	1011	2^{nd} Layer O_{3C}
10	847	0.25	0.95	847	2^{nd} Layer O_{4C}
11	818	0.16	0.56	818	3^{rd} Layer O_{4C}
12	880	0.27	0.28	880	3^{rd} Layer O_{4C}
13	881	0.28	0.22	881	3^{rd} Layer O_{4C}
14	818	0.16	0.81	818	3^{rd} Layer O_{4C}
15	878	0.09	0.55	878	Bulk like
16	886	0.29	0.95	886	Bulk like
17	887	0.30	0.97	887	Bulk like
18	878	0.12	0.63	878	Bulk like
19	877	0.10	0.50	877	Bulk like
20	876	0.19	0.09	876	Bulk like
21	876	0.19	0.19	876	Bulk like
22	877	0.11	0.47	877	Bulk like
23	878	0.13	0.05	878	Bulk like
24	879	0.18	0.63	878	Bulk like
25	879	0.18	0.63	879	Bulk like
26	878	0.13	0.16	878	Bulk like
27	874	0.13	0.46	874	Bulk like
28	879	0.16	0.07	879	Bulk like
29	879	0.16	0.25	878	Bulk like
30	874	0.14	0.35	874	Bulk like
31	878	0.13	0.04	878	Bulk like
32	878	0.18	0.65	878	Bulk like
33	879	0.18	0.64	879	Bulk like
34	878	0.13	0.16	878	Bulk like
35	877	0.10	0.48	877	Bulk like
36	876	0.19	0.10	876	Bulk like
37	874	0.20	0.13	874	Bulk like
38	877	0.11	0.47	877	Bulk like

39	878	0.09	0.56	878	Bulk like
40	887	0.29	0.94	886	Bulk like
41	887	0.30	0.87	887	Bulk like
42	878	0.12	0.65	878	Bulk like
43	818	0.16	0.55	818	11^{th} Layer O_{4C}
44	879	0.27	0.30	879	11^{th} Layer O_{4C}
45	881	0.28	0.21	881	11^{th} Layer O_{4C}
46	818	0.16	0.83	818	11^{th} Layer O_{4C}
47	839	0.17	0.85	839	12^{th} Layer O_{4C}
48	872	0.25	0.86	872	12^{th} Layer O_{4C}
49	1011	0.57	0.23	1010	12^{th} Layer O_{3C}
50	1012	0.52	0.20	1011	12^{th} Layer O_{3C}
51	847	0.25	0.98	847	12^{th} Layer O_{4C}
52	1002	0.48	0.91	1002	13^{th} Layer O_{3C}
53	1043	0.46	0.22	1042	13^{th} Layer O_{3C}
54	1036	0.38	0.97	1036	13^{th} Layer O_{3C}
55	858	0.77	0.88	857	13^{th} Layer O_{3C}
56	-8	7.81	0.93	-169	Surface H_2O

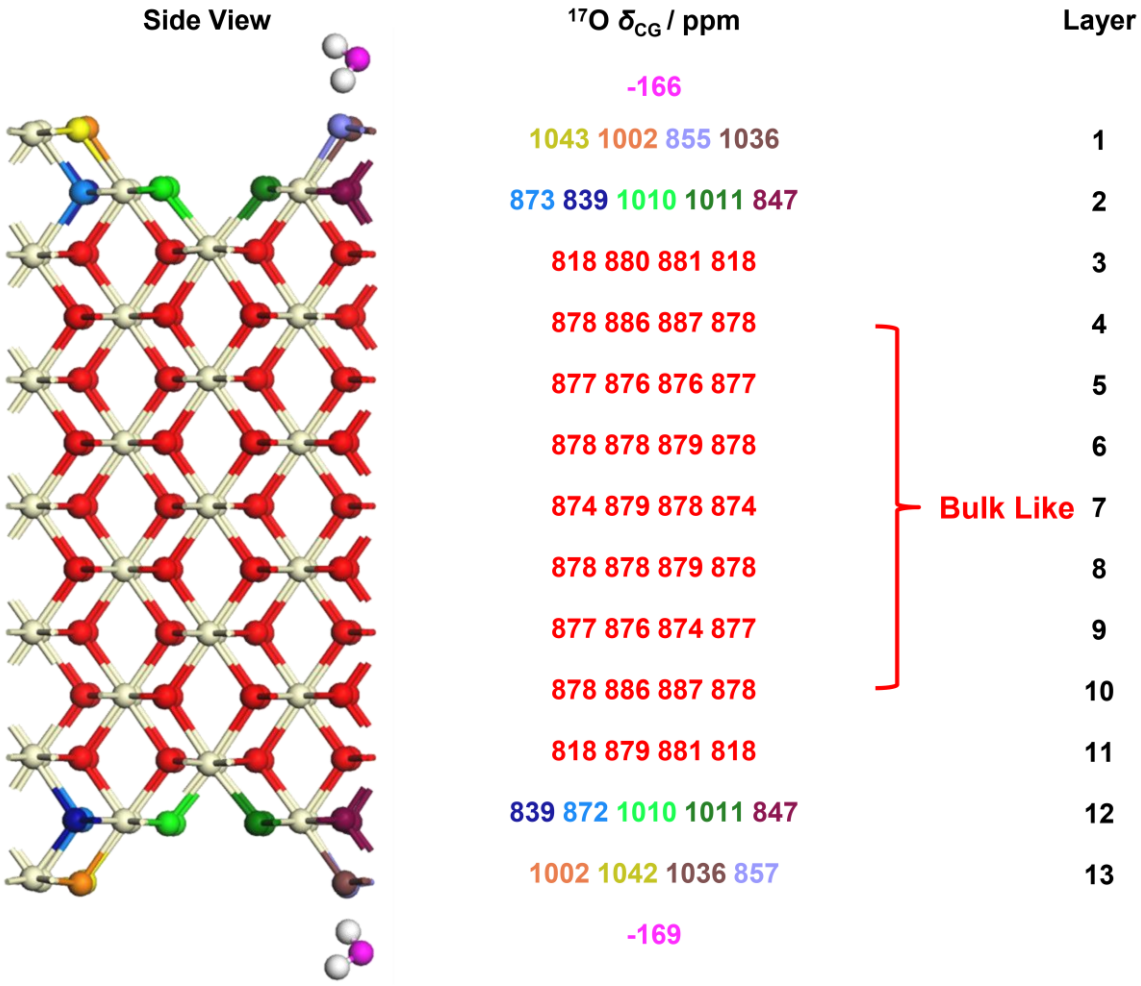

Fig. S24 The ROMb structure model of ceria employed in DFT simulations with calculated shifts (δ_{CGS}) for oxygen ions and the layer numbers displayed on the right. The spheres representing bulk oxygen, cerium and hydrogen ions consist with the color in Fig. S22. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Table S8.

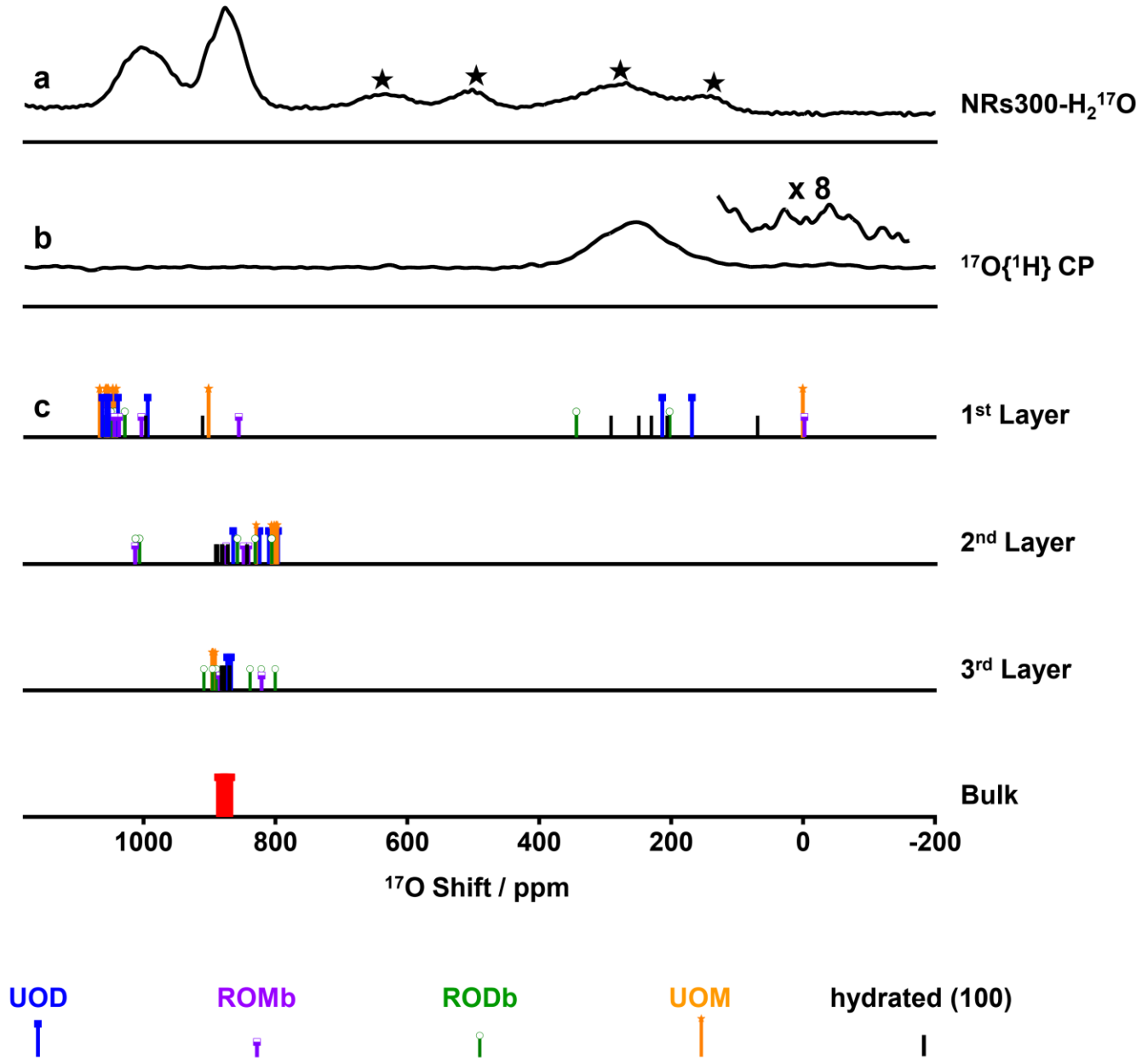

Fig. S25 ^{17}O NMR spectra and calculated ^{17}O NMR shifts from UOD, UOM, RODb and ROMb, which are the most possible models for each circumstance of hydrated ceria (110) surfaces (unreconstruction and reconstruction, molecular and dissociated water molecules). (a,b) ^{17}O single pulse and ^{17}O{^{1}H} cross polarization solid-state NMR spectra of $H_2{}^{17}O$-enriched ceria NRs300. (c) The summarized ^{17}O NMR shifts (δ_{CGS}) predicted with DFT simulations for UOD, UOM, RODb, ROMb and hydrated (100) surfaces[11a]. The simulated ^{17}O NMR parameters for each oxygen ion have been displayed in Tables S5 – S8.

Table S9 Predicted ^{17}O NMR shifts (δ_{CGS}) of the 1st layer oxygen ions interacting directly and indirectly with water (dissociated and molecular) in pristine and hydrated ceria (111), (110) and (100) surfaces, respectively, as well as corresponding calculated models.

		(111)		(110)				(100)	
				Unreconstructed		Reconstructed			
		Dissociated	Molecular	Dissociated	Molecular	Dissociated	Molecular	Dissociated	Molecular
Pristine	^{17}O δ_{CG} / ppm	1026		1052		1008	1033	968	—
	Model	P(111)[a]		PU(110)[b]		PR(110)[b]		$D(100)_2$[c]	—
Hydrated	Direct ^{17}O δ_{CG} / ppm	291	883	213	900	202	855	206	—
	Indirect ^{17}O δ_{CG} / ppm	997 984 974	1045 1019 1016	1063, 1057 1056, 1053 1039, 994	1065, 1056 1054, 1052 1045, 1040	1045 1026	1043 1036 1002	996 910	—
	Model	D(111)[a]	M(111)[a]	UOD	UOM	RODb	ROMb	$D(100)_3$[c]	—

[a] P(111) indicates a model with pristine (111) surface; D(111) or M(111) denotes a model with one dissociated or molecular water molecule per (111) surface unit, respectively, whose ^{17}O NMR shifts models are extracted from *Ref.*12.

[b] PU(110) or PR(110) represents a model with pristine (110) surface.

[c] $D(100)_2$ or $D(100)_3$ represents a model with two or three dissociated molecules per (100) surface unit, respectively. The ^{17}O NMR shifts models are extracted from *Ref.*12.

Section G: DFT calculated adsorption energies of CO on ceria (111) at dry and hydrous conditions

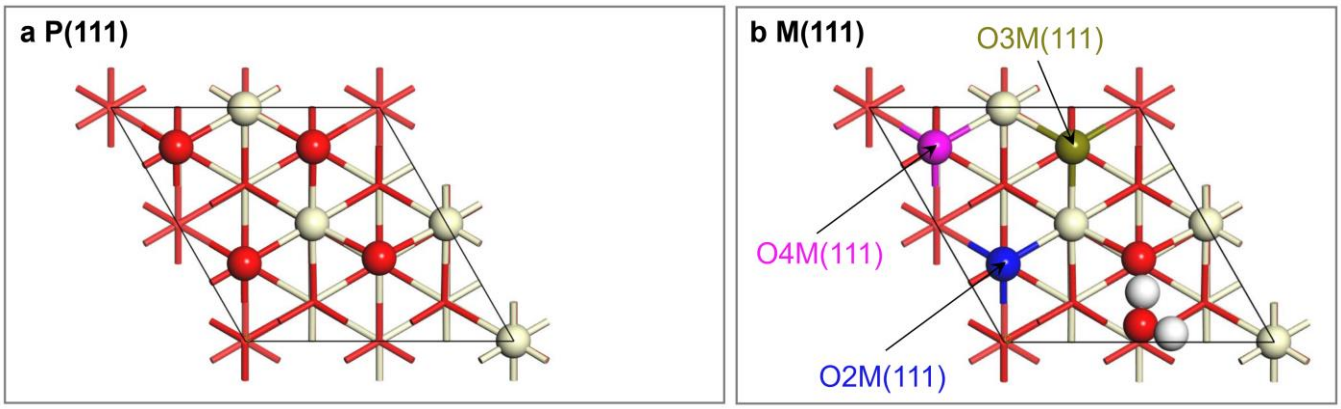

Fig. S26 Adsorption energies of CO on ceria (111) at dry and hydrous conditions. (a) CO adsorbed on P(111), the pristine CeO_2(111) surface; (b) CO adsorbed on M(111), in which one water molecule is pre-adsorbed molecularly per surface unit of CeO_2(111) (water coverage = 1/4 ML). Off-white and white spheres represent cerium and hydrogen ions, respectively. Surface oxygen groups with different chemical shifts are in different colors.

Table S10 Adsorption energies (E_{ads}) of CO on the 1st layer oxygen ions at P(111) and M(111) obtained with DFT calculations and the corresponding ^{17}O chemical shifts (δ_{iso}s) of bare oxygen ion.

Level of Hydration	Model	Adsorption Sites	δ_{iso} / ppm	Eads / eV
Dry	P(111)	O1P(111)	1026	-0.134
		O2M(111)	1016	-0.198
Hydrous	M(111)	O3M(111)	1019	-0.203
		O4M(111)	1045	-0.158

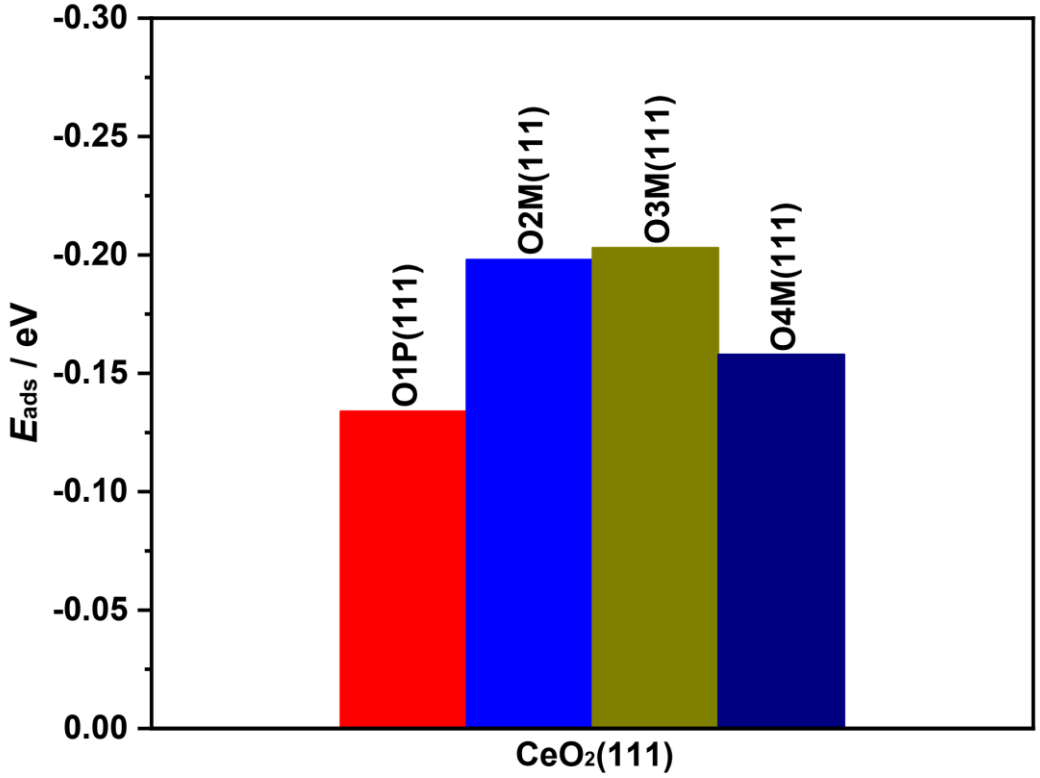

Fig. S27 Adsorption energies of CO on the different oxygen sites of different surfaces (P(111) and M(111)).

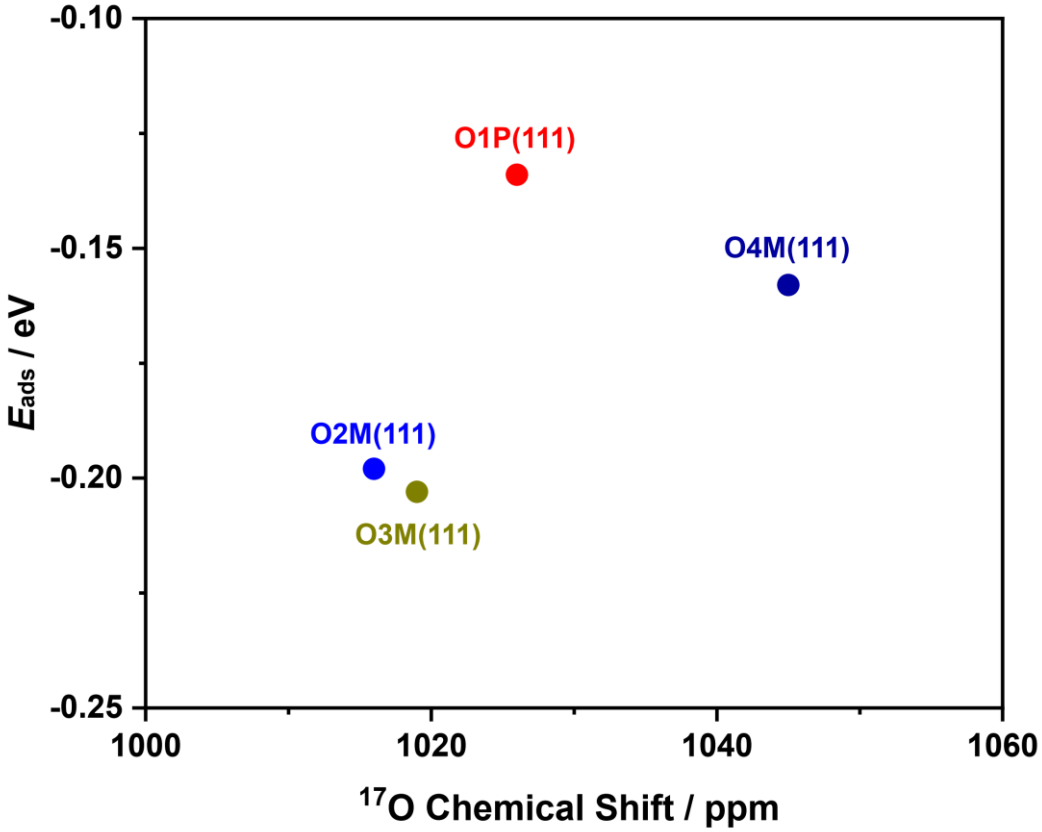

Fig. S28 CO adsorption energies and corresponding ^{17}O chemical shifts of the 1st layer bare oxygen ions at P(111) and M(111).

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