Supporting Information:

Ceria Nanocrystals Supporting Pd for Formic Acid Electrocatalytic Oxidation: Prominent Polar Surface Metal Support Interactions

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Table of Contents	page
SECTION S1 Synthesis of Ceria	
S1.1 Shape Controlled Synthesis of Ceria	3
S1.2 Synthesis of Palladium Modified Ceria	3
SECTION S2 Characterization	4
S2.1 Particle Size and Shape of Ceria	4
S2.2 Particle Size and Distribution of Pd Nanoparticles on Ceria	5
S2.3 Crystal Structure of Ceria	9
S2.4 Oxygen Defects on Ceria	10
SECTION S3 Formic Acid Electro-Oxidation by Electrochemical Techniques	13
SECTION S4 Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)	15
SECTION S5 Density Functional Theory (DFT) Modelling of Pd/CeO ₂ (100) Catalysts	18
SECTION S6 References	23

Ceria and palladium deposited on ceria (Pd/CeO₂) were controlled synthesized. The particle size, shape, composition and distribution of the obtained ceria and Pd deposited on ceria were characterized by various techniques, as detailed below. In addition, their catalytic activities towards electro-oxidation of formic acid were investigated. The relationship between shape of ceria support and the catalytic activity of Pd catalyst was also explored. The results and discussion have been shown below.

S1 Synthesis of Ceria

S1.1 Shape Controlled Synthesis of Ceria

Ceria nanocrystals were prepared in four different shapes; rod, cube, sphere and plate. The rods, cubes and sphere were prepared by following the literature with some modification.¹ In general cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) 0.868 g was dissolved in 35 mL of 6M aqueous solution of sodium hydroxide. The mixed solution was poured into a Teflon bottle and kept stirring for 30 min. During the reaction, the formation of milky slurry was observed. Rods can be prepared in oil bath at 100°C for 36 h while the spheres can be prepared at room temperature for 96 h. For cubes, the solution was transferred into Teflon lined stainless steel autoclave and the autoclave was heated in an oven at 180°C for 24h.

Ceria plates were prepared by following literature with some modification.² In general, 3 mmol cerium (III) nitrate and 2 mmol CTAB were mixed in a beaker under stirring. 4 mL of 25% (w/v) ammonium hydroxide solution was added. The mixture was transferred into a Teflon bottle and heated in oil bath at 100°C for 2 h. White precipitates of the products were separated by centrifugation and washed several with distillation water and ethanol. The obtained pale yellow powders were dried at 90°C for 5h and calcined at 500°C for 6h. (the BET surface areas of 22 and 75 m^2/g for cubes and rods samples, respectively were obtained).

S1.2 Synthesis of Palladium Modified Ceria

Palladium modified ceria nanocrystals were prepared by chemical reduction/deposition. In three neck round bottom flask, a mixture of 30 mg $\text{Pd}(\text{NO}_3)_2$ (7% w/w of CeO_2) and 60 mg of PVP was dissolved in 30 mL of ethylene glycol under stirring. Then, 0.20 g of the prepared ceria

were added to the solution and stirred for 10 min. The mixture was heated with stirring at 90°C for 1 h. Finally, the product was washed thoroughly with acetone, ethanol and dried under nitrogen atmosphere.

S2 Characterization

S.2.1 Particle Size and Shape of Ceria

TEM images and size distribution histograms of the synthesized ceria are shown in Figure S1

Figure S1. TEM images and size distribution histograms of the synthesized CeO₂ a) spheres b) cubes c) plates d) rods

S.2.2 Particle Size and Distribution of Pd Nanoparticles on Ceria

TEM images and size distribution histograms of Pd deposited on Pd/CeO₂ crystals are shown in Figure S2. It clearly demonstrated high dispersion of Pd particle on the surface of ceria. Pd particles display a spherical shape and narrow size distribution. Although activity of metal nanoparticles depends on their particle sizes, the different in size of Pd about 0.1 nm is assumed negligible change to their catalytic activity

Figure S2. TEM images and size distributions histograms of a) PVP-Pd b) Pd/cubes CeO₂

c) Pd/rods CeO₂

The results from EDX analysis are shown in Table S1. It can be confirmed that the amount of Pd loading on ceria obtained from theoretical calculation and experiment are similar. This indicated high dispersion of Pd nanoparticles on ceria surfaces.

Table S1. The percentage of Pd on the synthesized Pd/CeO₂

Ceria shapes	Percentage of Pd loading	
	Theoretical calculation	EDX analysis
Cubes	7.05	7.07±1.16
Rods	7.03	6.80±1.87
Plate	7.02	6.58±1.17
Sphere	7.05	6.65±1.47

An enlarge HRTEM image in Fig. S3 displays a lattice pattern with spacing between lattice fringes (bright stripes) of 2.75Å, indicating the crystal with an exposed of (200) face. For deposited Pd nanoparticles on ceria surface, the inter-planar spacing of 1.24 Å and 0.89 Å indicating exposed (300) and (330), respectively.

Figure S3. HRTEM image of Pd deposited on cube-shaped ceria

Although atomic arrangements of cerium cations and oxygen anions on (110) and (100) are clearly defined from modelling, high resolution scanning tunneling microscopy and diffraction data, as for a complete comparison, both high quality atomic images of HRTEM from polar (100) and non-polar (110) surfaces should be provided and analyzed. We applied exit wave restoration technique on a focal series of HRTEM images by reducing residual aberrations of the microscope. One of the main challenges in observing CeO_2 in the TEM is its notorious ability to reduce easily under irradiation from the electron beam and vacuum/atmosphere used. For (100) polar surface, it is relatively easier to differentiate the alternative layers of larger $\text{Ce}^{3+}/\text{Ce}^{4+}$ and smaller O^{2-} anions. We could get good atomic image of (110) surface with a sawtooth-like structure, as shown in Fig. 1(d) in the main manuscript but were however unable to obtain similar highest and comparable quality to that of the polar (100) on the inter-dispersed cerium cations and oxygen anions on the top surface of (110) facet by the exit wave restoration technique despite many attempts. The surface structure of this ceria facet is also not static, and the inherent mobility of atoms at ceria surfaces must be assessed for a better understanding of the temporal evolution of the atomic structure of facets. It may be possible to use the fast-pixelated detectors and data processing in the recent new electronic ptychography technique (Pennycook, T. J. et al. Ultramicroscopy 151, 160–167, 2015) which can allow simultaneous ADF and phase images for the detection of both light and heavy elemental species in a matrix. Our initial attempt on using the ptychography technique was still not yet able to differentiate the inter-dispersive cerium cation and oxygen anions on the same terminate surface. As a result, we have acknowledged the need for the complete comparison and difficulties we encountered.

S2.3 Crystal Structure of Ceria

Figure S4 shows the X-ray diffraction (XRD) patterns of the four types ceria, which can well indexed to the pure fluorite cubic structure (JCPDS card number 34-0394).

Figure S4. XRD patterns of different shapes of ceria

Although XRD is not the surface characterized techniques, the probability that one plane will be occurred predominantly in the sample can be estimated from the ratio of reflection intensity. For face center cubic structure, shape of crystals was mainly determined by the ratio between the growth rates along (100) and (111) directions. From the results in Figure S4, the intensity reflection of (100) to (111) was following the order; cube > sphere > rod > plate. The clearly exposed (100) plane on the surface of cube ceria is confirmed by HRTEM on section S1.3.

The XRD patterns of Pd nanoparticle compared with Pd deposited on rod and cube-shaped ceria are shown in Figure S5. Three peaks are observed at 40°, 46° and 68° corresponding to the

(111), (200) and (220) planes of Pd in face centered cubic (FCC) structure. In comparison with XRD pattern of Pd deposited on ceria, it was found that all the XRD-patterns only showed face center cubic structure of ceria without any of Pd phase. This may due to low loading of Pd nanoparticles (7 wt%) and ceria still maintain their original crystal structure after deposition. This result implies that Pd nanoparticles only deposits on the surface without intercalation into the lattice.

Figure S5 XRD patterns of the Pd nanoparticles and 7wt% Pd/ CeO_2 crystals

S2.4 Oxygen Defects on Ceria

The main defect in ceria is the formation of oxygen vacancies. The properties of the oxygen vacancies are essentially related to the catalytic activity of ceria. In addition, the crystal plane of ceria plays an essential role in determining its catalytic properties. Ceria can uptake and release oxygen via the transformation between Ce^{3+} and Ce^{4+} of surface defect (oxygen

vacancy). Ce^{3+} is paramagnetic species. Thus, ESR technique was used to study. The ESR spectra are shown in Figure S6

Figure S6. ESR spectra of different shapes of ceria

As seen from Figure S6, cubes and rods-shaped ceria show very intense paramagnetic signals at $g = 1.96$ respectively indicating a typical non-stoichiometric ceria with the existence of ceria Ce^{3+} from defective ceria structure. Very low ESR signal is observed in plates presumably due to passivated surface by surfactant molecules. Cubes show a broad peak at $g = 2.03$ which corresponding to superoxide radical ions (O_2^-) formation on the ceria surface.³

The ESR spectra and the quantitative analysis of spin concentration of CeO_2 and Pd modified CeO_2 are shown in Figure S7 and Table S2.

Figure S7. ESR spectra of Pd modified different shapes of ceria

Table S2. Quantitative analysis of spin concentration

Sample	G value	Spin/mg
CeO ₂ rods	1.96	1.14×10^{13}
Pd/CeO ₂ (rods)	1.96	8.27×10^{12}
CeO ₂ cubes	2.03/ 1.96	4.74×10^{13} / 1.61×10^{13}
Pd/CeO ₂	2.03/ 1.96	1.90×10^{13} / 5.04×10^{12}
CeO ₂ plates	-	non-detected

By consider at g value 1.96, higher spin concentration is found on Pd/CeO₂ cubes than rods, whereas the g value signal from plates cannot be detected. It is interesting that the signal at g value 2.03 is found only on cubes. There has been reported that this superoxide signal is found on ceria when the particle size is less than 5.3 nm.⁴ The high intensity of paramagnetic signal in cubs clearly shows high concentration of Ce³⁺ in the structure with contain high concentration of superoxide in lattice. This may due to the polar surface of oxygen layer on the (100) plane on the surface. The six (100) planes of cubes have the highest surface energy among the low-index crystal planes. This high surface energy originates from the instability of the top-layer oxygen,

which is located at the bridging positions between two cerium ions.⁵ The decreasing of spin concentration after depositing with Pd is found which may be oxidation/reduction between of Pd and oxygen at vacant sites.

S3 Formic Acid Electro-Oxidation by Electrochemical Techniques

For the electro-catalyst preparation, acid treated XC-72R carbon was used as carbon support in order to increase conductivity. The colloidal suspension of Pd/CeO₂ in ethanol was dropped onto the suspension of carbon in ethanol under sonication. Catalyst ink was prepared by ultrasonically dispersing catalyst in a mixture of ethanol and 5% w/w solution of Nafion. A three-electrode electrochemical cell was set up for the electrochemical measurements. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. Working electrode was prepared by coating a thin layer of catalyst ink (9.71 $\mu\text{g Pd cm}^{-2}$) on glassy carbon (surface area 0.0706 cm²).

All electrochemical measurements were carried out in the solution of 0.5 M H₂SO₄ (electrolyte) and 0.5 M formic acid (reactant) at a scan rate of 0.1 V/s. For CO stripping experiment, the electrodes were immersed in N₂ pre-saturated electrolyte, kept the potential at 0.02 V while ultra-pure CO was purged through the electrolyte for 30 min. Then N₂ was purged to expel CO in the electrolyte for another 30 min. The potential was scanned from 0.0 V to 1.2V vs. SHE at 50 mV·s⁻¹ for 2 cycles. Chronoamperometric experiments were performed in 0.5M H₂SO₄ aqueous solution in the presence of 0.5 M formic acid at room temperature. The measurement was carried out at 0.1 V vs. Ag/AgCl for a period of 1200 s.

Electrochemical surface area (ECSA) was applied to determine the total active catalyst surface. The ratio of the ECSA to the mass of catalyst indicates how effectively the metal precious catalyst is used total to geometrical surface area (specific activity). It is typically measured by

hydrogen adsorption/ desorption peak area or the oxidative CO stripping peak area. The ECSA can be calculated from region of hydrogen desorption peak according to the following equation.

$$ECSA = \frac{Q_H}{L_{Pd}Q_f} \times 10^{-4}$$

Where Q_H is Coulombic charge in unit mC, the Q_f is required coulombic charge to hydrogen desorption after clean Pd surface by hydrogen (0.21 mC/cm²) and L_{Pd} is amount of Pd loading on working electrode surface in gram unit. The evolution of the charge density (Q) during hydrogen oxidation on Pd surface is analyzed by integration of hydrogen desorption peak. The ECSA of Pd and Pd/CeO₂ different shapes are shown in Table S3. The mass activity is “normalized” from ECSA and presented in terms of the specific activity (the activity per unit surface area of catalyst).

Different shapes of ceria support may affect to the activity of Pd nanoparticles. Their catalytic mass activity and specific activity are shown in Table S3. From the results, it can be seen that the maximum mass activity of Pd/CeO₂ towards formic acid electro-oxidation can be enhanced to 1060 A/gPd which is 3 times than colloidal Pd catalyst. Pd/CeO₂ cubes not only showed high catalytic mass activity but also showed excellent specific activity.

Table S3. ECSA and catalytic activity Pd nanocatalyst deposited on different shapes of ceria

Shape of ceria support	Peak area (C)	ECSA (cm ² /g Pd)	Mass Activity (A/g Pd)	Specific Activity (mA/cm ²)
Non support	7.02×10^{-5}	48.73	360.20	7.98
Cubes	1.34×10^{-4}	93.02	1059.18	11.38
Plate	5.80×10^{-5}	40.26	441.84	10.97
Rod	6.04×10^{-5}	41.93	469.68	11.20
Sphere	3.75×10^{-5}	26.03	336.73	7.96

S4 Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

The Ce⁴⁺/Ce³⁺ composition of the ceria surface is commonly characterized by x-ray photoelectron spectroscopy (AP-XPS).⁶ The most frequently used method for determining the oxidation state of Ce is by measuring the Ce 3d core level. However, most of the XPS studies of ceria are done under ultra-vacuum conditions which might not reflect the sample under catalytic conditions. Hence, using ambient pressure (AP) XPS developed by Tao et. al., measurements of these catalysts could be performed in operando, where reducing or oxidizing gases could be fed into the sample.⁷ With this technique, the surface Ce⁴⁺/Ce³⁺ composition under reaction conditions could be determined. The catalyst samples were therefore heated in 1 Torr H₂ gas to 500 °C to reduce the surface oxygen for oxygen vacancy formation in Pd deposited ceria morphologies (Figure S8). The samples were cooled to 100 °C under H₂ before their XPS measurements were taken. The samples were also reoxidised by heating them in 1 Torr O₂ gas at 300 °C for 3 hours to investigate the oxygen replenishing of the reduced ceria samples.

Figure S8. XPS Ce 3d spectra of a) ceria cubes b) ceria rods c) 7% Pd/ceria cubes d) 7% Pd/ceria rods under UHV (UHV 100 °C), reduced (H_2 100 °C) and reoxidised (O_2 100 °C) conditions.

Figure S9 shows the Ce 3d XPS spectra for 7% Pd/CeO₂ cubes and rods and compared with their corresponding undeposited samples, under UHV, reduced and oxidised conditions. Under UHV, all their spectra correspond to the typical Ce 3d spectrum of fully oxidised CeO₂ sample (Figure S9a), which contains six peaks resulting from spin-orbit-splitting of 3d core level.

Additional peaks were also present which were due to ‘shake-down’ states where electrons are transferred from the O 2p level to the Ce 4f level in the excited state. On the other hand, the typical spectrum of fully reduced ceria, Ce_2O_3 shown in Figure S9a consists of 4 peaks which also resulted from spin-orbit splitting of 3d core level. Under reduced conditions, the spectra of all the samples (Figure S9b, labelled under H_2 100 °C) resemble to that of the partially reduced CeO_{2-x} (Figure S9a), where their spectra are the combination of CeO_2 and Ce_2O_3 .

Figure S9 (a) Typical XPS Ce 3d spectra of A) fully oxidised ceria, CeO_2 B) partially reduced ceria, CeO_{2-x} and C) fully reduced ceria, Ce_2O_3 ; (b) Calibrated O/Ce ratios of typical Figure 3(b) in the main text, the atomic ratio is normalized to the calculated value 1.91 at UHV RT. Notice that $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios of 0.3 ± 0.05 and 0.05 ± 0.02 under extensive H_2 pre-reduction and pre-oxidation in O_2 of the typical Pd/ceria rods sample shown in Figure S9(b), respectively correspond to O/Ce ratios of 1.4 ± 0.1 and 1.9 ± 0.1 on the top layer, matching with the boundary phases of Ce_2O_3 and CeO_2 within experimental errors.

Thus, the Ce 3d spectra are used to calculate the $\text{Ce}^{4+}/\text{Ce}^{3+}$ compositions of the samples under the different conditions (Figure S9b). Under UHV, all the samples suggested the presence of small amounts of Ce^{3+} (green) which could attribute to the existing oxygen vacancies in ceria. The oxygen vacancies increased after the samples were reduced to 500 °C in 1 Torr H_2 , which was indicated by the increase in Ce^{3+} and the decrease in Ce^{4+} compositions. In our method of calibration, we assumed that the photoelectrons from O 1s and Ce 3d below the Pd/PdO particles cannot be travelled through the particles; thus, the O area of the exposed Ce oxides were obtained by subtracting O 1s area of PdO from the total O1s peak.

S5 Density Functional Theory (DFT) Modelling of Pd/CeO₂ (100) Catalysts

Density Functional Theory (DFT) is one of the most used computational calculations to investigate the stability of the ceria surfaces, as their properties such as oxygen vacancy formation and oxygen mobility are dependent on the ceria surface energy. Figure S10 shows the structural models of (111), (110) and (100) ceria surfaces. The (100) surface has been reported by Kim et. al. to be terminated by O in their direct recoil spectroscopy / low energy ion scattering of Kr experiments.⁸ It also has been argued to produce a net dipole moment perpendicular to the surface due to alternately charged planes with a repeat unit consisting of only two planes which is termed a polar surface.⁹

Figure S10. Surfaces of ceria a) (111) b) (110) c) (100) and d) reconstructed (100) by removing half of surface oxygen to remove polarity.^[16]

To set the models, the calculations were performed by using the Vienna ab initio simulation package (VASP).^{1, 10} The projector-augmented wave (PAW) potentials¹¹ were used for the core electron interaction. The Perdew–Burke–Ernzerhof (PBE) functional¹² based on the generalized gradient approximation (GGA) with corrections for on-site Coulomb interactions for strongly correlated systems (GGA+U)¹³ was employed. For all structure optimizations and density of states (DOS) calculations, a plane wave basis set with a cutoff energy of 400 eV was used and all

the ionic positions were allowed to relax until the forces were less than 0.02 eV/Å. Spin polarization and dipole correction were also included in all these calculations.

A value of $U = 5.0$ eV was applied to the Ce 4f state.¹⁴ The unit cell model for the CeO₂ contained 4 CeO₂ units. A 6×6×6 k-point grid determined by the Monkhorst-Pack method was used in the bulk cell optimization, resulted in cell parameters 5.442 Å, in good agreement with the experimental values (5.411 Å). The CeO₂ (111) and (100) surface models were all modeled by 2×2 periodic slab models with 7 Ce atomic layers. The bottom two Ce atomic layers and the coordinated O layers are fixed and a vacuum layer of 12 Å along the z direction perpendicular to the surface was employed to prevent spurious interactions between the repeated slabs in all these models.

The calculations of CeO₂(111) surface, which is type II surface according to Tasker classification with no dipole moment,¹⁵ used a 4×4×1 k-point sampling grid. The CeO₂(100) is type III surface, which introduces a dipole perpendicular to the surface upon cleaving. Some computational studies remove the dipole moment by replacing every second row of oxygen atoms from one side of the slab to the other side and build a surface termination with a 50% missing oxygen layer.^{9a, 14, 16} This model was named (100)_ref in this work. We also named a (100)_ref_o model with an extra oxygen atom on the (100)_ref surface which sits at a removed surface oxygen site. Meanwhile some studies have considered cation or anion terminated (100).¹⁷ We built a non-stoichiometric ideal (100) model with symmetric top and bottom fully oxygen terminated surface layer, which is named (100)_ot. A 4×4×1 k-point sampling grid was utilized in all the (100) models.

The distances between defects in periodic slabs are 7.696 Å in both (111) and (100). The energy of oxygen vacancy formation in CeO₂ surfaces was computed from

$$E_{\text{ovf}} = (E_{\text{CeO}_{2-x}} + 1/2 E_{\text{O}_2}) - E_{\text{CeO}_2}$$

Here $E_{\text{CeO}_{2-x}}$ and E_{CeO_2} are the total energies of CeO₂ surface with and without an oxygen vacancy, respectively, and we reference to half the energy of an O₂ molecule ($1/2 E_{\text{O}_2}$).

The calculated surface energy of ceria shown in Table S4 indicates that stability is in the order (111) < (110) < (100). On the other hand, upon reconstruction of (100) to remove the dipole moment (100_{O-half}), the stability of (100) and (110) are reversed as suggested by the less favorable oxygen vacancy formation (2.40 and 1.99 eV, respectively). Furthermore, when one oxygen atom is added into the reconstructed (100) surface (100_{O-half} + 1), the oxygen vacancy formation becomes very favorable. This suggests that between the unconstructed (100) surface and one oxygen added to the reconstructed surface, the oxygen vacancy formation is more favorable than the (110) surface, implying (100) is the less stable surface in the surface CeO_x, $1 < x \leq 2$ range.

Table S4. DFT calculated energy of oxygen vacancy formation of ceria surfaces.

Surface	Calculated energy of oxygen vacancy formation (eV)
111	3.08
110	1.99
100	-1.98
100 _{O-half}	2.40
100 _{O-half} + 1	-1.56

The observations on the catalyst testing demonstrate that the ceria cubes support with polar surface is more superior to the rods and other shapes, in terms of oxygen mobility and oxygen vacancy formation. It could be postulated that these characteristics are attributed to the polarity of (100) surface, at which under reaction conditions, being at the state of more than half filled oxygen CeO_x ($1 < x \leq 2$), which gives them the higher degree of oxygen vacancy formation and oxygen mobility during catalysis. At this state, the ceria (100) surface has a non-zero dipole moment perpendicular to surface, therefore a polar surface which could possibly contribute to its surface properties through electrostatic interactions.

Due to greater sensitivity to changing gas environment over Pd surface than ceria, the Pd metal surface on CeO_2 can gain access to mobile oxygen atoms of (100) surface and beyond reversibly through the alternative cations and anions layers arrangement due to change in polarity with the same planes.

Scheme S1. Due to greater sensitivity to changing gas environment over Pd surface than ceria, the Pd metal surface on CeO_2 can gain access to mobile oxygen atoms of (100) surface and beyond reversibly through the alternative cations and anions layers arrangement due to change in polarity with the same planes.

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