Equilibrium oxygen storage capacity of ultrathin CeO$_2$-$\delta$ depends non-monotonically on large biaxial strain

Chirranjeevi Balaji Gopal$^1$, Max García-Melchor$^{2,3,4}$, Sang Chul Lee$^1$, Yezhou Shi$^1$, Andrey Shavorskiy$^5$, Matteo Monti$^1$, Zixuan Guan$^6$, Robert Sinclair$^1$, Hendrik Bluhm$^7$, Aleksandra Vojvodic$^{2,8}$ & William C. Chueh$^{1,9}$

Elastic strain is being increasingly employed to enhance the catalytic properties of mixed ion-electron conducting oxides. However, its effect on oxygen storage capacity is not well established. Here, we fabricate ultrathin, coherently strained films of CeO$_2$-$\delta$ between 5.6% biaxial compression and 2.1% tension. In situ ambient pressure X-ray photoelectron spectroscopy reveals up to a fourfold enhancement in equilibrium oxygen storage capacity under both compression and tension. This non-monotonic variation with strain departs from the conventional wisdom based on a chemical expansion dominated behaviour. Through depth profiling, film thickness variations and a coupled photoemission-thermodynamic analysis of space-charge effects, we show that the enhanced reducibility is not dominated by interfacial effects. On the basis of ab initio calculations of oxygen vacancy formation incorporating defect interactions and vibrational contributions, we suggest that the non-monotonicity arises from the tetragonal distortion under large biaxial strain. These results may guide the rational engineering of multilayer and core-shell oxide nanomaterials.
The tunable oxygen nonstoichiometry of mixed ionic and electronic conducting (MIEC) oxides underlies their application in solid oxide fuel cell electrodes, heterogeneous catalysis, solar fuel generation through thermochemical cycles and resistive switching-based memory devices. It governs the concentration of mobile oxygen vacancies and electronic defects that mediate oxygen exchange at the oxide/gas interface, store oxygen at the surface and in the bulk and facilitate transport. The oxygen nonstoichiometry can be tuned intrinsically through temperature and oxygen partial pressure, and extrinsically through composition, nanostructuring and lattice strain. Recent advances in achieving atomic-level control in thin-film growth techniques, the inherent layered architecture of solid-state devices and their rapid downsizing have rendered lattice strain an attractive and dopant-free alternative to enhance a wide array of properties of existing materials. Strain-induced modifications to the crystal symmetry of multilayered thin films and core–shell nanomaterials have led to dramatic enhancements in carrier mobilities of semiconductors, superconducting transition temperatures and ferroic properties of layered oxides.

In MIEC oxides, strain has an additional impact on the material properties through its coupling with oxygen chemical potential. The presence of oxygen vacancies is associated with an expansion of the lattice due to electron localization on the neighbouring cations, commonly known as chemical expansion. Thus, control of lattice volume through strain provides a means to tune the defect chemical properties of MIEC oxides. Numerous studies have investigated the effect of strain on the surface reactivity using substrate-supported films and on ionic transport using multilayered heterostructures. In the latter, a wide variation in the results is often observed depending on the volume fraction of the strained phases and the geometry of electrical contacts, among other parameters. It is generally recognized that compressive strain increases the migration barrier for oxygen ion transport and surface exchange, while tensile strain has the opposite effect. This hypothesis of a monotonic dependence of reaction barriers on strain has been corroborated by computational studies, and is believed to extend to oxygen vacancy formation energetics as well.

A trend is consistent with a chemical expansion-dominated behaviour. However, strain also affects the ligand field and distorts local bonding which can influence the vacancy formation and migration significantly. Yet another important consideration for MIECs with large point defect concentrations is the chemical strain effect that describes the alleviation of elastic strain energy through defect association and formation of concentration gradients. In Gd-doped ceria, for instance, defect association lowers the apparent elastic modulus by over an order of magnitude to accommodate large stresses. Decoupling the multiple effects of strain necessitates well-defined model systems and precise fabrication control, as elegantly pointed out by Yildiz and Wen in recent reviews.

An important metric of catalytic activity of MIEC oxides is the surface redox capacity, that is, the extent of change in oxygen nonstoichiometry with oxygen chemical potential. Changes to the surface chemistry and its ability to buffer oxygen can have dramatic implications for both the thermodynamics and kinetics of oxygen insertion reactions. To establish a definitive relationship between strain and a functional property, it is desirable to have the oxide film uniformly strained over a wide range of values, both compressive and tensile. This is challenging, because biaxially strained films undergo strain relaxation beyond a critical film thickness, rendering the strain fields inhomogeneous, or undergo a polymorphic transition due to large local strains. For instance, in a recent study using electron energy-loss spectroscopy to probe the incoherent $\text{CeO}_2$-$\text{YSZ}$ interface, Song et al. found that the Ce atoms are reduced to the $3+$ oxidation state near the misfit dislocation, regardless of the sign of the strain. However, Sun et al. used atomistic simulations and arrived at an opposite prediction. Donner et al. showed that strained $\text{La}_0.5\text{Sr}_0.5\text{CoO}_3$ thin films undergo cation ordering (unlike the bulk oxide), facilitated by lower oxygen vacancy formation energy and enhanced cation mobility under biaxial strain. Another recent ex situ study of strained $\text{SrCoO}_3$ observed an increase in oxygen nonstoichiometry with tensile strain, though the non-equilibrium nature of the experiment convolutes the kinetics and thermodynamics of oxygen vacancy formation. As can be seen, the difficulty of isolating strain effect from that of the buried interface and misfit dislocations, and the lack of in situ measurements, have precluded a clear connection between biaxial strain and oxygen storage capacity.

In this study, we quantify the effect of large biaxial strain on the surface redox capacity of $\text{CeO}_2$, a prototypical MIEC with wide-ranging applications in chemical catalysis and electrocatalysis. Ceria shows exceptional oxygen nonstoichiometry and phase stability in its bulk form over a range of reducing conditions and elevated temperatures, making it an ideal model system. Owing to the immense lattice mismatch between ceria and YSZ (5.6%), a coherent interface between the two has been regarded as impossible to stabilize. In fact, equilibrium theory predicts a critical thickness of $\sim 0.8$ nm ($< 2$ unit cells, see Supplementary Note 1). We successfully fabricated ultrathin cerium oxide films under biaxial compression on atomically flat, single-crystalline (001) YSZ, and under biaxial tension on (001) STO. Using in situ ambient pressure X-ray photoelectron spectroscopy (APXPS), we directly quantify the surface Ce$^{3+}$ and oxygen vacancy concentrations of the strained ceria films under conditions relevant to solid oxide fuel cells and catalysis, and compare them with those of fully relaxed films. Remarkably, both compressive and tensile strained films showed a significant enhancement in the Ce$^{3+}$ and oxygen vacancy concentrations near the surface compared with the unstrained films. Using depth profiled APXPS and by varying the thickness of strained films, we show that the buried interface does not contribute significantly to the observed strain effects. The use of coherently strained films (~ 5.6% and 2.1%) and measuring oxygen nonstoichiometry in chemical equilibrium with the gas phase capture the true effect of strain. This reproducible, non-monotonic behaviour goes against the conventional wisdom that defect chemical properties vary monotonically with lattice strain and opens up new means to engineer enhanced redox capacity in multilayer structures. By combining APXPS, coupled photoemission–space-charge analysis and density functional theory (DFT) calculations, we demonstrate a systematic framework for understanding and isolating the various thermodynamic contributions (apart from strain) to defect formation at the surface.

**Results**

**Characterization of strain and interface structure.** Three sets of $\text{CeO}_2$ films were studied: (1) 3.2 nm thick, compressively strained on (001) YSZ, (2) 350 nm thick, unstrained on (001) YSZ and (3) 3.0 nm thick, tensile strained on (001) STO. The strain state of the ceria films was quantified using X-ray reciprocal space measurements, have precluded a clear connection between strain effects. The use of coherently strained films (~ 5.6% and 2.1%) and measuring oxygen nonstoichiometry in chemical equilibrium with the gas phase capture the true effect of strain. This reproducible, non-monotonic behaviour goes against the conventional wisdom that defect chemical properties vary monotonically with lattice strain and opens up new means to engineer enhanced redox capacity in multilayer structures. By combining APXPS, coupled photoemission–space-charge analysis and density functional theory (DFT) calculations, we demonstrate a systematic framework for understanding and isolating the various thermodynamic contributions (apart from strain) to defect formation at the surface.
between, we conclude that the film is coherently strained. For CeO$_2$/YSZ, RSM was performed about the STO (103) and ceria (113) reflections, because of the 45° in-plane rotation for registry alignment (see Methods). As evident in Fig. 1c, the in-plane reciprocal lattice vectors of the film and substrate are once again matched, and the relaxed ceria feature expected at (2.15 2.15 1.02) is absent, confirming that the film is coherently strained on STO as well.

Additionally, we used high-resolution transmission electron microscopy (HR-TEM) to directly visualize the atomic structure of the interface. Cross-section TEM specimens were carefully prepared following conventional procedures (see Methods) and negative spherical aberration imaging was performed. Under these conditions, the cation columns appear brighter than the oxygen ion columns. Figure 2a,b shows typical images revealing the epitaxy of fluorite CeO$_2$ on YSZ (compressively strained) (b) 350 nm ceria on YSZ (unstrained/relaxed) and (c) about the (103) reflection of STO for the 3 nm ceria on STO (tensile strained). For the strained oxides, that is, (a,c), the film peak shows up directly below that of the substrate (same ‘h’), confirming identical in-plane lattice constants, that is, coherency. For the relaxed film, the film peak position corresponds to its equilibrium lattice constant; r.l.u., reciprocal lattice unit.

The FFT of the HR-TEM image of CeO$_2$/STO is shown in Fig. 2d. The (00l) peaks of CeO$_2$ and STO are clearly separated in the diffraction pattern, and the difference in d-spacing is verified using a cross-plane line cut (red curve). Along the in-plane direction (blue curve), the [h00] of ceria align with the [2[100] reflections of STO, confirming that the film is lattice matched with the substrate in-plane. The in-plane tension and the corresponding cross-plane Poisson compression are calculated to be 2.1% and 1.3%, respectively, implying a volume increase of 2.9% over the unstrained structure. Table 1 summarizes the strain state of the ultrathin and relaxed films. The magnitude of in-plane and cross-plane elastic strains, ranging from −5.6 to 4.2%, is exceptional. The residual strain due to differential thermal expansion is expected to be 0.1%, given the film’s growth temperature at 550°C in 0.5 mTorr O$_2$, since the coefficient of thermal expansion mismatch between bulk ceria and YSZ is only $\sim 2 \times 10^{-6}$ K$^{-1}$ (refs 44,45). Thus, the measured room temperature strain state is expected to be accurate at the APXPS measurement conditions as well.

The surface topography of the strained films was examined by atomic force microscopy before and after APXPS measurements (Supplementary Fig. 1). In both films, an atomically flat terrace-and-step structure is observed. The step heights are of the order of 2.5 and 4 Å for CeO$_2$ films grown on YSZ and STO, respectively. The fact that the ceria films conform to the substrate terraces shows that they retain their single termination, within the detection limit of atomic force microscopy. The topography was almost identical even after sustained exposure to reducing atmospheres (H$_2$/H$_2$O) and temperatures up to 550°C, suggesting that strain relief through surface roughening was not significant during the course of the experiment.

Quantification of surface nonstoichiometry by APXPS. The primary effect of strain is to modify the interatomic distances in a lattice that consequently modulates the potential energy landscape for electrons, and their energy levels. The tetragonal distortion, c/a of 1.1 for CeO$_2$/YSZ and 0.96 CeO$_2$/STO breaks the cubic symmetry and likely causes significant changes in the electronic structure. In CeO$_2$, the electronic structure has predicted by equilibrium theory (see Supplementary Note 1). We propose that the large nucleation barrier for misfit dislocations stabilizes the coherent film.

The FFT along [001] (in-plane direction, blue curve) shows singlet diffraction spots with a d-spacing of 2.55 Å (that is, 1/2 unit cell YSZ), confirming that the substrate and film have identical in-plane lattice parameter. In the line-cut along [001] (cross-plane direction, red curve), we observe doublets with d-spacings of 2.55 Å (1/2 unit cell YSZ) and 2.82 Å (1/2 unit cell ceria). From these data and equilibrium lattice constants, the in-plane compression and the cross-plane Poisson tension for the ceria films grown on YSZ were calculated to be 5.6% and 4.2%, respectively. This corresponds to a volume decrease of 7.1% from that of the relaxed structure. The 3.2 nm thin-film thickness is significantly greater than the expected critical thickness of 0.8 nm predicted by equilibrium theory (see Supplementary Note 1). We propose that the large nucleation barrier for misfit dislocations stabilizes the coherent film.

The FFT along [010] (in-plane direction, blue curve) shows singlet diffraction spots with a d-spacing of 2.55 Å (that is, 1/2 unit cell YSZ), confirming that the substrate and film have identical in-plane lattice parameter. In the line-cut along [001] (cross-plane direction, red curve), we observe doublets with d-spacings of 2.55 Å (1/2 unit cell YSZ) and 2.82 Å (1/2 unit cell ceria). From these data and equilibrium lattice constants, the in-plane compression and the cross-plane Poisson tension for the ceria films grown on YSZ were calculated to be 5.6% and 4.2%, respectively. This corresponds to a volume decrease of 7.1% from that of the relaxed structure. The 3.2 nm thin-film thickness is significantly greater than the expected critical thickness of 0.8 nm predicted by equilibrium theory (see Supplementary Note 1). We propose that the large nucleation barrier for misfit dislocations stabilizes the coherent film.

The FFT along [010] (in-plane direction, blue curve) shows singlet diffraction spots with a d-spacing of 2.55 Å (that is, 1/2 unit cell YSZ), confirming that the substrate and film have identical in-plane lattice parameter. In the line-cut along [001] (cross-plane direction, red curve), we observe doublets with d-spacings of 2.55 Å (1/2 unit cell YSZ) and 2.82 Å (1/2 unit cell ceria). From these data and equilibrium lattice constants, the in-plane compression and the cross-plane Poisson tension for the ceria films grown on YSZ were calculated to be 5.6% and 4.2%, respectively. This corresponds to a volume decrease of 7.1% from that of the relaxed structure. The 3.2 nm thin-film thickness is significantly greater than the expected critical thickness of 0.8 nm predicted by equilibrium theory (see Supplementary Note 1). We propose that the large nucleation barrier for misfit dislocations stabilizes the coherent film.
Figure 2 | HR-TEM characterization of the CeO$_2$-substrate interfaces. HR-TEM images of the (a) CeO$_2$-YSZ and (b) CeO$_2$-STO interface. Bright and dark spots correspond to cations and anions, respectively. Scale bars, 3 nm. No misfit dislocations were found at either interface, confirming that the coherently strained films of ceria were stable on both YSZ and STO even after several hours of exposure to temperatures up to 550 °C and reducing oxygen partial pressures. (c,d) The FFT patterns of CeO$_2$-YSZ and CeO$_2$-STO obtained from the corresponding TEM images. Line cuts along the in-plane direction (blue curve) show singlet peaks for both films, further confirming coherency with the substrate. Along the cross-plane direction (red curve), doublet peaks are observed, due to Poisson relaxation. Energy-dispersive spectroscopy line scan obtained in scanning TEM mode across the (e) CeO$_2$-YSZ interface and (f) CeO$_2$-STO interface of the strained, ultrathin films show no signs of significant interdiffusion of cations even after APXPS measurements at elevated temperatures. Lines are for guiding the eye.

Table 1 | Summary of crystallographic information obtained from TEM and X-ray diffraction.

| Substrate      | $\varepsilon_{\text{IP}}$ | $\varepsilon_{\text{CP}}$ | $\Delta V$ | c/a   | Thickness |
|----------------|-----------------|-----------------|--------|------|---------|
| Compression    |                 |                 |        |      |         |
| (001) YSZ      | $-5.6\%$        | $4.2\%$         | $-7.1\%$ | 1.1  | 3.2 nm  |
| Unstrained     | (001) YSZ       | 0%               | 0%      | 0    | 350 nm  |
| Tension        | (001) STO       | $2.1\%$         | $-1.3\%$ | 2.9% | 0.96    |

$\varepsilon_{\text{IP}}$ and $\varepsilon_{\text{CP}}$ denote the % strain along in-plane and cross-plane directions, respectively (minus sign denotes compressive strain), $\Delta V$ denotes change in unit cell volume with respect to the unstrained structure and c/a denotes the tetragonal distortion (ratio of cross-plane to in-plane lattice constant).
a direct impact on the redox capacity, since the formation of oxygen vacancies, the primary ionic defects, is accompanied by electron redistribution to render the system charge neutral (formation of Schottky pairs is unlikely under our experimental conditions). Specifically, the formation of an oxygen vacancy is accompanied by electron localization in the unoccupied 4f orbitals of two Ce4+. Using Kroger–Vink notation, the point defect reaction is given by:

$$O_O^– + 2Ce^{3+}_{Ce} \rightarrow V_O + 2Ce^{4+}_{Ce} + \frac{1}{2} O_2$$  \hspace{1cm} (1)

where the species, from left to right, denote O2−, Ce4+, Ce3+ and gaseous oxygen, respectively. Electron correlation causes the occupied (Ce3+) and unoccupied (Ce4+) Ce 4f states to split (Fig. 3a). The occupied Ce 4f state, which can be readily measured by XPS, provides a direct measure of reducibility of ceria.

The in situ APXPS measurements were performed at 450 and 550°C in both O2 and H2/H2O atmospheres to investigate the effect of strain on the equilibrium surface redox behaviour. 250 and 690 eV kinetic energy photoelectrons, with inelastic mean free paths of 0.6 and 1.2 nm respectively, were analysed for quantifying the extent of reduction at different depths from the surface (Supplementary Note 7). The photon energies were adjusted for the binding energies of the different core levels and valence band. Figure 3b,c shows representative valence-band spectra for the 3.2 nm CeO2-δ/YSZ. The spectra have been normalized by the integrated intensity of Ce 4d core-level spectra collected at identical kinetic energies. The reference spectra of oxidized CeO2 (black curve) was collected at $T = 450{\degree}\text{C}$ and $PO_2 = 1.3 \times 10^{-4}$ atm; the Ce 4f feature is absent. The broad feature, between 2 and 8 eV, is that of hybridized O 2p states. Upon lowering the oxygen partial pressure to $PO_2 = 4 \times 10^{-30}$ atm by introducing H2/H2O, a clear Ce 4f peak emerges, reflecting Ce reduction 46,47. Furthermore, this is accompanied by a corresponding decrease in the O 2p (and O 1s) intensity, a measure of the oxygen content (see Supplementary Note 2). Analysis of the unstrained and tensile samples yielded the same result, suggesting that the redox process in all films involves release of oxygen along with formation of Ce3+. The near-surface fraction of Ce3+ was quantified using Ce 4f feature in the valence-band spectra normalized by the Ce 4d peak area, based on a previously validated procedure (see Supplementary Note 3)46,47. The fraction of oxygen sites occupied by Ce3+ is determined by normalizing the O 1s or O 2p intensity against that under oxidizing conditions. Figure 3d plots semiquantitative $[O_O^–] / [Ce_{Ce}]$ versus $[Ce_{Ce}]$ and reveals that the values for all strain states and probing depths essentially fall on the same line (values tabulated in Supplementary Table 1). The slope, a measure of the electroneutrality of the thin films within the XPS probing depth, is 0.30 ± 0.02, close to the electroneutral site fraction of 0.25. We will return to this point later.

A comparison of the valence-band spectra of the compressive, unstrained and tensile strained films, at an information depth of 0.6 nm, is shown in Fig. 4a–c. For ease of comparison, the spectra have been normalized by the maximum intensity of the O 2p feature. Regardless of the strain state, the ceria films are all oxidized at $T = 450{\degree}\text{C}$ and $PO_2 = 1.3 \times 10^{-4}$ atm (dashed line).
Upon lowering the $p_{O_2}$ to $4 \times 10^{-30}$ atm, it is apparent even without quantification that the Ce 4f intensity in the valence-band spectra (solid line) of the strained ceria films is substantially larger (suggesting higher reducibility) as compared with the unstrained film. Additional spectra collected at information depths of 1.2 and 1.8 nm reveal similar strain-induced enhancement. This redox behaviour was also reversible (Supplementary Fig. 2).

Figure 4d,e shows $[\text{Ce}^3]$ as a function of in-plane strain for 0.6 and 1.2 nm information depths, respectively. At $p_{O_2} = 1.3 \times 10^{-4}$ atm (black curve), $[\text{Ce}^3] = 0$ regardless of the strain state. With decreasing oxygen chemical potential (lighter shades of brown), $[\text{Ce}^3]$ increases. Going from 0.6 to 1.2 nm depth, $[\text{Ce}^3]$ drops by a factor of two in strained ceria, and even more so in unstrained ceria. At both information depths, the dependence of $[\text{Ce}^3]$ on strain is consistently non-monotonic. The effect of biaxial tension is nearly twice as potent as that of compression, judging by the slope of the 'V' curves. In other words, 2.1% tension and 5.6% compression lead to similar increase in $[\text{Ce}^3]$ relative to the unstrained value.

At first glance, the enhancement in reducibility with respect to the unstrained sample seems small, since the reported increases in conductivity or surface reactivity often deemed significant are well over an order of magnitude. However, we note that the surface of ceria, even in the absence of strain, is already enriched in Ce$^{3+}$ compared with the bulk$^{45,46}$. Straining the lattice leads to further enrichment of surface oxygen vacancies and Ce$^{3+}$. The fourfold increase in the surface $[\text{Ce}^3]$ of ceria films upon biaxial straining translates to a decrease in the oxygen vacancy formation energy by $\sim 0.4$ eV per O (see Supplementary Note 4). For Sm-doped CeO$_2$,$\omega$ Chueh et al.$^{47}$ determined the reduction enthalpy at the surface to be 2.9 eV, nearly 1 eV lower than that in the bulk (>4 eV). Both compressive and tensile strains lead to a further decrease by 15%. A similar non-monotonic reduction in vacancy formation energies has been reported computationally by Donner et al.$^{40}$ in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ under compression and tension.

**Decoupling strain and space-charge effect on defect concentration.**

The surprising nature of these findings on ultrathin films begs the question of whether the enhancement in redox capacity is dominated by electrostatic or chemical effects arising from the ceria/substrate or ceria/gas interface. Next, we detail several experimental observations and simulations indicating that this is not likely the case. We first compare the redox behaviour of 3.0 nm versus 9.0 nm ceria on STO (Supplementary Fig. 3), both of which are under identical biaxial tension. Figure 5a shows the valence-band spectra at 550 °C and $p_{O_2} = 2 \times 10^{-24}$ atm. The variation of $[\text{Ce}^3]$ with strain and chemical potential are quantitatively unaffected by the film thickness. We also compared the redox behaviour of ~5 nm ceria grown on (001) La$_{0.18}$Sr$_{0.82}$Al$_{0.5}$Ta$_{0.4}$O$_{3}$ (LSAT, 0.7% biaxial tension) and 350 nm ceria grown on YSZ (the unstrained reference). APXPS of ultrathin CeO$_2$/LSAT revealed nearly identical valence-band spectra and $[\text{Ce}^3]$ as the 350 nm CeO$_{2-\omega}$/YSZ over a range of reducing atmospheres (Supplementary Fig. 4 and Supplementary Note 5). Hence, the nature of the substrate and the proximity of the buried interface do not have a discernible impact on the measured redox capacity.

To further confirm that the ceria/substrate interface does not contribute to the strain-dependent redox capacity, we varied the probing depth by changing the photoelectron kinetic energy
during APXPS. Figure 5a shows the Ce 4d spectra for 3 nm CeO$_2$-d/STO at inelastic mean free paths of 0.6, 1.2 and 1.8 nm, respectively, normalized by the two highest binding energy peaks (that do not have any contribution from Ce$^{3+}$). At greater information depths, the intensity of the lower binding energy peaks, which scale with total Ce content, decrease. This suggests that the extent of reduction is greatest at the surface and decreases with probing depth, providing further evidence that the influence of the buried interface on the enhanced reducibility, beyond introduction of uniform elastic strain, is negligible.

For completeness, we also examine the possibility that cations could diffuse from the substrate to the ceria films during growth and/or characterization at elevated temperatures. Diffusion of Zr or Ti into the ceria film, for example, could lead to the formation of Zr or Ti substituted ceria, both of which have a markedly lower enthalpy of reduction, and would hence favour higher Ce$^{4+}$. Using scanning TEM (STEM) analysis with energy-dispersive spectroscopy (with a detection limit of $\sim 1$ at.%) we find no trace of Zr or Ti in the ceria films even after APXPS measurements at elevated temperatures beyond 0.3 nm from the interface (Fig. 2e,f). For a $1\%$ Zr or Ti interdiffusion into ceria, bulk thermodynamics suggests that the Gibbs free energy of reduction will change by less than $1\%$–$2\%$ depending on the oxygen nonstoichiometry.

Finally, we consider the possibility that strain is coupled to space-charge effects at the surface of the film. An electrostatic potential gradient in the near-surface region modulates the binding energy of photoelectrons as a function of depth. The effective photoelectron spectrum, which exponentially integrates signal from different depths in the space-charge region, exhibits a broadening in the full-width at half maximum (FWHM) and a shift in the binding energy (Shavrovskiy et al., in preparation). Figure 5b overlays Ce 4d core-level spectra collected at information depths of 0.6, 1.2 and 1.8 nm, respectively, at $550 \degree C$ for 9 nm CeO$_2$-d/STO. The shift in binding energies of the spectra relative to one another (<0.04 eV) and the change in FWHM (<0.03 eV) with probing depth are within the error of APXPS measurement.

For a more quantitative assessment, we simulated the oxygen vacancy and electron distribution in the near-surface region using a thermodynamically consistent space-charge (SC) model (see Supplementary Fig. 5 and Supplementary Note 6), and calculated the corresponding X-ray photoelectron spectra. Taking a range of electron and oxygen vacancy segregation energies between 0 and $-1.5$ eV as the driving force for SC formation, we mapped out the resulting electrostatic potential in the SC region and in the core, and the concentration profiles (Supplementary Figs 6 and 7). We simulate the [V$_o$/Ce$^{4+}$] by XPS (Fig. 3d), which shows an experimental value of 0.20 ± 0.02, in slight excess of the expected 0.25 in the electroneutral limit. More importantly, the [V$_o$/Ce$^{4+}$] ratio is close to 0.20 ± 0.02 irrespective of the biaxial strain state of the oxide films, and the XPS probing depth (0.6 versus 1.2 nm). Based on the simulations, this experimental result corresponds to a negligible space-charge potential ($\Phi_0$) of <0.1 eV (in the limit that XPS only probes the
Ab initio vacancy thermodynamics under biaxial strain. The most direct impact of biaxial strain on a cubic crystal is to introduce tetragonal distortion, shifting the electronic energy levels and lifting band degeneracy. Ligand field splitting, which leads to a pronounced rearrangement of electronic energies in 3d transition metal perovskites, is negligible in ceria, as evidenced by the narrow Ce 4f bandwidth in ab initio calculations. Under biaxial strain, the bond lengths and bond angles within the oxygen-centred tetrahedra and the spacing between them are modified. Figure 6a illustrates the three stoichiometric unit cells under compression (blue), no strain (green) and tension (red). Also plotted alongside in Fig. 6b are percentage changes in the Ce-O and O-O distances, Ce-O-Ce angles and the spacing between tetrahedra as a function of strain, using the average crystal structure obtained from TEM. For reference, the oxygen at (0.25, 0.25, 0.25) position in unit cell coordinates has been set as the origin in all of the structures. Three salient features emerge. First, the Ce-O distances vary monotonically with biaxial strain and remain degenerate, by virtue of being oriented along the [111] direction. Second, the tetrahedron distortions such that distinct in-plane (Ce$_0$-O$_0$-Ce$_{IP}$) and cross-plane (Ce$_0$-O$_0$-Ce$_{CP}$) angles emerge, where subscripts ‘IP’, ‘CP’ and ‘0’ denote in-plane, cross-plane, and reference species, respectively. While the cross-plane bond angle is greater than the regular tetrahedral angle of 109.47° under compression, the in-plane angle is larger under tension. Third, the O-O distance, that is, the spacing between tetrahedra, is also split into in-plane and cross-plane values that scale oppositely with strain. Based on these simple geometric observations, two distinct oxygen vacancy pairs can be identified for nonstoichiometric ceria, whose formation energetics likely exhibit different dependencies on strain. Biaxial strain also likely exacerbates the tendency for oxygen vacancies to form along certain directions.

Yet another symmetry consideration ties into the relative stabilities of the two-oxidation states of Ce. The 4$^+$ oxidation state is favoured in the eightfold coordinated cubic fluorite structure, while the 3$^+$ oxidation state is more stable in the sixfold coordinated, hexagonal sesquioxide structure. Oxygen nonstoichiometry provides a natural means to lower the oxidation state of Ce to 3$^+$ to better accommodate the lower symmetry under biaxial strain, both compressive and tensile. The competing effects of chemical expansion and symmetry constrained Ce$^{3^+}$ formation could likely lead to the shallower dependence of [CeO$_{C2}$] on compressive strain.

To explore the role of tetragonal distortion under large biaxial strain, we performed DFT plus Hubbard $U$ (DFT + $U$) calculations of oxygen vacancy formation energies ($E_{\text{Vac}}$) in the relatively simpler bulk model system. Specifically, we subject bulk CeO$_{2.5}$ to
bcial versus isostatic strain (see Methods for details). At each value of bcial strain, Poisson relaxation and chemical expansion were explicitly accounted for. The magnitude of the isostatic strain was chosen to match the optimized cell volume under bcial strain for the stoichiometric and nonstoichiometric structures, enabling a meaningful comparison between the two. For instance, 5.0% bcial compression, after accounting for Poisson relaxation, corresponds to an equal change in volume as 2.2% isostatic compression. Figure 6c illustrates $E_{vac}$ as a function of volume (normalized by the corresponding unstrained value), and the values are also tabulated in Supplementary Table 2. Even for the bulk, the difference between isostatic versus bcial—a direct consequence of tetragonal distortion—is striking beyond a volume change of 2 to 3%. For small volume changes, the two modes of straining the lattice result in a monotonic, almost-linear decrease in oxygen vacancy formation energy, in agreement with a recent study on uniaxially strained bulk ceria by Sun et al.30 Under large bcial strain, on the other hand, the behaviour is asymmetric under compression and tension. Specifically, the oxygen vacancy formation energy displays a significantly shallower dependence on compression compared with tension. Interestingly, the vacancy formation energies approach an inflection point around a compressive strain of $\sim$5% (similar to the coherent CeO$_2$/YSZ). We also computed the vacancy formation energies at the (100) terminated surface of ceria under bcial strain (see Methods for details of the surface calculations). The most stable surface vacancies (of the many distinct positions), summarized in Supplementary Table 3, have lower formation energies relative to the bulk, in agreement with the literature, but the dependence on bcial strain is similar to that of the bulk.

To probe the interplay between bcial strain and oxygen vacancy–vacancy interaction, we computed the formation energy of a second oxygen vacancy in a unit cell of bulk ceria (that is, $\delta = 0.50$). We are aware that disordered ceria is likely not stable in its cubic/tetragonal crystal structure at such high oxygen nonstoichiometry. Nevertheless, to achieve a large vacancy concentration while keeping the electron localization problem tractable, this calculation remains insightful. The nonlinearity in the dependence of oxygen vacancy formation energies on volume persists under large bcial strain (Fig. 6c). Moreover, a weakly non-monotonic behaviour becomes apparent at $\delta = 0.50$ compared with $\delta = 0.03$ under large bcial compression. DFT + $U$ calculations reveal that for all values of bcial compressive strain, oxygen vacancy ordering is favoured in the cross-plane direction to minimize vacancy–vacancy repulsion. For low values of bcial tension (up to 2.5%), orienting oxygen vacancies in the cross-plane direction is still favoured, as the chemical expansion due to the significantly larger Ce$^{3+}$ ions is better accommodated along the unconstrained cross-plane direction. For large bcial tensile strain, there is no apparent preference in vacancy ordering in the in-plane and out-of-plane directions, as expected. The coupling between bcial strain and vacancy ordering/association can be inferred from Fig. 6c; cross-plane ordered vacancies become relatively more favoured under large bcial compression compared with tension. This suggests that defect association, enabled by high vacancy content, could be serving as a strain relaxation mechanism34,35.

Chemical expansion associated with oxygen vacancy formation makes the process vibrationally stabilized in the absence of geometric constraints32,33. To investigate the effect under bcial strain, we computed the vibrational entropy and free energy changes with oxygen vacancy formation as a function of temperature under the harmonic approximation at $-5, 0$ and 5% bcial strain. Figure 6d depicts the vibrational free energy and entropy change per oxygen as a function of bcial strain at 550 °C (the corresponding harmonic phonon density of states for the three strain states and two stoichiometries are plotted in Supplementary Fig. 11). The difference in the oxygen vibrational free energy ($E_{vib}$) between compressively strained and unstrained ceria, $\sim 0.1$ eV, is comparable in magnitude to the difference in the enthalpy ($E_{vac}$), also $\sim 0.1$ eV; between tensile strained and unstrained ceria, the difference in the $E_{vib}$, $\sim 0.3$ eV, is likewise significant in magnitude compared with the difference in the $E_{vac}$, $\sim 0.6$ eV. However, in contrast to $E_{vac}$, $E_{vib}$ becomes more favourable as lattice constants are decreased. Given the relative importance of vibrational contribution with increasing temperature, our calculations suggest that this could be another important factor in determining how compression enhances the redox capacity relative to the unstrained ceria.

With these insights, we can now look at the effect of bcial strain on the redox properties as being multipronged, affecting energetics, vibrations and ordering of oxygen vacancies. Under bcial tension, the larger lattice volume and the lowered crystal symmetry inherently favour reduction of ceria. Under bcial compression, Ce$^{3+}$ formation is hindered if the strain coupling works as the only driving force. However, the ability of 3+ oxidation state of Ce to better accommodate the tetragonal distortion from bcial strain and the lowering of vibrational free energy favour the creation of oxygen vacancies. The finding that the enhanced reducibility is insensitive to the type of bcial strain could explain the observation of Song et al.38 about the reduction of Ce in the heterogeneous strain fields surrounding a misfit dislocation.

To conclude, we fabricated ultrathin CeO$_2$-x films that are coherently strained under large bcial compression on (001) YSZ (-5.6%) and tension on (001) STO (2.1%), and characterized their oxygen redox chemistry. The in situ APXPS at 450–550 °C and conditions relevant for water splitting and hydrogen oxidation reactions revealed a dramatic, fourfold enhancement in the surface redox capacity of the ceria films under both compression and tension. Geometrical considerations and ab initio calculations indicate that bcial strain affects the redox capacity not only by its coupling with chemical expansion, but also by breaking the cubic symmetry of ceria through tetragonal distortion. This non-monotonic enhancement in the oxygen nonstoichiometry could be useful in applications relying on redox capacity. The decrease in oxygen vacancy formation energy by $\sim 0.4$ eV observed in this study could lower the operating temperature and/or overpotential of catalysts and electrocatalysts significantly. Our insights into the role of strain may guide the rational redox engineering using nanoscale strain fields such as that found near dislocations and in multilayer structures of nonstoichiometric oxides. In particular, the strain-enhanced redox capacity being largely agnostic to the type of strain could relax material requirements for fabrication.

**Methods**

**Materials and synthesis.** High-quality, ultrathin ceria films were grown on atomically flat single crystal (001) Y$_{2/3}$Sr$_{1/3}$O$_{1.95}$ (YSZ, CrystTec), and (001) SrTiO$_3$ (STO, Shinoda) substrates via pulsed-laser deposition (PLD/MBE 2300, PVD products). While ceria and YSZ crystallize in the cubic fluorite structure under conditions relevant in this study, STO adopts a cubic perovskite structure. The lattice constants of ceria, YSZ and STO are 5.414, 5.142 and 3.905 Å, respectively. The PLD target was pressed uniaxially from commercial CeO$_2$ powder (Sigma Aldrich, 99.999%) and sintered at 1350 °C in 21% O$_2$ balance Ar for 5 h. Single-terminated terraces on YSZ and STO surfaces were obtained using the following annealing procedures. For YSZ, the as-received substrates were sonicated in isopropanol for 15 min, followed by annealing in ultra-high purity Ar at 1,250 °C for 12 h. The STO substrates were sequentially sonicated in isopropanol for 15 min and 18 MΩ water for 30 min. Subsequently, they were etched in 1:6 HF/NH$_4$F mixture, and annealed at 1,000 °C in Ar atmosphere for 2 h to obtain atomically flat terraces.

Subsequently, ceria films were grown in 0.5 mTorr O$_2$ at $\sim 500$ °C in a PLD chamber equipped with a KrF excimer laser. Then, 2 J cm$^{-2}$ laser fluence, 1 Hz
repetition rate (10 Hz for the bulk-like films) and 100 mm target–substrate distance were used. After the deposition, the samples were cooled to room temperature in 0.5 mTorr O₂. The unstrained ceria film (350 nm) was grown on an as-received (001) YSZ substrate.

**X-ray diffraction.** In accordance with the substrate orientation, cross-plane X-ray diffraction scans (Xpert Pro, PANalytical, Cu Kα) revealed only (002) family of peaks for all the ceria films, Supplementary Fig. 8. Phi scans showed that CeO₂ grows epitaxially with perfect alignment registry on YSZ, and with a 45° 0.5 mTorr O₂. The unstrained ceria film (350 nm) was grown on an as-received (001) YSZ substrate.

**Computational methods**

Supplementary Note 3 and Supplementary Fig. 9. The effect of strain on surface oxygen vacancy formation was carried out by imposing biaxial strains of −5.0, 0.0 and +5.0%, and calculating the energy required to remove one oxygen atom. This corresponds to a vacancy concentration of 11% (1 out of 9 oxygen atoms missing) of the topmost 12 Å of the surface slab. We also explored all the possible O-vacancy positions within this probing depth (see Supplementary Fig. 10) for each strain to obtain the lowest energy configuration.

Spin-polarized calculations were performed and the supercell geometries were relaxed until a threshold force of 0.02 eVÅ⁻¹ was fulfilled. Details of electron localization can be found in the Supplementary Note 8. The bulk structures under biaxial strain were modelled by constraining the (x, y) lattice parameters. The cross-plane relaxation (z) was obtained by performing multiple constant-volume calculations at different values of ‘z’, and fitting a parabola to a plot of total energy versus ‘z’. The isostatic strain was chosen to match the volume of each structure obtained after energy minimization under biaxial strain.

Oxygen vacancy formation energies reported in this work were calculated as follows:

\[ E_{\text{vac}} = \frac{1}{n} (E_{\text{non-stoich}} - E_{\text{stoich}} + nE_{\text{O}_2}) \]

where \( E_{\text{non-stoich}} \) and \( E_{\text{stoich}} \) denote total energies of the simulated defect and defect-free cells, respectively, \( n \) denotes the number of oxygen vacancies and \( E_{\text{O}_2} \) denotes half the energy of an isolated oxygen gas molecule. The ordering of the oxygen vacancies along the in-plane and cross-plane directions was investigated using the \( 1 \times 1 \times 1 \) unit cell and creating a second adjacent oxygen vacancy in both directions of the space.

Phonon calculations were performed by means of density functional perturbation theory implemented in the VASP code. With the force constants output by VASP, we obtained the dynamical matrix at different \( q \) points and the phonon density of states (DOS) using Phonopy. Supplementary Fig. 11 shows the phonon DOS for a unit cell of bulk ceria without and with an oxygen vacancy, at strains of −5, 0 and 5%. Upon vacancy formation, compressive strained bulk ceria exhibits the largest softening of phonon frequencies (difference between the nonstoichiometric and stoichiometric phonon DOS). Supplementary Table 4 summarizes the extent of lattice expansion accompanying vacancy formation for the three strain states. For nonstoichiometry change from 0 to 0.25, there is 4.4% expansion along the c-axis under 5% compression as compared with 3.7% and 3.5% under no strain and 5% tension, respectively. Using the harmonic approximation, the vibrational free energies were calculated from the phonon DOS using the following equation:

\[ F_{\text{vb}}(T) = r k_B T \int_0^\infty g(v') \ln \left( \frac{2 \pi k_B T}{h} \right) \frac{h}{2e} \sinh \left( \frac{h v'}{2k_B T} \right) \frac{dv'}{v'} \]

where \( r \) is the number of degrees of freedom, \( g(v') \) is the normalized phonon density of states and \( k_B \) is the Boltzmann constant. The partial molar vibrational free energy of oxygen was computed as the difference in free energies of the nonstoichiometric and stoichiometric structures after accounting for the loss in the phonon modes due to the missing oxygen atoms. Mathematically, it can be expressed as:

\[ \Delta F_{\text{vb}} = F_{\text{vb, non-stoich}} - F_{\text{vb, stoich}} + \text{Fibras et al.}\]

The entropy change \( S_{\text{vb}} \) was calculated by taking the derivative of \( F_{\text{vb}} \) with respect to \( T \).

Data availability. The data supporting the findings in this study are available from the corresponding author on request.

**References**

1. Jacobson, A. J. Materials for solid oxide fuel cells. *Chem. Mater.* 22, 660–674 (2009).
2. Trovarelli, A. Catalytic properties of ceria and CeO₂-containing materials. *Catal. Rev.* 38, 439–520 (1996).
3. Scheffe, J. R. & Steinfeld, A. Oxygen exchange materials for solar thermochemical splitting of H₂O and CO₂: a review. *Mater. Today* 17, 341–348 (2014).
4. Waser, R. & Aono, M. Nanoelectronics-based resistive switching memories. *Nat. Mater.* 6, 833–840 (2007).
5. Tuller, H. L. & Bishop, S. R. Point defects in oxides: tailoring materials through defect engineering. *Annu. Rev. Mater. Res.* 41, 369–398 (2011).
6. Li, J., Shan, Z. W. & Ma, E. Elastic strain engineering for unprecedented materials properties. *MRS Bull.* 39, 108–117 (2014).
7. Chu, M., Sun, Y. K., Aghoram, U. & Thompson, S. E. Strain: a solution for higher carrier mobility in nanoscale MOSFETs. *Annu. Rev. Mater. Res.* 39, 203–229 (2009).
S.C.L. and R.S. were supported additionally by the Precourt Institute of Energy at Stanford. We thank W. Nix, A. Feng and W.E. Gent (Stanford University), Johannes Voss (SLAC) and E. Crumlin (ALS) for insightful discussions.

Author contributions
C.B.G. conceived the experiment. C.B.G. and Y.S. fabricated the thin films, following the procedures developed by the latter. C.B.G., M.M., Z.G. and H.B. carried out the APXPS experiment. S.C.L. performed HRTEM characterization. M.G.-M. and A.V. performed and interpreted the DFT calculations. W.C.C. supervised the project. All authors contributed to writing the manuscript.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Gopal, C. B. et al. Equilibrium oxygen storage capacity of ultrathin CeO$_2$-d depends non-monotonically on large biaxial strain. Nat. Commun. 8, 15360 doi: 10.1038/ncomms15360 (2017).

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material.

To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2017