Atomically-precise colloidal nanoparticles of cerium dioxide

Kylie J. Mitchell¹, Khalil A. Abboud¹ & George Christou¹

Synthesis of truly monodisperse nanoparticles and their structural characterization to atomic precision are important challenges in nanoscience. Success has recently been achieved for metal nanoparticles, particularly Au, with diameters up to 3 nm, the size regime referred to as nanoclusters. In contrast, families of atomically precise metal oxide nanoparticles are currently lacking, but would have a major impact since metal oxides are of widespread importance for their magnetic, catalytic and other properties. One such material is colloidal CeO₂ (ceria), whose applications include catalysis, new energy technologies, photochemistry, and medicine, among others. Here we report a family of atomically precise ceria nanoclusters with ultra-small dimensions up to ~1.6 nm (~100 core atoms). X-ray crystallography confirms they have the fluorite structure of bulk CeO₂, and identifies surface features, H⁺ binding sites, Ce³⁺ locations, and O vacancies on (100) facets. Monodisperse ceria nanoclusters now permit investigation of their properties as a function of exact size, surface morphology, and Ce³⁺:Ce⁴⁺ composition.

¹Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA. Correspondence and requests for materials should be addressed to G.C. (email: christou@chem.ufl.edu)
Since its introduction in 1976 as an oxygen-storage component to ensure the efficient activity of the noble metals used in three-way catalysis in automobile exhausts, cerium (IV) dioxide (CeO₂, ceria) has become of considerable utility as a catalyst or co-catalyst in industrial, petrochemical and environmental processes. In addition, CeO₂-containing materials are often used in oxide fuel cells, precision polishing materials, UV filters, corrosion prevention, and other applications.

This widespread use of Ce is partially due to its significant abundance (0.0046% by weight of the Earth's crust) and its Ce³⁺/Ce⁴⁺ redox couple, which is crucial to many applications by facilitating the formation of CeO₂⁻ₓ, containing highly reactive defect sites comprising O vacancies and attendant Ce³⁺ ions. Ceria can thus act as an efficient oxygen buffer, assisted by oxygen mobility within its layered fluorite structure. In fact, bulk ceria naturally contains relatively few Ce³⁺/O-vacancy defect sites at ambient temperatures, but their number increases at higher temperatures where Ce⁴⁺ reduction and oxygen release are favoured. Catalysis by bulk ceria is therefore normally carried out at temperatures > 450 °C.

In the last decade, interest in ceria nanoparticles (CNPs) has seen explosive growth due to their much greater reactivity and increased catalytic efficiencies at lower temperatures. Significant CNP activity at or near room temperature has also been established, as has facet-dependent reactivity. For example, appreciable oxygen storage capacity is observed at 150 °C on the cubic (100) face of nanoceria crystals, which is ~250 °C lower than for irregularly shaped nanoceria or the bulk material. CNPs are also under investigation as photovoltaic materials in solar cells whereas bulk CeO₂ has no photovoltaic response. Using CNPs instead of a cerium oxide support increases by two orders of magnitude the activity of a Au catalyst for the selective oxidation of CO.

In addition, the higher reactivity of CNPs at ambient temperatures is permitting many important biomedical applications to be developed, such as scavenging of reactive oxygen species (ROS). The CNP activity and toxicity to living tissue clearly depend on particle size and surface composition (e.g., Ce³⁺/Ce⁴⁺ ratios), but as is normally the case in all areas of nanoparticle science, the problems of polydispersity, agglomeration, and surface variations have plagued detailed study of these parameters. For CNPs, it is particularly challenging to determine the concentration and locations of Ce³⁺, attendant O vacancies, and protonated O (i.e., OH⁻, H₂O) species on the surface, and the relationship...
between them. A more controlled approach to monodisperse CeO2 nanoclusters and nanoparticles is clearly needed, especially at the ultra-small, sub-20 nm sizes that are of growing importance, particularly for biomedical applications.

We now describe development of procedures using simple Ce4+ salts and organic reagents that yield a family of monodisperse ceria nanoclusters of different sizes depending on the carboxylic acid employed. Such an approach was recently accomplished for monodisperse metal nanoclusters, primarily of Au, stabilized by thiolate ligands. It no work, the ligands of the carboxylate O atoms) with metal (excluding carboxylate O atoms) showing terminal pyridines ‘capping’ (binding to the center of) the (111) hexagons, and µ2-carboxylates bridging edges joining two (111) facets; f Ce38 (2) showing n2-µ2-carboxylates at edges joining (100) and (111) facets; and g Ce38 (3) showing n2-µ2- and µ1-carboxylates on edges of (110) facets, and µ2-carboxylates bridging edges joining (110) and (111) facets. Colour code: CeIV gold, CeIII sky-blue, O red, N blue, C grey, (100) facets dark blue; (110) facets violet; (111) facets green.

Fig. 2 Ligand binding modes on the surface of ceria nanoclusters. The different binding modes of surface carboxylate and pyridine groups in 1–3: a chelating (η2); b µ2-bridging; c η2-chelating and µ2-bridging; d µ3-bridging; e Ce38 (2) showing terminal pyridines ‘capping’ (binding to the center of) the (111) facets. Finally, the cores are enveloped within the carboxylate employed. Such an approach was recently accomplished for monodisperse metal nanoclusters, primarily of Au, stabilized by thiolate ligands. In our work, the ligands of choice for metal oxide nanoclusters are carboxylates, especially since oleic and similar acids are common surfactants in metal oxide nanoparticle syntheses. The solubility and monodisperse nature of the products we obtain allows molecular crystals to be grown, leading to structural characterization of the nanoclusters and their surface features to atomic precision by single-crystal X-ray diffractometry. The nanoclusters are Ce24O28(OH)8(PhCO2)30(py)4 (1; Ce24), Ce38O56(OH)8(EtCO2)36(py)8 (2; Ce38) and Ce40O56(OH)2(MeCO2)44(MeCO2H)4(py)4/MeCN (3a/b; Ce40), where py is pyridine. 3a/3b denote the two independent nanoclusters in the asymmetric unit of 3, which differ slightly in the organic ligation. 2 also contains two independent nanoclusters (2a/2b), but they have the same formulation.

Results

Nanocluster structures. Several pertinent points about the complete structures of 1–3 (Fig. 1a–c) will be summarized to allow for convenient comparisons. They all comprise CeO2 cores (excluding carboxylate O atoms) with metal (x) and total (x+y) atom counts of 24/60, 38/100 and 40/98 for 1–3, respectively, and they exhibit the same fluorite structure as bulk CeO2, i.e., alternating layers of 8-coordinate cubic Ce4+ and 4-coordinate tetrahedral O2− ions. Some surface Ce4+ ions are 7- or 9-coordinate (vide infra). From the viewpoint of Fig. 1d–f, the cores consist of five Ce layers in an A:B:C:B:A pattern (1, A = 2, B = 6, C = 8; 2, A = 4, B = 9, C = 12; 3, A = 4, B = 10, C = 12), leading to the Ce38 core of 2 being essentially spherical (1.12 × 1.12 × 1.12 nm) whereas those of Ce38 (1, 0.75 × 1.10 × 1.10 nm) and Ce40 (3, 1.13 × 1.13 × 1.61 nm) are ellipsoidal. The Ce38 can also be described as a ‘truncated octahedron’, a structure that is one of those recently predicted by DFT studies to be favoured for Ce3+ fragments of CeO2 in this size range. 2 contains only Ce4+, but 1 and 3 each also contain two 10-coordinate Ce3+ ions at opposite ends of the cores, as suggested by DFT calculations on Ce3+ in CeO2 fragments of CeO2. The Ce oxidation states were confirmed by bond valence sum (BVS) calculations (Supplementary Table 2) and the detection of Ce3+ (S = ½) EPR spectra for 1 and 3. The latter were measured on microcrystalline powders at 5 K (Supplementary Figs. 1 and 2) and are comparable with the few Ce3+ EPR spectra reported for CeO2 nanoparticles or Ce3+ doped into polymeric species. Nanoclusters 1–3 are large enough to display multiple facets (Fig. 1g–i), as do CNPs; the different faces for CeO2 and Ce40 are defined in Supplementary Fig. 3. 1 and 2 display only (100) and (111) facets, whereas 3 exhibits these and also (110) facets. Finally, the cores are enveloped within monolayer organic shells of carboxylate and py groups, which exhibit only minor positional disorder in some C and O atoms (Fig. 1a–c).
The structural results thus strongly support the description of 1–3 as atomically precise ceria nanoclusters in the ultra-small size range corresponding to the smallest CNPs synthesized to date, and stabilized to agglomeration by the organic monolayers. CNPs at this sub-20 nm size are being heavily targeted for use in various applications, especially in the biomedical field because they show enhanced catalytic activity and regenerative properties. 1–3 are larger than the few previously known Ce/O molecular species, most of which are Ce6 species and some with tridentate amino-alcohol N,O,O-chelates. It should be noted that the large family of monodisperse, crystalline polyoxometalates, some with extremely long (2.7–2.9 Å), which thus anchors the H+ on O15 and O16 and gives the expected O BVS of 2.12 (Supplementary Table 3). In contrast, the two Ce4+ O2- ions in 2 are ordered since there is no reason for H+ to favour particular Ce4+ O2- ions when so many are essentially equivalent. Slightly lowered BVS values (1.52–1.72) for the four μ2-O2- ions at O18/O39 and the four at O49/O60 in 2a and 2b, respectively (Supplementary Table 4), suggest that the 2H+ are randomly distributed primarily among these positions to give partial μ2-OH- occupancies.

In body Ce4 atoms, each edge is oxide-bridged, but at the surface the edges are carboxylate-bridged. These are the (100) facets (Fig. 1g–i) and occur in three slightly different forms. The six separated Ce4+ squares in 2 (Fig. 3b), the two Ce4+Ce3+Ce4+ squares in 3 (Fig. 3c), and two Ce4+, Ce3+ squares in 3 (Fig. 3c) are all bridged by a μ2-OH- ion with rare tetragonal pyramidal geometry (the O is 0.7–0.8 Å above the Ce4 plane). All μ2-OH- ions have similar O BVS values of 0.52–0.71 (Supplementary Tables 3–5), intermediate between those of OH- and H2O. In 1 (but not 2 or 3), the μ2-OH- protons (H12 and H14) were observed in different observation modes, informing them (and by extension those in 2 and 3) to be OH-, not H2O. The Ce4+-OH- and Ce3+-OH- distances are extremely long (2.7–3.0 Å; Supplementary Table 7) and suggest minimal Ce-O bonding; for comparison, Ce4+-μ2-O22- = 2.2–2.3 Å, Ce4+-μ2-O2- = 2.3–2.5 Å, and Ce4+-μ2-OH- = 2.3–2.45 Å. The very long Ce-μ2-OH- distances suggest an essentially free OH- ion acting as a weakly docked ‘lid’ on the Ce4 surface (and thus rationalizing its small BVS). Space-filling representations (Supplementary Fig. 6) show the OH- to be encapsulated by the surrounding carboxylates and cannot move from its μ2 central position to become more strongly bound μ2 or μ3.

3 also contains planar double-square units (Fig. 3d, e), and these do not contain μ1-OH- ions. Instead, those in 3a (Fig. 3d) have η2-carboxylates attached to one Ce that act as lids, tilting inwards so that one O atom approaches the mid-point of each square; the three resulting Ce-O separations (∼3.0 Å) indicate extremely weak contacts (Supplementary Table 8). In 3b, one η2-carboxylate of each double-square is replaced by a MeCN, as described above, and this again tilts over the center of the square to act as a lid, giving a very unusual bent binding mode. The three resulting Ce-N separations (>3.0 Å) again indicate only very weak contacts. Interestingly, these planar double squares in 3 are each fused at their Ce4+ corners to the μ2-O2- bridged Ce4+,Ce3+ squares (Fig. 3c) described above, so that 3 contains two asymmetric L-shaped (86.1°) triple squares with the Ce3+ lying at the inner point of the L. For charge balance, 3a must also contain two additional H+. Since the O BVS values indicate they are not on surface μ1-O2- ions, we suspected them to be on ligand groups. Indeed, three carboxylate O atoms

### Table 1: Type of surface ligands in nanoclusters 1–3

| Type   | Binding mode | Found | Surface location |
|--------|--------------|-------|-----------------|
| O2-    | μ2-bridging  | 1-3   | (111) or (110) Ce3 triangle |
| OH-    | μ2-bridging  | 1, 2  | (111) Ce3 triangle |
| OH-    | μ4-bridging  | 1-3   | Lid on (100) Ce4 square |
| py     | terminal     | 1-3   | Capping of (111) hexagon |
| MeCN   | terminal     | 3b    | Lid on (100) Ce4 square |
| RCO2-  | η2-chelating  | 3     | Lid on (100) Ce4 square |
| RCO2-  | η2-μ2-chel/brid | 1-3 | Ce3 edge joining (100) (111) |
| RCO2-  | μ2-bridging  | 1-3   | Ce3 edge joining (110) (111) |
| RCO2-  | μ3-bridging  | 3     | V-shaped Ce3 edge of (110) |

The surface features are the multi-faceted surface structure, including py groups completing ligation where necessary. Both types of μ2-carboxylates occur in all three nanoclusters and bridge Ce2 edges joining two facets, one of which is always a (111) facet (Table 1 and Fig. 2e–g). Interestingly, the η2-μ2 mode is found only at (100)(111) and (110)(111) edges, whereas the μ2 mode is found only at (111)(111) and (110)(111) edges. In contrast, μ3-carboxylates occur only in 3, bridging a V-shaped edge of the (110) facets. The η2-chelating mode is also only found in 3, always bound to one Ce of a (100) Ce4 square (vide infra). Terminal py ligands occur in all three nanoclusters, always ‘capping’ a (111) hexagon, i.e., attached to its central Ce (Fig. 2e). The two independent Ce3+ nanoclusters in 2 are identical in formula and structure, but the two Ce40 units in 3 provide the benefit of slightly differing organic monolayer shells, revealing one way the latter can vary for a given nanocluster core. Thus, the chelating carboxylates (Fig. 2a) on two Ce4+ ions (Ce9) in 3a are each replaced by a terminal MeCN (on Ce32) in 3b, converting 9-coordinate Ce9 into 8-coordinate Ce32.

There are two distinct Ce surface subunits in 1–3 resulting from the fluorite structure, Ce3 triangles and Ce4 squares, and these will be described in turn. Ce3 triangles are very common surface units in (111) and (110) facets and are bridged primarily by pyridyl μ3-O2- ions (Table 1), from tetrahedral body O2- ions now binding one less Ce. Some in 1 and 2 are instead bridged by μ2-OH- ions (Fig. 3a); the four in 1 are obvious from their O–H–N hydrogen bonding to lattice py molecules (O–N = 2.7–2.9 Å), which thus anchors the H+ on O15 and O16 and gives the expected O BVS of 1.21 (Supplementary Table 3). In contrast, the CeO2- ions in 2 are disordered since there is no reason for H+ to favour particular CeO2- ions when so many are essentially equivalent. Slightly lowered BVS values (1.52–1.72) for the four μ2-O2- ions at O18/O39 and the four at O49/O60 in 2a and 2b, respectively (Supplementary Table 4), suggest that the 2H+ are randomly distributed primarily among these positions to give partial μ2-OH- occupancies.

In body Ce4 atoms, each edge is oxide-bridged, but at the surface the edges are carboxylate-bridged. These are the (100) facets (Fig. 1g–i) and occur in three slightly different forms. The six separated Ce4+ squares in 2 (Fig. 3b), the two Ce4+Ce3+Ce4+ squares in 3 (Fig. 3c), and two Ce4+, Ce3+ squares in 3 (Fig. 3c) are all bridged by a μ2-OH- ion with rare tetragonal pyramidal geometry (the O is 0.7–0.8 Å above the Ce4 plane). All μ2-OH- ions have similar O BVS values of 0.52–0.71 (Supplementary Tables 3–5), intermediate between those of OH- and H2O. In 1 (but not 2 or 3), the μ2-OH- protons (H12 and H14) were observed in different observation modes, informing them (and by extension those in 2 and 3) to be OH-, not H2O. The Ce4+-OH- and Ce3+-OH- distances are extremely long (2.7–3.0 Å; Supplementary Table 7) and suggest minimal Ce-O bonding; for comparison, Ce4+-μ2-O22- = 2.2–2.3 Å, Ce4+-μ2-O2- = 2.3–2.35 Å, and Ce4+-μ2-OH- = 2.3–2.45 Å. The very long Ce-μ2-OH- distances suggest an essentially free OH- ion acting as a weakly docked ‘lid’ on the Ce4 surface (and thus rationalizing its small BVS). Space-filling representations (Supplementary Fig. 6) show the OH- to be encapsulated by the surrounding carboxylates and cannot move from its μ2 central position to become more strongly bound μ2 or μ3.

3 also contains planar double-square units (Fig. 3d, e), and these do not contain μ1-OH- ions. Instead, those in 3a (Fig. 3d) have η2-carboxylates attached to one Ce that act as lids, tilting inwards so that one O atom approaches the mid-point of each square; the three resulting Ce-O separations (∼3.0 Å) indicate extremely weak contacts (Supplementary Table 8). In 3b, one η2-carboxylate of each double-square is replaced by a MeCN, as described above, and this again tilts over the center of the square to act as a lid, giving a very unusual bent binding mode. The three resulting Ce-N separations (>3.0 Å) again indicate only very weak contacts. Interestingly, these planar double squares in 3 are each fused at their Ce4+ corners to the μ2-O2- bridged Ce4+,Ce3+ squares (Fig. 3c) described above, so that 3 contains two asymmetric L-shaped (86.1°) triple squares with the Ce3+ lying at the inner point of the L. For charge balance, 3a must also contain two additional H+. Since the O BVS values indicate they are not on surface μ1-O2- ions, we suspected them to be on ligand groups. Indeed, three carboxylate O atoms
attached to Ce$^{3+}$, namely O40, O40′ and O83, form a triangle and all show lowered BVS values of 1.78, 1.78 and 1.65, respectively, suggesting an H$^+$ is capping each of the two triangles in 3a by interacting with the O atoms in a trifurcated fashion (Supplementary Table 5). The formulation of 3b can now be rationalized as resulting from loss of some of the chelating MeCO$_2^-$ groups in 3a, assisted by protonation to MeCO$_2$H by these H$^+$, and replacement by MeCN solvent molecules in 3b.

The two Ce$^{3+}$ each in 1 and 3 are thus all at surface sites, as suggested to also be the case in CNPs$^{10,38}$. The lower Ce$^{3+}$ charge favors fewer O$_2^-$ ligands than Ce$^{4+}$ and thus disfavors body sites. In contrast, 2 contains no Ce$^{3+}$. Interestingly, all Ce$^{3+}$ occur within (100) Ce$^{3+}$Ce$^{4+}$ square facets. In 3 (Fig. 3c), the Ce$^{3+}$-OH$^-$ and Ce$^{4+}$-OH$^-$ distances are identical (~2.7 Å), again supporting weak contacts by the μ$_4$-OH$^-$. In 1, the V-shaped double-square joined at the Ce$^{3+}$ corner (Fig. 3f) has a Ce$^{3+}$-OH$^-$ distance of ~2.7 Å on one side, but this causes a longer Ce$^{3+}$-OH$^-$ on the other (~3.0 Å; Supplementary Table 7). It is also extremely interesting that when Ce$^{3+}$ ions are present, the surface H$^+$ (i.e., OH$^-$ ions, and H$^+$ hydrogen bonding to carboxylate groups) are located very close to them. The presence and positions of H$^+$ on nanoparticles are extremely challenging to determine$^{39}$, but in nanoclusters 1 and 3 most of them are directly observed and clearly accumulate on O atoms near Ce$^{3+}$ (Fig. 1d, f). The effect is likely synergistic, i.e., the lower Ce$^{3+}$ charge favors accumulation of H$^+$ nearby, which in turn mollify the O$_2^-$ and carboxylate charges and stabilize the lower Ce$^{3+}$ charge. In contrast, with no Ce$^{3+}$ in 2, the H$^+$ spread out over the surface (Fig. 1e), although they again favor Ce$_4$ squares. H$^+$ are expected to be mobile on the nanocluster surfaces, as recent work has concluded from studies of hydrogen mobility (‘hopping’) on surface O atoms of CeO$_2$ thin films$^{40}$. Double protonation of an O$_2^-$ and desorption of surface H$_2$O was suggested as the means of forming O vacancies.

**Discussion**

We have shown that a bottom-up synthetic approach in solution at ambient temperatures using readily available reagents can be successfully applied to obtain a family of monodisperse metal oxide nanoparticles of ultra-small dimensions. This thus achieves for metal oxides what was previously accomplished for the distinctly different area of metal nanoparticles, particularly of Au. In the present work, monodisperse CeO$_2$ nanoclusters with the fluorite structure and monolayer organic ligand shells can be synthesized and structurally characterized to atomic resolution. They exhibit multifaceted structures consisting mainly of (100) and (111) facets, but 3 also has (110) facets giving noticeable surface kinks/edges/trenches. The surface location of any Ce$^{3+}$ ions and the H$^+$ positions on μ$_3$- and μ$_4$-OH$^-$ groups, as well as ligand groups, are particularly welcome to know. The μ$_4$-OH$^-$ are weakly attached with long Ce···O distances to the (100) facets, acting as lids on Ce$_4$ squares, as also do O (carboxylate) and N (MeCN) lids on other (100) facets. Such surface features are likely of great relevance to CNP reactivity: Under heterogeneous catalysis conditions, or in solution or colloidal suspension, one can
envisage the ready loss or ‘opening’ of such weakly interacting lids (e.g., by protonation of OH\(^-\), detachment of MeCN, or tilting away of the chelating carboxylate, perhaps by becoming monodentate) exposing Ce\(_4\) square faces for reaction. We thus propose these weakly lidded Ce\(_4\) sites as resting states of some of the catalytically highly reactive, surface O-vacancy sites in CNPs. In addition, when Ce\(^{3+}\) ions are present, their locations in 1 and 3 corner-linking two (100) Ce\(^{3+}\)-Ce\(^{3+}\) squares, and the concomitant accumulation nearby of mobile H\(^+\), \(\mu_2\)-OH\(^-\), \(\mu_4\)-OH\(^-\) and/or ligand groups, together offer a possible picture for the high catalytic activity of surface Ce\(^{3+}\) in CNPs. Similarly, the kinks/edges/trenches associated with the (110) facets in CNPs is the most thermodynamically stable while the (100) facet is highly reactive due to its lower stability and is therefore a proposed site for O vacancies and Ce\(^{3+}\) ions\(^{37,29,43}\), observations that are consistent with the surface features we have identified in 1–3.

Even on the basis of only the three nanoclusters described herein, it is already apparent how CNPs with similar sizes can have very different properties and reactivities. Although 2 and 3 are essentially the same size and metal nuclearity, they differ significantly in their overall shape, the variety of facets they exhibit, the resulting surface morphology, and their Ce\(^{3+}\) content. On the other hand, the availability now of samples of identical, monodisperse nanoclusters makes possible the study of activity vs. exact size, surface morphology and Ce\(^{3+}\) content. In addition, while dispersions of CNPs in water are often unstable, leading to agglomeration that can affect their transport, distribution and reactivity, particularly for ultra-small CNPs in biomedical studies, 3 is completely water soluble and affords the opportunity to study reactivity in biologically relevant media\(^{27,44}\).

Finally, 1–3 contain either Ce\(^{4+}\)-\(\mu_4\)-OH\(^-\) or Ce\(^{3+}\)-Ce\(^{3+}\)-\(\mu_4\)-OH\(^-\)(100) squares, or both, and this variation may also be responsible for the recognized redox-dependent ROS-scavenging ability and toxicity of CNPs with different amounts of surface Ce\(^{3+}\)\(^{21,22,45,46}\). In contrast, recent suggestions that 1.1–3.5 nm CNPs should have a defect-fluorite structure and a fluorite structure and a nanocrystals with cubic facets. Furthermore, the conventional wisdom that smaller CNPs have more surface Ce\(^{3+}\) may reflect the greater number of such V-shaped units present in smaller nanoparticles of lower symmetry as a result of their increased number of points of high curvature. We are currently seeking to extend the family to larger nanoclusters and higher Ce\(^{3+}\)-Ce\(^{3+}\) ratios, and exploring the reactivity of 1–3 with ROS.

Methods

Syntheses. [\(\text{Ce}_2\text{O}_2\text{O}(\text{OH})(\text{PhCO}_2\text{O})_2\text{py}(\text{py})_4\)] \(^1\) was prepared by the reaction of (NH\(_3\))\(_2\)[Ce(NO\(_3\))]\(_3\) and PhCO\(_2\)H in a 1:2 molar ratio in pyridine at room temperature. The yellow-golden solution was stirred for 30 mins, diluted with 2 volumes of MeCN, and maintained undisturbed for 1 week. The resulting yellow square plates of 1 were collected by filtration, washed with MeCN, and dried in vacuum. The yield was 14% based on Ce. Anal. Calc. (Found) for dried 1: 2py (C\(_{24}\)H\(_{18}\)O\(_{15}\)Ce\(_2\)N\(_{10}\)O\(_{10}\)) \(\times\) C, 35.79 (35.63); H, 2.35 (2.00); N, 1.04 (0.98). [\(\text{Ce}_2\text{O}_2\text{O}(\text{OH})(\text{EtCO}_2\text{O})_2\text{py}(\text{py})_4\)] \(\times\) MeCN (2\(\times\)MeCN), and [\(\text{Ce}_2\text{O}_2\text{O}(\text{OH})(\text{MeCO}_2\text{H})_2\text{MeCN}\)]\(_2\) (py\(_4\)) \(\times\) 48MeCN have been deposited at the Cambridge Crystallographic Data Centre with deposition codes CCDC 1529955-1529957 for 1–3, respectively.

Received: 9 August 2017 Accepted: 6 October 2017
Published online: 13 November 2017

References

1. Flytzani-Stephanopoulos, M. Nanostructured cerium oxide “ecocatalysts”. MRS. Bull. 26, 885–889 (2001).
2. Trovarelli, A. Catalytic properties of ceria and CeO\(_2\)-containing materials. Catal. Rev. 38, 439–520 (1996).
3. Wang, Q., Zhao, B., Li, G. & Zhou, R. Application of rare earth modified Zr-based ceria-zirconia solid solution in three-way catalyst for automotive emission control. Environ. Sci. Technol. 44, 3870–3875 (2010).
4. Qi, X. M. & Flytzani-Stephanopoulos, M. Activity and Stability of Cu-CeO\(_2\) Catalysts in high-temperature water-gas shift for fuel-cell applications. Ind. Eng. Chem. Res. 43, 3055–3062 (2004).
5. Sharma, S., Hilaire, S., Vohs, J. M., Gorte, R. J. & Jen, H. W. Evidence for oxidation of ceria by CO\(_2\). J. Catal. 190, 199–204 (2000).
6. Murray, E. P., Tsai, T. & Barnett, S. A. A direct-methane fuel cell with a ceria-based anode. Nature 400, 649–651 (1999).
7. Panagiotopoulou, P., Papavasiliou, J., Avgouropoulos, G., Ioannides, T. & Kondarides, D. I. Water-gas shift activity of doped Pt/CeO\(_2\) catalysts. Chem. Eng. J. 134, 16–22 (2007).
8. Fan, L., Wang, C., Chen, M. & Zhu, B. Recent development of ceria-based (nano)composite materials for low temperature ceramic fuel cells and electrolyte-free fuel cells. J. Power Sources 234, 154–174 (2013).
9. Sun, C., Li, H. & Chen, L. Nanostructured ceria-based materials: synthesis, properties, and applications. Energy Environ. Sci. 5, 8475–8505 (2012).
10. Reed, K. et al. Exploring the properties and applications of nanoceria: is there still plenty of room at the bottom? Environ. Sci. Nano 1, 390–405 (2014).
11. Castano, C. E., O’Keeffe, M. J. & Fahrenholtz, W. G. Cerium-based oxide coatings. Curr. Opin. Solid State Mater. Sci. 19, 69–76 (2015).
12. Perullini, M., Aldabe Bilmes, S. A. & Jobbagy, M. in Nanomaterials: A Danger or a Promise? (eds Brayner, R., Fiévet, F. & Coradin, T.) 307–333 (Springer, London, 2012).
13. Beckers, J. & Rothenberg, G. Sustainable selective oxidations using ceria-based materials. Green. Chem. 12, 939–948 (2010).
14. Lawrence, N. J. et al. Defect engineering in cubic cerium oxide nanoclusters for catalytic oxidation. Nano Lett. 11, 2666–2671 (2011).
15. Tabakova, T. et al. A comparative study of nano sized IB/ceria catalysts for low-temperature water-gas shift reaction. Appl. Catal. A 298, 127–143 (2006).
16. Mann, A. K. P., Wu, Z., Calaza, F. C. & Overbury, S. H. Adsorption and reaction of acetaldehyde on shape-controlled CeO\(_2\) nanocrystals: elucidation of structure-function relationships. ACS Catal 4, 2437–2448 (2014).
17. Zhang, J. et al. Extra-low-temperature oxygen storage capacity of CeO\(_2\) nanocrystals with cubic faces. Nano Lett. 11, 361–364 (2011).
18. Corma, A., Atienzar, P., Garcia, H. & Chane-Ching, J.-Y. Hierarchically mesostructured doped CeO\(_2\) with potential for solar-cell use. Nat. Mater. 3, 394–397 (2004).
30. Dutta, P. et al. Concentration of Ce³⁺ and oxygen vacancies in cerium oxide crystallites. *ACS Nano* **6**, e90 (2014).

31. Canevali, C. et al. Stability of luminescent trivalent cerium in silica host glasses modified by boron and phosphorus. *J. Am. Chem. Soc.* **127**, 14681–14691 (2005).

32. Martos, M., Julián-López, B., Folgado, J. V., Cordoncillo, E. & Escrigano, P. Sol–gel synthesis of tunable cerium titanate materials. *Eur. J. Inorg. Chem.* **2008**, 3163–3171 (2008).

33. Chen, J., Patil, S., Seal, S. & McGinnis, J. F. Rare earth nanoparticles prevent retinal degeneration induced by intracellular peroxides. *Nat. Nano* **1**, 142–150 (2006).

34. Ju-Nam, Y. & Lead, J. R. Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Sci. Total Environ.* **400**, 396–414 (2008).

35. Mathey, L., Paul, M., Copéret, C., Tsurugi, H. & Mashima, K. Cerium(IV) hexameric clusters from cerium(III) precursors. Molecular models for oxidative growth of ceria nanoparticles. *Chem. Eur. J.* **21**, 13454–13461 (2015).

36. Estes, S. L., Antonio, M. R. & Soderholm, L. Tetravalent Ce in the nitrate-decorated hexanuclear cluster [Ce₆(O₂)₂(µ₄-OH)₄]₁₂⁺: A structural end point for ceria nanoparticles. *J. Phys. Chem. C* **120**, 5810–5818 (2016).

37. Malasteen, I. L., Ellern, A., Baca, S. & Kogerler, P. Cerium oxide nanoclusters: commensurate with concepts of polyoxometalate chemistry? *Chem. Commun.* **48**, 1499–1501 (2011).

38. Loschen, C., Bromley, S. T., Neyman, K. M. & Illes, F. Understanding ceria nanoparticles from first-principles calculations. *J. Phys. Chem. C* **111**, 10142–10145 (2007).

39. Zherebetskyy, D. et al. Hydroxylation of the surface of PbS nanocrystals passivated with oleic acid. *Science* **344**, 1380–1384 (2014).

40. Shahed, S. M. F. et al. STM and XPS study of CeO₂(111) reduction by atomic hydrogen. *Surf. Sci.* **628**, 30–35 (2014).

41. Lu, J. L., Gao, H. J., Shahkhdinov, S. & Freund, H. J. Gold supported on well-ordered ceria films: nucleation, growth and morphology in CO oxidation reaction. *Catal. Lett.* **114**, 8–16 (2007).

42. Nilius, N. et al. Formation of one-dimensional electronic states along the step edges of CeO₂(111). *ACS Nano* **6**, 1126–1133 (2012).

43. Mullins, D. R. The surface chemistry of cerium oxide. *Surf. Sci. Rep.* **70**, 42–85 (2014).

44. Karakoti, A. S. et al. Nanoceria as antioxidant: synthesis and biomedical applications. *JOM* **60**, 33–37 (2008).

45. Pulido-Reyes, G. et al. Untangling the biological effects of cerium oxide nanoparticles: the role of surface valence states. *Sci. Rep.* **5**, 15613 (2015).

46. Pirmohamed, T. et al. Nanoceria exhibit redox state-dependent catalytic mimic activity. *Chem. Commun.* **46**, 2736–2738 (2010).

47. Hallstone, R. K., DiFrancesco, A. G., Leong, J. G., Allston, T. D. & Reed, K. J. A study of lattice expansion in CeO₂ nanoparticles by transmission electron microscopy. *J. Phys. Chem. C* **113**, 15155–15159 (2009).

48. Baranchikov, A. E., Polezhaeva, O. S., Ivanov, V. K. & Tretyakov, Y. D. Lattice expansion and oxygen non-stoichiometry of nanocrystalline ceria. *Cryst. Eng. Comm.* **12**, 3531–3533 (2010).