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Towards the Sub-15nm CeO₂ Nanowires with Increased Oxygen Defects and Ce³⁺ Sites for Selective Oxidation of Aniline at Roomtemperature with a Non-Noble Metal Catalyst

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Abstract

We described herein the facile synthesis of sub-15 nm CeO₂ nanowires based on a hydrothermal method without the use of any capping/stabilizing agent, in which an oriented attachment mechanism took place during the CeO₂ nanowires formation. The synthesis of sub-15 nm CeO₂ nanowires could be achieved on relatively large scales (~ 2.6 grams of nanowires per batch), high yields (> 94 %), and low cost. To date, there are only a limited number of successful attempts towards the synthesis of CeO₂ nanowires with such small diameters, and the reported protocols are typically limited to low amounts. The nanowires displayed uniform shapes and sizes, high surface areas, increased number of oxygen defects sites, and a high proportion of Ce^{3+}/Ce^{4+} surface species. These features make them promising candidates for oxidation reactions. To this end, we employed the selective oxidation of aniline as a model transformation. The sub-15 nm CeO₂ nanowires catalyzed the selective synthesis of nitrosobenzene (up to 98 % of selectivity) from aniline at room temperature using H_2O_2 as oxidant. The effect of solvent and temperature during the catalytic reaction was investigated. We found that such parameters played an important role in the control of the selectivity. The improved catalytic activities observed for the sub-15 nm nanowires could be explained by: i) the uniform morphology with typical dimensions of 11 ± 2 nm in width, which provide higher specific surface areas relative to conventional catalysts; ii) the significant concentration of oxygen vacancies and high proportion of Ce^{3+}/Ce^{4+} species at the surface that represent highly active sites towards oxidation reactions, *iii*) the crystal growth through (110) highly catalytically active crystallographic directions, and iv) the mesoporous surface which is easily accessible by liquid substrates. The results reported herein demonstrated high activities under ambient conditions, provided novel insights over

selectivities, and may inspire novel metal oxides-based catalysts with desired performances.

Introduction

Metal oxide nanowires have received tremendous attention due to their interesting and unique electronic, optical, thermal, mechanical, magnetic, and catalytic properties.^{1–4} Among them, cerium oxide (CeO₂) has been widely employed in the field of heterogeneous catalysis applications due to its intrinsic oxygen storage capability at the surface and the presence of Ce³⁺/Ce⁴⁺ ions, which are crucial in several catalytic redox cycles.^{5–11} For example, CeO₂ catalysts have widely been used in automotive three-way catalytic systems to oxidize toxic organic compounds (CO, NO_x and hydrocarbons),^{12,13} and also towards the partial oxidation of a variety of organic compounds with commercial value and industrial applications.^{7,14–16}

In order to improve the redox cycle and increase the oxygen storage capability of CeO₂ catalysts for oxidation reactions, researchers have focused efforts on the manipulation of their physicochemical features by controlling their size, shape, morphology and surface area.^{17–20} It has been demonstrated that control over the nanoparticle size and shape (*e.g.*, nanocubes, nanorods, nanowires, etc) strongly affects their properties,^{9,11,21,22} endowing nanoparticle shape-control as an efficient strategy for maximizing performance. For example, CeO₂ nanomaterials with sizes below 20 nm display substantial enlargement in their cell parameters and an increased quantum confinement effect.²³ This tends to facilitate the reduction of Ce⁴⁺ to Ce³⁺ ions, and as a consequence generating an increased amount of oxygen vacancies.²⁴

In particular, one-dimensional (1D) CeO₂ nanowires have attracted great attention in catalysis^{25,26} for the following reasons: (i) the higher specific surface areas relative to commercial catalysts;²⁶ (ii) the crystal growth through (110) and (100) highly catalytically active crystallographic directions,²⁷ (iii) the surface of nanowires is easily accessible by gas and liquid substrates due to their porous structures,²⁸ and (iv) sintering processes, which normally are responsible for major decreases of the surface area in several catalysts and they can be significantly retarded in nanowires as compared to other shapes.²⁸ Moreover, increasing the aspect ratio offers an effective strategy for further improving several interesting properties of CeO₂ nanowires (surface area, oxygen vacancies, $Ce^{3+/}Ce^{4+}$ ions, etc).^{26,27} However, it has been difficult to generate CeO₂ nanowires with high aspect (length/diameter) ratio and diameters smaller than 15 nm, which, due to the small sizes, are highly desirable in catalytic applications. In fact, there are a number of successful attempts reported for the synthesis of CeO_2 nanowires in large scale. In an earlier report, Zhang and co-workers prepared Ba-doped CeO₂ nanowires in gram quantities using the composite-hydroxide-mediated approach in a one-step and lowcost procedure.²⁹ However, this and most of these reported protocols for the synthesis of CeO_2 nanowires do not display thin diameters (< 20 nm) and high aspect ratios (ratio of length to diameter > 50).²⁹⁻³² Moreover, the synthesis of thin CeO₂ nanowires are usually restricted by the low yields of produced materials (limited to mg).^{26,27,33,34}

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The selective oxidation of anilines with hydrogen peroxide to produce oxygenated derivatives (hydroxylamine, nitroso, nitro, azo, and azoxy compounds) is an attractive alternative approach to the selective reduction of nitrobenzenes.³⁵

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Given that other functional groups could undergo unwanted reduction reactions, the chemoselectivity of the oxidation reaction provides an alternative synthetic strategy to circumvent this problem.³⁵ Selective catalytic oxidation of aniline is a relevant reaction for the synthesis of intermediates of industrial interest, leading to the formation of valuable oxygenated products typically employed in the fabrication of dyes, drugs, reducing agents, chemical stabilizers and polymerization inhibitors.^{36,37} The activation of molecular oxygen (O_2) and hydrogen peroxide (H_2O_2) at the catalyst surface represents a great challenge in achieving high activity towards the selective oxidation of aniline.^{37,38} In order to overcome this barrier, gold (Au) and silver (Ag) nanoparticles (NPs) have been widely employed to improve activities towards the aniline oxidation.^{36–42} However, practical applications of Au and Ag NPs have been limited due to its relatively high costs and sensitivity to poisoning.⁴³ The use of nonnoble metals-based catalysts are still limited and only few reports have been demonstrated towards the aniline oxidation.^{43–46} More specifically, CuCr₂O₄ spinel nanoparticles, graphene oxide supported MnO₂ nanorods, Cu–CeO₂ NPs, titanium silicate molecular sieves and Nb₂O₅ micro and nanoparticles have been employed as alternatives in this reaction. 43-47

It has been demonstrated that nitrosobenzenes are versatile compounds for synthetic chemistry.⁴⁸ Their application in many organic reactions has been reviewed.⁴⁸ The preparation of nitrosobenzenes is not a trivial task although some reasonable success has been achieved by the oxidation of aniline with peracids,⁴⁹ by hydrogen peroxide in the presence of phosphotungstate catalyst,⁵⁰ and by ozone.⁵¹ There are a few reports describing the aerobic oxidation of aniline with molecular oxygen leading to azobenzene without the direct isolation of nitrosobenzene.^{36,52} In

contrast, a photocatalytic protocol achieved high selectivity's for the formation of nitrosobezene under mild conditions and without significant azobenzene formation.⁵³ Here, we report a facile and versatile route to the gram-scale production of CeO₂ nanowires with diameters below 15 nm presenting increased oxygen vacancies and Ce³⁺ sites to achieve superior catalytic performances towards the selective oxidation of aniline at room-temperature and using hydrogen peroxide (H_2O_2) as the oxidant. The synthesis of sub-15 nm nanowires are interesting as it leads to an increase in the aspect ratio of nanowires (defined as the ratio of length to diameter), offering an effective strategy for improving their catalytic activities because this parameter is directly proportional to the surface area. The sub-15 nm CeO₂ nanowires catalyzed the selective synthesis of nitrosobenzene (up to 97 % of selectivity) from aniline at room temperature using H_2O_2 as oxidant. This is especially interesting as one of the most employed approaches for producing nitroso-based compounds is based on the Caro's acid synthesis,⁵¹ which is a dangerous procedure and involves the oxidation of anilines in the presence of peroxymonosulfuric acid, followed by distillation.

Experimental

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Materials and Instrumentation

Analytical grade chemicals cerium(III) nitrate hexahydrate (Ce(NO₃)₃.6H₂O, 99.5%,Sigma-Aldrich), sodium hydroxide (NaOH, 99%, Sigma-Aldrich), aniline (H₂NC₆H₅ >97.0%, Sigma-Aldrich), acetonitrile anhydrous (CH₃CN, 99.8%, Sigma-Aldrich) ethanol (C₂H₆O, 99.5%, Sigma-Aldrich), acetone (C₃H₆O, 99.5%,Sigma-

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Aldrich), chloroform anhydrous (CHCl₃, \geq 99%, Sigma-Aldrich), dimethylformamide anhydrous (DMF, 99.8%, Sigma-Aldrich), hydrogen peroxide aqueous solution (H₂O₂, 30 % (w/w), Sigma-Aldrich), azoxybenzene (C₁₂H₁₀N₂₀, >99%, Sigma-Aldrich), azobenzene, (C₁₂H₁₀N₂, 98%, Sigma-Aldrich), nitrosobenzene (C₆H₅NO, >97%, Sigma-Aldrich), nitrobenzene (C₆H₅NO₂, >99%, Sigma-Aldrich), phenylhydroxilamine (C₆H₇NO, >97%, Sigma-Aldrich) were used as received. All aqueous solutions were prepared using deionized water (18.2 M Ω cm).

The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. The high-resolution transmission electron microscopy (HRTEM and STEM-HAADF) images were obtained with a Tecnai FEI G20 microscope operated at 200 kV. Samples for HRTEM were prepared by drop-casting an aqueous suspension of the materials over a carboncoated copper grid, followed by drying under ambient conditions. Specific surface areas were determined by the Brunauer-Emmett-Teller equation (BET method) from adsorption isotherm generated in a relative pressure range 0.07 < P/Po < 0.3. The total pore volume was calculated from the amount of N_2 adsorbed at a relative pressure close to unity. The average pore diameter was determined by the Barrett-Joyner-Halenda (BJH) method from the N_2 desorption isotherms. The X-ray diffraction (XRD) data were obtained using a Rigaku-Miniflex II equipment, Cu Ka radiation. The diffraction pattern was measured in the range of 20-80° 20 with a 1° min^{-1} angular speed scan. Temperature-programmed reduction with hydrogen (H₂-TPR) was carried out in a Quantachrome ChemBET-Pulsar instrument equipped with

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a thermal conductivity detector. Typically, 0.1 g of a catalyst was dried with N_2 flow at 125 °C for 1h and then cooled down to room temperature. The TPR profiles were obtained between 50 and 1200 °C in a flow of 5% H_2/N_2 , the temperature increasing linearly at a rate of 10 °C min⁻¹. Raman spectra were collected using a in a Renishaw InVia Reflex coupled to a Leica DM 2500 M microscope and a CCD detector. The laser excitations used were 632.8 nm (He/Ne source) and the objective was a 63× objective (NA=0.9). The infrared absorption spectra were obtained on Bruker model ALPHA interferometric spectrometer. The samples were placed directly into the sample compartment using an attenuated total reflectance accessory of single reflection (ATR with Platinium-crystal diamond). Eighty spectra were accumulated for each sample, using spectral resolution of 4 cm⁻¹. X-ray photoelectron spectroscopy (XPS) data of the samples was obtained with an SPECSLAB II (Phoibos-Hsa 3500 150, 9 channeltrons) SPECS spectrometer, with Al Ka source (E = 1486.6 eV) operating at 12 kV, pass energy (Epass) = 40 eV, 0.1 eV energy step and acquisition time of 1 s per point. The samples were placed on stainless steel sampleholders and were transferred under inert atmosphere to the XPS pre-chamber and held there for a 2 h in a vacuum atmosphere. The residual pressure inside the analysis chamber was $\sim 1 \times 10^{-9}$ Torr. The binding energies (BE) of the Ce 3d and O 1s spectral peaks were referenced to the C 1s peak, at 284.5 eV, providing accuracy within ± 0.2 eV. Textural characteristics for the catalysts were determined from nitrogen adsorption isotherms, recorded at -196 °C in a Micromeritics (Norcross, GA) Gemini III 2375 surface area analyzer. The samples (ca. 100 mg) were degassed for 3 h at 150 °C before analysis.

Synthesis of CeO₂ nanowires and nanocubes

The CeO₂ nanowires were obtained by a hydrothermal approach.³⁴ In a typical procedure for the synthesis of nanowires, 19.6 g of NaOH were dissolved in 35 mL of deionized water and then transferred to a 100 mL Teflon-lined stainless steel autoclave. After that, 6.95 g of Ce(NO₃)₃.6H₂O were dissolved in 5 mL of deionized water and transferred gradually to the autoclave containing the NaOH solution. The autoclave was heated at 110 °C for 24 h and then allowed to cooled down to room temperature. The products were collected by centrifugation and washed three times with ethanol (15 mL) and three times with water (15 mL) by successive rounds of centrifugation and removal of the supernatant. As prepared materials were then dried at 110 °C for 6 h in air. The same procedure was employed in the synthesis of CeO₂ nanocubes, except that the reaction in the autoclave was performed at 140 °C.

Aniline oxidation

In a typical experiment, a mixture of 100 μ L of aniline, 150 μ L of H₂O₂ (30 % (w/w), Sigma-Aldrich) 10 mg of CeO₂ catalyst, and 3 mL of solvent (acetonitrile, ethanol, chloroform or acetone) was transferred to a 10 mL round-bottom flask connected to a septum-inlet Flask. This catalytic system was kept under stirring for 12 h at room-temperature. During the reaction, aliquots of 100 μ L were taken and diluted to 1 mL with the same solvent to monitor the conversion of aniline and selectivity for the products by a Shimadzu GC-2010 Plus Tracera – BID equipment. After the reaction was completed, the products were also analyzed by CG-MS GCM-QP2010SE Shimadzu instrument with low-resolution electron impact (EI, 70eV)

equipped with a RTx[®]-5MS capillary column and quantified a by calibration curve by injection of different concentrations of each pure product. GC/MS conditions: injector 260 °C; detector: 110 °C pressure: 100 kPa; Column temperature: 80 °C, 1 °C/min up to 280 °C. In the control experiments, the volume of H_2O_2 was varied from 0 to 250 µL, while the weight of CeO₂ catalyst was varied from 0 to 20 mg. In order to check the reusability of the CeO₂ nanowires as catalyst, they were recovered from the reaction mixture by centrifugation at the end of the reaction and washed three times with ethanol and three times with water by successive rounds of centrifugation at 5000 rpm and removal of the supernatant.

Results and Discussion

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Our investigations started with the hydrothermal synthesis of sub-15 nm CeO_2 nanowires. Our approach enabled their synthesis in gram scale (approximately 2.6 grams of nanowires), high yields (> 94 %), and using inexpensive reactants (as described in the experimental section). They displayed well-defined shapes and uniform sizes (11 ± 2 nm in width) as shown in Figure 1A-B. Figure 1C shows the HRTEM image of an individual CeO_2 nanowire, revealing that they are structurally uniform with a growth direction along the [110] axis. In the hydrothermal synthesis of CeO_2 nanowires, it is well established that the Ce^{3+} ions present in the $Ce(NO_3)_3$ precursor are less stable relative to Ce^{4+} in the presence of a sodium hydroxide solution (alkaline medium).³⁰ Therefore, an oxidation reaction of Ce^{3+} ions, leading to the formation of hydrated CeO_2 (Ce^{4+}) as shown in the following equation during the hydrothermal synthesis is expected to occur:³⁰

$$4 \operatorname{Ce}^{3^{+}} + 12 \operatorname{OH}^{-} + \operatorname{O}_{2} + (4n-6) \operatorname{H}_{2}\operatorname{O} \to 4 (\operatorname{CeO}_{2} \cdot \operatorname{nH}_{2}\operatorname{O})$$
(1)

As the hydrothermal reaction proceeds, the hydrated ceria (CeO₂·xH₂O) is then converted to CeO₂ at elevated temperatures (> 100 °C) according to Equation $2:^{30}$

$$CeO_2 \cdot xH_2O \rightarrow CeO_2 + xH_2O$$
 (2)

Figure S1 displays the effect of reaction time on the morphology of the CeO₂ nanowires by stopping the reaction after 1, 3, and 6 h. Firstly, CeO₂ nanorods were detected after 1 h of reaction, with typical dimensions ~ 8 nm in width and > 20 nm in length. Moreover, an increase in the length of the nanorods could be observed by allowing the reaction to proceed for 6 h (Figure S1A-C), leading to the formation of CeO₂ nanowires after 12 h of reaction with typical dimensions of 11 ± 2 nm in width and > 500 nm in length (Figure 1). Nanowires and nanorods can be defined as a function of their aspect ratios (length/diameter).¹ In this case, while nanowires typically show aspect ratios greater than 10, nanorods present aspect ratios lower than 10.¹ Therefore, this observation indicates that the sub-15 nm CeO₂ nanowires were produced by an oriented attachment mechanism, in which individual CeO₂ nanoparticles can be self-connected by assembling at the interface between neighboring particles.^{54–56} This result is in agreement with previously reported mechanisms for the formation of CeO₂ nanowires.^{27,33}

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After the synthesis of sub-15 nm CeO₂ nanowires, we were interested in investigating how their structural, textural, and surface properties may influence the catalytic performances towards the oxidation of aniline under mild conditions. For the sake of comparison, we also employed a commercial CeO₂ catalyst (Figure 1D-F) to probe the influence of the nanowire morphology on the structural features and catalytic properties. TEM images for the commercial CeO₂ catalyst (Figure 1D-F) shows that the material is polycrystalline and comprised by large, elongated, and irregularly-shaped CeO₂ particles (no dominant surface orientation could be detected for this material).

The values for the surface area, pore volume, and average pore size obtained by BET analysis of CeO₂ nanowires are shown in Table 1. The specific surface area for the sub-15 nm CeO₂ nanowires was much higher (87 m²/g) relative to the commercial CeO₂ sample (9 m²/g), which agrees with the formation of a uniform nanosized material. The CeO₂ nanowires also displayed a smaller average BJH pore diameter (36 Å) as compared to commercial CeO₂ (142 Å). The adsorption isotherms for sub-15 nm CeO₂ nanowires and commercial CeO₂ samples (Figure S2) corresponded to type IV (IUPAC classification),^{57,58} which is typical of mesoporous materials. The shape of the hysteresis loop corresponded to type H3 with welldefined loops that did not level off at relative pressures close to the saturation vapor pressure.^{57,58} This is also in agreement with the HRTEM images for a single sub-15 nm CeO₂ nanowire S3), in which several 1-2 nm mesoporous could be detected at the nanostructure surface.

The X-ray diffractograms for commercial CeO_2 (Figure 2A) shows well-defined peaks corresponding to the (111), (200), (220), (311), (400), (311) and (420) planes of

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a face-centered cubic fluorite structure of CeO_2 (JCPDS 34-0394).^{7,27} It can be observed in the XRD pattern for the sub-15 nm CeO_2 nanowires a significant broadening of all diffraction peaks (Figure 2A), which is agreement with the formation of smaller crystallites.⁷

The presence of oxygen vacancies and the reducibility of heterogeneous catalyst play an important role over their catalytic activities towards a variety of chemical reactions.^{59–61} In order to gain further insights into these properties, the sub-15 nm CeO₂ nanowires and commercial CeO₂ materials were investigated by temperature programmed reduction (TPR) and Raman Spectroscopy. (Figure 2B and 2C, respectively). The TPR profile for the commercial CeO_2 displayed a single peak centered at 1005 °C assigned to the reduction of bulk ceria (Figure 2B).⁷ Surprisingly, the TPR profile for the CeO₂ nanowires presented a noticeable difference. The reduction of bulk CeO₂ was shifted to 954 °C and an intense peak centered at 654 °C corresponding to the reduction of CeO_2 due to the movement of oxygen anions through vacancies could be observed (Figure 2B).^{7,27} These results are in agreement with previous data that smaller nanoparticles and high surface area nanomaterials lead to an increase in their reducibility properties as result of a more effective gas adsorption and faster surface reduction processes.^{61,62} The intense peak at 654 °C observed for the CeO₂ nanowires also indicate enrichment of the surface oxygen ions in this sample, which is very attractive for catalytic applications.^{63,64} It is important to note that, CeO_2 nanostructures exposing planes with higher surface energy, such as the {110} facet, generate increased concentration of oxygen vacancies relative to nanostructures exposing {111} and {100} facets, which leads to improved catalytic activities towards oxidation reactions.^{63,64} These sites are expected to be more reactive, shifting the reduction reaction with H_2 to lower temperatures, which is in agreement with the TRP results.^{63,64} The Raman spectra for CeO₂ nanowires and commercial CeO₂ further support this evidence (Figure 2C). The spectrum of commercial CeO₂ displays an intense and sharp peak at 463 cm⁻¹, which is assigned to the symmetric stretching vibration of the oxygen atoms around Ce^{4+} ions (F_{2g} mode for the fluorite structure).^{7,65} However, the same F_{2g} peak for the sub-15 nm CeO₂ nanowires was broadened and shifted to a lower wavenumber (458 cm⁻¹).⁶⁶ Such an effect has been assigned to the formation nanoparticles having reduced Ce³⁺ species in their structure.⁶⁶ The substitution of Ce^{+4} ions by Ce^{3+} tends to cause an expansion of the lattice and thus, shifting F_{2g} peak to lower wavenumbers as previous reported.^{7,65} Additionally, the Raman spectra for the sub-15 nm CeO₂ nanowires presented a low intensity and broad band centered at 598 cm⁻¹ (Figure 2C), which corresponds to oxygen vacancies produced by reduced cerium ions (Ce^{3+}) in the ceria structure.^{7,65} Figure 2D presents the ATR-IR spectra for the sub-15 nm CeO_2 nanowires and commercial CeO_2 samples. While the broad band around 3200 cm-¹ are due to the OH stretching vibrations of residual water in the sample, the absorption bands at the 1300-1700 cm⁻¹ can be assigned to physically adsorbed water molecules or the presence of partially non-reacted nitrate from the metal precursor.^{67,68} The intense absorption bellow 600 cm⁻¹ could be assigned to the asymmetric and symmetric vibrations of Ce-O in the CeO₂ structure.^{67,68} Interestingly, all absorption peaks for the sub-15 nm nanowires are shifted relative the commercial CeO_2 sample (Figure 2D), which is in agreement with the TPR and Raman observations.

In order to further investigate the presence of oxygen vacancies and Ce³⁺ ions in both nanowires and commercial CeO_2 samples, we performed X-ray photoelectron spectroscopy (XPS) analysis to probe surface composition and oxidation states. We were interested in probing surface structural changes that possibly could be observed for the CeO₂ nanowires relative to the commercial CeO₂ sample. The XPS spectra are shown in Figure 3 and XPS parameters and assignments are listed in Table 2. Figure 3 shows the Ce 3d (Figure 3A), and O 1s (Figure 3B) core-level spectra for sub-15 nm CeO₂ nanowires and commercial CeO₂. The binding energies (BE) of Ce $3d_{3/2}$ and Ce $3d_{5/2}$ regions for the CeO₂ nanowires indicated shifts relative to commercial CeO₂, which can be explained by the formation of nanostructured particles that often change surface properties.^{60,69} Such results indicate the coexistence of Ce³⁺ and Ce⁴⁺ species, in which they can be differentiated with distinct lines in the following manner: (i) $Ce^{III} \rightarrow v_0$, $v' + u_0$, and u'; and (ii) $Ce^{IV} \rightarrow v$, v', v''', u, u', and u'''.^{70,71} While the u''' component is a fingerprint of Ce⁴⁺ions, the u' is equivalent for Ce^{3+} ions.^{70,71} Analysis of experimental data indicated that u'/ u''' ratio was significantly higher for the CeO_2 nanowires when compared to commercial CeO_2 (0.42 vs 0.23, respectively as depicted in Table 2), indicating the enrichment of Ce^{3+} ions and, consequently, higher oxygen vacancies at the CeO_2 nanowires surface. To confirm this evidence, we investigated the O 1s XPS spectra of commercial CeO_2 and CeO₂ nanowires (Figure 3B). The analysis of O 1s XPS spectra indicated that three different surface oxygen species were detected. The BE between 529.9-529.5 eV was assigned to lattice oxygen (O_L) while the BE 532.0–531.4 eV corresponded to surface oxygen ions or oxygen vacancies $(O_s)^{60}$, and BE around 533.9 eV are characteristic of adsorbed water (O_w).⁶⁰ As expected, the O 1s XPS spectra match with the Ce 3d XPS results. The sub-15 nm CeO₂ nanowires showed a significant decrease in the O_L/O_S ratio relative to the commercial CeO₂ sample. This evidence further supports the enrichment of oxygen vacancies at the CeO₂ nanowires surface, in agreement with both TPR and Raman spectroscopy analyses. It is important to note that the high surface area, the uniform thin cross-sections (11 ± 2 nm in width), the crystal growth towards (110) highly energy crystallographic direction, and the enrichment of oxygen vacancies at sub-15 nm nanowires make them interesting for applications in heterogeneous catalysts. Indeed, the observed features of the ceria nanowires are important for achieving high activities and selectivities towards several oxidations reactions.^{7,60,72,73}

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Therefore, we decided to probe the catalytic activities of sub-15 nm CeO₂ nanowires towards the aniline oxidation under mild conditions (low temperatures and using H_2O_2 as the oxidant). We also compared their activities with the commercial CeO₂ sample under the same conditions. The catalytic oxidation of aniline is highly relevant as several oxidation products are widely used for industrial production of dyes, pigments, and pharmaceuticals.^{36,38,39,74} For such applications, it is imperative the use highly active, selective, and stable heterogeneous catalysts, as aniline oxidation can lead to the formation of different oxidation products, ³⁴ as illustrated in Figure 4A. Figures 4B and 4C show the conversion (%) for the oxidation of aniline as a function of both the H_2O_2 volume and the weight of sub-15 nm CeO₂ nanowires catalyst. The utilization of the sub-15 nm CeO₂ nanowires resulted in conversion > 60 % at room-temperature after 12 h of reaction, with an optimal

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weight of CeO₂ nanowires and volume of added H_2O_2 corresponding to 10 mg and 150 µL, respectively.

In order to further examine the catalytic properties we investigated the conversion (%) for the oxidation of aniline and the respective selectivities (%) for oxidation products as a function of time for both sub-15 nm CeO₂ nanowires and commercial CeO₂ materials (Figure 5). The experimental results indicated that the sub-15 nm nanowires led to a much higher aniline conversion (%) as function of time relative to the commercial CeO₂ catalyst (64 % vs 9 % after 12 h, respectively as shown in Figure 5A). The sub-15 nm CeO₂ also displayed higher selectivity (only one product was quantitatively produced), leading to the preferentially formation of nitrosobenzene after 12 h of reaction (96 % of selectivity, Figure 5B). On the other hand, the commercial CeO₂ sample produced a mix of nitrosobenzene and nitrobenzene with a lower selectivity, highlighting the superior catalytic performance of sub-15 nm CeO₂ nanowires.

We also investigated the effect of solvent in the catalytic activity (conversion and selectivity) of sub-15 nm CeO₂ nanowires catalyst towards the aniline oxidation reaction as depicted in Table 3. The aniline conversion (%) decreased in the following order: ethanol > acetone > acetonitrile > chloroform, in which a correlation with their polarity could be detected. In this case, it is suggested that the aniline conversion (%) increased with the solvent polarity. Previous reports have also observed an increase in the activity and selectivity for both protic and aprotic polar solvents (with a more pronounced effect for aprotic solvents).^{7,75} In this case, a positive effect of polar solvents can be explained as a result of a better stabilization

In addition to conversion (%), it has been reported that the selectivity for the oxidation products can also be highly dependent on the nature of the solvent.^{7,75} Results depicted in Table 3 are in agreement with this observation. Using acetonitrile as solvent, 64 % of conversion with 95.7% of selectivity for nitrosobenzene was achieved, while 74% of conversion with 70.2 and 16.8 % of selectivity for nitrosobenzene and azoxybenzene, respectively, were obtained with ethanol as solvent. Such a difference can be assigned to the formation of higher amounts of reactive metal-peroxo complexes that is expected to be more pronounced in the presence of protic polar solvents such as ethanol.^{7,75} This solvent would inevitably promote subsequent condensation of aniline with the formed nitrosobenzene, favoring the formation of azoxybenzene and azobenzene as product, as shown in Scheme S1. An increase in the reaction temperature is expected to promote the similar effect in the selectivity. In order to confirm this evidence, we measured the catalytic activities (conversion and selectivity) of sub-15 nm nanowires in the aniline oxidation as a function of the reaction temperature as shown in Figure 6. Interestingly, it was observed that the conversion of aniline slightly decreased as the reaction temperature was increased (Figure 6A). This result can be explained due to the higher decomposition rate of H_2O_2 to molecular O_2 and H_2O at higher temperatures.^{7,75} Thus, an increase in the temperature may inhibit the stabilization of reactive intermediates species and a lower formation of metal-peroxo species, which are considered the highly catalytically active species for oxidations reactions.

On the other hand, their selectivities displayed expressive changes as a function of temperature. For instance, the selectivities for nitrosobenzene decreased from 71 to 13% using ethanol as solvent and 98 to 86% using acetonitrile, leading to the formation of azoxybenzene instead (68 % using ethanol and 10 % using acetonitrile). Such a decrease is in agreement with the higher rates of aniline condensation with the preformed nitrosobenzene, leading to the formation of higher amounts of azoxybenzene in the presence of protic polar solvents. Furthermore, the sub-15 CeO₂ nanowires displayed good catalytic stability towards the aniline oxidation as shown in Figure S4A. No significant loss of catalytic activity was detected after 5 catalytic cycles for both sub-15 nm CeO₂ nanowires and commercial CeO₂ samples, showing that the nanowires are a promising candidate for liquidphase oxidation transformations (Figure S4A-C). The TEM images of the sub-15 nm nanowires after 5 catalytic cycles (Figure. S5A-B) are in agreement with this observation, showing no change on the morphological features after the stability studies. XRD pattern for both sub-15 nm CeO₂ nanowires and commercial CeO₂ samples also indicated that the fluorite structure of CeO2 also did not present a detectable change (Figure S6A). However, the selectivities towards the oxidation products changed upon reuse of the catalyst (Figure S4B-C). While the sub-15 nm nanowires increased their selectivities for nitrosobenzene as a function of the number of completed catalytic cycles (from 95.2 to 99.7% after the 5th cycle, Figure S4B), the commercial sample presented an opposite tendency (selectivity for nitrosobenzene decreased from 75.1 to 68.7% after the 5th cycle, Figure S4C). Even though no change in the morphological features were observed, we speculate that the observed differences in selectivities may be related to changes in their surface properties. To confirm this hypothesis, we investigated the O 1s XPS spectra of sub-15 nm CeO₂ nanowires (Figure S6B) commercial CeO₂ (Figure S6C) before and after the catalytic cycles. Interestingly, the O 1s XPS spectra for sub-15 nm CeO₂ nanowires after the catalytic cycles showed an increase in the O_L/O_S ratio relative to the freshly prepared nanowires (O_L/O_S ratio increase from 11.2 to 16.4, Figure S6B). This data suggests that the enrichment of oxygen vacancies on the CeO₂ nanowires surface took place, which may be responsible for the increase in the selectivity for nitrosobenzene. Conversely, the O 1s XPS spectra for the commercial CeO₂ after the catalytic cycles showed a decrease in the O_L/O_S ratio relative to the commercial CeO₂ sample in the first cycle (O_L/O_S ratio increase from 4.1 to 2.9, Figure S6C).

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In order to gain further insights, the observed performance of the sub-15 nm nanowires with the Ce³⁺/Ce⁴⁺ ratio in the materials and the presence of preferential exposed crystallographic facets at the CeO₂ surface was correlated. Thus, CeO₂ nanocubes was prepared by a similar approach as described for the nanowires (only increasing the temperature of synthesis from 110 to 140 °C) as shown in Figure S7. The CeO₂ nanocubes presented uniform sizes and shapes (Figure S7A-C) enclosed by monocrystalline {100} side facets (Figure S7D). X-ray diffractograms for CeO₂ nanocubes (Figure S8A) shows well-defined peaks corresponding to the (111), (200), (220), (311), (400), (311) and (420) planes of a face-centered cubic fluorite structure, confirming the formation of CeO₂ structure.^{7,27} Interestingly, the TPR profile for the CeO₂ nanocubes displayed noticeable difference relative to the sub-15 nm nanowires (Figure S8B). Whilst the reduction of bulk CeO₂ was centered at 963 °C, the peak around 600-800 °C corresponding to the reduction of CeO₂ the reduction of CeO₂ due to the movement of oxygen anions was significantly decreased (Figure S8B). XPS spectra for the CeO₂

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nanocubes (Figure S8C-D) are in agreement with the TPR results. Analysis of experimental data indicated that u'/ u''' and O_s/O_L ratio was significantly lower for the CeO₂ nanocubes as compared to the sub-15 nm CeO₂ nanowires, corresponding to 0.30 and 5.4, respectively. Conversely, these values were higher relative to the commercial CeO₂ sample. This tendency had a direct implication on the catalytic oxidation of aniline under the same conditions. The experimental results indicated that the sub-15 nm nanowires led to a much higher aniline conversion (%) relative to the CeO₂ nanocubes (64 % vs 18 % after 12 h, respectively). The CeO₂ nanocubes also displayed significant lower selectivity for the formation of nitrosobenzene after 12 h of reaction (81 % of selectivity), in agreement with the observations that CeO₂ nanostructures exposing planes with high surface energy {110} facets generate increased concentration of oxygen vacancies relative to nanostructures exposing {100} facets, leading to improved catalytic activities and selectivities.

As previously abovementioned, the use of non-noble metals-based catalysts are still limited but in contrast Au and Ag NPs have been employed towards the aniline oxidation.^{43–46} The absence of noble-metals, the use of H₂O₂ as the oxidant under atmospheric conditions, and the proper reusability of the sub-15 nm nanowires produced by a simple method based on a hydrothermal method make the present catalytic protocol a promising alternative for the selective oxidation of aniline. The reasonably high activities, selectivities, and stability observed for the sub-15 nm CeO₂ nanowires may be assigned to a variety of factors: *i*) the morphology comprised of long one-dimensional nanowires and sub-15 nm crosssections; which provide higher specific surface area than that of the conventional CeO₂-based catalysts; *ii*) the crystal growth through (110) highly catalytically active crystallographic directions towards oxidation reactions; *iii*) the surface of nanowires is easily accessible by gas and liquid substrates due to the presence of mesoporous as demonstrated by BET analysis, *iv*) the significant concentration of oxygen vacancies, resulting in an enhancement of surface oxygen mobility, and high proportion of Ce^{3+} species at the surface relative to commercial samples that represent highly active sites towards oxidation reactions; and *v*) the uniform shapes and sizes of sub-15 nm CeO_2 nanowires is generally crucial to achieve high catalytic activities. Moreover, the catalytic activity, selectivity, and stability at mild reaction conditions described herein meet the principles of heterogeneous catalysis.

Conclusions

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We have demonstrated the synthesis of CeO₂ nanowires with small diameter (11 ± 2 nm in width), high aspect ratios, high surface areas, increased number of oxygen defects sites and high proportion of Ce³⁺ species at the surface. They were obtained through a facile hydrothermal method, which allowed the synthesis at relatively large scales (~ 2.6 grams of nanowires per batch), high yield (> 94 %), and low cost without the use of any capping/stabilizing agents. The key to this efficient synthesis is the control of the nucleation and growth of the sub-15 nm CeO₂ nanowires that are formed by an oriented attachment mechanism. The sub-15 nm CeO₂ nanowires exhibited excellent catalytic performances towards the selective oxidation of aniline at room-temperature and hydrogen peroxide (H₂O₂) as the oxidant. Owing to their 1D morphology, large specific surface area, thin crosssections, high concentration of oxygen vacancies, with a high fraction of Ce³⁺, and the highly active surface due to preferential crystal growth along [110] direction, we

found that the sub-15 nm CeO₂ nanowires have improved activities, selectivities, and stabilities towards the aniline oxidation under mild conditions to produce nitrosobenzene relative to the commercial CeO₂ sample. It is worth noting that the high selectivities towards the formation of nitrosobenzene are outstanding and have seldom been achieved. Selectivities above 97% were observed when using a nanostructured CeO₂ catalyst and furthermore these excellent selectivities were accompanied by high conversion levels. The catalytic performances and mild reaction conditions described herein will inspire the development of novel nanomaterials with high catalytic activities via facile procedures at relatively larger scales.

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Figure 1. (A) SEM and (B-F) HRTEM images of sub-15 nm CeO₂ nanowires (A-C) and commercial CeO₂ (D-F).

Table 1. Textural properties measured by N_2 -physisorption for sub-15 nmCeO2 nanowires and commercial CeO2 catalysts.

Catalyst	Specific Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Pore Diameter (Å)	
Sub-15 nm CeO ₂ nanowires	87	0.35	36	
Commercial CeO ₂	9	0.05	142	



Figure 2. (A) X-ray diffraction (XRD) patterns (B) Temperature programmed reduction profiles (TPR),(C) Raman spectra, and (D) ATR-IR spectra for sub-15 nm CeO₂ nanowires and commercial CeO₂.

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Figure 3. Deconvoluted Ce 3d (A) and O 1s (B) spectra for sub-15 nm CeO₂ nanowires and commercial CeO₂.

	Sample	Binding energy Ce 3d (eV)			u'/ u'''	0,/0,	
		u'	u‴	OL	Os	.,.	03, 01
	Sub 15pm CoO, popowiros	905,0	916,7	916,7 528.2	530.0	0.42	11 2
Sub-15mm CeO ₂ nanowires	(5)*	(12)*	(6)*	(67)*	0.42	11.2	
		905,1	916,4	527.9	529.5	0.22	. 1
commercial CeO ₂	(3)*	(3)* (13)*	(14)*	(58)*	0.23	4.1	

Table 2. XPS binding energies, u'/ u''', and O 1s/C 1s ratio obtained from the Ce 3d

and O 1s regions for sub-15 nm CeO_2 nanowires and commercial $CeO_2.$

*percentages of Ce^{δ^+} or O species.



Figure 4. (A) Scheme for the aniline oxidation catalyzed by sub-15 nm CeO_2 nanowires and commercial CeO_2 . (B-C) aniline conversion (%) as function of volume of H_2O_2 (A) and weight (B) of sub-15 nm CeO_2 nanowires (black line) and commercial (red line) catalysts added into the reactions at room-temperature. Solvent: acetonitrile.



Figure 5. Aniline conversion (A) and selectivity for the room-temperature oxidation products (B) as function of time for the sub-15 nm CeO₂ nanowires and commercial CeO₂ materials employed as catalysts. The weight of sub-15 nm CeO₂ nanowires and volume of added H_2O_2 corresponding to 10 mg and 150 µL, respectively. Solvent: acetonitrile.

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Table 3. Effect of solvent in the catalytic activity (conversion and selectivity) of sub-

15 nm CeO₂ nanowires catalyst towards the aniline oxidation reaction.

	Conversion*	Selectivity (%)*				
Solvent	(%)	Azobenzene	Nitrobenzene	Nitrosobenzene	Azoxybenzene	phenylhydroxyilamine
Acetone	66.0	1.3	10.2	78.2	10.3	-
Acetonitrile	64.1	0.7	3.6	95.7	0	-
Chloroform	58.4	1.4	-	98.6	-	-
Ethanol	73.0	1.6	10.8	70.2	17.4	-

*Reaction conditions: 100 μ L of aniline, 150 μ L of H₂O₂, 10 mg of CeO₂ catalyst, and 3 mL of solvent (acetonitrile, ethanol, chloroform or acetone). Reaction time: 12 h and room-temperature.



Figure 6. Aniline conversion (A) and selectivity for oxidation products (B) as function of temperature for the sub-15 nm CeO₂ nanowires employed as catalysts. The weight of sub-15 nm CeO₂ nanowires and volume of added H_2O_2 corresponding to 10 mg and 150 µL, respectively.

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Higher Concentration of Oxygen Vacancies



Higher Catalytic Activity and Selectivity

119x62mm (300 x 300 DPI)