Sustainable and Surfactant-Free High-Throughput Synthesis of Highly Dispersible Zirconia Nanocrystals

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Herein, a cost-effective and tailored synthesis route for the preparation of cubic ZrO₂ nanocrystals with high dispersibility (up to 45% by weight in H₂O) is reported. The synthetic procedure is straightforward and produces uniform 2-3 nm particles of excellent yield when applying microwave dielectric heating as a “green” method. Also, it can be applied to a wide range of batch sizes (from 0.5 to 20 g ZrO₂), which makes it interesting for industrial applications. Hier einen kurzen Verweis auf die Herstellung von YSZ einfügen. Overall, the paper aims at unravelling all relevant reaction steps by means of nuclear magnetic resonance and gas chromatography-mass spectrometry. Furthermore, two innovative synthesis routes are presented, which have not been considered in previous studies. Both the microstructure and chemical composition of the nanocrystals were analyzed via electron microscopy, X-ray diffraction and dynamic light scattering as well as Raman, X-ray absorption and X-ray photoelectron spectroscopy. Besides, it is demonstrated that alcoholic ZrO₂ dispersions are highly suited for the preparation of nanoscale materials with different morphologies, including fibers as well as ordered mesoporous and macroporous thin films and powders. Collectively, this work provides a blueprint for the preparation of high-quality nanoparticles and structured materials thereof and is likely to trigger further research in the field of solution-processed metal oxides.

Introduction

The field of nanostructured metal oxides has experienced significant advances in recent years, both in research and application.¹⁻⁴ This progress can be attributed to a large extent to innovative developments in sol-gel chemistry, allowing for the preparation of a variety of nanocrystalline oxides and non-oxides with different functionalities and morphologies (e.g., nanoparticles, fibers, thin films etc.).⁵⁻⁸ However, sol-gel syntheses are often environmentally unfriendly for several reasons. For example, a major drawback in the preparation of nanoparticles is the inherent use and release of solvents, thus requiring elaborate waste management strategies. Also, the recovery of solvent(s) from reaction mixtures consumes considerable amounts of energy. Furthermore, sol-gel syntheses usually suffer from moderate yields, leading again to an overall poor waste and energy balance.

In this work, a novel synthesis route for the preparation of ZrO₂ nanocrystals is presented, aiming at minimizing waste and (electrical) energy consumption. ZrO₂ is used as a model material to demonstrate that advances in the design and understanding of the underlying sol-gel chemistry enable the preparation of high-quality products with reduced environmental footprint.

At atmospheric pressure, pure zirconia (ZrO₂) exists in three solid polymorphs.⁹ In the monoclinic (*P*₂₁/*c* – *C*_{2h}⁵, *Z* = 4) low-temperature structure – which naturally occurs in the mineral baddeleyite – the Zr atoms are sevenfold coordinated by oxygen atoms. This modification is stable up to about 1170 °C and can be considered a distorted form of the fluorite (CaF₂) structure. Above around 1170 °C, it undergoes a phase transition to the tetragonal (*P*₄₂/*nmc* – *D*_{4h}¹⁵, *Z* = 2) polymorph and transform at *T* > 2370 °C into the cubic (*Fm* $\bar{3}$ *m* – *O*_h⁵, *Z* = 4) form. In both high-temperature modifications, the Zr atoms are eightfold coordinated by oxygen, as in the ideal fluorite type structure; however, in the tetragonal form the oxygen atoms are displaced along the *c*-axis.

Nanocrystalline ZrO₂-based ceramics, in particular, gain more and more importance in industrial applications.¹⁰⁻¹² The primary reasons are the enhanced mechanical, electrical, magnetic, optical and catalytic properties compared to their bulk counterparts.¹³⁻¹⁵ Among others, solid solutions of ZrO₂ and Y₂O₃ are widely used in oxygen sensors, hip-joint replacements, thermal barrier coatings and as electrolyte in solid oxide fuel cells due to the unique combination of high

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fracture resistance, low thermal and high ionic conductivity.¹⁶⁻¹⁸

The main feature of the sol-gel approach described in the present work is the use of a microwave device for heating. Microwave processing has been shown to be advantageous in nanoparticle synthesis as it enables very rapid heating and cooling as well as fine control over and monitoring of individual process parameters (time, pressure, temperature etc.), unlike conventional heating methods.^{19, 20} Recently, several studies have reported strategies towards the large scale (multigram) synthesis of ZrO₂ nanoparticles and dispersions thereof, thus increasing their application potential.²¹⁻²³ Yet, these routes still have certain shortcomings such as prolonged reaction times, leading again to increased energy consumption.

Here, we report the microwave synthesis of ZrO₂ nanocrystals based on rational design of sol-gel reactions, using tailored precursors and solvents with the goal to reduce the reaction time to the minute-scale and to achieve high yield. Furthermore, the procedure was developed to generate dispersions in environmentally friendly solvents (e.g., H₂O). Overall, with this work we aim at targeting the requirements for “green chemistry”, as proposed by Anastas and Warner.^{24, 25} While the sol-gel synthesis of nanoscale metal oxides suffers from intrinsic environmental issues, we show that significant advances can be achieved with regard to “atom economy”, “safer solvents and auxiliaries” and “design for energy efficiency” to name three important principles defined by Anastas and Warner.

In order to demonstrate that the rational design of reaction pathways provides many possibilities to reduce the environmental impact of these materials, the individual synthesis steps were studied on the molecular level by means of various state-of-the-art characterization techniques, including nuclear magnetic resonance and chromatographic analysis of intermediate species. The nanoparticles themselves were analyzed via electron microscopy, X-ray diffraction, dynamic light scattering, Raman spectroscopy, X-ray absorption spectroscopy and X-ray photoelectron spectroscopy. Finally, the excellent dispersibility of the nanocrystals in water and other polar solvents was used to produce mesoporous and macroporous materials, thereby revealing their versatility as building blocks.

Experimental

Materials

Anhydrous zirconium(IV) chloride (≥99.5%), zirconium(IV) propoxide solution (70 wt% in C₃H₇OH) and 1-propanol (99%) were purchased from ABCR; yttrium(III) isopropoxide, yttrium(III) nitrate hexahydrate (99.8%), ethanol (99.8%) and diethyl ether (99%) from VWR International GmbH; dimethylformamide (99.8%), *n*-pentane (≥99%), methanol (99.8%), acetonitrile (99.8%), acetyl chloride (≥99.0%), isopropyl alcohol (99.5%), poly(ethylene oxide) [PEO; *M_w* = 300.000 g/mol] and polyacrylonitrile [PAN; *M_w* = 150.000

g/mol] from Sigma Aldrich; anhydrous benzyl alcohol (99%) from Grüssing GmbH Analytika; and dimethyl sulfoxide-d₆ (99.9 at% D) with 1 vol% TMS from Acros Organics. Polyvinyl butyral (PVB; Mowital B 60 H) was provisioned by Kuraray Europe GmbH.

H[(CH₂CH₂)_{0.67}(CH₂CHCH₂CH₃)_{0.33}]₈₉(OCH₂CH₂)₇₉OH, referred to as KLE [Kraton-liquid-*b*-poly(ethylene oxide)],²⁶ was used as structure-directing agent.

Synthesis of Nanoparticles

Both an appropriate amount of ZrCl₄ and a short-chain primary alcohol (e.g., ethyl or propyl alcohol) are heated to 150 °C for 1 min under microwave irradiation. After cooling to 70 °C, Zr(OC₃H₇)₄ in 1-propanol is added to the solution and heated at 150 °C for 3 min in order to produce ZrCl₂(OC₃H₇)₂ or ZrCl₂(OC₃H₇)_{4/3}(OC₂H₅)_{2/3}. Alternatively, ZrCl₂(OC₃H₇)₂ can be prepared by chlorination of Zr(OC₃H₇)₄ using CH₃COCl via microwave heating at 120 °C for 1 min (see **Table S2**, ESI). Then, 1-hexanol (and optionally a dopant) is added to the solution and heating at 150 °C for 1 min. Finally, benzyl alcohol is introduced to the reaction mixture, followed by heating at 200 °C for several minutes. In all reaction steps, the stirring rate is set to 300 rpm and kept constant. **Tables S1-S4** (ESI) summarize reagent masses, reaction times and microwave reactors used for different batch sizes. To disclose the composition of samples, a short summary of the most important parameters along with batch numbers is given in **Table 1**. Representative heating profiles are shown in **Figures S1-S3** (ESI). Purification methods for the preparation of high-quality powders and dispersions are given in section 1.2 (ESI).

Table 1. Summary of sample description, including precursors and target compositions.

Batch name	Precursor	Dopant	Target composition
BN1#	ZrCl ₄ /Zr(OPr) ₄	-	ZrCl ₂ (OPr) ₂
BN2#	ZrCl ₄ /Zr(OPr) ₄	-	ZrO ₂
BN3*	ZrCl ₄ /Zr(OPr) ₄	-	ZrO ₂
BN4#	Zr(OPr) ₄ /CH ₃ COCl	-	ZrCl ₂ (OPr) ₂
BN5#	Zr(OPr) ₄ /CH ₃ COCl	-	ZrO ₂
BN6#	ZrCl ₄ /Zr(OPr) ₄	Y(OPr) ₃	Zr _{0.97} Y _{0.03} O _{2-δ} (3YSZ)
BN7#	ZrCl ₄ /Zr(OPr) ₄	Y(OPr) ₃	Zr _{0.94} Y _{0.06} O _{2-δ} (6YSZ)
BN8#	ZrCl ₄ /Zr(OPr) ₄	Y(OPr) ₃	Zr _{0.88} Y _{0.12} O _{2-δ} (12YSZ)
BN9#	ZrCl ₄ /Zr(OPr) ₄	Y(OPr) ₃	Zr _{0.82} Y _{0.18} O _{2-δ} (18YSZ)
BN10#	ZrCl ₄ /Zr(OPr) ₄	Y(NO ₃) ₃ × H ₂ O	Zr _{0.97} Y _{0.03} O _{2-δ} (3YSZ)
BN11#	ZrCl ₄ /Zr(OPr) ₄	Y(NO ₃) ₃ × H ₂ O	Zr _{0.88} Y _{0.12} O _{2-δ} (8YSZ)
BN12#	ZrCl ₄ /Zr(OPr) ₄	Y(NO ₃) ₃ × H ₂ O	Zr _{0.84} Y _{0.16} O _{2-δ} (16YSZ)

Notation of microwave reactors: Monowave 300 (#) and Masterwave BTR (*) with total container volumes of 30 mL (borosilicate glass vial) and 1000 mL (PTFE-TFM reaction vessel), respectively.

Synthesis of Mesoporous Thin Films and Powders

40 mg of KLE are added to 90 mg of ZrO₂ nanoparticles (BN2#) dispersed in 2 mL of methanol and 0.3 mL of water. Thin films can be produced via dip-coating onto polar substrates. Optimal conditions include 80-90% relative humidity and constant withdrawal rates of 1-10 mm/s. The as-prepared films are heated to 300 °C using a 5 h ramp, followed by aging for 12 h. Then, they can be heated to temperatures as high as 900 °C (using a 65 min ramp) while retaining nanoscale order. Powder

materials are prepared in a Petri dish using 120 mg of KLE but under otherwise identical conditions. Removal of the structure-directing agent is achieved by heating in air above 500 °C.

Synthesis of Fibers

2.5 mL of a methanolic dispersion with 60 mg/mL solid content are combined with 240 mg of 10 wt% PVB in isopropyl alcohol. Nanofibers can be produced via electrospinning at room temperature onto Si(100) wafers and aluminium foil. Removal of the carrier polymer and solidification of the inorganic material are achieved by heating in air above 500 °C. Additional preparation methods using PEO and PAN – in place of PVB – are described in section 1.3 (ESI).

Characterization Methods

Atomic force microscopy (AFM) images were collected on a multimode atomic force microscope from Veeco Instruments, employing Olympus microcantilevers. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were taken using a CM30-ST from Philips and MERLIN from Carl Zeiss, respectively. Diffuse reflectance ultraviolet-visible spectra were collected on a Lambda 750 UV-vis-NIR spectrophotometer (PerkinElmer) equipped with a Praying Mantis diffuse reflectance accessory. Gas chromatography-mass spectrometry (GC-MS) was performed on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 MSD. Grazing-incidence small-angle X-ray scattering (GISAXS) data were obtained at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4. Both ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in dimethyl sulfoxide- d_6 on a Bruker AM 400 spectrometer. N_2 -physisorption measurements were conducted at 77 K on an Autosorb-6-MP automated gas adsorption station from Quantachrome Instruments. Raman spectra were collected on a SENTERRA dispersive Raman microscope from Bruker Optics equipped with an objective from Olympus MPlan N 100x and a Nd:YAG laser. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC. The thermobalance was coupled to a Balzers QMG 421 quadrupole mass spectrometer. The ionization energy was set to 70 eV. X-ray diffraction (XRD) measurements were carried out on an X'Pert PRO diffractometer from PANalytical instruments. FullProf software was used for Rietveld refinement (size-microstrain analysis). The reflections were described by the Thompson-Cox-Hastings pseudo-Voigt profile function assuming that line broadening was a result of both the small crystallite size and lattice microstrain. The profile half-width parameters V , W and X were kept constant at values determined using LaB_6 as an internal standard. X-ray photoelectron spectroscopy (XPS) data were obtained on a Perkin-Elmer $\Phi 5600\text{Ci}$ spectrometer with an Al-K α radiation source. The C1s signal from adventitious hydrocarbon at 284.6 eV was used as the energy reference to correct for charging. X-ray absorption (XAS) measurements at the Zr K-edge (17998 eV) and Y K-edge (17038 eV) were performed at beamline BM08 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France, in 7/8-bunch mode

(200 mA). For energy selection, a Si(311) double-crystal monochromator was used. Spectra were collected in transmission mode using two ionization chambers placed upstream and downstream of the sample. Prior to measurements, the samples were pressed into homogeneous pellets using cellulose as a dispersant. Data reduction and analysis were performed using the freeware package Demeter. The amplitude factor (S_0^2) was calibrated against metallic foil and determined to be 0.9 for Zr and 0.85 for Y. Both the Zeta potential and hydrodynamic particle diameter were determined using a Zetasizer Nano from Malvern Instruments (for dispersions with 1-10 wt% ZrO_2 in H_2O).

Results and discussion

ZrO_2 nanoparticles were prepared by solvent-controlled sol-gel synthesis using zirconium(IV) chloride (ZrCl_4) and zirconium(IV) propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$) as precursors along with 1-hexanol ($\text{C}_6\text{H}_{13}\text{OH}$) and benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) as solvents. Notably, only a single step is required to disperse the ZrO_2 nanocrystals in polar solvents without the need for time-consuming post-functionalization. In a nutshell, the synthesis involves three chemical process steps: (1) ligand exchange, (2) alcoholysis and (3) alkyl halide elimination.

In the first synthesis step, a zirconium(IV) chloro-alkoxide complex is synthesized, in which the ligand chlorine to alkoxide (primary alkoxy group) ratio is exactly one (i.e., $\text{ZrCl}_2(\text{OR})_2$). While comparable $\text{TiCl}_2(\text{OR})_2$ compounds can be readily prepared by alkoxylation of TiCl_4 with primary alcohols (ROH), this method is not applicable to the preparation of $\text{ZrCl}_2(\text{OR})_2$, as shown in Eqs. (1,2).²⁷⁻²⁹

However, this obstacle can be overcome through a ligand exchange process – known as metathesis – by the reaction of $\text{ZrCl}_3(\text{OR})_1$ and $\text{Zr}(\text{OR})_4$, as shown in Eq. (3).

Here, we used different microwave reactors with 30 mL and 1 L containers to prepare $\text{ZrCl}_3(\text{OC}_3\text{H}_7)_1 \times 2\text{C}_3\text{H}_7\text{OH}$ by reacting ZrCl_4 (solid) with 1-propanol ($\text{C}_3\text{H}_7\text{OH}$) at 150 °C, followed by treatment with $\text{Zr}(\text{OC}_3\text{H}_7)_4$ to obtain the desired $\text{ZrCl}_2(\text{OC}_3\text{H}_7)_2$, as proven by NMR spectroscopy (see ^1H and ^{13}C NMR spectra in **Figures 1** and **S4**, respectively, as well as **Tables S5** and **S6** for assignment of signals).

Interestingly, $\text{ZrCl}_2(\text{OC}_3\text{H}_7)_2$ (along with propyl acetate ($\text{CH}_3\text{COOC}_3\text{H}_7$)) can alternatively be produced by controlled chlorination of $\text{Zr}(\text{OC}_3\text{H}_7)_4$ with acetyl chloride (CH_3COCl) at 120 °C via esterification, as shown in Eq. (4). This approach is also straightforward and further prevents the release of HCl as an unwanted side product.²⁸

The corresponding ^1H and ^{13}C NMR spectra are shown in **Figures S5** and **S6**, respectively (see also **Tables S7** and **S8** for assignment of signals).

In the second synthesis step (alcoholysis), 1-hexanol (b.p. 156°C) is introduced to the $\text{ZrCl}_2(\text{OC}_3\text{H}_7)_2$ solution and the mixture heated to 150°C , thereby ensuring that most of the short-chain propoxy groups (OC_3H_7) are replaced by long-chain hexyloxy moieties (OC_6H_{13}), as described in Eq. (5).

In this context, we note that 1-hexanol (or other medium-chain alcohols) affects the particle size and dispersibility of ZrO_2 , because the bulky alkoxy groups have a profound effect on the last processing step. In the final step of the synthesis, benzyl alcohol (b.p. 205°C) is added as a higher boiling reactant (oxygen donor) to the solution, followed by heating to 200°C , to introduce benzyloxy groups ($\text{OCH}_2\text{C}_6\text{H}_5$) via alkoxy-alkoxy exchange, as illustrated in Eq. (6).

Under these conditions, only benzyloxy groups are capable of producing oxo bridges (i.e., Zr-O-Zr bonds) via benzyl chloride elimination at temperatures of 140 – 250°C (Eqs. 7, 8). This is a vital prerequisite for the formation of crystalline ZrO_2 at low temperatures (e.g., at 200°C) on the time-scale of minutes.

As can be seen from Eq. (8), an equal ratio of chlorine to alkoxide ligands is crucial for the condensation process. In the case of an “unequal” ratio (e.g., $\text{ZrCl}_3(\text{OCH}_2\text{C}_6\text{H}_5)_1$ or $\text{ZrCl}_1(\text{OCH}_2\text{C}_6\text{H}_5)_3$), only amorphous or semi-crystalline material is obtained. To confirm our delineated reaction pathway, we analysed the organic solution after synthesis by means of GC-MS. As expected, solely benzyl chloride was found as the main product along with small quantities of benzyl ether species, as shown in **Figure 2** and **Table S9**. Their formation can be attributed to the etherification of benzyl chloride by alcoholic solvent molecules.

We believe that 1-hexanol reduces the reaction rate of the condensation, thereby facilitating the formation of highly crystalline nanoparticles and promoting the steric stabilization in water and other polar solvents such as short-chain alcohols, glycol ethers and so forth. A scheme summarizing the key mechanistic steps is presented in **Figure 3**.

The synthesis method employed here also allows for the incorporation of Y_2O_3 into ZrO_2 to produce solid solutions of the type $(\text{ZrO}_2)_{1-x}(\text{YO}_{1.5})_x$. Suitable dopants are $\text{Y}(\text{NO}_3)_3 \times \text{H}_2\text{O}$ and $\text{Y}(\text{OPr}^i)_3$, which are added simultaneously along with 1-hexanol to the reaction mixture (**Tables S3** and **S4**). Diese Tatsache ist sehr Vorteilhaft, da das Dotieren dazu genutzt

werden kann, gezielt Materialeigenschaften wie z.B. die Temperaturbeständigkeit (Stichwort Phasenumwandlung, Wärmeausdehnungskoeffizient) oder auch die ionische Leitfähigkeit zu verändern. Gleichzeitig erhöht sich damit das Einsatzpotential der Nanopartikel.[Vorschlag für Textbaustein.] Apart from the synthesis method itself, here we also introduce a processing strategy that allows for simple and environmentally friendly preparation of particle dispersions in water. The addition of non-polar solvents (e.g., *n*-pentane) is often necessary to isolate particles from alcoholic reaction solutions. After collecting them by centrifugation or filtration and subsequent washing, the purified particles can be processed into dispersions. The major drawback is the use/consumption of large quantities of liquid alkanes as precipitation agents, which are – because of their toxicity and flammability – no good with respect to waste management and economic efficiency. However, in our process, the precipitation step can be avoided by extracting the particles with water, resulting in stable and highly concentrated colloidal ZrO_2 dispersions with solid contents of $> 30 \text{ wt}\%$. If necessary, both 1-hexanol and benzyl alcohol, which are inevitably dissolved to some degree in the aqueous dispersion, can be removed by solvent extraction using diethyl ether. Also, the particle dispersion can be processed into ultrafine powders via freeze drying or gentle evaporation (e.g., at 50°C in vacuo). We emphasize that the ZrO_2 nanoparticles obtained in this way can be redispersed in water and organic solvents, without the need for any additional surfactants. More information on these procedures can be found in section 1.2 (ESI).

To gain insight into the morphology and microstructure of the nanoparticles, TEM, XRD, DLS, XAS and XPS measurements were carried out. We note again that our synthesis route allows for the preparation of up to 20 g of pure ZrO_2 (BN3*) in less than 1 hour . The corresponding consumption of electric energy needed for the dielectric microwave heating is only around 1 kWh . As can be seen from the TEM images in **Figures 4a** and **b**, the nanoparticles are almost spherical in shape with diameters ranging from 3 – 4 nm . Virtually identical observations were made for both the small-scale synthesis (BN2#; **Figure S7**) and the modified approach using acetyl chloride instead of ZrCl_4 (BN5#, **Figure S8**). The structure and composition of pure ZrO_2 and $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ solid solutions before and after heating to 700°C ($5^\circ\text{C}/\text{min}$) were investigated via XRD. The XRD pattern of a representative ZrO_2 sample (BN3*) was also analyzed by Rietveld refinement assuming both tetragonal and cubic structure types with space groups $137 (P4_2/nmc)$ and $225 (Fm\bar{3}m)$, respectively. The results are summarized in **Table S10**; the Rietveld plots are shown in **Figures 4c** and **S9**. The smallest R_p , GoF and R_{wp} values were obtained for the cubic polymorph although the differences between the cubic structure and the tetragonal structure are relatively small. The size-microstrain analysis indicated an average crystallite size of 2.5 nm and an average maximum microstrain of 77.61×10^{-4} . These values are in fair agreement with data obtained on 2.8 – 2.9 nm ZrO_2 nanoparticles described in the literature.^{21, 22} As mentioned above, the modified synthesis approach (BN5#) produced nanoparticles of similar

size (**Figure S10**). Overall, we found that the average crystalline domain sizes can be tailored from about 2.0 nm to 2.5 nm by adjusting the time of the final synthesis step, as shown in **Figure 4d**. XRD patterns of pure ZrO_2 and $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ solid solutions after heating to 700 °C are presented in **Figures 5a-c** and **S11**. From these data, it is evident that cubic ZrO_2 is metastable and transforms into tetragonal and monoclinic ZrO_2 at elevated temperatures ($\theta > 550$ °C). The conversion to monoclinic ZrO_2 is completed at around 1000 °C (data not shown). However, even minor amounts of solutes such as Y_2O_3 (e.g., 3 mol% Y) are sufficient to stabilize the tetragonal phase at 700 °C, as indicated by Raman spectroscopy in **Figure 5d**.³⁰

³¹ Besides, no parasitic phases such as cubic Y_2O_3 (JCPDS card no. 043-0661) were found, irrespective of doping level. The chemical composition of the $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-\delta}$ solid solutions was analysed via XPS. A summary of the quantitative analysis is given in **Table 2**. As seen, all samples exhibit a non-negligible amount of carbon, which can be ascribed to both superficial contaminations and surface ligands (i.e., hexyloxy and benzyloxy groups). However, the ligands were largely removed after heating in air, since the carbon content decreased noticeably. A further residue from the sol-gel synthesis is chlorine, which was also detected for all samples (approx. 9 at%). The Zr/Y atomic ratio is, for 3YSZ (BN6#) and 6YSZ (BN7#), in reasonable agreement with the expected ratio, while samples with higher Y content show indeed a higher Zr/Y ratio with respect to the nominal one. Typically, upon annealing to 700 °C, the yttrium dopant shows some tendency for migration towards the surface. This is a well-known phenomenon in YSZ materials.^{32, 33} In addition, Figure 6 shows representative XPS detail spectra of the Zr 3d and Y 3d core level regions obtained from a 6YSZ sample (BN7#). As demonstrated, the Zr 3d core level is represented by a doublet, the components of which ($3d_{5/2}$ and $3d_{3/2}$) are separated by $\Delta E = 2.4$ eV. After deconvolution of the Zr 3d signal, three different chemical environments are obtained. The $3d_{5/2}$ peak at about 181.5 eV corresponds to non-stoichiometric $\text{ZrO}_{2-\delta}$, while for stoichiometric ZrO_2 the corresponding peak is located at 182.5 eV.^{34, 35} The highest laying component ($3d_{5/2} = 183.4$ eV) is due to the presence of hydroxyl surface groups. A similar description can also be provided for the Y 3d core level (doublet splitting $\Delta E = 2.1$ eV). In this case, the different chemical environments give rise to $3d_{5/2}$ signals at binding energies of 156.1 eV, 157.3 eV and 158.3 eV for non-stoichiometric $\text{Y}_2\text{O}_{3-\delta}$, defect-free Y_2O_3 and Y-OH, respectively. The relative amount for the different species in pure ZrO_2 (BN2#) and YSZ samples (BN6#-BN9#) is indicated in **Figures S12** and **S13**. To conclude, the XPS data provide evidence that a large fraction of Y can be successfully incorporated into the ZrO_2 nanoparticles to prevent the formation of monoclinic ZrO_2 at temperatures above 550 °C.

Table 2. Chemical composition from XPS analysis.

Batch name	Sample	Zr (at%)	Y (at%)	O (at%)	C (at%)	Cl (at%)	Zr/Y ratio
BN2#	ZrO_2	18.6x	-	38.2	33.6	9.6	-

BN6#	(as-made) ZrO_2 (700 °C)	24.2	-	45.0	21.5	9.3	-
	3YSZ (as-made)	18.8	0.5	38.9	32.3	9.5	97.2/2.8
	3YSZ (700 °C)	23.9	1.0	45.3	20.7	9.1	95.8/4.2
BN7#	6YSZ (as-made)	17.7	1.0	38.6	32.4	10.3	94.8/5.2
	6YSZ (700 °C)	24.4	1.9	47.3	17.0	9.3	92.3/7.3
	12YSZ (as-made)	16.4	1.2	35.3	38.3	8.8	93.5/6.5
BN8#	12YSZ (700 °C)	21.9	3.6	44.1	21.6	8.9	86.0/14.0
	18YSZ (as-made)	15.4	2.5	34.5	38.3	9.3	86.1/13.9
	18YSZ (700 °C)	20.8	4.1	41.8	24.4	8.9	83.4/16.6

To better assess the local structural environments of Y^{3+} and Zr^{4+} in yttria-stabilized zirconia, XAS measurements were performed on both 6YSZ (BN7#) and 12YSZ (BN8#). Representative XANES spectra of the YSZ specimens (taken at room temperature) are shown in **Figures 6c-d** and **S14**, revealing the Y K-edge at about 17.051 keV and the Zr K-edge at about 18.014 keV in agreement with reported values for YSZ.³⁶ In comparison to Y_2O_3 (used as reference), the Y K-edge XANES spectra of the as-made samples exhibit a significantly narrower linewidth and a much more intense white line, thus implying that the coordination number of Y^{3+} is larger than in Y_2O_3 with cubic bixbyite structure (i.e., > 6) and confirming the incorporation into the host lattice.³⁷ After heat-treatment at 700 °C, the XANES edges become broader and split into two components, suggesting a more ordered environment around Y.³⁸ The EXAFS spectra of the as-made samples shown in **Figure S15** are characterized by a single decaying oscillation, corresponding to the Y-O shell, while the heat-treated samples show features characteristic of cubic YSZ.³⁹ The feature characterizing the as-made samples is likely related to a size-effect, given that the particles are very small and thermal disorder dominates.³⁸ After heat-treatment, it was possible to assess the presence of a second shell, which we attribute to an increase in crystallite size (see XRD patterns in **Figure S11**). In addition, the Y local environment is known to be less sensitive to the host structure.³⁷ Moreover, the size-effect is also supported by the fitting data of the EXAFS curves (**Table S11**). The XANES spectra collected at the Zr K-edge are practically identical for the pristine samples, which is indicative of a similar local environment around the Zr ions and comparable to cubic ZrO_2 . After heat-treatment, the observed features slightly change; a bump at 18.057 keV becomes evident in the 6YSZ sample, which can be associated with tetragonal ZrO_2 .^{37, 38} The partial phase transformation is also corroborated by the fitting data of the EXAFS curves (see **Figure S16** and **Table S12**). Interestingly, the pristine samples are solely composed of cubic YSZ, with Zr-O and Zr cation distances typical of these compounds.^{37, 40} On the other hand, both materials convert into a mixed cubic-tetragonal structure upon heating, with the extent of conversion increasing with decreasing Y content.

To demonstrate the excellent dispersibility of the ZrO_2 nanocrystals in water, a series of DLS measurements were performed. The hydrodynamic size distributions of two samples (BN3* and BN5#) are shown in **Figures 7a** and **b**. Both dispersions exhibit very narrow size distributions with an average hydrodynamic particle diameter of (4.0 ± 2.0) nm at a solid content of 10 wt%. The monomodal distribution leads us to conclude that particle aggregation (settling or clumping) can be ruled out. We believe that this is due to the combination of electrostatic and steric stabilization, a hypothesis that is supported by the fact that the particles exhibit a positive zeta potential of 40 meV in water. The latter can be explained by the formation of trace amounts of HCl through hydrolysis of Zr-Cl species. A photograph of a nanoparticle dispersion (BN3*) with 45 wt% (pure) ZrO_2 is shown in **Figure 6c**.

From TGA-MS (**Figure 6d**), it can be seen that mostly hexyloxy ligands are present on the particle surface. This finding helps to explain why the particle dispersions are stable over years and no additional stabilizing agents such as fatty acids, phosphonates or *n*-alkylamines to name but a few are required.⁴¹⁻⁴³ The TGA-MS data further indicate a total mass loss of 17.2% by 1000 °C. A significant loss of around 5% due to adsorbed water is noticed at temperatures below 150 °C. The combustion of large amounts of covalently bound hexyloxy groups is apparent at 235 °C, while minor amounts of benzyl alcohol and benzyloxy groups decompose at 180 °C and 250 °C. In addition, the presence of small amounts of chlorine, released by cleavage of Zr-Cl species above 300 °C can be observed, in accordance with findings from XPS. Overall, an approximate composition of 88% ZrO_2 , 2% Cl and 10% organics is determined from TGA-MS, which underlines the high quality of the nanoparticles with a reasonable carbon-to-metal oxide ratio.

Apart from the microstructure, the optical properties of the ZrO_2 nanoparticles (BN3*) were probed as well. The UV-Vis data in **Fig. S17** indicate an indirect band gap of (5.05 ± 0.05) eV at room temperature, in agreement with both theoretical predictions (approx. 5.0 eV) and experimental results for cubic stabilized zirconia (approx. 5.2 eV).^{44, 45} As pointed out in previous works, the optical band gap arises from the excitation of electrons from the O 2p valence band to the Zr 4d conduction band.^{44, 45}

In summary, compared to previous studies on the advanced synthesis of ZrO_2 nanoparticles, our procedure possesses advantages as far as energy consumption and utilization of non-toxic substances are concerned. Joo et al. developed a synthesis of high-quality ZrO_2 nanoparticles at 340 °C (2 hours) using trioctylphosphinoxide as a capping ligand.²¹ The synthesis route developed by Garnweitner et al. is also based on benzyl alcohol, but requires treatment at 210 °C for 2 days.²² Cheema et al. reported a synthesis requiring autoclave conditions at 220-250 °C for 3-4 days and post-functionalization with 2-[2-(2-methoxyethoxy)ethoxy] acetic acid to achieve good dispersibility.²³

Finally, we demonstrate that the as-made ZrO_2 nanoparticles are highly suited for use as preformed building blocks to prepare thermally stable fiber mats as well as mesoporous thin

films and powders through electrospinning and co-assembly strategies, respectively. Such materials are believed to be beneficial for application as industrial catalysts and/or catalyst supports.⁴⁶⁻⁴⁸ Thin films and powders were prepared via evaporation-induced self-assembly (EISA) using the amphiphilic diblock copolymer KLE as the structure-directing agent.⁴⁹⁻⁵² The morphology and nanoscale structure of the polymer-templated mesostructured ZrO_2 thin films were investigated by a combination of SEM, TEM, AFM, and GISAXS. **Figure 8** present top view SEM, bright-field TEM and tapping mode AFM images at different magnifications of a thin film sample heated to 600 °C in air. Both SEM and AFM show an ordered cubic network of 20 nm pores at the top surface. On the basis of these data, the presence of a sealing layer can be ruled out. The lateral (in-plane) pore size is also confirmed by TEM. In addition, it can be seen that the pore-solid architecture persists throughout the bulk and the pore walls have a thickness of approx. 16 nm. These results are further supported by GISAXS. **Figure S18** shows GISAXS data obtained at an angle of incidence of 0.2° as a function of temperature. Samples calcined at 300 °C produced patterns with strong scattering maxima along the *z*- and *y*-directions. They can be clearly indexed to a face-centered-cubic (pore) structure with (111) orientation relative to the substrate. We note that even third order maxima can be observed, thus emphasizing the degree of ordering. Furthermore, GISAXS indicates that the periodicity, and thus the pore structure, can be preserved up to 850 °C, which underlines the exceptional thermal stability of the polymer-templated mesostructured thin films. In this content, we want to mention briefly that macroporous films can be made from the preformed ZrO_2 building blocks as well, as shown in **Figure S19**.

Besides, the synthesis method employed here is also applicable to the preparation of materials in powder format. **Figure 9a** shows a low-magnification TEM image of a polymer-templated mesostructured powder sample heated to 600 °C in air. The average pore diameter is 12 nm, which is slightly smaller compared to the thin films described above. The primary reasons are likely the different polymer-to-precursor ratio used and the different drying conditions. In this case, we found by XRD (**Figure S20**) that the crystalline domain sizes can be tailored from 2 nm (as-made) to about 6 nm (600 °C). The porosity was also examined by N_2 -physisorption. **Figure S21** shows adsorption/desorption isotherms along with the corresponding cumulative surface area plot. The shape of the isotherms (type IV) is characteristic of mesoporous materials, and the distinct hysteresis loop indicates the presence of pores of uniform size and shape. The Brunauer-Emmett-Teller (BET) surface area was determined to be some 140 m²/g, in good agreement with theoretical predictions assuming a low micropore fraction. From the data in **Figure S22**, it is evident that the micropore fraction is in fact negligible. Overall, this is not surprising given that these materials were made from preformed building blocks rather than molecular precursors. For comparison, a non-templated (as-made) powder material (BN2#) exhibits a BET surface area of around 170 m²/g (**Figure S22**). The total pore volume (0.135 cm³/g) was determined

from the adsorption branch using a non-local density functional theory (NLDFT) model for porous silica.

As mentioned previously, the good dispersibility of the nanocrystals in various solvents also enables the preparation of thermally stable high-aspect-ratio fibers via electrospinning using different carrier polymers (PVB, PAN and PEO). The electron microscopy images in **Figures 9b, S23 and S24** as well as the porosity data in **Figure S25** reveal very uniform, porous fibers (after polymer removal) of diameter > 100 nm and a length of several micrometers. Collectively, the data shown in this section clearly demonstrate the versatility of the dispersible ZrO₂ nanocrystals, which we believe significantly increases their application potential.

Conclusions

An efficient multigram scale microwave synthesis of ZrO₂ nanocrystals with narrow size distribution using non-toxic solvents was reported. The simplicity and robustness of the synthetic procedure also enabled the preparation of high-quality ZrO₂-Y₂O₃ solid solutions. More importantly, because of the excellent dispersibility of the nanocrystals, they could be processed in the form of nanofibers as well as mesoporous and macroporous powders and thin films.

Apart from both the material preparation and characterization, it was shown that rational design of sol-gel reactions can lead to significant improvements in the ecological footprint of metal oxide syntheses. As a major advance, neither intricate post-functionalization steps nor additional surface-active species were required to achieve long-term stable dispersions in water and organic solvents due to electrosteric stabilization. Also, only about 0.05 kWh per gram of synthesized ZrO₂ nanoparticles were consumed by the microwave dielectric heating, and other energy-intensive steps were avoided.

In summary, the number of processing steps and chemicals (additives, stabilizers etc.) required for the synthesis was small, thus leading to improved atom efficiency, in line with the principles of “green chemistry”. Overall, our study demonstrates clearly that a profound understanding of the reaction mechanism(s) is vital for the development of synthesis routes with reduced environmental impact.

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TOC

Fig. 1. ^1H NMR spectrum of $\text{ZrCl}_2(\text{OC}_3\text{H}_7)_2 \times 2.3\text{C}_3\text{H}_7\text{OH}$ (BN1#) prepared by metathesis of $\text{ZrCl}_3(\text{OC}_3\text{H}_7)_1$ and $\text{Zr}(\text{OC}_3\text{H}_7)_4$ [70 wt% in $\text{C}_3\text{H}_7\text{OH}$] after distilling off excess propyl alcohol under vacuum at 80 °C for 12 hours.

Fig. 2. Gas chromatogram of the organic solution after the final synthesis step (3 min at 200 °C, BN2#). For analytical reasons, the ZrO_2 nanoparticles were separated from the solution by precipitation with chloroform- d . Benzyl chloride is found as the main organic component along with small quantities of mixed benzyl ethers (ethyl, propyl, hexyl) formed by etherification of benzyl chloride.

Fig. 3. (a) Propoxylation of ZrCl_4 . (b) Ligand exchange between $\text{ZrCl}_3(\text{OPr})_1$ and $\text{Zr}(\text{OPr})_4$. (c) Alkoxy-alkoxy exchange. (d) Proposed mechanism for the formation of Zr-O-Zr bonds via benzyl chloride (BnCl) elimination.

Fig. 4. (a,b) Bright-field TEM images at different magnifications of ZrO_2 nanoparticles (BN3*). (c) XRD pattern of ZrO_2 nanoparticles (BN3*). The observed (black) and simulated (red) patterns as well as the difference profile of the fit (blue) are shown. The vertical lines indicate the Bragg reflections expected for cubic ZrO_2 . (d) XRD patterns of ZrO_2 nanoparticles with average sizes of 2.0 nm (A) and 2.5 nm (B) obtained at different synthesis times (2 min or 3 min at 200 °C, BN2#). The reflections are indexed according to JCPDS card no. 01-081-1551 (ICSD collection code 072956) for cubic ZrO_2 .

Fig. 5. XRD pattern of (a) ZrO_2 (BN2#), (b) 3YSZ (BN10#) and (c) 16YSZ (BN12#) nanoparticles before (A) and after heating to 700 °C (B) at 5 °C/min. The XRD patterns in (a), (b) and (c) are indexed according to JCPDS reference cards no. 01-081-1551 (cubic ZrO_2), 37-1484 (monoclinic ZrO_2), 01-083-0113 (tetragonal YSZ) and 030-1468 (cubic YSZ). Please note that some Miller indices are omitted for clarity. (d) Raman spectrum of tetragonal 3YSZ particles (BN10#) after heating to 700 °C. A Raman spectrum of non-stabilized ZrO_2 particles (BN2#) heated to 700 °C is also shown for comparison. The asterisks indicate monoclinic ZrO_2 (baddeleyite).

Fig. 6. Detailed XPS scans of the Zr 3d (a) and Y 3d core level regions (b) for as-made 6YSZ (BN7#). Y K-edge and Zr K-edge XANES spectra (c,d) obtained on YSZ samples (BN7# and BN8#) before and after heating to 700 °C.

Fig. 7. (a,b) Particle size distributions of ZrO₂ (left BN3*, right BN5#; 10 wt% solid content) in water from dynamic light scattering. The insets show dispersions with solid contents of 20 wt%. (c) Photograph of a 45 wt% ZrO₂ dispersion (BN3*). The powder material used is shown in the inset. (d) TGA-MS of as-made ZrO₂ nanoparticles (BN3*) in synthetic air at 5 °C/min. The dashed black line is the TG curve. The MS analysis shows H₂O ($m/e = 18$) in red, CO₂ ($m/e = 44$, $I \times 0.5$) in blue, Cl⁺ ($m/e = 35$, $I \times 10$) in green, C₄H₈⁺ ($m/e = 56$, $I \times 10$; fragmentation ion of C₆H₁₃OH) in gray, and C₇H₇⁺ ($m/e = 91$, $I \times 100$; fragmentation ion of C₆H₅CH₂OH) in black. Prior to TGA-MS, the nanoparticles were dried at room temperature under high vacuum and then stored in a closed vial.

Fig. 8. Morphology of polymer-templated mesostructured ZrO_2 thin films made from preformed nanocrystalline building blocks (BN2#). (a) Top view SEM image. (b) Bright-field TEM image indicating that the pore structure persists throughout the bulk. (c) Tapping mode AFM image. The contrast covers height variations in the 1–10 nm range. (d) 3D-AFM image with a sample tilt of 55° .

Fig. 9. Morphology of polymer-templated mesostructured ZrO_2 powder and electrospun nanofibers made from preformed nanocrystalline building blocks (BN2#). The powder material was calcined at 600°C , while the nanofibers were heated to 1100°C in air. (a) Bright-field TEM image showing 12 nm pores. The inset is an electron diffraction pattern from the same area. (b) SEM image.