## **Supporting Information**

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

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### 1. Experimental

### 1.1 Recipes for the synthesis of $ZrO_2$ and YSZ

Batch number	Precursor 1	Solvent 1	Heating 1	0	Cooling 1	Precursor 2	Heating 2		Cooling 2	Solvent 2	Heating 3	0	Cooling 3	Solvent 3	Heating 4	D	Workup
Monowave 300	ZrCl4	1-Propanol	Length of time / min	Temp. / °C	Temp. / °C	Zr(OPr) <sub>4</sub>	Length of time / min	Temp. / °C	Temp. / °C	1-Hexanol	Length of time / min	Temp. / °C	Temp. / °C	Benzyl- alcohol	Length of time / min	Temp. [°C]	Precipitation and washing
BN1#	624.5 mg (2.68 mmol)	2.5 mL	1	150	70	627.1 mg (1.34 mmol)	ŝ	150	70	ı		I	ı	·	ı	ı	The solvent was removed by distillation in vacuo (6 hours at 100 °C)
BN2#	624.5 mg (2.68 mmol)	2.5 mL	1	150	70	627.1 mg (1.34 mmol)	ŝ	150	70	6 mL	-	150		6 mL	3 (2)	200	(1) 200 mL <i>n</i> -pentan (2) $1 \times 50$ mL diethyl ether
Masterwave Pro	ZrCl4	Ethanol	Length of time / min	Temp. / °C	Temp. / °C	Zr(OPr) <sub>4</sub>	Length of time / min	Temp. / °C	Temp. / °C	1-Hexanol	Length of time / min	Temp. / °C	Temp. / °C	Benzyl- alcohol	Length of time / min	Temp. [°C]	Precipitation and washing
BN3*	25.64 g (110 mmol)	100 mL	1	150	70	25.74 g (55 mmol)	б	150	70	250 mL	m	150	70	250 mL	ς	70	See description in 1.2

Tab. S1 Synthesis of ZrO<sub>2</sub> nanoparticles.

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

BN5#	BN4#		Batch number
1.87 g (4 mmol)	1.87 g (4 mmol)	Zr(OPr)4	Precursor 1
628.0 mg (8 mmol)	628.0 mg (8 mmol)	CH3COCI	Precursor 2
2.5 mL	ı	Ethanol	Solvent 1
1	1	Length of time / min	Hooting 1
120	120	Temp. / °C	
70	70	Temp. / °C	Cooling 1
10 mL (6 mL)		1-Hexanol	Solvent 2
1	ı	Length of time / min	Heating 2
150	ı	Temp. / °C	D D
70	ı	Temp. / °C	Cooling 2
2 mL (6 mL)	I	Benzyl alcohol	Solvent 3
22 (3)	ı	Length of time / min	Heating 3
200	ı	Temp. / °C	0
70		Temp. / °C	Cooling 3
(1) 100 mL <i>n</i> -pentane and 100 mL diethyl ether (2) $1 \times 50$ mL diethyl ether	NMR analysis	Precipitation and washing	Workup

Tab. S2 Synthesis of ZrO<sub>2</sub> nanoparticles using acetyl chloride.

Workup	Precipitation and washing	(1) 200 mL <i>n</i> -pentan (2) $2 \times 50$ mL diethyl ether and ethanol	(1) 200 mL <i>n</i> -pentan (2) $2 \times 50$ mL diethyl ether and ethanol	(1) 200 mL <i>n</i> -pentan (2) $2 \times 50$ mL diethyl ether and ethanol	(1) 200 mL <i>n</i> -pentan (2) $2 \times 50$ mL diethyl ether and ethanol
0	Temp. [°C]	200	200	200	200
Heating 4	Length of time / min	5.5	6	7	12
Solvent 3	Benzyl alcohol	6 mL	6 mL	6 mL	6 mL
Cooling 3	Temp. / °C	70	70	70	70
D	Temp. / °C	150	150	150	150
Heating 3	Length of time / min	1	1		1
Precursor 3	Y(O- <i>i</i> -Pr) <sub>3</sub>	34.6 mg (0.13 mmol)	69.2 mg (0.26 mmol)	135.7 mg (0.51 mmol)	205.0 mg (0.77 mmol)
Solvent 2	1-Hexanol	6 mL	6 mL	6 mL	6 mL
Cooling 2	Temp. / °C	70	70	70	70
	Temp. / °C	120	120	120	120
Heating 2	Length of time / min	ę	e	c	c
Precursor 2	Zr(OPr)4	650.5 mg (1.39 mmol)	627.1 mg (1.34 mmol)	589.6 mg (1.26 mmol)	547.5 mg (1.17 mmol)
Cooling 1	Temp. / °C	70	70	70	70
nteamig 1	Temp. / °C	150	150	150	150
Uootina 1	Length of time / min	1	1	1	1
Solvent 1	1-Propanol	2.5 mL	2.5 mL	2.5 mL	2.5 mL
Precursor 1	ZrCl4	645.5 mg (2.77 mmol)	626.9 mg (2.69 mmol)	587.3 mg (2.52 mmol)	545.3 mg (2.34 mmol)
Batch number		BN6# (3YSZ)	BN7# (6YSZ)	BN8# (12YSZ)	BN9# (18YSZ)

**Tab. S3** Recipes for the synthesis of YSZ nanoparticles using yttrium(III) isopropoxide.

Heating 4 Workup	Length of time / min Temp. [°C] Precipitation and washing	5.5 200 (1) 200  mL <i>n</i> -pentan $(2) 2 \times 50 \text{ mL}$ diethyl ether and ethanol	6 200 (1) 200  mL <i>n</i> -pentan $(2) 2 \times 50 \text{ mL}$ diethyl ether and ethanol	7 200 (1) 200 mL <i>n</i> -pentan (2) $2 \times 50$ mL diethyl ether and ethanol
	Length of time /	۲ ک	ý	L
Solvent 3	Benzyl alcohol	6 mL	6 mL	6 mL
Cooling 3	Temp. / °C	70	70	70
IICamigo	Temp. / °C	150	150	150
Hooting 3	Length of time / min	1	1	1
Precursor 3	Y(NO <sub>3</sub> ) <sub>3</sub> ×H <sub>2</sub> O	35.2 mg (0.12 mmol)	93.7 mg (0.32 mmol)	190.4 mg (0.65 mmol)
Solvent 2	1-Hexanol	6 mL	6 mL	6 mL
Cooling 2	Temp. / °C	70	70	70
	Temp. / °C	150	120	120
Heating 2	Length of time / min	°,	ŝ	Э
Precursor 2	Zr(OPr)4	608.3 mg (1.3 mmol)	575.6 mg (1.23 mmol)	412.2 mg (1.13 mmol)
Cooling 1	Temp. / °C	70	70	70
ncamig 1	Temp. / °C	150	150	150
Hooting 1	Length of time / min	1	1	1
Solvent 1	Ethanol	2.5 mL	2.5 mL	2.5 mL
Precursor 1	ZrCl4	605.9 mg (2.6 mmol)	573.3 mg (2.46 mmol)	526.7 mg (2.26 mmol)
Batch number		BN10# (3YSZ)	BN11# (8YSZ)	BN12# (16YSZ)

Tab. S4 Recipes for the synthesis of YSZ nanoparticles using yttrium(III) nitrate monohydrate(\*).

 $*Y(NO_3)_3 \times H_2O$  is not commercially available; however, it can be prepared as follows: An appropriate amount of commercially available  $Y(NO_3)_3 \times 6H_2O$  is dehydrated in a drying closet at 170 °C for 12 hours.<sup>[1, 2]</sup> Then, the resulting hygroscopic  $Y(NO_3)_3 \times H_2O$  is dissolved under exclusion of moisture in anhydrous 1-hexanol and used for synthesis.

#### **1.2 Powders and dispersions**

#### 1.2.1 Work-up procedure I (suitable for small batch sizes)

The nanoparticles (e.g., BN2#, BN6# and BN10#) can be isolated from the organic reaction solution by precipitation with *n*-pentane, followed by centrifugation (4000 rpm), washing with small amounts of diethyl ether (50 mL) and drying in air. To this end, 200 mL of precipitation agent are needed. The obtained material ( $\sim$ 0.6 g) can be dispersed in polar solvents (e.g., water and ethanol) with solid contents of at least 20% by weight.

#### 1.2.2 Work-up procedure II (suitable for large batch sizes)

1.5 L of *n*-pentane is placed in a 2 L separating funnel with PTFE stopcock plug. Then, 50 mL of a 600 mL reaction solution (e.g., BN3\*) are added and stirred slowly with a glass rod. After 5 min, the formed precipitate is collected by releasing the lower phase. The remaining supernatant is filled to a total volume of 1.5 L with *n*-pentane so that further 50 mL of the reaction solution can be precipitated. By employing this procedure, 300 mL of the reaction solution can be precipitated. Around 5 liters of the precipitation agent is required for the entire solution. The low boiling point alkane is recovered by distillation. After 1 hour, the combined precipitates are decanted to remove the supernatant. Then, 0.8 L of diethyl ether are added to the solution and transferred into a separating funnel. After repeated shaking and venting, the collected precipitate is isolated by centrifugation (at 4000 rpm). Finally, the powder is dried in air under ambient conditions. The obtained white material (approx. 25 g) can be dispersed in water, yielding a transparent sol with a solid content of up to to 825 g/L.

#### **1.2.3 Work-up procedure III (solvent exchange)**

600 mL of the reaction solution (BN3\*) consisting of approx. 25 g of  $ZrO_2$ , 100 mL of ethanol, 250 mL of 1-hexanol and 250 mL of benzyl alcohol are transferred to a 2 L separating funnel. After adding 100 mL of deionized water, the mixture is shaken so that the nanoparticles pass into the aqueous phase. After phase separation (approx. 30 min), 71 mL of an aqueous dispersion are obtained and then washed 5 times using 80 mL of diethyl ether. The resulting transparent dispersion (57.5 mL) is subjected to distillation (at 50 °C) to remove minor amounts of diethyl ether and ethanol. Depending on the distillation period, a volume of 47.5 mL can be obtained, which contains 22.6 g of nanoparticles (i.e., approx. 33.7 wt%  $ZrO_2$  in H<sub>2</sub>O). Higher solid contents can be achieved through subsequent water evaporation.

#### 1.2.4 Work-up procedure IV (lyophilisation)

600 mL of the reaction solution (BN3\*) consisting of approx. 25 g of  $ZrO_2$  are transferred to a 2 L separating funnel. 250 mL of deionized water are added, followed by shaking and frequent venting. After phase separation, the aqueous phase is cooled to -20 °C. 25 g of fine powder material are isolated by sublimation of ice and frozen solvent. The home-built freeze drying system used for this purpose is shown below. Lastly, the powder can be dispersed in water and other polar solvents with solid contents of 45% by weight.



Home-built freeze drying apparatus used for lyophilisation.

#### 1.3 Nanofibers

#### 1.3.1 PEO as carrier polymer

For the synthesis of nanofibers, a suspension of as-prepared nanoparticles (BN2#) in methanol was mixed with a solution of poly(ethylene oxide) (PEO) in water. The solution contained 2.8 wt% of PEO, 2.2 wt% of  $ZrO_2$ , 39 wt% of water, and 56 wt% of methanol. The solution was stirred until it was homogeneous and then loaded into a plastic syringe equipped with a steel needle. The syringe was placed inside a syringe pump and the needle was connected to a high voltage power supply. The counter electrode (aluminium foil) was connected to a high voltage power supply of opposite polarity. The power supplies were used to create an electric field of

about 1 kV/cm. The distance between the electrodes was about 10 cm. This set-up was placed inside a chamber flushed with compressed air to reduce the humidity. The as-spun fibers were heated at 550  $^{\circ}$ C (5  $^{\circ}$ C/min) for 3 hours.

#### 1.3.2 PAN as carrier polymer

In a typical experiment, 160 mg of polyacrylonitrile (PAN) was dissolved in 840 mg of DMF and subsequently 1000 mg of an 5 wt% dispersion of ZrO<sub>2</sub> (BN2#) in methanol and water (80/20) was added dropwise. The resulting solution was homogenized for several minutes using a shaker. Electrospinning was carried out using a home-built set-up consisting of a humidity controlled chamber including high voltage supply (scientific instruments, TSI-HV), syringe pump (Harvard Apparatus, 11 Plus MAI 70-2208), syringe, 4.73 mm diameter needle, and 10 cm diameter circular counter electrode covered with aluminium foil. The applied voltage was set to 7 kV at a tip-to-collector distance of 10 cm. The pumping rate of the spinning solution was 0.3 mL/h. The relative humidity in the chamber was approx. 35%. The as-spun PAN/ZrO<sub>2</sub> fibers were heated with a rate of 5 °C/min to 900 °C and aged for 2 hours at this temperature to achieve complete combustion of the PAN.

# NMR data of dipropoxyzirconium dichloride obtained by metathesis reaction of zirconium(IV) chloride and zirconium(IV) propoxide

Assignment	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-X	C <sub>3</sub> H <sub>7</sub> OH
PrOH	$\delta = 0.83$	$\delta = 1.41$	$\delta = 3.33$	$\delta = 4.35$
(X = H)	(t, J = 7.4  Hz, 3H)	(sxt, J = 7.1  Hz, 2H)	( <i>m</i> , 2H)	(t, J = 5.2  Hz, OH)
$Zr(OPr)_4^*$	$\delta = 0.84$	$\delta = 1.42$	$\delta = 3.83$	$\delta = 4.38 (m, OH)$
(X = Zr)	(t, J = 7.4  Hz, 3H)	(sxt, J = 6.9  Hz, 2H)	( <i>m</i> , 2H)	0 = 4.38 (m, 011)
$ZrCl_1(OPr)_3$ (X = Zr)	-	-	$\delta = 3.86$	
$ZrCl_2(OPr)_2$	$\delta = 0.89$	$\delta = 1.51$	$\delta = 3.90$	
(X = Zr)	(t, J = 7.3  Hz, 3H)	(sxt, J = 6.9  Hz, 2H)	(t, J = 6.2  Hz, 2H)	$\delta = 4.41 \ (m, OH)$
$ZrCl_3(OPr)_1$ $(X = Zr)$	-	-	$\delta = 3.95$	

Tab. S5 <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) data of ZrCl<sub>2</sub>(OPr)<sub>2</sub>×2.3PrOH (BN1#).

(\*) Reference data for comparison

Tah	<b>S6</b> <sup>13</sup> C NMR	(100.3  MHz)	DMSO-dc)	data of ZrCl <sub>2</sub> (	$(OPr)_{2} \times 2$ 3PrOF	H (BN1#)
I av.		(100.5  mmz)	$D_{1100}$ $u_0$		$(011)_{2}^{-2}.51101$	$\mathbf{I}$ ( $\mathbf{D}$ $\mathbf{I}$ $\mathbf{I}$ $\mathbf{I}$ $\mathbf{I}$ $\mathbf{I}$ $\mathbf{I}$

Assignment	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-Zr	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–Zr	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–Zr
PrOH	$\delta = 10.40 \ (s)$	$\delta = 25.59 (s)$	$\delta = 62.38 (s)$
$Zr(OPr)_4^*$	$\delta = 10.38 (s)$	$\delta = 25.66 (s)$	$\delta = 62.54 (s)$
ZrCl <sub>1</sub> (OPr) <sub>3</sub>	-	-	-
ZrCl <sub>2</sub> (OPr) <sub>2</sub>	$\delta = 10.49 (s)$	$\delta = 26.31 (s)$	$\delta = 72.24 (s)$
ZrCl <sub>3</sub> (OPr) <sub>1</sub>	-	-	-

(\*) Reference data for comparison

# NMR data of dipropoxyzirconium dichloride obtained by halogenation of zirconium(IV) propoxide with acetyl chloride

Assignment	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-X	C <sub>3</sub> H <sub>7</sub> OH / CH <sub>3</sub> CO-R
PrOH (X = H)	$\delta = 0.84$ ( <i>t</i> , <i>J</i> = 7.4 Hz, 3H)	$\delta = 1.42$ ( <i>sxt</i> , <i>J</i> = 7.1 Hz, 2H)	$\delta = 3.34$ ( <i>t</i> , <i>J</i> = 6.0 Hz, 2H)	
$ZrCl_1(OPr)_3^*$ (X = Zr)	$\delta = 0.85$ ( <i>t</i> , <i>J</i> = 7.3 Hz, 3H)	δ = 1.48 ( <i>m</i> , 2H)	$\delta = 3.88$ ( <i>t</i> , <i>J</i> = 6.2 Hz, 2H)	$\delta = 4.45$
$ZrCl_2(OPr)_2 (X = Zr)$	$\delta = 0.89$ ( <i>m</i> , 3H)	δ = 1.50 ( <i>m</i> , 2H)	$\delta = 3.90$ ( <i>t</i> , <i>J</i> = 6.3 Hz, 2H	(s, OH)
$\frac{\text{ZrCl}_{3}(\text{OPr})_{1}^{*}}{(X = \text{Zr})}$	$\delta = 0.89$ ( <i>m</i> , 3H)	δ = 1.59 ( <i>m</i> , 2H)	δ = 3.95 ( <i>m</i> , 2H)	
$PrOAc$ $X = CH_3CO$ $R = C_3H_7$	$\delta = 0.89$ ( <i>t</i> , <i>J</i> = 7.4 Hz, 3H)	$\delta = 1.58$ ( <i>sxt</i> , <i>J</i> = 7.2 Hz, 2H)	$\delta = 3.95$ ( <i>t</i> , <i>J</i> = 6.7 Hz, 2H	$\delta = 2.00$ (s, 3H)

Tab. S7 <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) data of ZrCl<sub>2</sub>(OPr)<sub>2</sub>×CH<sub>3</sub>COOC<sub>3</sub>H<sub>7</sub> (BN4#).

(\*) Reference data for comparison

We note that a ratio of approx.  $\frac{2}{3}$  ZrCl<sub>2</sub>(OPr)<sub>2</sub> to  $\frac{1}{3}$  ZrCl<sub>3</sub>(OPr)<sub>1</sub> was found by comparing the proton NMR integrals (see **Fig. S6**). This is likely due to weighing errors of the acetyl chloride.

Assignment	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O-X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–X	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O–X	CH <sub>3</sub> CO–R	CH <sub>3</sub> CO-R
PrOH V – H	$\delta = 10.40$	$\delta = 25.81$	$\delta = 62.61$	-	-
X = II $ZrCl_1(OPr)_3^*$ X = Zr	$\delta = 10.54$	$\delta = 27.42$	$\delta = 70.90$	-	-
$ZrCl_2(OPr)_2$ $X = Zr$	$\delta = 10.51$	$\delta = 26.37$	$\delta = 72.31$	-	-
$\operatorname{ZrCl}_{3}(\operatorname{OPr})_{1}^{*}$ X = Zr	δ=10.55	$\delta = 25.70$	δ = 74.16	-	-
$PrOAc$ $X = CH_3CO$ $R = C_3H_7$	$\delta = 10.20$	$\delta = 20.65$	δ = 21.54	δ = 170.36	δ = 65.28

Tab. S8 <sup>13</sup>C NMR (100.3 MHz, DMSO-d<sub>6</sub>) data of ZrCl<sub>2</sub>(OPr)<sub>2</sub>×CH<sub>3</sub>COOC<sub>3</sub>H<sub>7</sub> (BN4#).

(\*) Reference data for comparison

Retention time (min)	Compound	<i>m</i> / <i>z</i> [MP]	<i>m</i> / <i>z</i> [BP]	<i>m</i> / <i>z</i> [FP]
1.692	Ethanol	46	31	45, 29, 27
1.880	1-Propanol	60	59	42, 41, 39
2.125	Chloroform-d	119	84	86, 49, 47
(4.348)	1-Chlorohexane	120	91	69, 55, 41
4.489	1-Hexanol	102	56	69, 55, 43
6.557	Benzyl chloride	126	91	92, 65, 39
6.816	Benzyl alcohol	108	107	79, 77, 51
7.133	Benzyl ethyl ether	136	91	92, 79, 77
(8.279)	Benzyl propyl ether	150	91	92, 79, 65
11.469	Benzyl hexyl ether	192	91	92, 83,43
13.326	Dibenzyl ether	198	92	91, 79, 65

MP = molecule peak, BP = base peak, FP = fragment peak, m/z = mass/charge ratio, () trace amounts

Phase	ZrO <sub>2</sub> (BN3*)	
Space group	<i>Fm</i> 3 <i>m</i> (SG 225)	P4 <sub>2</sub> /nmc (SG 137)
Crystal system	Cubic	Tetragonal
Lattice parameters (Å)	<i>a</i> = 5.095(1)	a = 3.631(1) c = 5.065(3)
Unit-cell volume (Å <sup>3</sup> )	132.28(3)	66.79(2)
Calc. density (g/cm <sup>3</sup> )	6.188	6.127
Average grain size (nm)	2.5	2.4
Average maximum microstrain ( $\times 10^{-4}$ )	77.61	81.20
$R_{wp}$ [Bragg contributions] (%)	5.45	6.42
Goodness of fit (GoF), $\chi^2$	2.1, 4.38	2.5, 6.30

Tab. S10 Refined structural parameters for  $ZrO_2$  nanoparticles from Rietveld analysis.

Tab. S11 Structural parameters of YSZ from fitting of Y K-edge EXAFS data.

Batch name	Sample	Pair	Distance / Å	N <sub>CN</sub>	$\sigma / 10^{-3} \text{ \AA}^2$
BN7#	6YSZ (as-made)	Y-0	$2.35 \pm 0.02$	8	6.4 ± 1.2
	6YSZ (700 °C)	Ү-О	$2.35\pm0.02$	8	$6.0 \pm 1.0$
		Y-cation	$3.66\pm0.02$	12	$22.0 \pm 5.1$
BN8#	12YSZ (as-made)	Ү-О	$2.32 \pm 0.01$	8	8.8 ± 0.6
		Y-cation	$3.64\pm0.01$	12	$10.0\pm0.9$
	12YSZ (700 °C)	Ү–О	$2.32\pm0.01$	8	$9.1 \pm 1.1$
		Y-cation	$3.63\pm0.01$	12	$11.8 \pm 0.9$

Batch name	Sample	Pair	Distance (Å)	N <sub>CN</sub>	$\sigma(10^{-3}\text{\AA}^2)$	Phase	
BN7#	6YSZ (as-made)	Zr–O	$2.15 \pm 0.01$	7	$10.3 \pm 2.0$	Cubic	
		Zr-cation	$3.56\pm0.02$	12	$13.2 \pm 2.1$		
BN8#	12YSZ (as-made)	Zr–O	$2.15\pm0.01$	7	9.9 ± 1.8	Cubia	
		Zr-cation	$3.56\pm0.02$	12	$12.8 \pm 1.8$	Cubic	
BN7#	6YSZ (700 °C)	Zr–O	$2.23\pm0.01$	7	$2.4 \pm 1.0$	Cubic (26%)	
		Zr-cation	$3.63 \pm 0.02$	12	$18.6 \pm 2.9$		
		Zr–O	$2.09\pm0.01$	4	$2.4 \pm 1.0$	Tetragonal (74%)	
		Zr–O	$2.36 \pm 0.01$	4	$9.8 \pm 1.8$		
		Zr-cation	$3.62\pm0.01$	12	$18.6 \pm 2.9$		
BN8#	12YSZ (700 °C)	Zr–O	$2.22 \pm 0.01$	7	5.4 ± 1.0	Cubic	
		Zr-cation	$3.63\pm0.02$	12	$15.1 \pm 1.7$	(33%)	
		Zr–O	$2.08\pm0.01$	4	$5.4 \pm 1.0$	Tetragonal (67%)	
		Zr–O	$2.35\pm0.01$	4	8.3 ± 1.3		
		Zr-cation	$3.61 \pm 0.02$	12	$15.1 \pm 1.7$		

Tab. S12 Structural parameters of YSZ obtained by fitting of Zr K-edge EXAFS data.



**Fig. S1** Monowave 300 synthesis protocol (BN2#) showing the temperature and power profiles used in the small-scale nanoparticle synthesis of  $ZrO_2$ . The heat up, holding and cooling time regions are denoted as I., II. and III., respectively. The maximum pressure observed in each reaction step (heating 1-4) was 7.3 bar, 6.5 bar, 4.3 bar and 8.4 bar, respectively.



**Fig. S2** Masterwave BTR synthesis protocol (BN3\*) showing the temperature and power profiles used in the large-scale nanoparticle synthesis of ZrO<sub>2</sub>. The heat up, holding and cooling time periods are denoted as I., II. and III., respectively. The maximum pressure observed in each reaction step (heating 1-4) was 9.3 bar, 8.9 bar, 5.3 bar and 10.4 bar, respectively.



**Fig. S3** Monowave 300 synthesis protocol (BN5#) showing the temperature and power profiles used in the small-scale nanoparticle synthesis of ZrO<sub>2</sub>. The heat up, holding and cooling time periods are denoted as I., II. and III., respectively. The maximum pressure observed in each reaction step (heating 1-3) was 4.5 bar, 4.0 bar and 9.5 bar, respectively.



Fig. S4 <sup>13</sup>C NMR spectrum of ZrCl<sub>2</sub>(OPr)<sub>2</sub>×2.3PrOH prepared by metathesis (BN1#).



**Fig. S5** <sup>1</sup>H NMR spectrum of  $ZrCl_2(OPr)_2 \times CH_3COOC_3H_7$  (BN4#) prepared by chlorination of  $Zr(OPr)_4$  using CH<sub>3</sub>COCl. A ratio of about 33%  $ZrCl_3(OPr)_1$  and 67%  $ZrCl_2(OPr)_2$  can be inferred when comparing the integrals between  $\delta = 3.95$ -3.90 ppm.



**Fig. S6** <sup>13</sup>C NMR spectrum of ZrCl<sub>2</sub>(OPr)<sub>2</sub>×CH<sub>3</sub>COOC<sub>3</sub>H<sub>7</sub> (BN4#) prepared by chlorination of Zr(OPr)<sub>4</sub> using CH<sub>3</sub>COCl.



Fig. S7 Electron microscopy of as-prepared  $ZrO_2$  nanoparticles (BN2#). (a) Bright-field TEM image and (b) SAED pattern demonstrating the crystallinity. Diffraction rings are indexed according to JCPDS card no. 01-081-1551 for cubic  $ZrO_2$ .



**Fig. S8** Electron microscopy of as-prepared  $ZrO_2$  nanoparticles (BN5#). (a) Bright-field TEM image and (b) SAED pattern demonstrating the crystallinity. Diffraction rings are indexed according to JCPDS card no. 01-081-1551 for cubic  $ZrO_2$ .



**Fig. S9** XRD data obtained on  $ZrO_2$  nanoparticles (BN3\*). The observed (red) and simulated (black) patterns as well as the difference profile of the fit (blue) are shown. The vertical lines indicate the Bragg reflections expected for cubic (a) and tetragonal (b)  $ZrO_2$ . Significant peak broadening is observed, thereby masking neighbouring Bragg reflections.



**Fig. S10** XRD pattern obtained on as-prepared ZrO<sub>2</sub> particles (BN5#). The reflections are indexed according to JCPDS card no. 01-081-1551 for cubic ZrO<sub>2</sub>.



**Fig. S11** XRD patterns of  $Zr_{1-x}Y_xO_{2-\delta}$  solid solutions with Y contents (*x*) of 0.03 (A), 0.06 (B), 0.12 (C) and 0.18 (D) (BN6#-BN9#) after heating to 700 °C (5 °C/min). As can be seen in the inset, there is a gradually shift in peak position to smaller scattering angles with increasing doping level. This is due to the fact that Y<sup>3+</sup> ions have a larger ionic radius than Zr<sup>4+</sup> ions (0.90 Å *vs.* 0.72 Å). The average crystallite sizes were determined to be 10 nm (A), 8 nm (B), 6 nm (C) and 5 nm (D).



**Fig. S12** Relative amount of Zr species as a function of the Zr content for as-made (left) and 700 °C annealed (right) samples of ZrO<sub>2</sub> (BN2#) and YSZ (BN6#-BN9#).



**Fig. S13** Relative amount of Y species as a function of the Zr content for as-made (left) and 700 °C annealed (right) samples of YSZ (BN6#-BN9#).



**Fig. S14** Zr K-edge XANES spectra of the first derivative obtained on YSZ samples (BN7# and BN8#) before and after heating to 700 °C.



**Fig. S15**  $k^3$ -weighted Y K-edge EXAFS curves (left) and corresponding plots of the Fouriertransform patterns of the uncorrected raw data obtained on YSZ samples (BN7# and BN8#) before and after heating to 700 °C.



**Fig. S16**  $k^3$ -weighted Zr K-edge EXAFS curves obtained on YSZ samples (BN7# and BN8#) before and after heating to 700 °C.



Fig. S17 UV-Vis data of as-made  $ZrO_2$  nanoparticles (BN3\*). The inset shows *Tauc* plots for direct (n = 2) and indirect ( $n = \frac{1}{2}$ ) optical transitions.



Fig. S18 Synchrotron-based GISAXS on polymer-templated mesostructured ZrO<sub>2</sub> (BN2#) thin films. Patterns were collected at  $\beta = 0.2^{\circ}$  and show the evolution of the face-centered-cubic pore network with (111) orientation with thermal treatment. Scattering vector *s* components are given in 1/nm.



Fig. S19 Nanoscale structure of macroporous films prepared by hard templating using dispersions of polystyrene beads and  $ZrO_2$  nanoparticles (BN#2) according to ref [3]. (a) SEM and (b) TEM images showing spherical pores of diameter (50 ± 25) nm with wall thicknesses of 12-22 nm.



**Fig. S20** XRD patterns obtained on polymer-templated mesostructured  $ZrO_2$  (BN2#) powder calcined at 300 °C for 12 hours (A) and 600 °C (B) for 30 min in air. The crystalline domain sizes can be tailored from 2 nm (as-prepared) to about 6 nm. The XRD patterns in (a) and (b) are indexed according to JCPDS reference cards no. 01-081-1551 (cubic  $ZrO_2$ ) and 01-080-0965 (tetragonal  $ZrO_2$ ). It should be noted that only the most instense reflections are indexed.



**Fig. S21** (a) N<sub>2</sub>-adsorption/desorption isotherms for polymer-templated mesostructured  $ZrO_2$  (BN2#) powder heated at 600 °C. (b) Cumulative surface area plot.



Fig. S22 N<sub>2</sub>-adsorption/desorption isotherms for as-made ZrO<sub>2</sub> nanoparticles (BN2#).



Fig. S23 Morphology of electrospun  $ZrO_2$  nanofibers made from polyacrylonitrile and preformed nanocrystalline building blocks (BN2#) after thermal treatment at 900 °C. (a) SEM and (b,c) TEM images at different magnifications showing a porous structure.



**Fig. S24** Morphology of electrospun  $ZrO_2$  nanofibers made from poly(ethylene oxide) and preformed nanocrystalline building blocks (BN2#). SEM images collected (a) before and (b) after heating at 550 °C (5 °C/min) by 3 hours in air.



Fig. S25 N<sub>2</sub>-adsorption/desorption isotherms obtained on the ZrO<sub>2</sub> nanofibers shown in Figure S24b.

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