

Scaling-Up a Confined Jet Reactor for the Continuous Hydrothermal Manufacture of Nanomaterials

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Supplementary text S1.

Extra information on the design of the pilot plant:

Pulsation dampeners:

The pulsation dampeners (Pulseguard, uk) consisted of a rubber bladder (Viton or EPDM elastomers) set within a high pressure carbon steel vessel (volume 0.3 L). The vessel was pressurised to 196 Bar with nitrogen (80% of the normal operating pressure of 240 Bar). During an outlet stroke the bladder expanded to accumulate a small volume of liquid, which was released again during the subsequent intake stroke of the pump. On each pump, the pressure was continuously measured immediately downstream of the pulsation dampener using fast-response pressure transducers (A10 series, Wika); it was found that pulsation

dampeners were extremely effective in reducing pressure/flow fluctuations to +/- 2% (5 Bar at operating pressure of 240 Bar).

Cooler construction and performance:

From the reactor, the nanoparticles mixture subsequently flowed upwards (3/4" OD, 0.103" wall thickness, length 0.5 m), where it turned 180 degrees downwards before entering a cooled pipe (1/4" OD, 0.049" wall thickness, length 1.5 m), then turned 180 degrees upwards again through an identical section of cooled pipe. Around these cooled pipes, cooling water flowed co-currently (flowrate 100 L min⁻¹, inlet T = 15 °C).

Heater construction and performance:

The four heaters on the pilot plant were arranged in parallel. Each heater consisted of a coil of tubing (Inconel alloy 625, 1/2" outside diameter, 0.065" wall thickness, 3 m length uncoiled) cast into a bronze block. Cast into the bronze block, through the centre of the coil, were several heating rods providing a thermal input of up to 6 kW per heater, yielding a total thermal input of 24 kW from the four units. The supercritical water exiting each heater, at a temperature of up to 500 °C, was recombined and subsequently flowed through insulated pipework (1/4" OD, 0.049" wall thickness) to the inlet of the confined jet reactor. The temperature of the supercritical water was measured before it entered the reactor, by a thermocouple (J-type, 1/8" OD, stainless steel sheath) protruding into the flow. This measurement was used as the input to a PID algorithm controlling a solid state relay (Din-A-Mite C, Watlow) which in turn regulated the power supplied to the heaters.

Safety Precautions:

Pressure safety:

In accordance with the European Union (EU) Pressure Equipment Directive, the equipment was classified as an 'assembly' *i.e.* designed and constructed only for use within UCL; nevertheless, the spirit of the PED was followed, as if it were for sale on the market. The pilot plant also fell under the scope of the United Kingdom Pressure Systems Safety Regulations, thus it was subject to a Written Scheme of Examination and annual inspection by a competent authority (Strata Technology Ltd.). The EU Low Voltage and Machinery Directives were also followed. Owing to the moderately high pressure and temperature used in the continuous hydrothermal process, compared with many industrial processes, a high degree of care was taken over the design, construction and operation of the pilot plant, which had a relatively high stored volume (~ 1 L) compared with the laboratory scale process (only a few mL). The outlet of each pump was fitted with a safety relief valve (SRV) set at 276 bar (Parker HPRV type rated category IV under the PED) to prevent the pulsation dampeners and pipework from overpressuring in the case of a partial or complete blockage *e.g.* of the back-pressure regulator. Two check valves were installed downstream of these safety valves, to prevent backflow of the hot fluid in the reactor through the pumps in the event that a pump suddenly stopped (*e.g.* due to an electrical or mechanical failure). Procedures were put in place to ensure these non-return valves provided a tight shut-off. In fact, the pumps also contained 4 internal check-valves (2 located on the outlet and 2 on the inlet), which must provide tight shutoff for the pump to work properly. Thus the Swagelok check valves simply provided further assurance that backflow would not occur in the event of a pump stopping.

An additional SRV, set at 300 Bar, was located after the Swagelok non-return valves, on the cold water feed to the electrical heaters. This SRV provided a route to accommodate thermal expansion of the water inside the heaters (potentially at a temperature higher than the

contents) in the event that flow ceases due to a complete blockage upstream. The outlet from this SRV was routed into a tank of water, in case the SRV failed to re-seat after lifting resulting in discharge of the heater contents.

Safety cut outs:

A shutdown system operated independently of the Labview control system. Each of the 4 heaters was fitted with a thermocouple to measure the temperature of the metal. In the event that any of the heaters went above 500 °C, power was automatically cut to all the heaters whilst the pumps continued to run. A thermocouple was also located on the outlet of the cooler; in the event this rose above 100 °C (*e.g.* due to steam breakthrough resulting from sudden loss of cooling water or system pressure) the power was cut to all the pumps and heaters.

Nanoparticle exposure and waste disposal considerations:

The continuous hydrothermal process produced a slurry of nanoparticles in water, as well as unreacted metal salts (typically small, due to the high yield) and counter-ions (*e.g.* potassium and nitrate). The nanoparticles tended to agglomerate and settle out readily, leaving a clear supernatant. Sodium chloride was added to 'salt out' the stable suspension of nanoparticles if agglomeration did not occur.

The toxicity of nanoparticles, irrespective of their composition, both to humans (and flora and fauna generally) remains a topic of great debate. Guidelines for their safe handling have been issued by the UK Health and Safety Executive. Two layers of disposable gloves (latex or nitrile) were worn when handling the slurries. Unwanted slurry was disposed of as hazardous waste and the supernatant was disposed of as aqueous waste.

Supplementary Table ST1: Summary of the synthesis conditions used for the production of ZnO on the laboratory scale CHFS process:

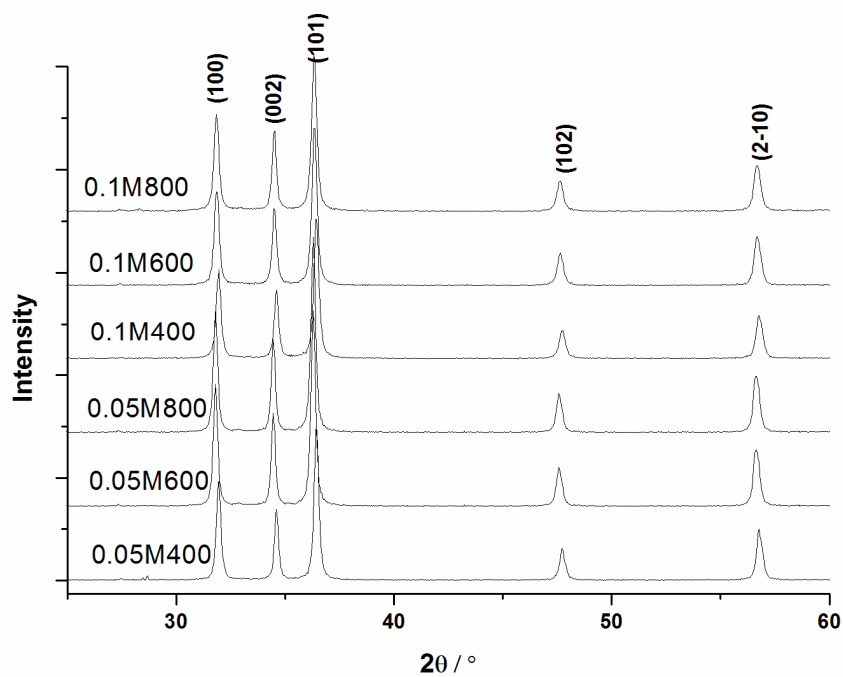
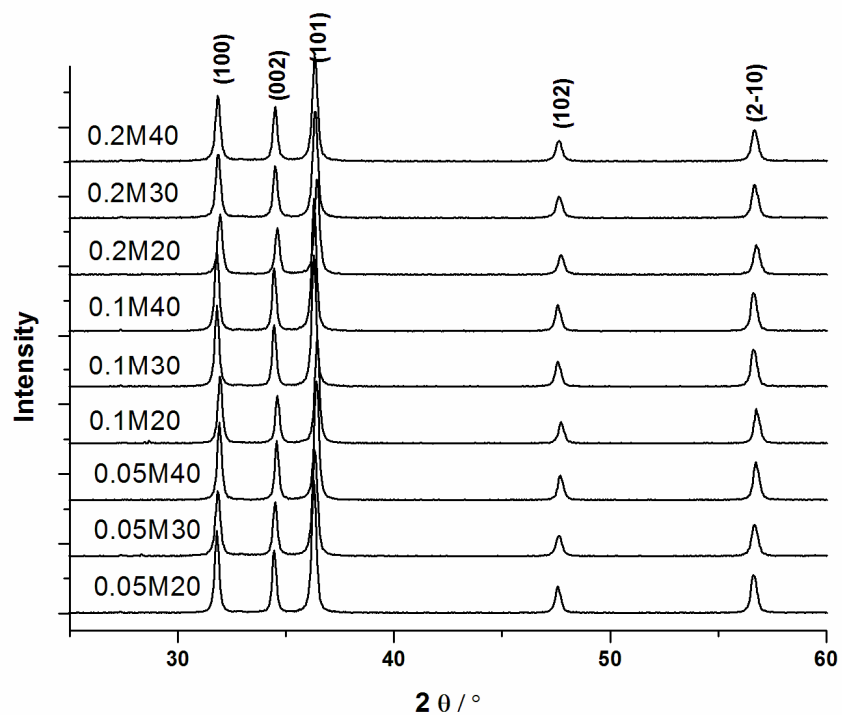
ID	[Zn] (M)	Q _{sw}	Q _{p(zn)}	Q _p (KOH)	Phase	Cs (nm)	BET (m ² g ⁻¹)	ESD (nm)	TE M (nm)	TEM SD (nm)	AR	Eg (eV)	Yield (%)
0.05M40	0.05	20	10	10	ZnO	32.03	10.8	99.1	68.8	14.2	1.01	3.27	92
0.1M40	0.1	20	10	10	ZnO	37.78	14.4	74.3	64.6	11.9	1.06	3.26	88
0.2M40	0.2	20	10	10	ZnO	33.66	14.2	75.4	60.1	9.7	1.2	3.26	91
0.05M30	0.05	15	7.5	7.5	ZnO	37.82	14.6	73.3	67.1	13.5	1.04	3.26	90
0.1M30	0.1	15	7.5	7.5	ZnO	34.11	12.1	88.5	62.1	15.8	1.08	3.26	83
0.2M30	0.2	15	7.5	7.5	ZnO	33.22	12.1	88.5	59.3	14.8	1.1	3.26	96
0.05M20	0.05	10	5	5	ZnO	34.01	12.1	88.5	63.9	10.3	1.16	3.27	94
0.1M20	0.1	10	5	5	ZnO	33.64	12.5	85.6	69.2	11.7	1.18	3.27	92
0.2M20	0.2	10	5	5	ZnO	35.52	12.0	89.2	64.6	9.3	1.08	3.27	95

NOTES: Phase= the crystallographic phase of the product determined by XRD, Cs is the crystallite size determined from application of the scheerer equation to the most intense reflection, ESD = the equivalent sphere diameter determined from $6000/(S_{BET} \cdot \rho)$, where ESD (nm) is the equivalent sphere diameter, S_{BET} (m² g⁻¹) is the BET surface area and ρ (g cm⁻³) is the density of the material, AR is the particle aspect ratio, Eg = the direct bandgap of the material determined using the KM method.

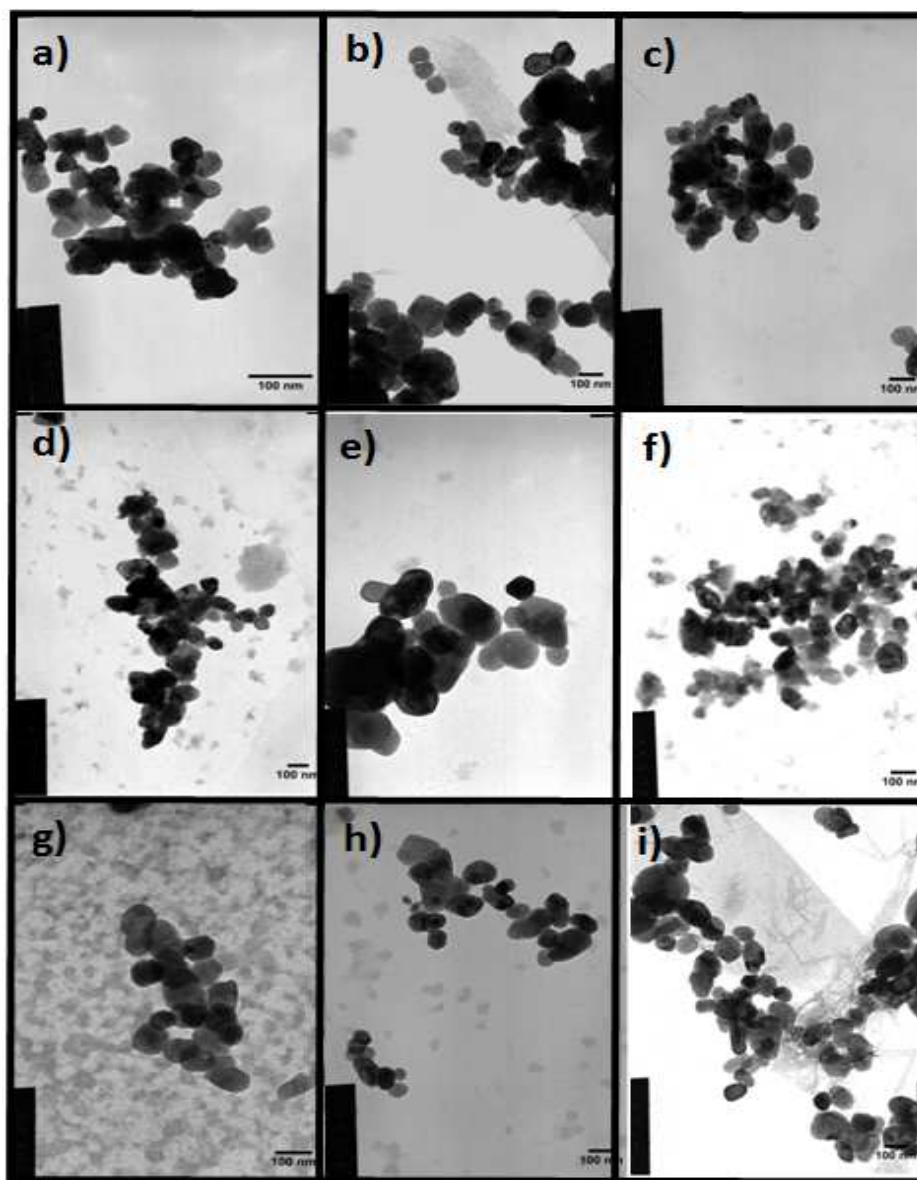
Supplementary Table ST2: Summary of the synthesis conditions used for the production of ZnO on the pilot scale CHFS process:

Sample i.d.	[Zn] (M)	Flowrates / mL min ⁻¹				Phase (XRD)	Cs(nm)	BET		TEM			E _g (eV)	Yield (%)
		Q _{sw}	Q _{Zn}	Q _K	Q _d			(m ² g ⁻¹)	ESD (nm)	Avg. (nm)	S.D (nm)	AR		
0.05M800	0.05	400	200	200	-	ZnO	33.61	16.30	65.6	59.51	18.04	1.13	3.26	92
0.05M600	0.05	300	150	150	-	ZnO	33.47	15.00	71.3	58.57	16.30	1.15	3.26	88
0.05M400	0.05	200	100	100	-	ZnO	34.17	15.79	67.7	59.65	16.76	1.11	3.26	91
0.10M800	0.1	400	200	200	-	ZnO	30.45	18.69	57.2	51.84	13.84	1.19	3.27	96
0.10M600	0.1	300	150	150	-	ZnO	30.85	17.55	60.9	55.93	15.79	1.20	3.27	92
0.10M400	0.1	200	100	100	-	ZnO	29.61	20.84	51.3	48.79	12.32	1.27	3.26	90
0.20M700	0.2	350	35.0	35.0	280	ZnO	-	17.16	62.33	81.88	37.84	1.32	3.25	93
0.30M700	0.3	350	52.5	52.5	245	ZnO	-	14.13	75.70	91.10	45.17	1.87	3.26	87
0.40M700	0.4	350	70.0	70.0	210	ZnO	-	12.47	85.76	94.52	45.17	1.90	3.26	94
0.50M700	0.5	350	87.5	87.5	175	ZnO	-	13.03	82.10	103.72	40.10	1.82	3.24	89
0.60M700	0.6	350	105.0	105.0	140	ZnO	-	12.58	85.03	112.53	48.27	1.90	3.26	93
0.70M700	0.7	350	122.5	122.5	105	ZnO	-	12.00	89.14	114.04	55.63	2.10	3.26	89
0.80M700	0.8	350	140.0	140.0	70	ZnO	-	11.68	91.62	112.37	44.29	2.10	3.26	93
0.90M700	0.9	350	157.5	157.5	35	ZnO	-	11.58	92.41	121.96	47.49	2.04	3.26	90

NOTES: Phase= the crystallographic phase of the product determined by XRD, Cs is the crystallite size determined from application of the scheerer equation to the most intense reflection, ESD = the equivalent sphere diameter determined from $6000/(S_{BET} \cdot \rho)$, where ESD (nm) is the equivalent sphere diameter, S_{BET} (m² g⁻¹) is the BET surface area and ρ (g cm⁻³) is the density of the material, AR is the particle aspect ratio, E_g = the direct bandgap of the material determined using the KM method.

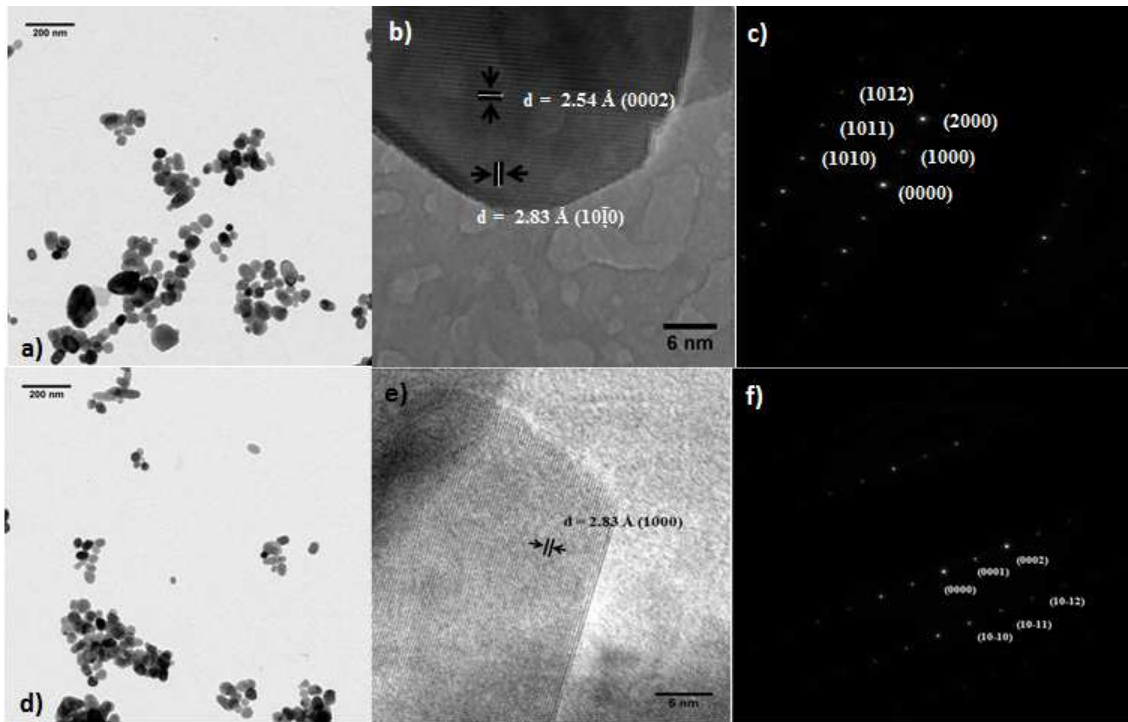


Supplementary Figure S1: Top) XRD patterns of ZnO nanoparticles synthesis using the laboratory scale CHFS process (Experimental runs 0.05M20 to 0.2M40) **bottom)** XRD patterns of ZnO nanoparticles produced at different volumetric scale up ratios (Experimental runs 0.05400 to 0.1M800).

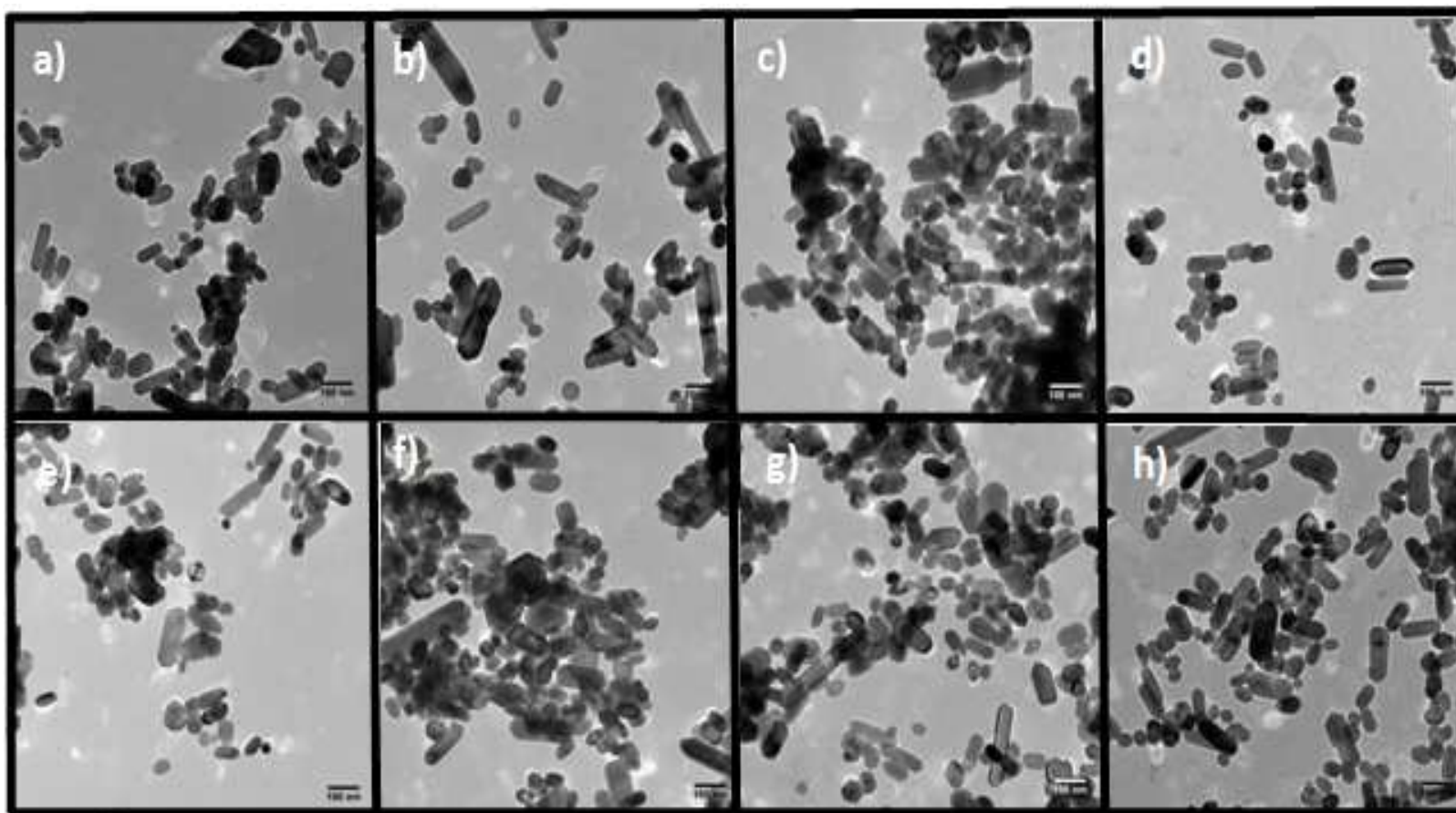


Supplementary Figure S2

TEM images representative of ZnO nanoparticles produced on the laboratory scale CHFS process through a variation of flow rate and precursor concentration **a)** 0.05M40 **b)** 0.1M40 **c)** 0.2M40 **d)** 0.05M30 **e)** 0.1M30 **f)** 0.02M30 **g)** 0.05M20 **h)** 0.1M20 **i)** 0.2M20

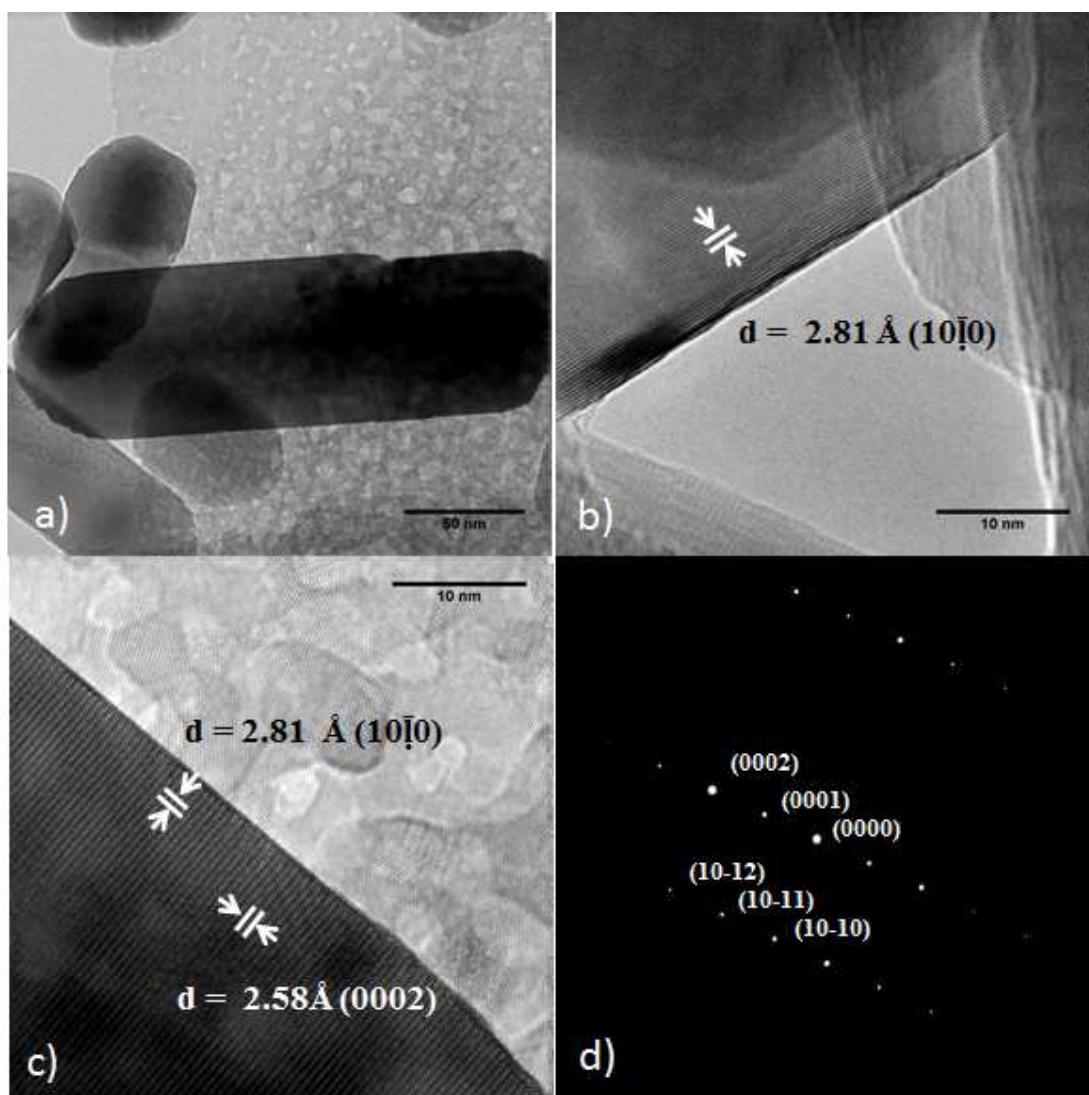


Supplementary figure S3: Compilation of HREM images of the ZnO sample produced in runs 0.1M40 and 0.1M800 **a)** and **d)** Low magnification image representative of the particles 0.1M40 and 0.1M800 **b)** and **e)** HREM images of ZnO nanoparticles produced in runs 0.1M40 and 0.1M800, respectively. **c)** and **f)** Electron diffraction pattern of the single crystallite presented in image [b and e] the spot patterns could be indexed to the (0001) and (10-10) planes confirming the growth direction presented in images **b)** and **e)**.



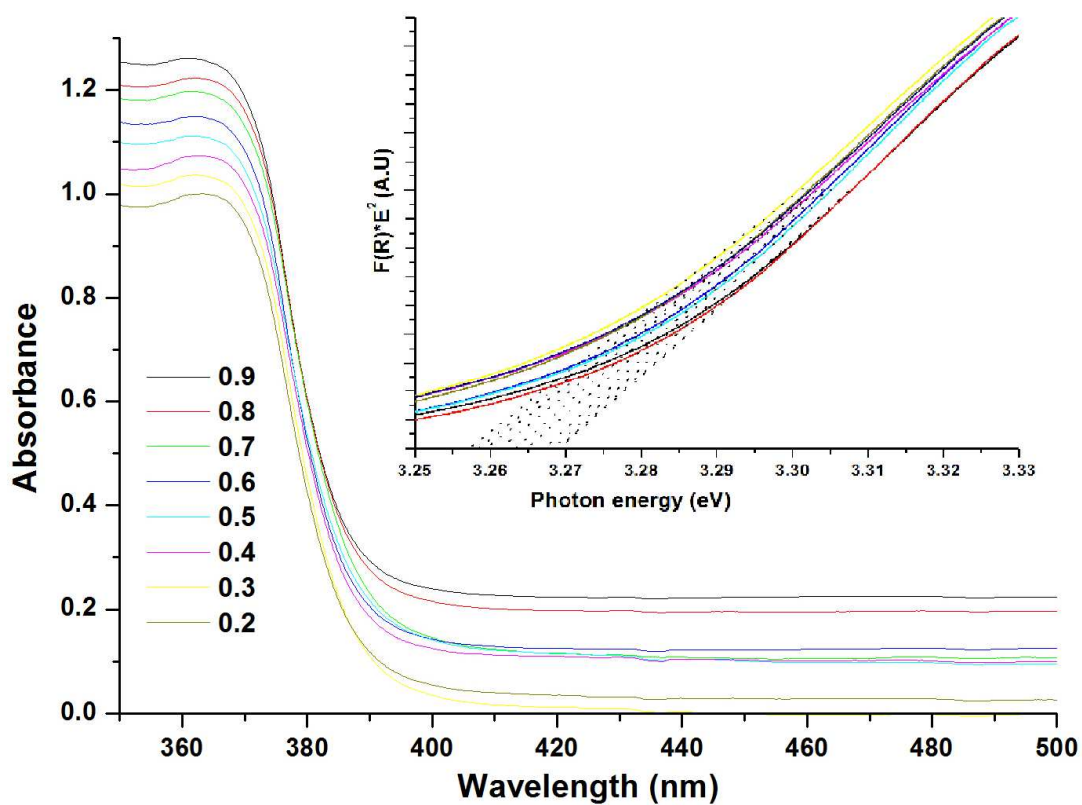
Supplemen

tary Figure S4: TEM images of ZnO nanoparticles produced through concentration based scale-up of the CHFS process. a) 0.2M700 b) 0.3M700 c) 0.4M700 d) 0.5M700 e) 0.6M700 f) 0.7M700 g) 0.8M700 h) 0.9M700



Supplementary Figure S5

Compilation of HREM images of the ZnO sample produced in run 0.9M700 **a)** Low magnification image of a typical rod like particle **b)** HREM image of a hexagonal particle **c)** HREM image of the facets of the rod like particle visualised along a zone axis showing intersecting lattice planes **d)** Indexed electron diffraction pattern of the single crystallite presented in image [a].



Supplementary Figure S6: Normalised UV-VIS spectra of ZnO nanoparticles produced as a function of precursor concentration. Figure inset, shows the KM function of the data (Both figure and inset have a common key)