SUPPORT INFORMATION

Impacts of the reactants on the synthesis of ZnO particles in glycerol-based solvent

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SI-1. Tables

Table S1: Rietveld refinement results*. Phase/Space group, lattice parameters (a, b, c), lattice volume (V), ZnO phase average crystallite size (D_{ZnO}) calculated by Highscore**, TEM images average particle size (D_{TEM}), microstrain percentage (ε_{ZnO}). Rietveld converge R values (R_{exp}, R_p, R_{wp}, and X^2) for different mole ratios of Zn^{2+}:HO^-.

Base / Temperature	Phase weight % (Space group)	a, b, c (Å)	V (Å³)	D_{ZnO} (nm)	D_{TEM} (nm)	ε_{ZnO} %	R values
1:0.5 25°C	ZnO hexagonal (P63mc) 15.4%	a=b=3.2518(4) c=5.2116(9)	47.7(5)	28.9(5)		0.009(3)	R_{exp}=8.07
	$Zn_5(OH)_8(NO_3)xH_2O$ monoclinic (C12/m1) 84.6%	a=19.509(4) b=6.253(11) c=5.5237(7)	672.9(7)	36.4(3)	38(10)	0.210(20)	R_p=12.74 R_{wp}=16.13 X^2 = 1.99
1:0.5 70°C	$Zn_5(OH)_8(NO_3)xH_2O$ orthorhombic (Imm2) 13.0%	a=6.73(2) b=21.82(3) c=3.173(9)	466.2(7)	34(2)		1.17(8)	R_{exp}=8.16 R_p=9.19
	ZnO hexagonal (P63mc) 46.3%	a=b=3.2552(6) c=5.2108(9)	47.82(5)	16(1)	37(5)	~0	R_{wp}=12.00
	$Zn_5(OH)_{10}xH_2O$ monoclinic (C12/c1) 40.7%	a=15.388(3) b=6.22(2) c=10.992(9)	1032.1(5)	4(1)		~0	X^2 = 1.47
1:1 25°C	ZnO hexagonal (P63mc) 88.3%	a=b=3.2559(9) c=5.2144(3)	48.87(7)	83(5)		0.022(3)	R_{exp}=5.36
	$Zn(NO_3)_2xH_2O$ monoclinic (P121/c1) 17.2%	a=19.512(4) b=6.258(15) c=5.516(13)	672.5(7)	41(3)	124*(60)	0.184(4)	R_p=7.14 R_{wp}=9.39 X^2 = 1.75
1:1 70°C	ZnO hexagonal (P63mc) 100%	a=b=3.2533(3) c=5.2122(6)	47.77(3)	16(1)	12(3)	0.304(9)	R_{exp}=5.47 R_p=6.78 R_{wp}=9.09 X^2 = 1.66
1:1.5 25°C	ZnO hexagonal (P63mc) 100%	a=b=3.2556(6) c=5.2136(3)	47.85(2)	27.9(4)	31(15)	0.132(3)	R_{exp}=5.36 R_p=8.33 R_{wp}=12.49 X^2 = 2.21
1:1.5 70°C	ZnO hexagonal (P63mc) 100%	a=b=3.2542(3) c=5.2131(5)	47.81(6)	21.6(5)	12(4)	0.252(4)	R_{exp}=5.22 Rp=6.56 R_{wp}=8.56 X^2 = 1.64

*The deviations were calculated by the Rietveld method and are presented between ( ), i.e. 2.78 ± 0.04 nm is 2.78(4) nm.** Highscore software calculates the average crystallite size and microstrain by the Williamson-Hall Method.

Table S2: Rietveld refinement results*. Phase/Space group, lattice parameters (a, b, c), lattice volume (V), ZnO phase average crystallite size (D_{ZnO}) calculated by Highscore**, TEM images average particle size (D_{TEM}), microstrain percentage (ε_{ZnO}). Rietveld convergence R values (R_{exp}, R_p, R_{wp}, and X^2) for different urea substitutes and glycerol-NH_3 bubbling method.

Solvents	Phase weight % (Space group)	a, b, c (Å)	V (Å³)	D_{ZnO} (nm)	D_{TEM} (nm)	ε_{ZnO} %	R values
TU - Tiourea	ZnS cubic (F4-3m) 100%	a=b=c= 5.358(4)	153.86(5)	3.7(3)	-	0.771(8)	R_{exp} =5.74 R_p =6.01 R_{wp} =7.73 X^2 = 1.54
DMU - Dimethylurea	ZnO hexagonal (P63mc) 88.3%	a=b=3.2578(4) c=5.2148(7)	47.93(7)	16.6(5)	24(8)	0.353(4)	R_{exp} =5.19
	$Zn_5(OH)_8xH_2O$ monoclinic (C12/c1) 11.7%	a=14.1044(4) b=6.33(4) c=10.85(6)	951.27(4)	4.4(8)		0.742(7)	R_p =6.09 R_{wp} =7.73 X^2 = 1.49
TMU - Tetramethylurea	ZnO hexagonal (P63mc) 51.5%	a=b=3.2557(5) c=5.2104(6)	47.83(9)	20.6(3)	20(5)	0.353(9)	R_{exp} =5.11
	$Zn_5(OH)_8xH_2O$ (C12/c1) 48.5%	a=13.967(20) b=6.22(3) c=11.214(18)	961.5(8)	9.7(4)		0.742(3)	R_p =5.64 R_{wp} =7.19 X^2 = 1.40
Glycerol:Amonia	ZnO hexagonal (P63mc) 86.3%	a=b=3.2510(5) c=5.2103(2)	47.7(2)	47(5)	~50 nm (rod thickness)	0.402(3)	R_{exp}=3.42 R_p=7.89 R_{wp}=11.45 X^2 = 3.34
	$Zn5(OH)_8(NO_3)xH_2O$ monoclinic (C12/m1) 13.4%	a=b=3.2528(12) c=5.2215(23)	670.6(5)	17(3)		0.402(3)	

*The deviations were calculated by the Rietveld method and are presented between ( ), i.e. 2.78 ± 0.04 nm is 2.78(4) nm.** Highscore software calculates the average crystallite size and microstrain by the Williamson-Hall Method.

Table S3: Rietveld refinement results*. Phase/Space group, lattice parameters (a, b, c), lattice volume (V), ZnO phase average crystallite size (D_{ZnO})**, microstrain percentage (ε_{ZnO}). Rietveld convergence R values (R_{exp}, R_p, R_{wp}, and X^2) for different mole ratios of G:I variations.

Glycerol: Isopropanol (G:I)	Phase weight % (Space group)	a, b, c (Å)	V (Å³)	D_{ZnO} (nm)	ε_{ZnO} %	R values
1:1	ZnO hexagonal (P63mc) 100%	a=b=3.2534(4) c=5.2145(7)	47.78(5)	25.5(8)	0.3420(11)	R_{exp} =8.69 R_p =12.03 R_{wp} =16.55 X^2 = 1.91
2:1	ZnO hexagonal (P63mc) 100%	a=b=3.2534(4) c=5.2145(7)	47.74(3)	33.25(10)	0.2190(6)	R_{exp} =8.66 R_p =11.23 R_{wp} =15.90 X^2 = 1.84
10:1	ZnO hexagonal (P63mc) 100%	a=b=3.2534(4) c=5.2145(7)	47.57(7)	37.11(5)	0.065(4)	R_{exp} =3.55 R_p =4.29 R_{wp} =5.94 X^2 = 1,68

*The deviations were calculated by the Rietveld method and are presented between ( ), i.e. 2.78 ± 0.04 nm is 2.78(4) nm.** Highscore software calculates the average crystallite size and microstrain by the Williamson-Hall Method.

Note that Highscore software calculates the average crystallite size from the average minimum diffraction planes from the samples, which generates the broadening of the diffraction peaks profile. Sometimes, for nanoparticles, we can compare TEM images with the calculated average crystallite size by XRD. In this case, SEM images tend to show larger agglomerates which can be difficult to compare.
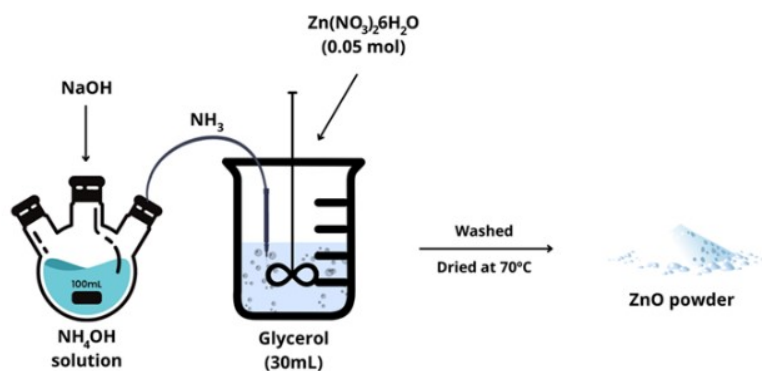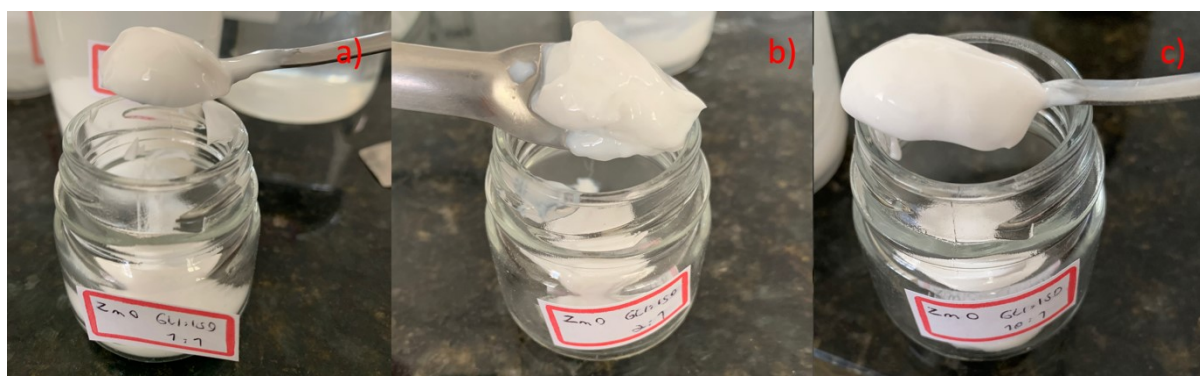
SI-2 Schemes and Pictures
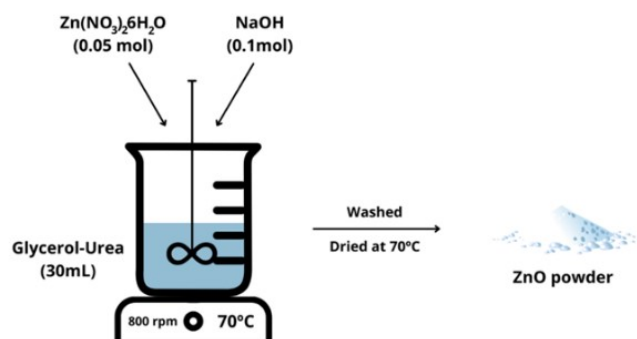
Fig. S1. General procedure to synthesize ZnO nanoparticles in glycerol-urea:

Fig.S2. Images of the gels in the preparations at varying glycerol-isopropanol mole ratios: (a) 1:1, (b) 2:1, (3) 10:1:


Fig. S3. Synthesis of the ZnO needles by bubbling ammoni

SI 3 – Histograms

Histograms were obtained by measuring all TEM images for the samples on ImageJ Software. The average TEM size was obtained by simple statistics and maximum and minimum values were also displayed below.

Fig.S4. Average size histograms of ZnO TEM images for different mole ratios of Zn^{2+}:HO^-. Preparations in the GU solvent.
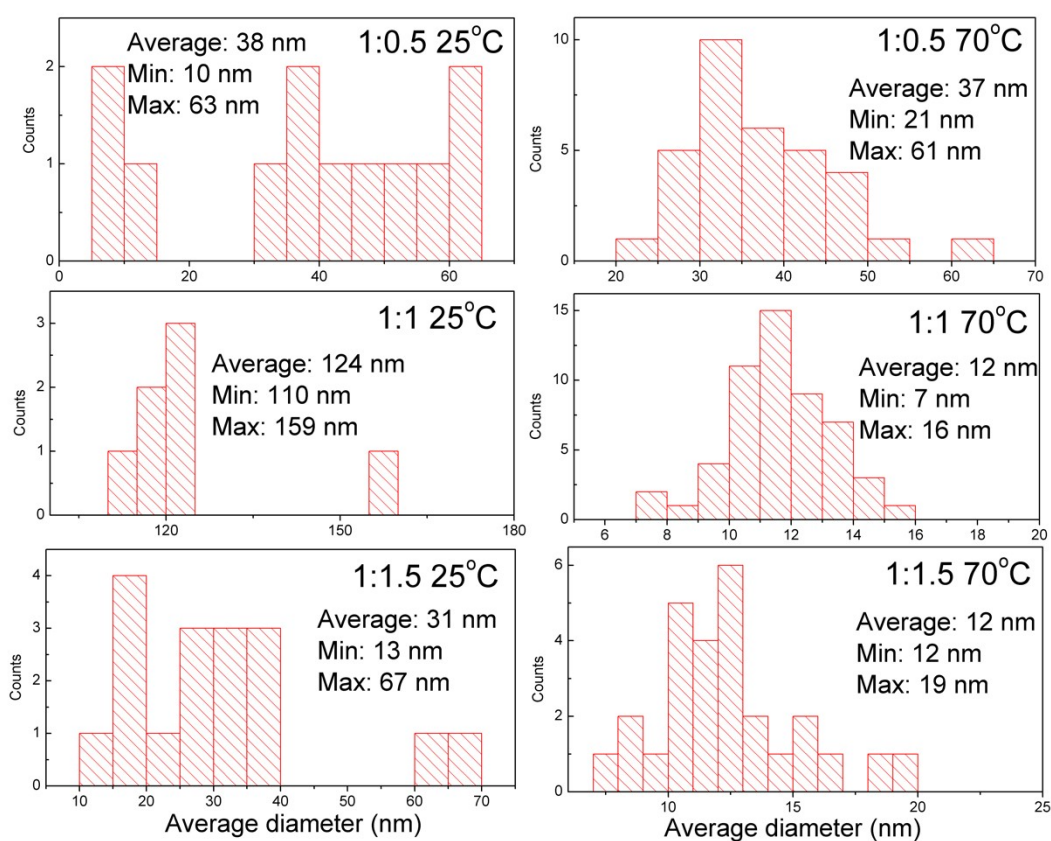
SI-4 UV-Vis characterization

UV-Vis spectra were measured in an Shimadzu 1900 equipment by using 2 mg of ZnO nanoparticles suspended in 10 mL of isopropanol prepared in a ultrasonic bath for 10 min. The spectra were acquired with 3 mL of each sample placed in quartz cuvettes of 10.0 mm optical path.

Fig.S5. UV-vis spectra of the ZnO particles obtained in (a) different Zn^{2+}:HO^- mole ratios and temperatures, and (b) at varying glycerol:isopropanol mole proportion.
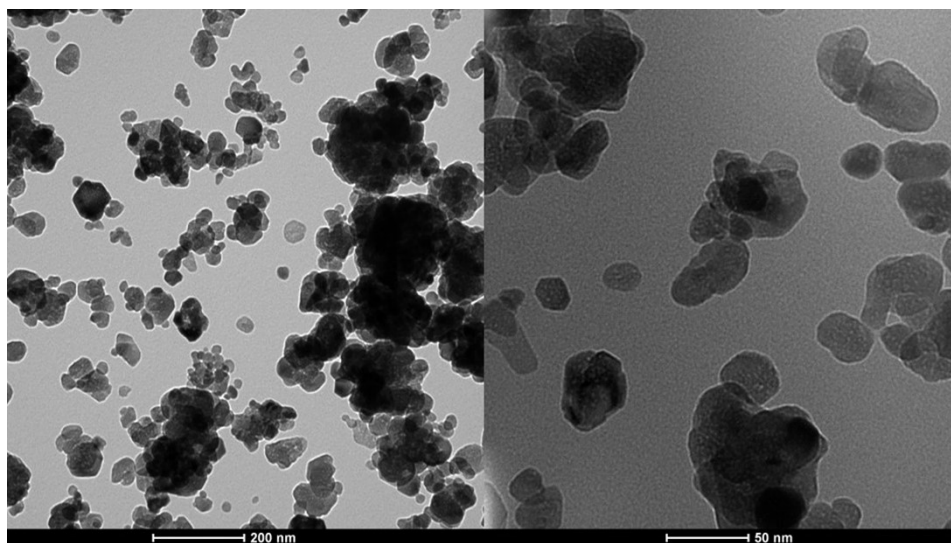
a)

b)
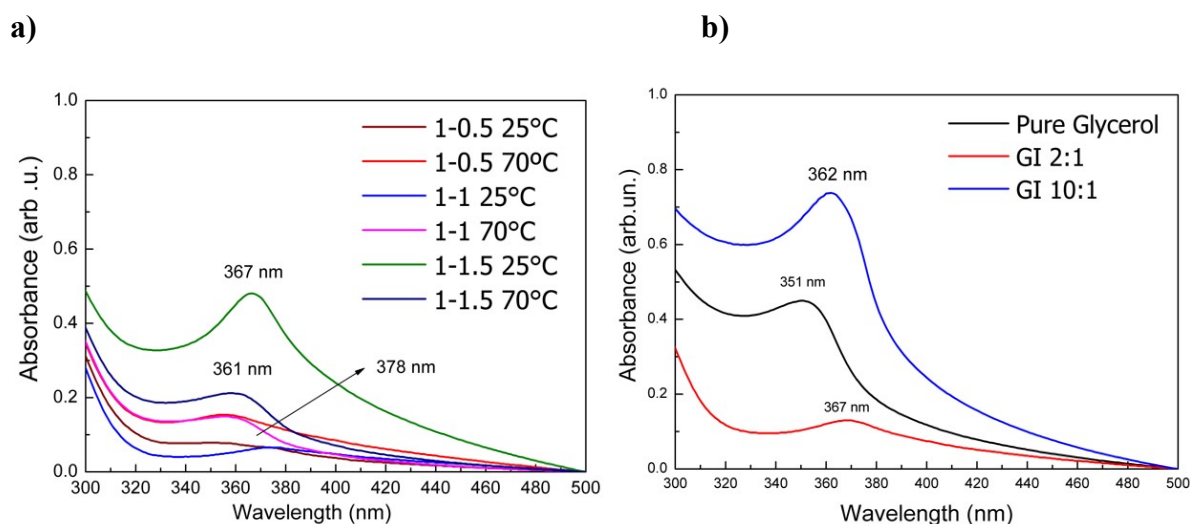
SI 5 – SEM and TEM images

Fig.S6. SEM images of ZnO particles synthesized in the pure glycerol solvent
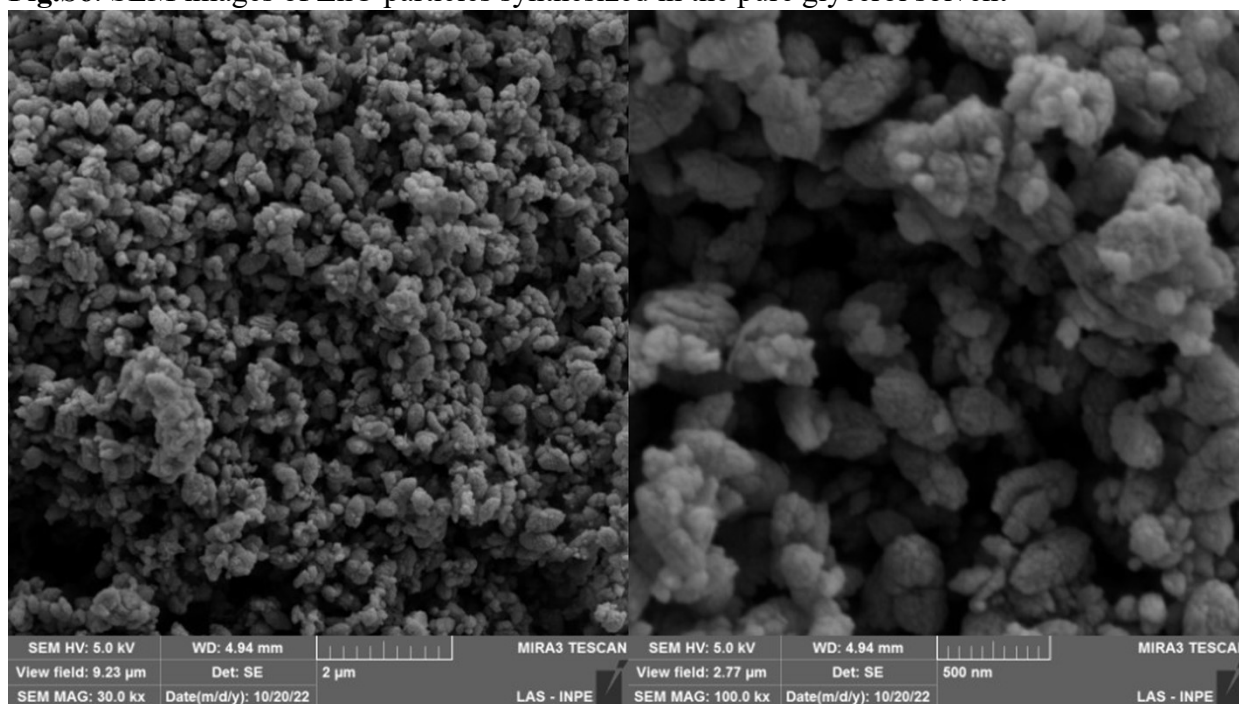
Fig.S7. TEM images of ZnO particles synthesized in the G:I 10:1 mole ratio.

This proportion of solvent represents a synthesis limit, above this condition the particles begin to become larger and more dispersed.