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Facile Synthesis of Inorganic Nanoparticles by Precipitation Method in Molten ε-caprolactam Solvent

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Table 1 Dipole moment and dielectric constant of some polar solvents and molten CL, Data Extracted from Ref [1].

Solvent [a]	Boiling point (°C)	Polarity Dipole moment μ (Debye)	Dielectric constant ε
Water	100	1.85	80.3
ethanol	78	1.68	25
ethylene glycol	197	2.28	37
N,N-Dimethylformamide	153	3.86	32.7
Molten CL (95 ^{0}C)	270	2.1	14

[a] The parameters of the solvents correspond to room temperature, unless noted otherwise.

[1] (a) M.Z.C. Hu, E.A. Payzant, C.H. Byers, *J. Colloid Interface Sci.*, 2000, **222**, 20-36.

(b) O. Madelung, Numerical Data and Functional Relationships in Science and Technology, New Series IV/6; Springer-Verlag: New York, 1996.

(c) X.M. Fang, R. Hutcheon, D.A. Scola, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 1379-1390.

(d) R. Hutcheon, J. Mouris, X.M. Fang and D.A. Scola, Measurements of the high-temperature microwave (400-3000 mhz) complex dielectric constants of monomers ε-caprolactam and ε-caprolactone, Second World Congress on Microwave and Radio Frequency Procesing, Ceramic Transactions Vol. III , 109 (2000).

Table 2 Solubility of salts in molten CL at 100 °C [2]

Salts	Solubility (g/100g CL)
$ZnCl_2$	27.5
$CuSO_4 \cdot 5H_2O$	5.0
$MgCl_2 \cdot 5H_2O$	21.0
NaOH	4.5
NaCl	<0.1
Others ($AgNO_3$, $CdCl_2$, $Nd(NO_3)_3 \cdot 6H_2O$)	>50

[2] The method used for determining the solubility of salts in molten CL was the following: An excess of an inorganic salt was added to 100 g of molten CL and the mixture was magnetically stirred at 100°C for 1 h till the equilibrium was reached. The system stood still for another 1 h for complete separation. Next, about 1 g of the supernatant of the CL solution of the inorganic salt was removed from the flask and was diluted to a ppm level with deionized water. The metal element concentration of the diluted solution was determined by atomic absorption spectroscopy (Perkin Elmer AA800). Finally, the solubility of the salt in molten CL was back-calculated.

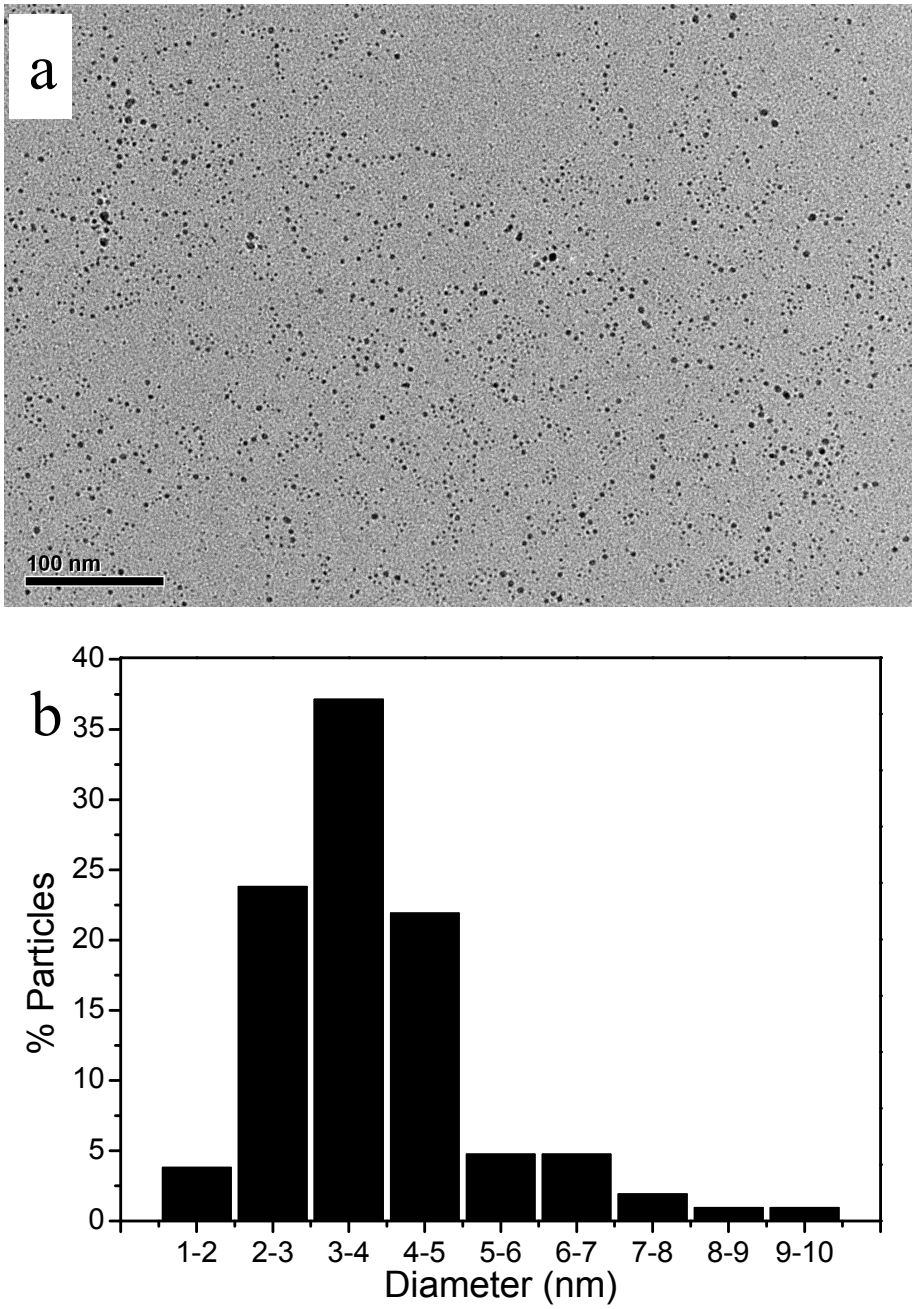

Figure S1. (a) TEM micrograph of Ag_2O NPs (b) Particle size distribution obtained by a statistical analysis of the TEM image.

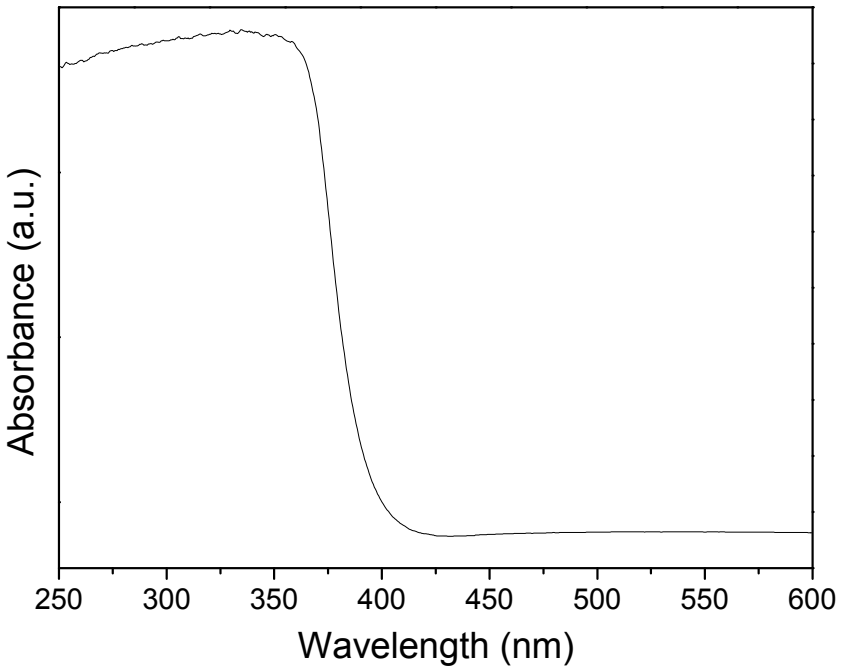

Figure S2. UV-vis absorption spectrum of ZnO NPs.

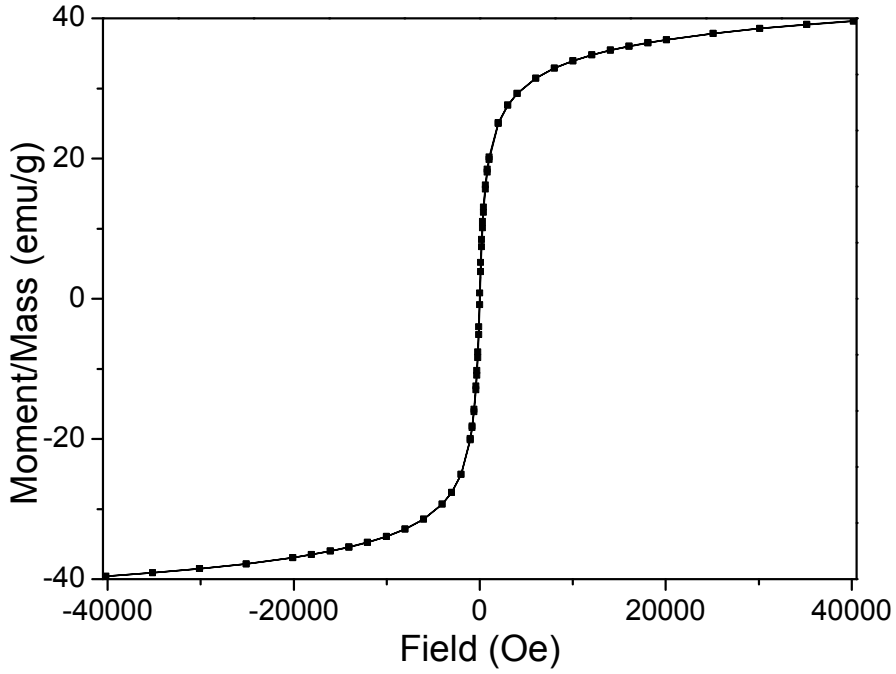

Figure S3. Field-dependent magnetization curve of Fe_3O_4 NPs at room temperature.

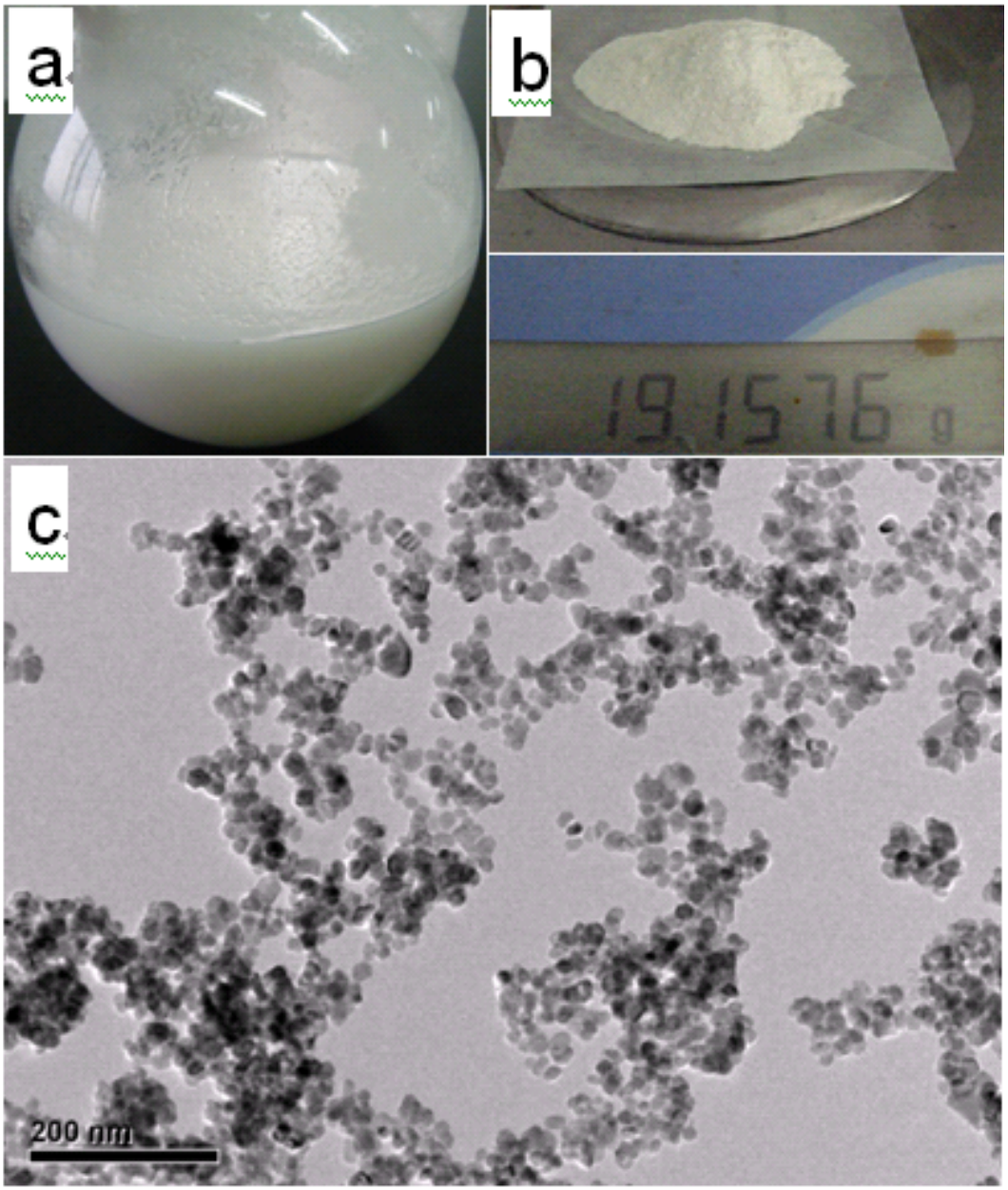

Figure S4. Photographs of a) the as-prepared ZnO/CL suspension obtained by a single run from 1000 g of molten ε-caprolactam using a 2000 mL flask, b) ~19 g of ZnO powder collected by washing and drying the as-prepared ZnO/CL suspension; c) the TEM image of the resulting ZnO NPs.

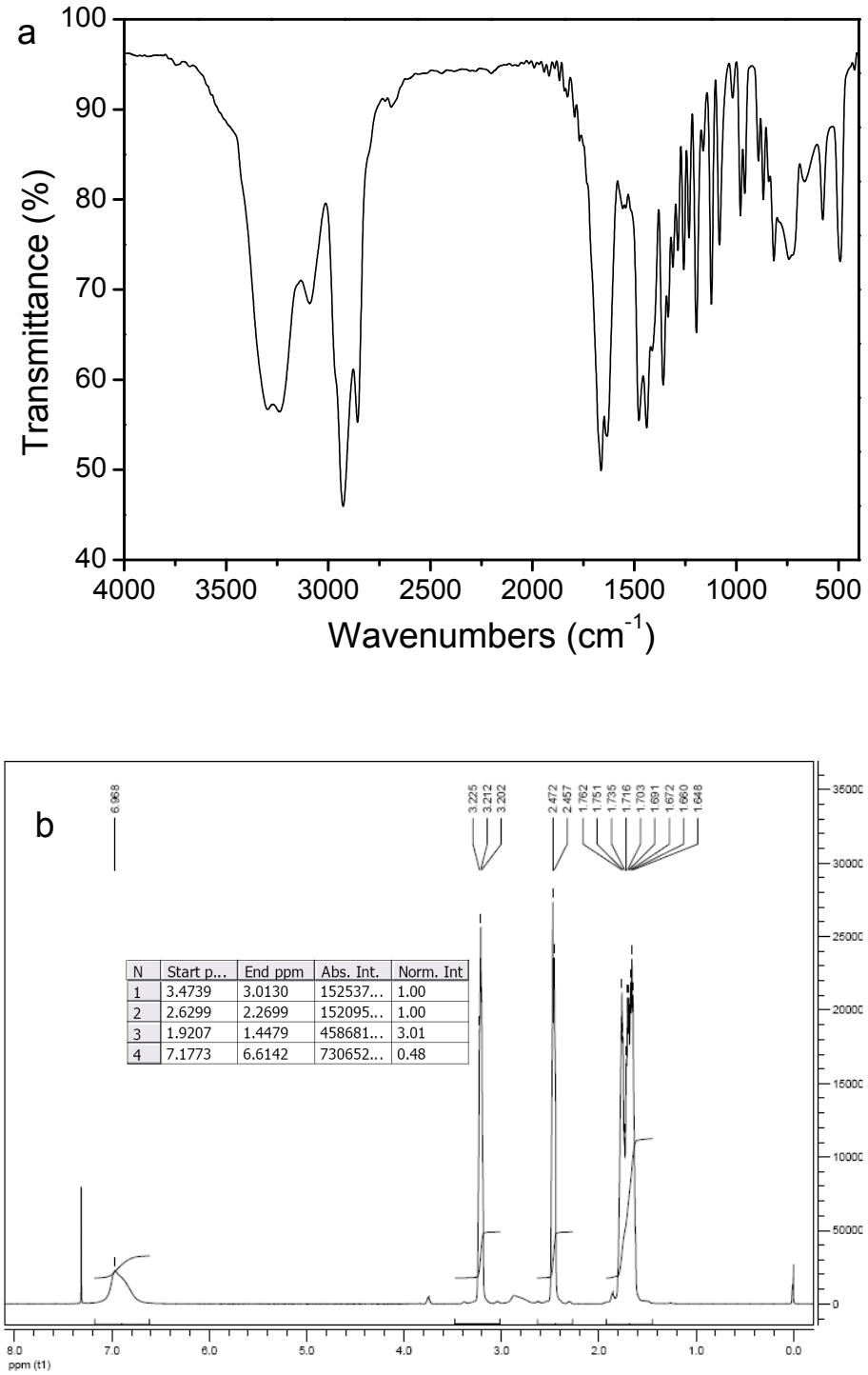

Figure S5. FT-IR and ^{1}H-NMR spectra of recycled ε-caprolactam. NMR solvent: $CDCl_3$. (a) FT-IR: 3280 (N-H), 2800-2900 (C-H), 1664 (C=O), 1300-1450, 1220; (b) ^{1}H-NMR: 1.5-2.1(m), 2.3-2.7 (m), 3.0-3.5 (m), 7.7 (broad band).

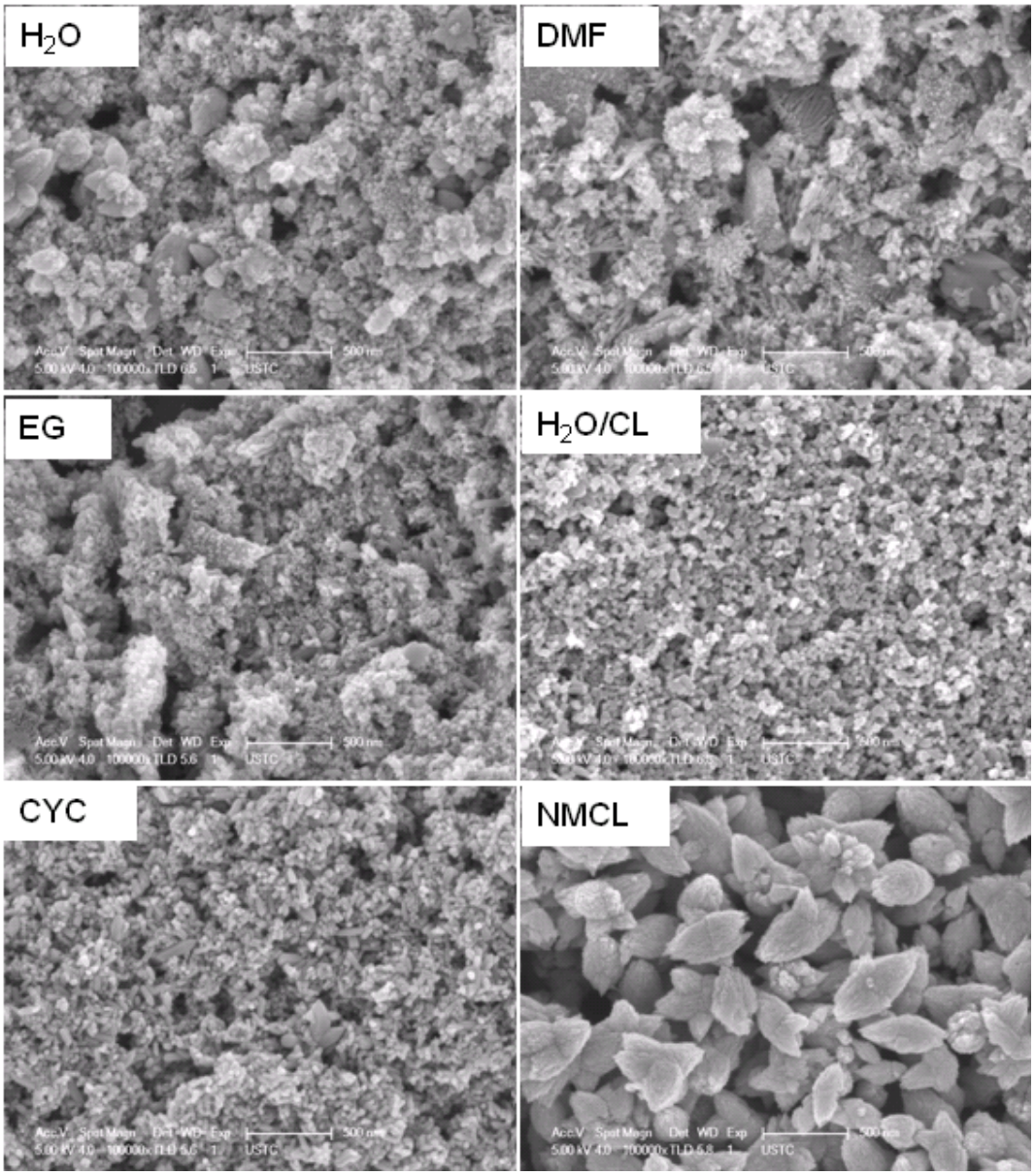

Figure S6. FE-SEM micrographs of ZnO samples synthesized in water (H_2O), N,N-Dimethylformamide (DMF), ethylene glycol (EG), an aqueous solution of 5 wt% ε-caprolactam (H_2O/CL), cyclohexanone (CYC), and N-Methyl caprolactam (NMCL).

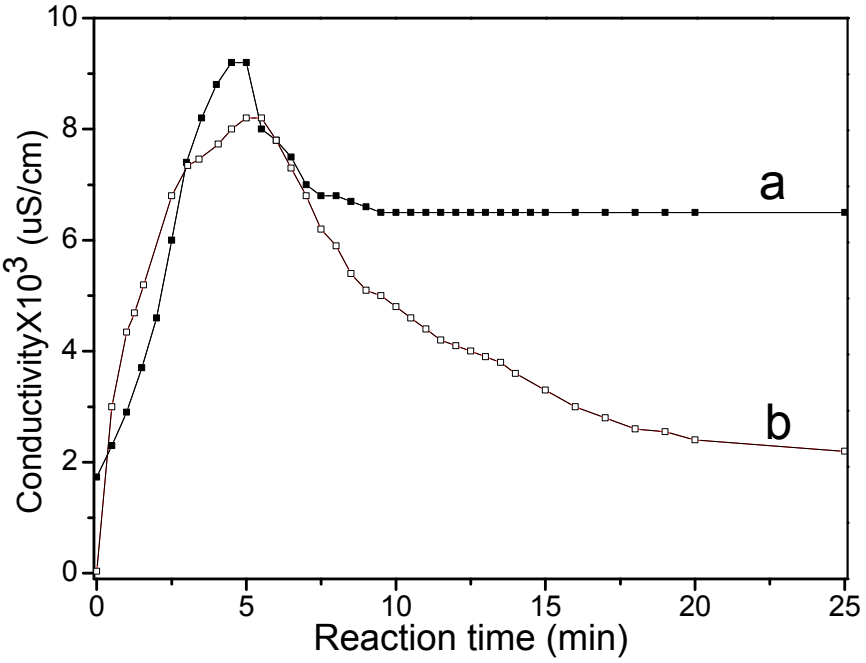

Figure S7 Time-dependent curve of conductivity for a) ethylene glycol solution containing 25 mM of $ZnCl_2$ after addition of a stoichiometric amount of NaOH pellets and b) molten CL solution containing 25 mM of $ZnCl_2$ after addition of a stoichiometric amount of NaOH aqueous solution (0.2g/ml) at 100□.

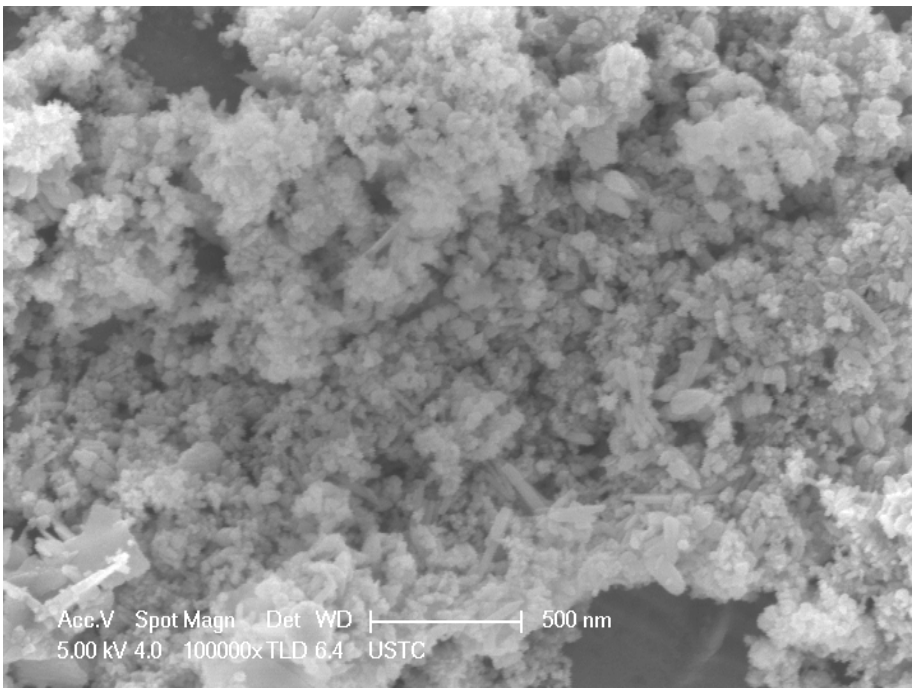

Figure S8. SEM image of ZnO sample synthesized by the same procedure as ZnO NPs except that the solid NaOH pellets was substituted by an aqueous solution of NaOH (0.2g/ml) with the same molar number of NaOH. .

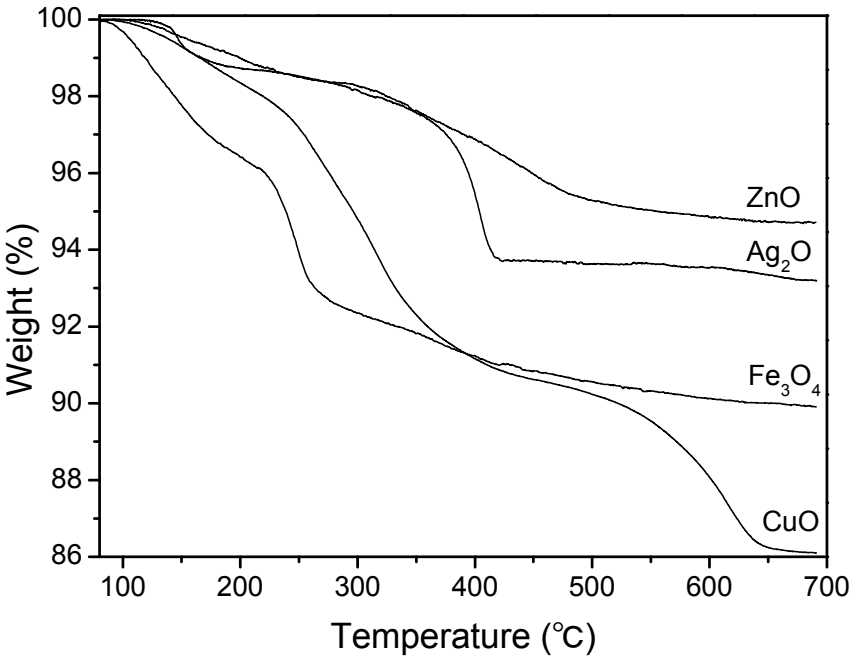

Figure S9. TGA curves of metal oxides NPs synthesized in molten CL.