Supplementary Material (ESI) for Journal of Materials Chemistry

Microwave assisted synthesis of ZnO micro-javelins

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Electronic Supplementary Information

ESI 1; Fig. 1: SEM of sample prepared by 20 min. of MW irradiation between 40 mL each of 10 mM zinc nitrate and 10 mM urea (1:1)

ESI 1; Fig. 2: SEM of sample prepared by 20 min. of MW irradiation between 40 mL each of 100 mM zinc nitrate and 100 mM urea (10:10)

ESI 2; Fig. 1: XRD of samples prepared by varying time of irradiation (● - $Zn_5(CO_3)_2(OH)_6$ / $Zn_4CO_3(OH)_6.H_2O$; ■ – from the instrument)

ESI 2; Fig. 2: XRD of sample prepared by 12 and 13 min of MW irradiation (● - $Zn_5(CO_3)_2(OH)_6$ / $Zn_4CO_3(OH)_6.H_2O$; ■ – from the instrument)

ESI 3; Fig. 1: FTIR spectra of ZnO micro-javelins prepared at various reaction times

ESI 4; Table 1: Details of MW conditions and corresponding pH, % yield and soluble zinc species concentrations.

ESI 4; Fig. 1: SEM of sample prepared by irradiating the already microwaved solution (150W 14 min) for 18 min. after adjusting the pH to 10 (*). The surface texture is rough due to the dissolution of the particles. (size ~13 μm)

ESI 5; Fig. 1: SEM image of 500 °C calcined product of the ammonium carbamate and zinc nitrate reaction.

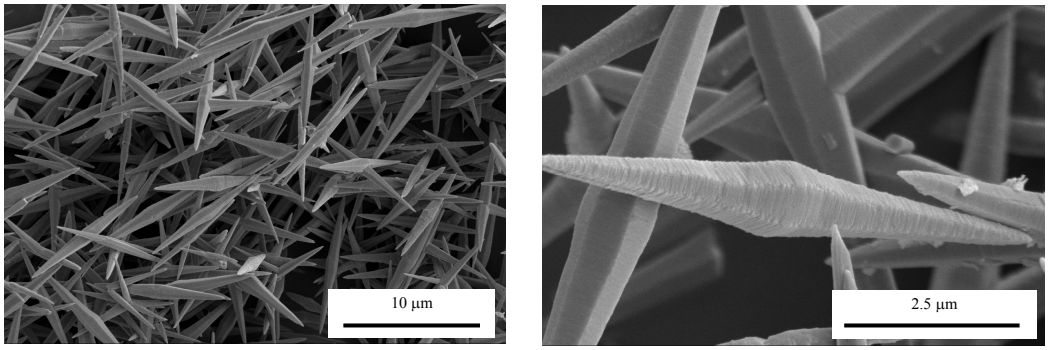
ESI 6; Table 1: Thermodynamic equilibria for ZnO(s)-H_2O and $Zn(OH)_2$(s)-H_2O systems.

ESI 6; Table 2: Thermodynamic data for ZnO(s), $Zn(OH)_2$(s) and soluble species at 298 K.

ESI 6; Fig. 1: Phase stability diagrams for the $ZnO_{(s)}$-H_2O (a) and $Zn(OH)_{2(s)}$-H_2O (b) systems at 25 ^oC as a function of pH. An equilibrium between $Zn(OH)^{3-}$ and the solid phase is out of the range (Taken from references mentioned in 36. Thermodynamic data of the phases can also be found therein).

ESI 7; Fig. 1: Carbonate-bicarbonte phase distribution diagram. Solubility product of carbonate at pH 8 is 8.5 x 10^{-4}.

ESI 1: SEM images of particles prepared by varying the concentrations of zinc nitrate and urea.



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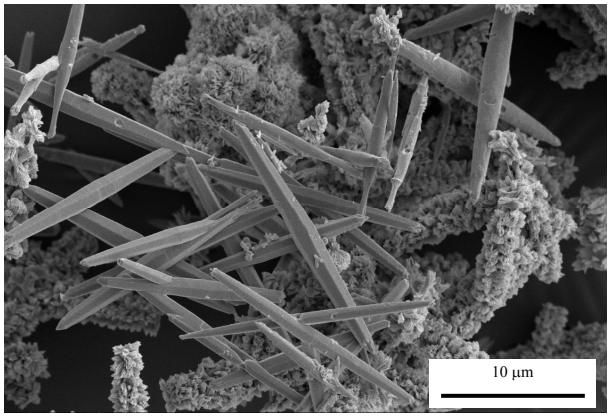
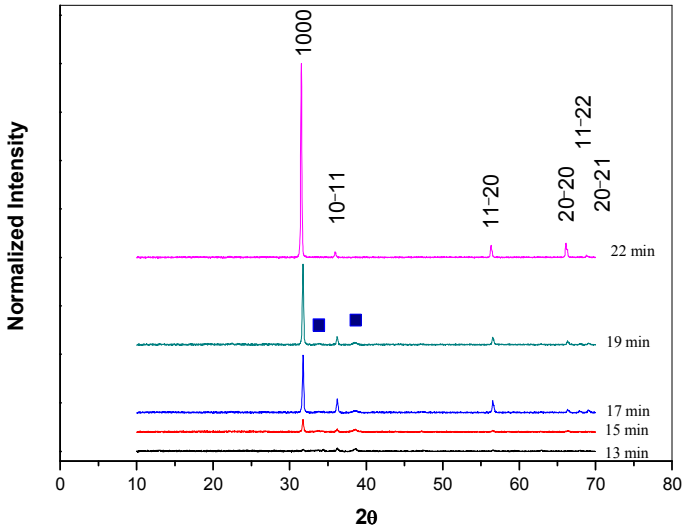


ESI 1; Fig. 2: SEM of sample prepared by 20 min. of MW irradiation between 40 mL each of 100 mM zinc nitrate and 100 mM urea (10:10)

ESI 2: XRD patterns



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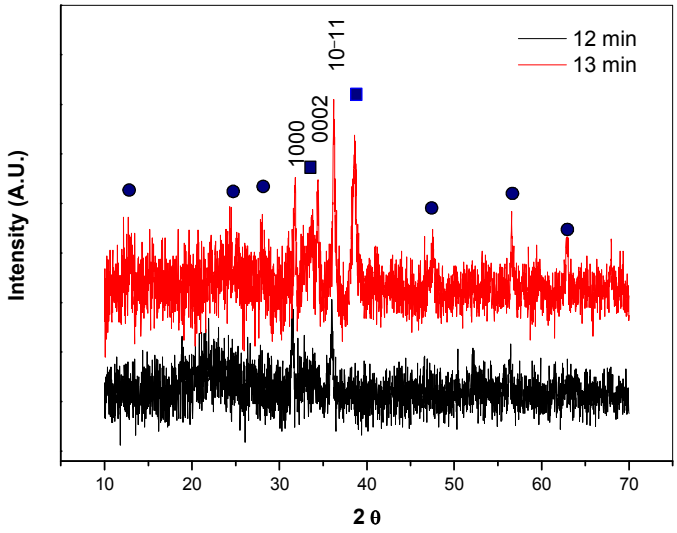

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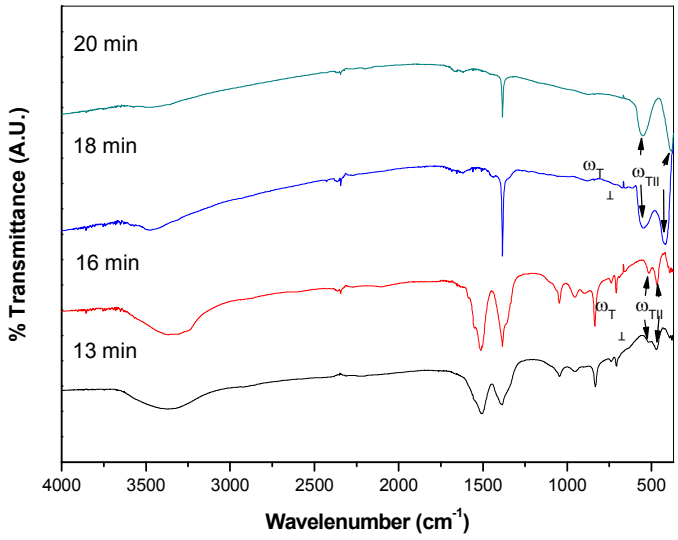
ESI 3: FTIR spectra of ZnO micro-javelins prepared at various reaction times



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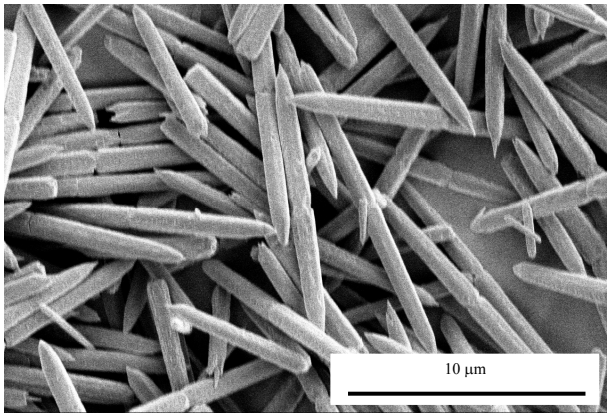
ESI 4: Details of reactions and products.

ESI 4; Table 1: Details of MW conditions and corresponding pH, % yield and soluble zinc species concentrations.

Irradiation Time (min)	pH	Yield (%)	Soluble Zn^{2+} ion concentration (mg)
10	6.11	--	21.9170
11	6.81	5	18.4423
12	6.88	41	13.364
13	7.04	110	3.2074
14	7.38	82	2.9401
15	8.62	95	2.6728
16	8.72	94	1.6037
17	9.01	93	1.6037
18	9.05	92	1.6037
19	9.13	82	2.6728
20	9.31	84	2.4055
22	9.56	80	3.4746
24	9.75	82	4.2765
14, 18*	9.87	73	5.8802
18#	10.37	26	16.571

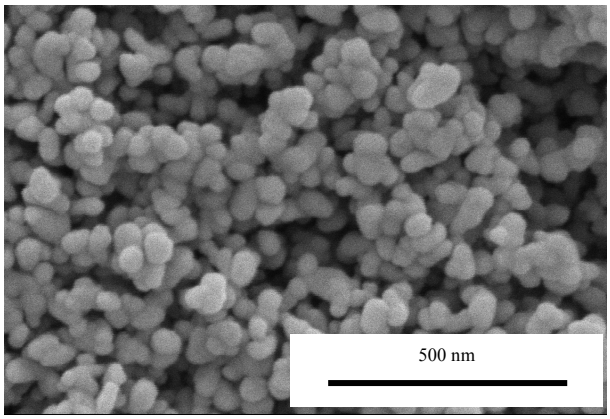
*Preparation sequence: 150W 14 min. Allowed cooling. Adjusted the pH to ~10 with NH_4OH. Microwaved again at 150 W for 18 min.

Preparation sequence: Adjusted the pH of reactant mixture to ~10. Microwaved at 150 W for 18 min.



ESI 4; Fig. 1: SEM of sample prepared by irradiating the already microwaved solution (150W 14 min) for 18 min. after adjusting the pH to 10 (*). The surface texture is rough due to the dissolution of the particles. (size ~13 μm)

ESI 5: SEM image of 500 °C calcined product of the ammonium carbamate reaction.



ESI 5; Fig. 1: SEM image of 500 °C calcined product of the ammonium carbamate and zinc nitrate reaction.

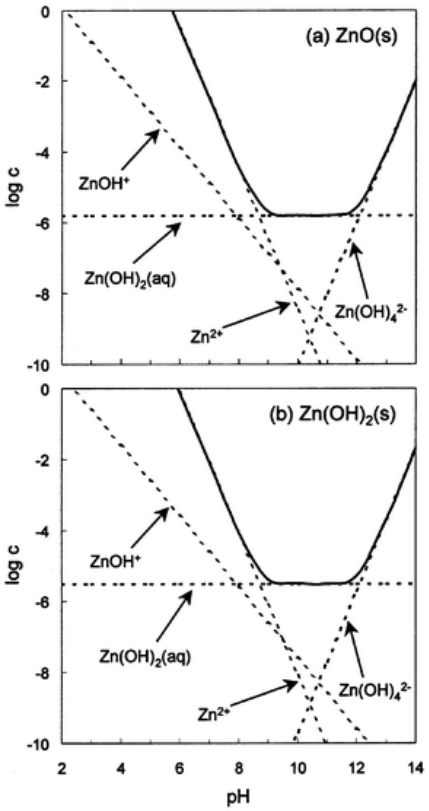
ESI 6: Thermodynamic data and phase diagrams of ZnO(s) and $Zn(OH)_2$(s).

ESI 6; Table 1: Thermodynamic equilibria for ZnO(s)-H_2O and $Zn(OH)_2$(s)-H_2O systems.

ZnO(s)–H_2O	$Zn(OH)_2$(s)–H_2O
$Zn^{2+} + H_2O \leftrightarrow$ $ZnO(s) + 2H^+$	$Zn^{2+} + 2H_2O \leftrightarrow$ $Zn(OH)_2(s) + 2H^+$
$ZnOH^+ \leftrightarrow$ $ZnO(s) + H^+$	$ZnOH^+ + H_2O \leftrightarrow$ $Zn(OH)_2(s) + H^+$
$Zn(OH)_2(aq) \leftrightarrow$ $ZnO(s) + H_2O$	$Zn(OH)_2(aq) \leftrightarrow$ $Zn(OH)_2(s)$
$Zn(OH)_3^- + H^+ \leftrightarrow$ $ZnO(s) + 2H_2O$	$Zn(OH)_3^- + H^+ \leftrightarrow$ $Zn(OH)_2(s) + H_2O$
$Zn(OH)_4^{2-} + 2H^+ \leftrightarrow$ $ZnO(s) + 3H_2O$	$Zn(OH)_4^{2-} + 2H^+ \leftrightarrow$ $Zn(OH)_2(s) + 2H_2O$

ESI 6; Table 2: Thermodynamic data for ZnO(s), $Zn(OH)_2$(s) and soluble species at 298 K.

Species	$\Delta_f G^\circ$/kJ mol^{-1}	Species	$\Delta_f G^\circ$/kJ mol^{-1}
ZnO(s)	−318.3	Zn^{2+}(aq)	−147.0
$Zn(OH)_2$(s)	−553.6	$ZnOH^+$(aq)	−330.1
		$Zn(OH)_2$(aq)	−522.3
H^+(aq)	0	$Zn(OH)_3^-$(aq)	−694.3
H_2O(l)	−237.2	$Zn(OH)_4^{2-}$(aq)	−858.7



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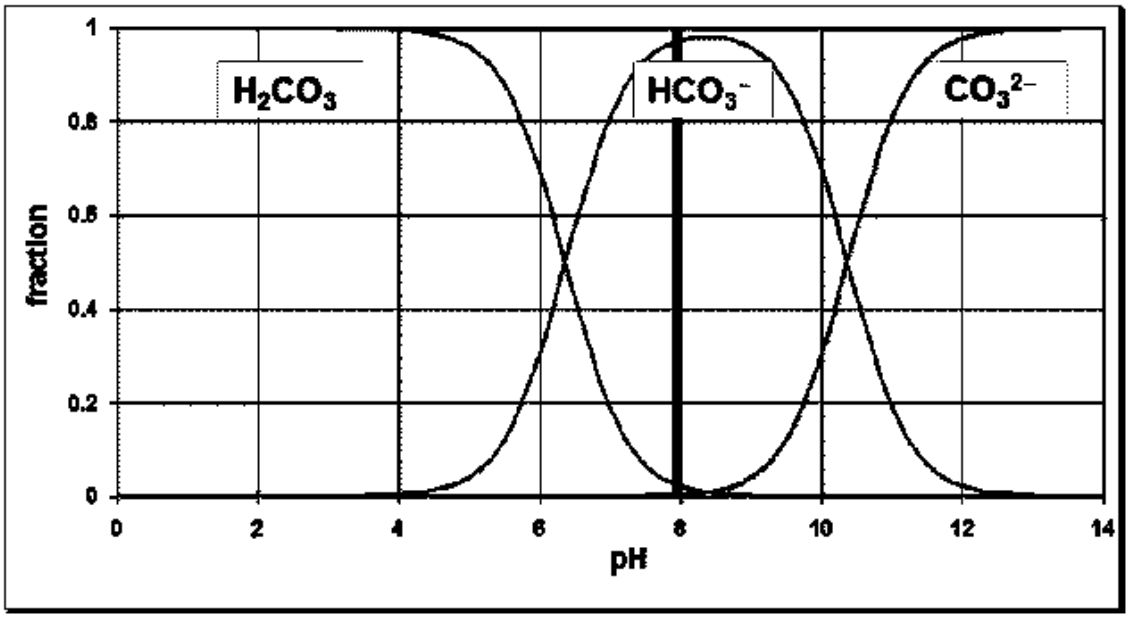

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