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Morphology Control of ZnO with Citrate: A Time and Concentration Dependent Mechanistic Insight

Somnath Das, Kingshuk Dutta and Amitava Pramanik*

Unilever R and D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, India.

E-mail: amitava.pramanik@unilever.com

Tel: +91-080-39830988

**Corresponding author: A. Pramanik*

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S1. Experimental details for measurement of the photocatalytic activity of the ZnO samples:

Photocatalytic activity of the ZnO powders synthesized at citrate/Zn molar ratio of 0 to 0.5 was studied by following the degradation of methylene blue dye. The samples were calcined at 700 °C for 5 hours to ascertain complete removal of adsorbed citrate. 100 mL of 20 μM dye was taken in a photocatalytic reactor, to which 5 mg of the synthesized ZnO was added and stirred for 30 minutes at 400 rpm and 25 °C in dark to establish adsorption–desorption equilibrium between the dye and ZnO surface. The suspension was then irradiated with UV light from a mercury lamp (60 W, 365 nm) under stirring condition (at 400 rpm, 25 °C). Aliquots were taken out from the reactor at every 5 minutes during irradiation, centrifuged and their absorbance were recorded at 664 nm (absorbance maxima of methylene blue in water) using a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer. Blank dye degradation was also carried out under similar condition without adding the catalyst.

Table S2. *Effect of citrate on the morphology control of zinc oxide: Literature Survey*

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Zn conc (mM)	Zn co-anion	(mM)	Base	(mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
50	Nitrate	100	HMTA	50	0	0.000	95	4, 8	rods		this work
50	Nitrate	100	HMTA	50	0.1	0.002	95	8	hexagonal cakelike		
50	Nitrate	100	HMTA	50	0.5	0.010	95	8	hexagonal cakelike		
50	Nitrate	100	HMTA	50	1	0.020	95	1, 4, 8, 24	hexagonal cakelike		
50	Nitrate	100	HMTA	50	2.5	0.050	95	8	hexagonal cakelike and porous spheres		
50	Nitrate	100	HMTA	50	5	0.100	95	1, 4, 8, 24	porous spheres		
50	Nitrate	100	HMTA	50	10	0.200	95	8			
50	Nitrate	100	HMTA	50	25	0.500	95	1, 4, 8, 24	solid spheres		
50	Nitrate	100	HMTA	50	33.3	0.666	95	8, 24	rhombic plates		

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Zn conc (mM)	Zn co-anion	(mM)	Base	(mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
4.83	Nitrate	9.67	HMTA	4.83	0.16	0.033	95	1, 2.5, 5, 12, 24, 48	microsphere, hexagonal microrod with stacked nanoplates	porous spheres, hexagonal cakelike morphology	35
30	Nitrate	60	HMTA	100	1.07	0.036	95	24	nanoplates		
30	Nitrate	60	HMTA	100	0.17	0.006	95	24	Micro structures		
30	Nitrate	60	HMTA	30	1.07	0.036	60	48	bilayer structure		32
1	Nitrate	2	HMTA	10	0.2	0.200	80 (≤0.5 atm)	6,24	nanorose	Porous microspheres.	42

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Zn conc (mM)	Zn co-anion	(mM)	Base	(mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
10	Nitrate	20	HMTA	10	130	13.000 **	90 (micro wave)	0.25	nanodisk		
10	Nitrate	20	HMTA	10	130	13 **	90 (micro wave)	0.25 (aged at RT for 100 min)	nanonuts		
10	Acetate	20	Ammonia	160	10	1 **	90 (micro wave)	0.25	nanoUFO		
10	Acetate	20	Ammonia	320	10	1 **	90 (micro wave)	0.25	nanoballs		
20	Nitrate	40	HMTA	20	130	6.5 **	90 (micro wave)	0.25	nanocakes		36

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Zn conc (mM)	Zn co-anion	(mM)	Base	(mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
20	Nitrate	40	HMTA	20	0.06-0.27	0.00283, 0.0133	60	6	secondary nanoplates on primary ZnO rods		40
30	Nitrate	60	HMTA	100	1	0.033	95	24	helical nano structures on ZnO rods		33
10	Nitrate	20	HMTA	10	100	10.000 **	RT	0.5 (ultra sonication)	nanodisk		56
10	Acetate	20	Ammonia	1570	10	1.000 **	RT	0.5 (ultra sonication)	Nano spheres		
30	Nitrate	60	HMTA	300	0.17	0.006	60	36	Micro patterns of Single Crystal ZnO		57
10	Nitrate	20	HMTA	10	20 , 50		80	6	Stacking nano plates		38

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Zn conc (mM)	Zn co-anion	(mM)	Base	(mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
20	Nitrate	40	HMTA	20	0.17	0.009	60		larger primary crystals		53
10	Acetate	20	Ammonia	300	15 , 25	1.5, 2.5 **	90	1	confeito like structures		
10	Acetate	20	Ammonia	300	0.5	0.050 #	90	1	sphere like structures	when citrate is used 0.5mM and 1 mM	
10	Acetate	20	Ammonia	300	10	1 #	90	1	anisotropic smooth ZnO crystals		
10	Acetate	20	Ammonia	300	20	2 $	90	1	twinned hexagonal structures		34
10	Nitrate	20	HMTA	10	10 , 40 µM	1, 4	75	2.5	hexagonal rods		41

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Zn conc (mM)	Zn co-anion	(mM)	Base	Base conc (mM)	citrate (mM)	Citrate/Zn	Temp	Ageing time (hr)	Morphology	Analogy	Reference
50	Acetate	100	Ammonia	1.06	37.5	0.75	120	8	doughnut micro particles		37
5	Nitrate	10	HMTA	5	1.36	0.272	90	0.83, 2	microsphere	solid microsphere	58
25	Nitrate	50	HMTA	25	6.8	0.272	85	1	core shell microsphere		59
500	Nitrate	1000	Sodium hydroxide	500	500	1.000 ┼	50	0.33	ZnO film		60
38	Acetate	76	Sodium hydroxide, Ammonia	168	20	0.53	85	12	rod, slick, flower	flower like structure	61
90	Acetate	180	HMTA	90	9	0.1	95	3	microspheres	porous microspheres	43

N.B. Wherever citrate is not mentioned it can be taken as sodium citrate; ** tri ethyl citrate; ┼ ammonium citrate tri basic; # tri potassium or sodium citrate; $ tri-ammonium citrate or citric acid.

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S3. Thermogravimetric analyses:

Figure S3 (a-b) contains the thermogravimetric plot and differential thermogram respectively. From Figure S3 (a), it is clear that in the absence of citrate the ZnO formed is of high purity and does not undergo any significant weight loss upon heating upto 600 ^{o}C. For the materials grown in presence of citrate, there is quite significant amount of weight loss upon heating. There are two major regions of weight loss, the first in the range 25 ^{o}C and 150 ^{o}C, presumably because of desorption of adsorbed moisture in the porous matrix, and the second in the range of 250 ^{o}C and 500 ^{o}C. We believe this is because of the loss of the adsorbed citrate. Pure crystalline zinc citrate itself undergoes weight loss in this temperature region, as shown in Figure S3 (b) E. The DTG profile of the zinc citrate is, however, quite different from that of the citrate adsorbed ZnO samples.

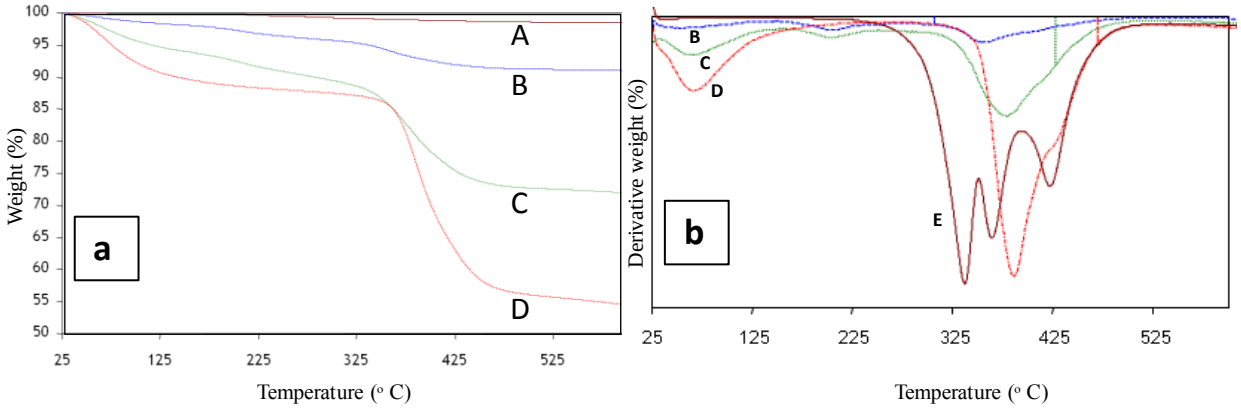

Figure S3. Thermo gravimetric plot (a) and DTG peaks (b) of synthesized ZnO particles with citrate/ Zn ratio of- A: 0; B: 0.02; C: 0.10: D: 0.50; E: commercial zinc citrate [$Zn_3(citrate)_2$].

The extents of weight loss in the 8 hour samples in these two temperature regions are collected in Table S3. It is clearly evident from the data that both adsorbed moisture and adsorbed citrate went up with increase in citrate concentration during synthesis. For the sample prepared in presence of 25 mM citrate, the loss in weight because of citrate decomposition is as high as 31.9%, the corresponding number for pure crystalline zinc citrate being 47.4%.

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Table S3. Weight loss (%) of the synthesized ZnO on heating using a thermogravimetric analysis.

[Citrate], mM	citrate/ Zn	25 to 150°C	250 to 500°C
0	0.00	0.1	0.9
1	0.02	1.9	5.1
2.5	0.05	5.0	13.8
5	0.10	6.0	18.2
15	0.30	4.3	33.8
25	0.50	10.3	31.9
33	0.67	8.2	36.5
Zn citrate (commercial)		0.1	47.4

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S4. Infrared Spectroscopy:

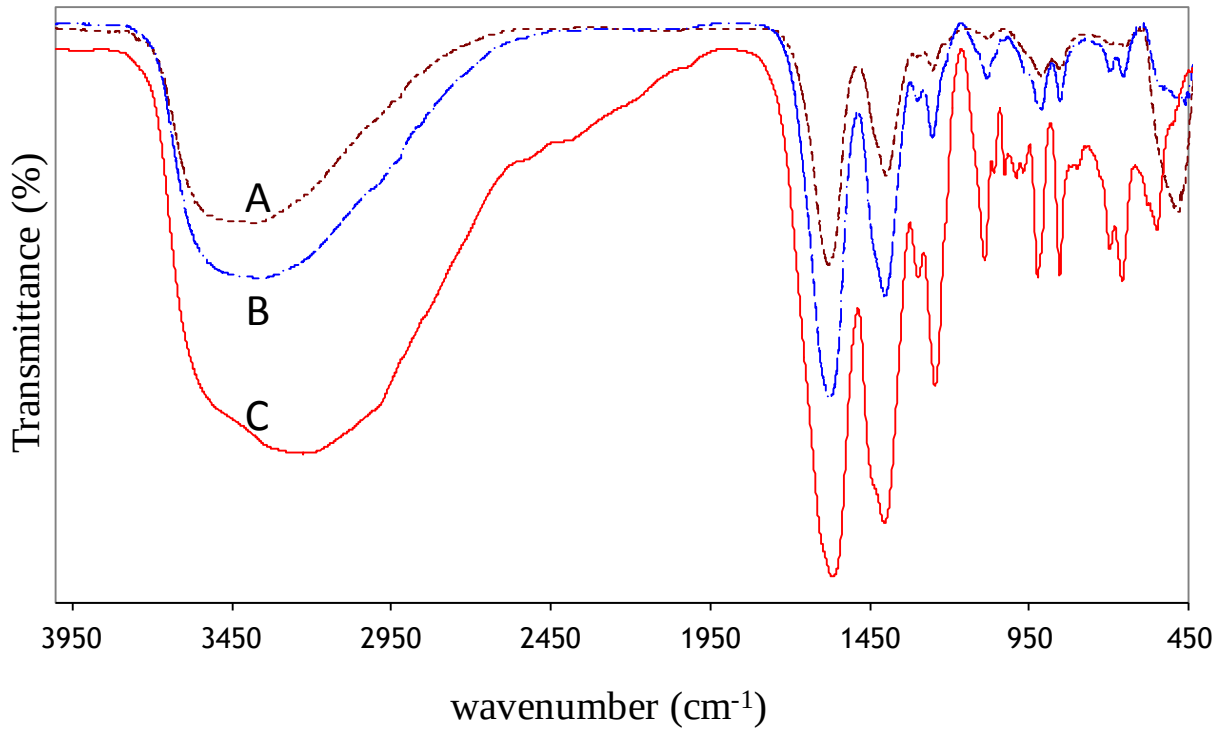

Figure S4. FT-IR plot of synthesized ZnO particles with citrate/ Zn ratio of- A: 0.02; B: 0.10: C: 0.50.

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S5. Effect of acetate ions:

In earlier studies, although remarkable effect of citrate in modifying ZnO morphology have been highlighted, the authors seemed to have ignored the effect of acetate, which also binds with zinc ions quite effectively, potentially either as terminal or as bridging mode.[45] Using zinc acetate as starting material would mean a ratio of acetate to zinc of 2, and therefore the ratio of acetate to citrate will be very high in cases where small concentration of citrates were used. Thus although citrate is a much stronger ligand compared to acetate, high ratio of acetate-to-citrate may induce some acetate-derived effect different from that by citrate alone.

We observed that acetate ions, even at a low concentration, could play a major role in modifying ZnO morphology. Figure S5 contains the SEM micrograph of ZnO particles formed with 5 mM of acetate (by using Zn nitrate as the zinc source, sodium acetate in place of trisodium citrate as the crystal habit modifier, acetate/Zn ratio of 0.1, other conditions remaining the same). Wafer thin plate-like particles with 50-60 nm thickness were observed in this condition. In absence of acetate, it would have been hexagonal rods, and use of citrate of the same concentration produced spherical aggregates.

Thus, use of zinc acetate along with smaller concentration of citrate would make acetate and citrate ions compete with each other for binding with zinc, and enforce morphology change. It is important to decouple the effects of these ions with different concentrations. We will report more detailed investigations on effects of ions like acetate in further studies.

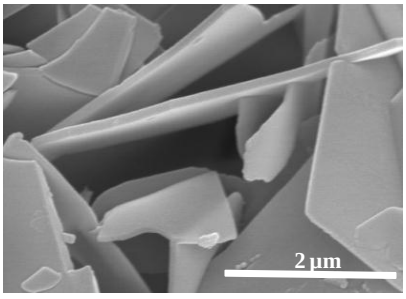

Figure S5. FE-SEM images of ZnO particles grown for 24 hours in presence of 5 mM acetate ions (acetate/Zn molar ratio of 0.1).