Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Complete Study of the Composition and Shape Evolution in the Synthesis of CZTS Semiconductor Nanocrystals

Claudia Coughlan,[a] and Kevin M. Ryan*[a]

[a]*Materials and Surface Science Institute and Department of Chemical and Environmental Sciences, University of Limerick, Limerick, Ireland.*

**Corresponding Author: E-mail: Kevin.M.Ryan@ul.ie*

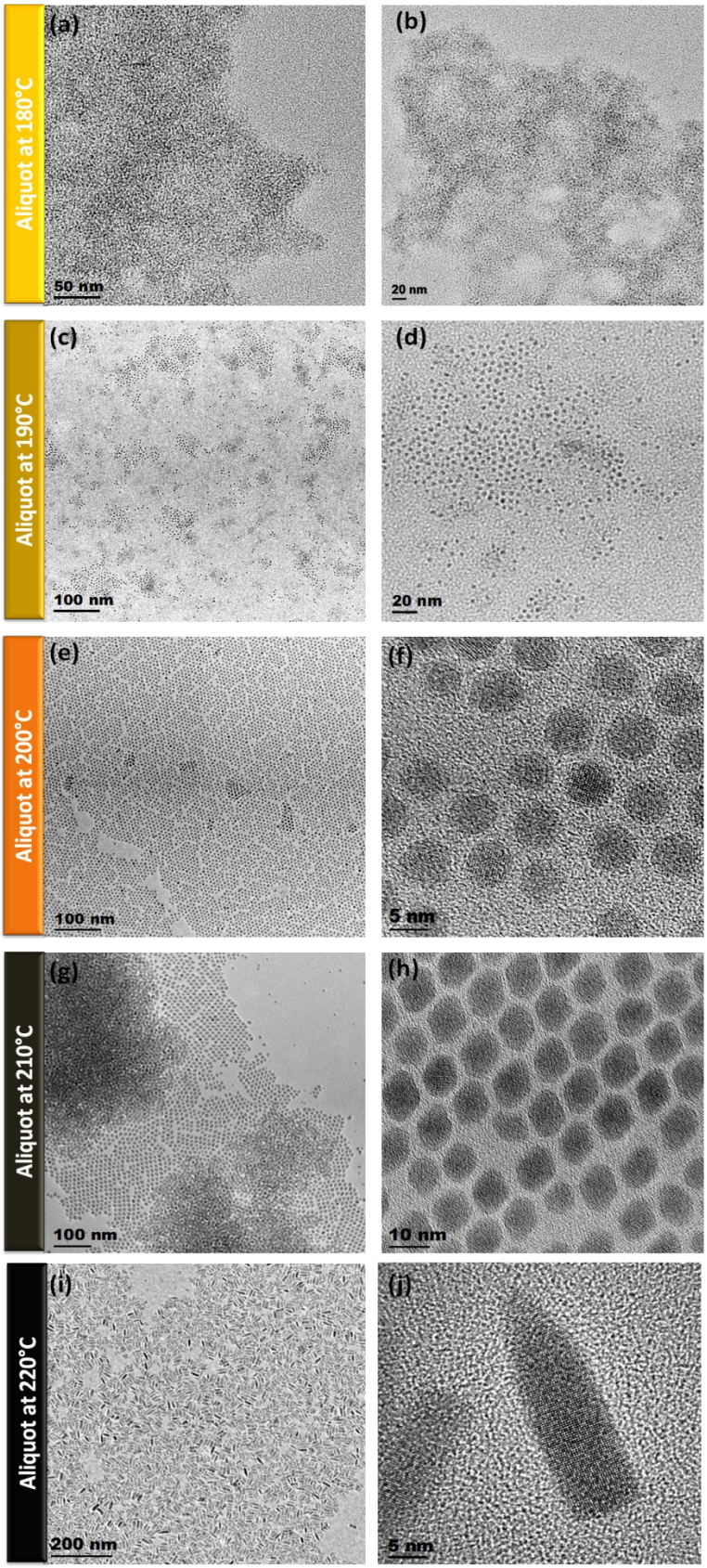

Figure S1. Low and higher resolution TEM images of aliquots withdrawn from the reaction at (a-b) 180°C, (c-d) 190°C, (e-f) 200°C, (g-h) 210°C and (i-j) 220°C.

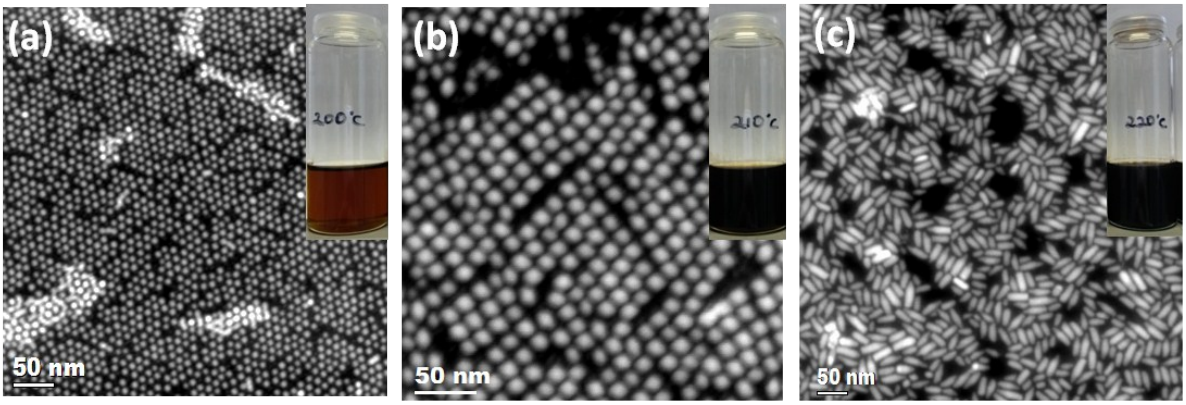

Figure S2. DF-STEM images of aliquots taken at (a) 200°C, (b) 210°C and (c) 220°C, with the associated solution colour changes shown in the photographs in the inset of each image.

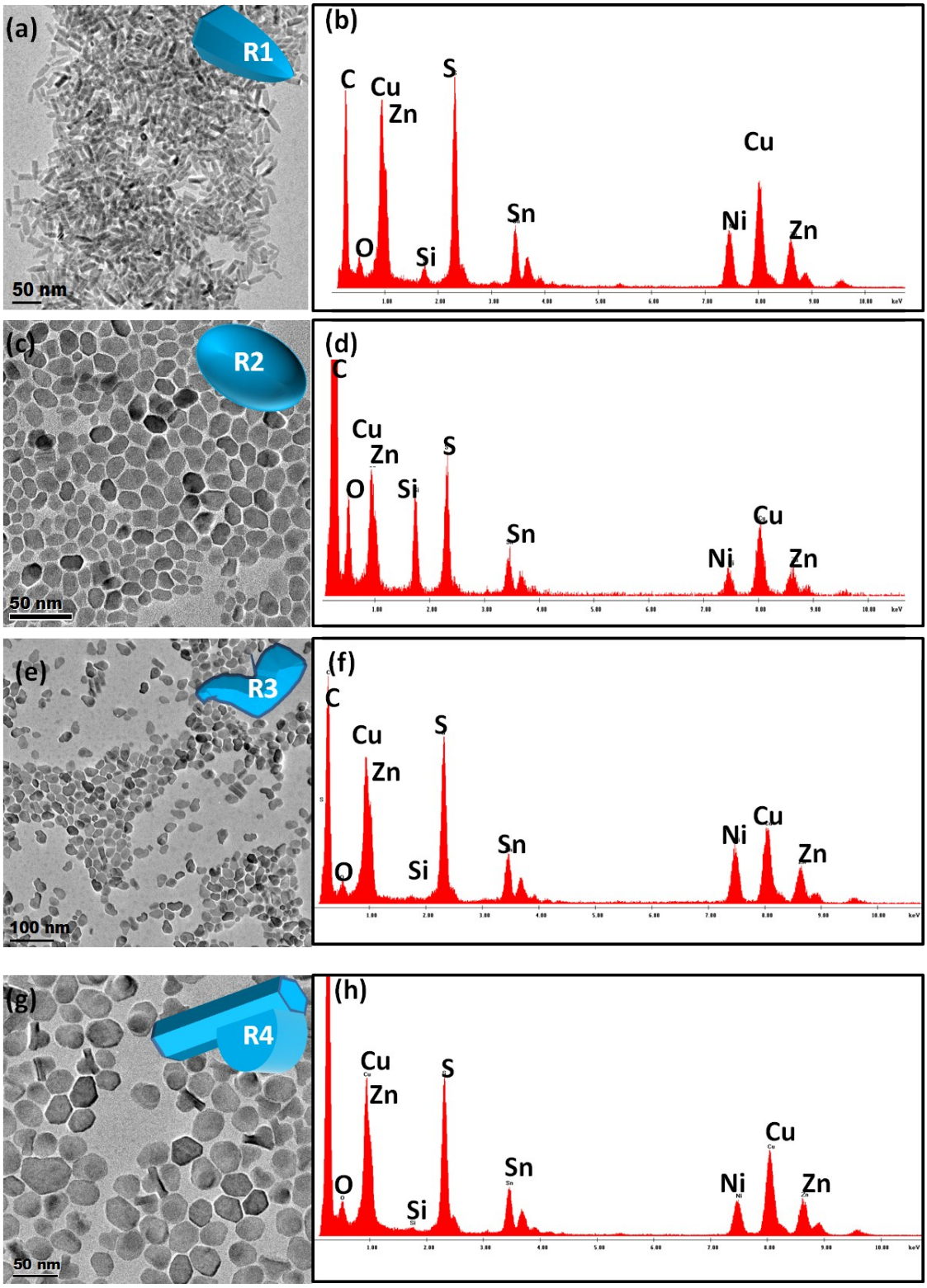

Figure S3. TEM and the corresponding Energy-dispersive X-ray spectroscopy (EDX) analysis of the four different shapes of CZTS nanocrystals, specifically (a-b) nanorods formed in route R1, (c-d) ellipsoids formed in route R2 (e-f) tadpole-shaped nanocrystals formed in route R3, (g-h) P-shaped nanocrystals formed in route R4.

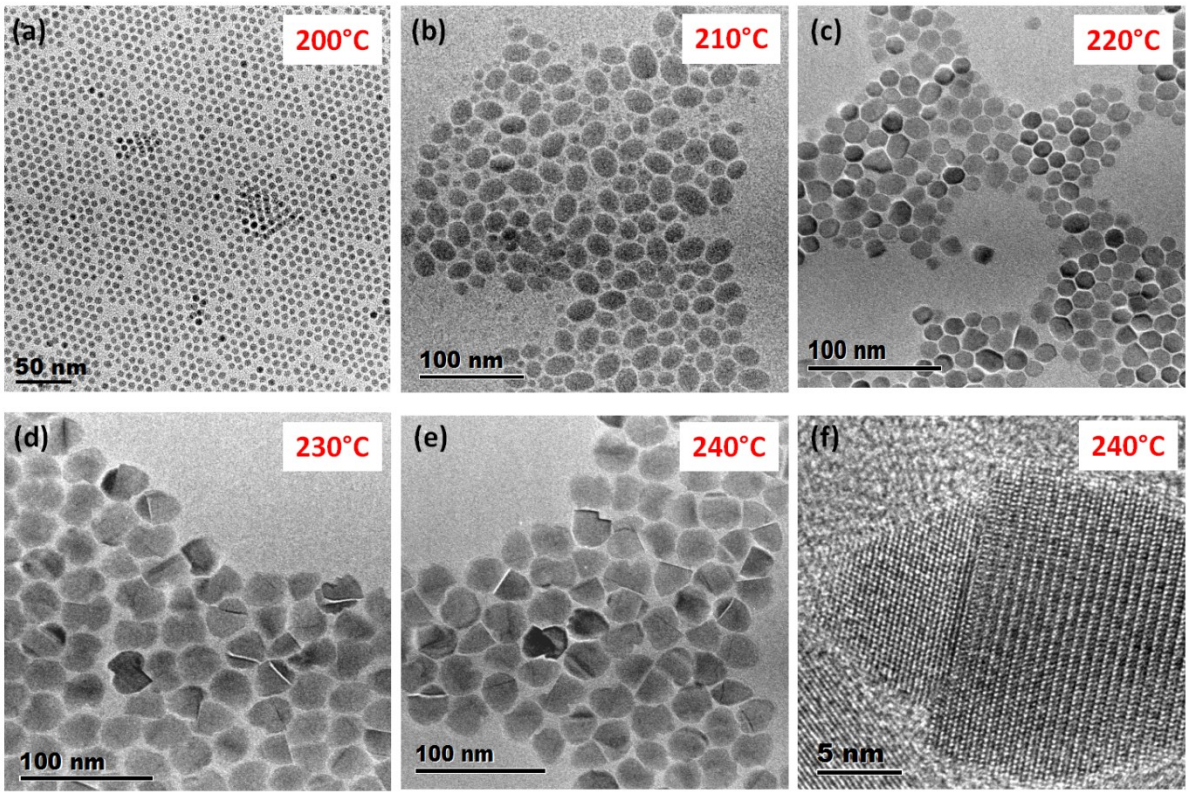

Figure S4. TEM images of aliquots withdrawn from the reaction at (a) 200°C, (b) 210°C, (c) 220°C, (d) 230°C and (e-f) 240°C. The first indication of polytypic nanocrystal growth is evident in the TEM image in (d), taken at 230°C and proceeds with the increasing reaction temperature.

Simulated Diffraction Patterns for the Wurtzite and Zinc Blende Structures of CZTS

Crystal Formula: Cu_2ZnSnS_4

Crystal System: Hexagonal

Space Group: $P6_3mc$ (no.186)

Unit Cell dimensions:

a = b = 3.8076Å and c = 6.2749Å

α = β = 90°, γ = 120°

Atomic Co-ordinates

Atom	Wyck.	x/a	y/b	z/c
Cu	2b	1/3	2/3	3/8
Zn	2b	1/3	2/3	3/8
Sn	2b	1/3	2/3	3/8
S	2b	1/3	2/3	0

hkl	d-spacing / Å	2-Theta / deg
100	3.29748	27.0168
002	3.13745	28.4230
101	2.91898	30.6004
102	2.27298	39.6164
110	1.90380	47.7303
103	1.76627	51.7092
200	1.64874	55.7022
112	1.62759	56.4903
201	1.59461	57.7673
400	1.56872	58.8132
202	1.45949	63.7076

Table S1. Summary of Simulated data for Wurtzite CZTS.

Crystal Formula: Cu_2ZnSnS_4

Crystal System: Cubic

Space Group: F -43 m (no.216)

Unit Cell dimensions:

a = b = c = 5.4507Å

α = β = γ = 90°

Atomic Co-ordinates

Atom	Wyck.	x/a	y/b	z/c
Cu	4a	0	0	0
Zn	4a	0	0	0
Sn	4a	0	0	0
S	4c	1/4	1/4	1/4

hkl	d-spacing / Å	2-Theta / deg
111	3.14696	28.3353
200	2.72535	32.8338
220	1.92711	47.1177
311	1.64345	55.8972
222	1.57348	58.6180
400	1.36267	68.8391

Table S2. Summary of Simulated data for Zinc-Blende CZTS.