Multi-Step Non-Classical Crystallization Pathway under Conditions Far from Equilibrium

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In the past decade, experimental and molecular modelling studies of protein crystals, small molecule organic materials, colloids, polymers and biominerals have indicated that nucleation of solids from solution under *quiescent* conditions proceeds following a two-step nucleation mechanism, whereby the nucleation of the crystalline phase is preceded by the formation of metastable dense liquid-like clusters. However, under *dynamic, far from equilibrium* conditions (e.g. in evaporative drying and electrodeposition), nucleation and growth mechanisms for polycrystalline structures are not well understood.

To explain a novel observation [1] of polycrystalline residual surface patterns with a plethora of microstructures (Fig.1; e.g. dendrites (b,c), branched fibres (d), and chiral twists (e)) upon dynamic evaporative drying of a droplet containing ZnO nanoparticles in a chloroform/methanol/isobutylamine mixture, we have proposed a multi-step crystallization pathway. Therein, rapid ZnO dissolution led to the formation of molecular *primary clusters* and then multilayered *secondary nanoclusters*. Subsequently, evaporation induced the secondary nanoclusters to form transient gels with dendritic micromorphologies. Further solvent removal from the gels manifested in the ultimate polycrystalline dendritic surface patterns. The observations we have made and the multi-step non-classical crystallization mechanism we have proposed [2], both unprecedented, offer new insight into the formation of complex hierarchical surface patterns with polycrystalline structures under conditions far from equilibrium.

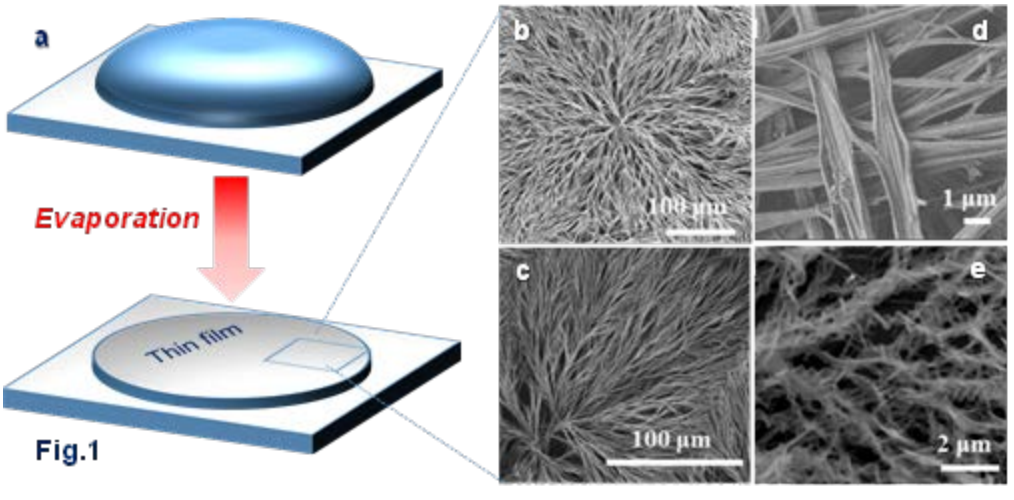

Figure 1 (a) Upon dynamic evaporative drying of a ZnO nanofluid, a residual hierarchical thin film forms, with a plethora of micromorphologies, including dendrites (b & c), fibres (d) and chiral twists (e).

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[1] H. Wu, L.X. Chen, X.Q. Zeng, T.H. Ren, and W.H. Briscoe, *Soft Matter*, 2014, **10**, 5243
[2] H. Wu and W.H. Briscoe, 2016, manuscript submitted