

Blowing unstable nanocrystals into being

Jincheng Tong¹, Nathan de Bruyn¹, Adriana Alieva¹, Elizabeth. J. Legge^{2,3},
Matthew Boyes¹, Xiuju Song¹, Alvin J. Walisinghe⁴, Andrew J. Pollard²,
Michael W. Anderson^{1,4}, Thomas Vetter⁵, Manuel Melle-Franco⁶, Cinzia Casiraghi¹

.....
1 – Department of Chemistry, University of Manchester, UK.
2 – National Physical Laboratory, Teddington, UK.
3 – Advanced Technology Institute, University of Surrey, UK.
4 – Curtin Institute for Computation, School for Molecular and Life Sciences, Curtin University, Australia.
5 – Department of Chemical Engineering and Analytical Sciences, University of Manchester, UK.
6 – CICECO & Department of Chemistry, University of Aveiro.
.....

Under different, thermodynamic and kinetic, conditions molecules may adopt different packings in the solid state. This phenomenon, known as polymorphism, is relevant for crystals used in, for instance, health and electronic applications, where producing selected polymorphs with enhanced properties may be a key to better performance. At the atomic level, molecules confined near surfaces may naturally arrange into layers. This can be used to access molecular layers and their distinct properties by producing molecular layered crystals. A method based on crystallization in ultra-thin puddles enabled by gas blowing was devised and tested. With this method, molecular layered crystals with, for instance,

glycine, the simplest amino acid, are easily produced with thickness down to the monolayer, Figure 1. This finding was rationalized with the help of computer models from the *Advanced Modelling Laboratory* at CICECO which allowed us to analyze and compare the intermolecular interactions holding together molecules in glycine polymorphs. Overall, in α -glycine, bulk crystals are formed by loosely bonded 2D layers showing stronger intermolecular interactions while in β -glycine, these interactions form a 3D network crystalline form, Figure 2. This simple molecular picture accounts for how pressure can be successfully used to obtain the, otherwise, less likely polymorph, α -glycine, Figure 1.

FIGURE 1

Schematic of the experimental setup. Gas pressure and solution concentration can be used to tune the crystal morphology and polymorph outcome.

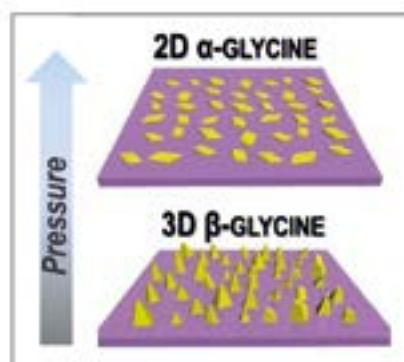
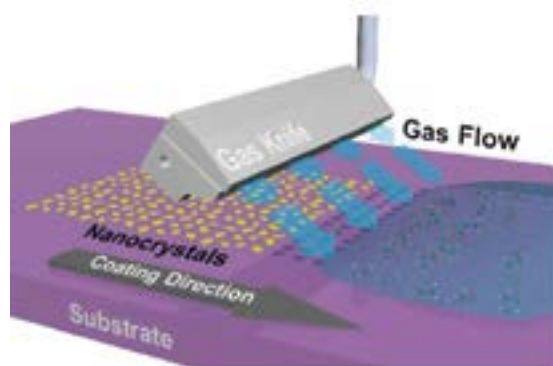


FIGURE 2

Binding interactions depicted as blue cylinders in glycine polymorphs revealing strong 2D and 3D interaction networks from computer models.

