

### 9 - Predicting synthesizability

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#### Status

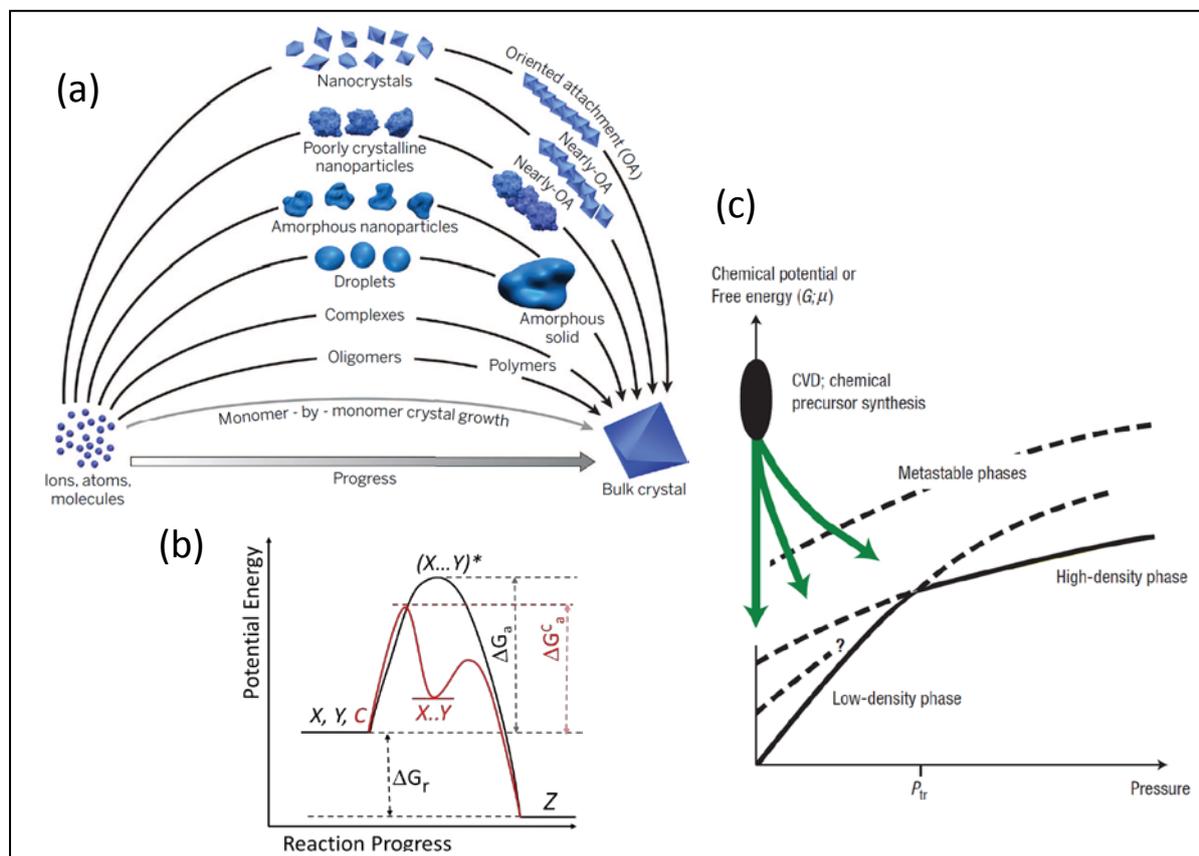


Fig. 1 (a) Crystal growth model, “Crystallization by Particle Attachment” (CPA), shows multiple pathways of crystal growth from solution. Unlike a classical monomer-by-monomer growth model (gray curve), CPA operates with higher-order species (black curves) and involves the interplay between thermodynamic factors and reaction dynamics [2]. (b) Potential energy profile from reactants X and Y to product Z with and without catalyst C.  $(X...Y)^*$  is high-energy transition state,  $X..Y$  is a metastable product;  $\Delta G_r$  is the Gibbs energy for the  $X+Y \rightarrow Z$  reaction;  $\Delta G_a^c$  and  $\Delta G_a$  are energies for activating transition states with and without catalyst C, respectively. (c) Generalized free-energy – pressure phase diagram with superimposed synthetic routes (bold green arrows) for obtaining metastable phases [3]

Advancements in multiscale multi-physics computational materials design have led to the accelerated discovery of advanced materials for energy, electronics and engineering applications [1]. For many common bulk materials synthesizing and processing procedures are reasonably well established. This also applies to modelling tools that can be utilized for the understanding of phenomena occurring in these procedures. However, theoretical approaches have limited analytical power for predicting viable synthetic routes towards making entirely new materials. The knowledge about growth mechanisms, free-energy landscape and dynamics of chemical and physical processes during synthesis is quite limited. This uncertainty is exemplified in Fig 1 (a) by showing multiple pathways for crystallization from solution, where a mechanism of forming bulk crystal depends on the interplay between thermodynamic and kinetic factors [2]. Therefore, the state-of-the-art in *materials design* needs to be complemented

with substantial efforts in advancing the field of *synthesis design*. To increase the predictive ability of material synthesizability, it is necessary to define both equilibrium and out-of-equilibrium descriptors that control synthetic routes and outcomes. The key metrics include free-energy surfaces in multidimensional reaction variables space (e.g., activation energies for nucleation and formation of stable and metastable phases in Fig 1 ((b) and (c)), composition, size and structure of initial and emerging reactants, and various kinetic factors such as diffusion rates of reactive species and the dynamics of their collision and aggregation.

### Current and Future Challenges

To identify and quantify key descriptors towards predictable synthesis design, it is essential to integrate (i) exploratory synthesis and (ii) *in situ* process monitoring with (iii) computational design of synthetic routes.

(i) Challenges of experimental exploratory synthesis are associated with the complexity of chemistries and reaction routes that depend on the interplay between equilibrium and out-of-equilibrium processes. Crystalline material growth methods, which span from condensed matter synthesis (all-solid-state synthesis and crystallization from melt or solution) to physical or chemical deposition from vapour (sputtering, e-beam deposition, pulsed laser deposition, atomic layer deposition, chemical vapour deposition), often proceed at non-equilibrium conditions, e.g., in highly supersaturated media, at ultra-high pressure, or at low temperature with suppressed species diffusion. Identification of chemical evolution reactions and the associated physical processes followed by their “equilibrium vs. metastable” classification is extremely difficult but is an essential step towards assessing material synthesizability. An illustration of possible reaction pathways to realize stable and metastable states of material is illustrated in Fig 1(c) where highly non-equilibrium synthetic routes are superimposed on a generalized phase diagram [3].

(ii) Developing *in situ* multi-probe measurements to capture important steps along the synthetic route is critical to make the synthesis design and its validation more efficient. For all-solid-state synthesis it is important to develop high spatial and temporal resolution 3D tomographic mapping of phase evolution. The same applies for developing in-line diagnostics for solid growth under extreme environments, including synthesis in supercritical fluids, at extreme pressures, temperatures, photon/radiation fluxes or electromagnetic fields. This is noteworthy since real-time multi-probe diagnostics generates massive sets of data, which need to be promptly utilized in a closed-loop-feedback with synthesis, data curation protocols and machine learning techniques, need to be advanced.

(iii) On the modelling side, the idea of extending computational material discovery to *in silico* synthesis design is still in its nascent state. Assessment of equilibrium and dynamic key variables for predicting the lowest activation energies and fastest routes for fabricating targeted material remains to be exceptionally challenging. The availability of data needed for modelling of new materials and processes poses another challenge.

### Advances in Science and Technology to Meet Challenges

The challenge of operating in multidimensional space of material fabrication can be addressed by integrating exploratory synthesis with multimode dynamic process monitoring to define key growth process parameters. Experimental synthesis and *in situ* measurements should be further integrated with computational tools to enable robust predictive synthesis of materials with tailored properties. This unified “experimental/*in situ*/*in silico*” synthesis concept is emphasized in the Department of Energy report [4] with focus on materials for energy, including experimentally verified design of novel thermoelectric and battery materials, metal nanoparticle catalysts, and transparent conducting oxides.

To address emerging materials needs exploratory synthesis is focusing more and more on metastable, hybrid, and hierarchical structures, such as thin film heterostructures, nanoparticle superlattices, and core-shell nanostructures. For example, the core-shell nanowire in Fig 2(a) demonstrates how thermodynamically favoured phase separation in GaAsSb alloy can be suppressed by strain from the GaAs shell layer [5]. Similarly, metastable rock-salt structure in SnSe thin film in Fig. 2(b) can be stabilized by depositing it epitaxially on a suitable substrate [6].

Advances in *in situ* diagnostics include application of multi-probe optical spectroscopies and neutron/X-ray scattering and diffraction for real-time process monitoring, *e.g.*, for crystal growth from melt [7], roll-to-roll solution drying of organic photovoltaic films, solvothermal synthesis of metal-organic frameworks, *etc.* In addition, *in situ* scanning probe and electron microscopies can provide direct insight into synthetic phenomena with atomic scale resolution [8].

Theory-guided data science has shown great potential for discovery and design in diverse scientific disciplines [9]. A recent example of theory-guided synthesis is shown in Fig. 2(c): *ab initio* modelling has predicted a new metastable allotrope of two-dimensional boron, a.k.a. “borophene”, and suggested a synthetic route via epitaxial deposition on a metal substrate, which was subsequently validated by the experiment [10]. Efficient *in silico* synthesis of new materials requires the availability of data. A need for reliable data makes integration of experiments, computation and theory imperative and machine learning and artificial intelligence methodologies will be needed to fill modelling and data gaps.

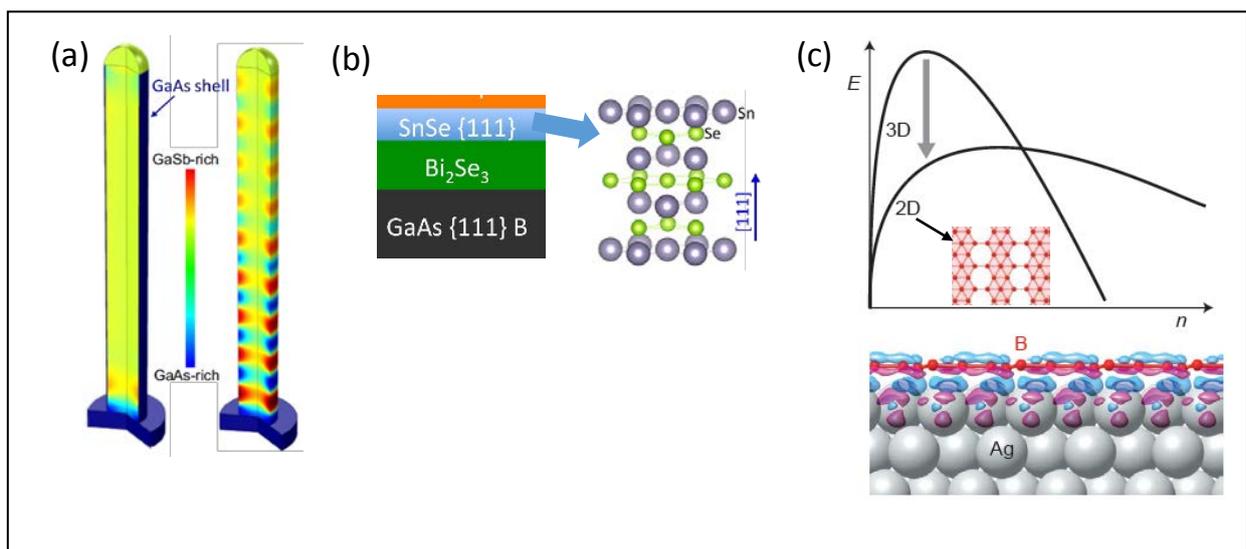


Figure 2. (a) GaAsSb semiconductor nanowire with (left) and without (right) GaAs shell. GaAs shell suppresses GaAsSb phase segregation, while the alloy without shell decomposes into GaSb-rich (red) and GaAs-rich (light blue) alternating segments. [5]; (b) crystal structure of topological insulator SnSe in its metastable rock-salt structure, stabilized by low-temperature molecular beam epitaxy on GaAs substrate [6]. (c) (top) The energies of the growing nuclei versus the number of atoms,  $E(n)$ , show how the substrate steers the synthesis from the 3D towards 2D route by suppressing the nucleation barrier; (bottom) computed charge density shows how the Ag substrate donates electrons (from pink to blue) to the boron layer to stabilize its 2D structure [10].

### Concluding Remarks

Even though the prediction of material synthesizability is an extremely challenging task, advances in modelling, *in situ* measurements and increasing computational power will pave the way for it to become a reality. *In silico* design of advanced materials will have to combine theory guided data science with statistical and theoretical computational methods. However, it is an open question whether it will be possible even with the most advanced modelling and simulation techniques to predict completely unknown pathways for synthesizability. For example, is an additional crystal growth route possible other than those shown in Fig. 1(a)? The development of techniques and tools to propose most efficient synthetic pathways will remain one of the major challenges for predicting new material synthesizability.

### Acknowledgements

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