

developed, such a vision might become a reality. Their use could then further advance applications such as thermoelectrics and wearable electronics. □

Bernard Kippelen 

School of Electrical and Computer Engineering,

Georgia Institute of Technology, Atlanta, Georgia 30332, USA.

e-mail: [kippelen@gatech.edu](mailto:kippelen@gatech.edu)

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## CRYSTAL ENGINEERING

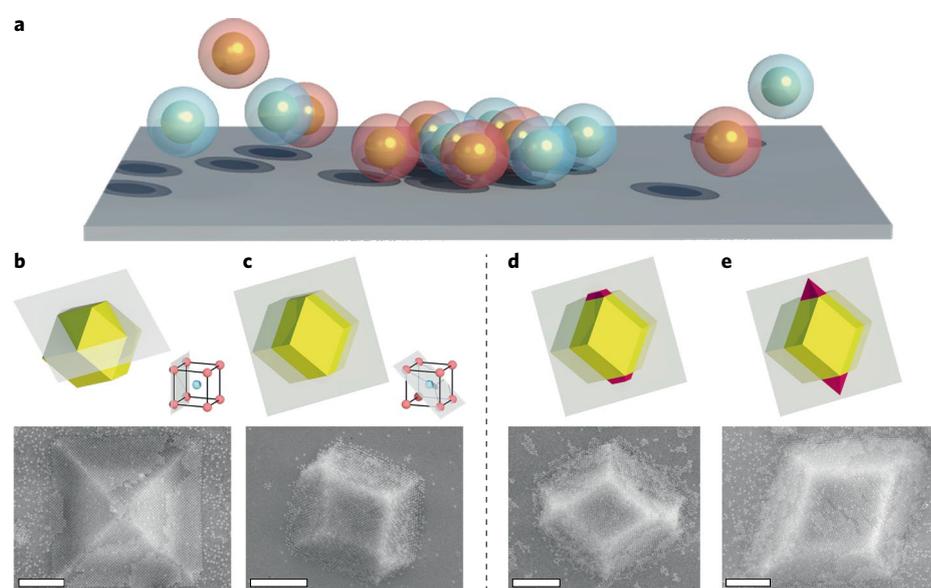
# Interfacial crystallization under DNA control

Programmable DNA hybridization is used to mediate the self-assembly of substrate-bound DNA-grafted gold nanoparticles into single-crystalline Winterbottom and non-Winterbottom constructions with particular size, shape and orientation.

Chang Liu and Qian Chen

In 1929, Linus Pauling published a seminal article<sup>1</sup> that notably advanced our understanding of how a substrate can break the spatial symmetry in crystal growth, and thus introduce complexities in structure and properties at all length scales. Since then, several models on how the shape of atomic crystal grown on a substrate can be controlled have been proposed<sup>2,3</sup>. However, when it comes to crystals formed by nanoparticles — that is, supracrystals — the control over the crystal shape (or habit) grown on substrates remains a fundamental gap. Now, writing in *Nature Materials*, Robert J. Macfarlane and colleagues<sup>4</sup> describe single-crystal Winterbottom shapes of DNA-grafted gold nanoparticles by exploring the programmability of DNA hybridization between the nanoparticles and substrate-bound DNA strands.

It is now universally acknowledged that crystallization is significantly modulated by the substrate on which crystals are being grown. Substrates can take the form of macroscopic container walls or microscopic impurities, and enhance or expedite phenomena such as cloud condensation and ice formation on airplane wings. Substrates can also template the development of a crystal's interior and exterior morphology. For example, the  $\gamma$ -tubulin complexes in the centrosome nucleate helicity in microtubule growth, and in atomic crystal synthesis crystal seeds guide crystal shape formation. Beyond structural effects, substrates can also be active players of crystal assemblies, namely in supported nanocrystal catalysts, where epitaxy on the support surface can provide



**Fig. 1 | Single-crystalline supracrystal shapes of DNA-grafted gold nanoparticles on a solid substrate.** **a–c**, DNA hybridization between nanoparticles and a functionalized substrate containing complementary DNA strands (**a**) enables the formation of single-crystalline Winterbottom constructions in the  $\langle 100 \rangle$  (**b**) and  $\langle 110 \rangle$  (**c**) orientations. **d,e**, Structures deviating from the thermodynamically favourable Winterbottom shapes can also be assembled due to kinetic effects, introduced by modulation of the DNA grafting density of the nanoparticles or the substrate loading with DNA strands. Scale bars, 1  $\mu\text{m}$ . Figure adapted with permission from ref. <sup>4</sup>, Springer Nature Ltd.

electronic coupling with the catalysts, thereby modulating catalytic activity<sup>5</sup>.

The scientific relevance of crystal growth on substrates and extensive industrial focus on thin film growth and substrate-integrated devices have pushed

the maturation of theories on the shape control of atomic crystal grown on a substrate. Here an important concept is the Winterbottom construction<sup>2</sup>. It builds on the even older Wulff construction, which predicts the thermodynamically

stable shape of a free crystal grown in a homogeneous environment by considering the surface energy for different facets of a crystal<sup>6</sup>. In the presence of a substrate, the Winterbottom construction predicts a Wulff shape truncated at a plane by the substrate. Pioneering work by Marks and co-workers validated the Winterbottom construction for atomic crystal catalysts grown on substrates by transmission electron microscopy (TEM)<sup>5</sup>. Besides thermodynamics, kinetic growth mode models such as the Stranski–Krastanov, Frank–van der Merwe, and Volmer–Weber models predict whether atoms deposit on a substrate layer by layer or as islands<sup>7</sup>. These theories coupled with experiments render shape prediction a largely solved puzzle for atomic crystals. However, the same is not true when it comes to nanoparticle supracrystals. These materials, formed by nanoscale ‘artificial atoms’ — nanocrystals that interact non-covalently — have key roles in several applications such as lasing and plasmonic photonic crystals<sup>8</sup>. Despite that, the factors determining the shapes of such crystals when grown on substrates are still not fully understood. The challenges are twofold. Assuming that the supracrystal can arrive at a thermodynamic equilibrium, the Winterbottom rule requires the surface energies of supracrystalline facets as inputs for prediction. These energies have not yet been experimentally measured and thus are typically estimated by a broken-bond model assuming all nanocrystal–nanocrystal contacts are local and equal or by computer simulations. In contrast, atomic crystals have these values well-established. Second, nanoscale building units diffuse orders of magnitude slower than atoms, can encounter high diffusion barriers, and fall into kinetic traps that do not reconcile with Winterbottom predictions<sup>9</sup>.

Macfarlane and co-workers use the high tunability of DNA hybridization and a combination of DNA-grafted nanoparticles, known as programmable atom equivalents (PAEs), and a substrate functionalized by DNA strands<sup>4</sup>, to precisely control the interfacial energies between the crystal and the fluid ( $\gamma_{cf}$ ), the substrate and the

crystal ( $\gamma_{sc}$ ), and the substrate and the fluid ( $\gamma_{sf}$ ), and thus assemble single-crystal Winterbottom shapes of nanoparticles (Fig. 1). Because the PAEs follow the broken-bond model and exhibit Wulff shapes when grown freely in solution, the authors were able to use calibrated facet-dependent surface energies as input for the Winterbottom construction. Kinetic traps are eliminated by thermal annealing via melting of DNA hybridization bonds. As a major demonstration of the precision of this approach, truncated body-centred cubic rhombic dodecahedra along {100} or {110} planes were grown by maximizing the number of DNA bonds between PAEs and the substrate with mono- or bi-functionalization (Fig. 1b, c). Parameters such as the PAE concentration, salt concentration and DNA grafting density were shown to control the supracrystals’ size and degree of anisotropy, all following the thermodynamic Winterbottom rule. Other Winterbottom shapes of face-centred cubic and AIB<sub>2</sub> lattices were also achieved, because the two-dimensional hexagonally close-packed monolayer, a common component of both lattices, can be stabilized by the substrate.

Moreover, the authors further show that kinetic effects can be used to make supracrystal shapes beyond the Winterbottom prediction. For instance, when the DNA grafting density on PAEs is decreased and/or the active linker loading on the substrate is increased, the <110> oriented crystals extend (110) edge facets to form ‘diamond’ shapes (Fig. 1d, e). The formation of these shapes was attributed to surface diffusion of PAEs, suggesting potential crystal engineering routes exploring diffusion-mediated crystal growth. These findings about the influence of kinetic effects in crystallization call for real-space and real-time studies of the crystal growth modes. Low-dose liquid-phase TEM has had recent success in mapping nucleation of supracrystals in a free environment<sup>10</sup>. The liquid chamber windows can serve as the substrate to accommodate grafted DNA or other modalities, on which crystal grows. Similarly, liquid-phase atomic

force microscopy<sup>11</sup>, prevalently on oxides, can be extended to map kinetic events for nanosized building units.

The work of Macfarlane and colleagues also opens opportunities to realize device integrations. For example, nanosized hexagonal boron nitride superlattices on a graphene layer have been shown as a versatile platform to modulate the band structures of graphene without substantial mobility degradation<sup>12</sup>. One can foresee the use of assembled nanoparticle superlattice patterns to achieve a similar goal. The substrate can be varied, such as curved or patterned to have geometric and chemical epitaxy to achieve exotic shapes and property coupling. The experimental realizations can serve as inputs or validations for simulations to guide minimal modelling of nanoscopic crystal growth, and to identify key parameters among the many, such as the morphology and interaction of the building units as well as energetic and mass transport contributions — surface diffusion, defects and strain. □

Chang Liu<sup>1</sup> and Qian Chen<sup>1,2,3,4</sup>✉

<sup>1</sup>Department of Materials Science and Engineering, University of Illinois, Urbana, IL, USA. <sup>2</sup>Materials Research Laboratory, University of Illinois, Urbana, IL, USA. <sup>3</sup>Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL, USA. <sup>4</sup>Department of Chemistry, University of Illinois, Urbana, IL, USA.

✉e-mail: qchen20@illinois.edu

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