

BIOMINERALIZATION

Ion binding and nucleation

The visualization of organic-acid-induced crystal growth by means of liquid-cell transmission electron microscopy can provide key insights into the nucleation of calcium carbonate in an organic matrix.

Roland Kröger

Both organic molecules and amorphous precursor phases play significant roles in the control of biomineralization¹. And both the specific crystallization pathways and the specific combination of materials involved give mineralized biocomposites — such as nacre, bone or limpet teeth — their remarkable mechanical properties^{2–4}. Yet much remains to be revealed about the mechanisms by which acidic organic molecules — such as polysaccharides, proteins or amino acids — affect the composition, microstructure, shape and size of the biominerals. This is mostly because a lack of high-resolution imaging tools in fluid environments has made it difficult to obtain nanometre-level details of the early stages of mineralization, in particular the impact of additives on the nucleation-and-growth dynamics. Writing in *Nature Materials*, de Yoreo and colleagues now demonstrate that liquid-cell transmission electron microscopy (TEM) can be used to examine the role of organic acidic additives (in their case, polystyrene sulphonate, PSS) on the formation of CaCO₃ from aqueous solutions of calcium and carbonate ions⁵.

Transmission electron microscopy has in the past three decades been established as a vital materials-characterization and imaging tool, and has become a core technique for the investigation of the structure of amorphous solids relevant to biological or polymeric systems, as well as of crystalline metal, semiconductor, ceramic and composite materials. This is largely due to the atomic-level resolution of TEM together with the powerful structural information that can be derived from electron diffraction and associated analytical techniques. The recent development of liquid-cell TEM holders has pushed the capabilities of this technique further by providing access to the early stages of particle and crystal formation in a wide range of material systems, from nanoparticles to bioinspired composites. Liquid-cell TEM uses thin membranes of either silicon nitride or graphene^{6,7} to separate the fluid from the ultrahigh vacuum in the microscope so as to prevent electron scattering (which would otherwise deteriorate resolution power). Also, it is possible to modify the composition and flow of the liquid phase by mixing fluids

of different composition while performing microscopy. The electron beam passes through membranes and fluid, allowing the study of materials and processes at the membrane/fluid interface (Fig. 1a). In fact, liquid-cell TEM is exclusively employed to probe materials attached to the membrane/fluid interface because direct high-resolution imaging of nanoparticles that are not immobilized by the membrane and undergo Brownian motion is virtually impossible⁸ (this typically occurs for nanoparticles smaller than 10 nm).

De Yoreo and co-authors find that hydrated, Ca-rich Ca–PSS globular complexes form in an aqueous solution containing PSS and Ca ions (in fact, it is known that Ca ions bind to carboxyl groups in organic acids), and that the globules act as preferred nucleation sites for amorphous calcium carbonate after a carbonate-rich solution is added. The authors discuss these findings in conjunction with results obtained using complementary techniques such as Fourier transform infrared spectroscopy, atomic force microscopy and isothermal titration, and conclude that the PSS-stabilized amorphous calcium carbonate tends to lead to the formation of nanocrystals of vaterite (Fig. 1b), the least stable CaCO₃ polymorph. Importantly, the authors also

suggest that the binding of Ca ions to PSS reduces the dependence of vaterite nucleation on kinetic barriers. This contrasts with their previous observations, obtained by using atomic force microscopy and optical microscopy, of barrier-dependent calcite nucleation with different negatively charged additives (alkylthiol and polysaccharides). De Yoreo and colleagues attribute the discrepancy to the lower Ca–PSS binding energy when compared with that between the ions and other acidic organic additives. It would, however, be interesting to investigate whether other additives would also result in calcite formation when observed by liquid-cell TEM.

De Yoreo and collaborators' liquid-cell TEM data and electron-diffraction patterns of vaterite nanocrystals are impressive, particularly in light of the difficulties in avoiding strong scattering of electrons by the surrounding fluid. When using liquid-cell TEM, care also needs to be taken to prevent any effects of the electron flux on crystal nucleation and growth. The researchers worked with plane-wave illumination at an operation voltage of 200 kV, and refer to electron doses of 50–300 e Å⁻² (low-dose conditions are generally identified to lie in the range of 1–10 e Å⁻²; refs 9,10). In general,

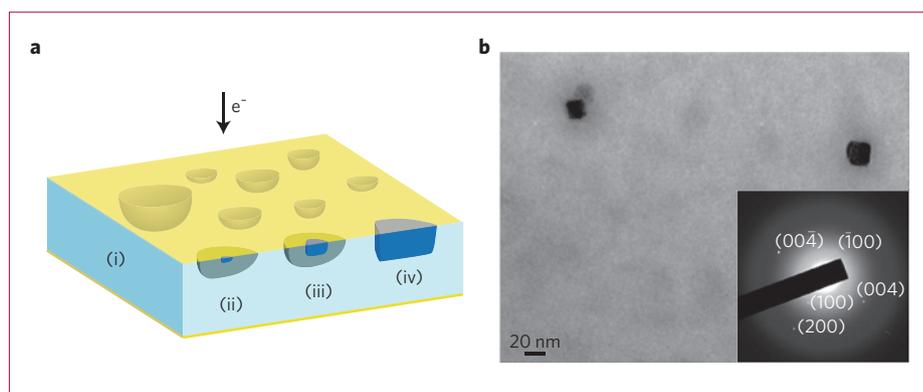


Figure 1 | Calcium carbonate nucleation and growth in the presence of polystyrene sulphonate (PSS). **a**, Schematic of the sample in a liquid-cell TEM (silicon nitride membrane, yellow; liquid, blue). The formation of Ca–PSS globular complexes at the liquid/membrane interface and the depletion of Ca ions outside the globules (i) leads to the nucleation of vaterite nanoparticles inside the complexes after CO₃²⁻ is added (ii), to continued nanoparticle growth (iii), and to the formation of vaterite nanocrystals (iv). The arrow indicates the direction of the electron flux. **b**, Bright-field TEM image and diffraction pattern (inset) of vaterite nanocrystals. Panel **b** reproduced from ref. 5, Nature Publishing Group.

liquid-cell TEM imaging with electron doses of several hundred $e\text{\AA}^{-2}$ is associated with a significant level of electron–sample interaction (which can be minimized for example, by using scanning TEM¹¹), and crystal nucleation can be triggered by extremely low electron doses, making the study of the relevant interaction mechanisms difficult¹². Such considerations thus require further study. In any case, it is clear that liquid-cell TEM has great potential for studying the dynamics of crystallization, as showcased by de Yoreo and colleagues’

work, and more widely for performing wet-chemistry experiments within the microscope. □

Roland Kröger is in the Department of Physics, The University of York, Heslington, York YO10 5DD, UK. e-mail: roland.kroger@york.ac.uk

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NANOLASERS

Lasing from 2D atomic crystals

The coupling of monolayer tungsten diselenide and a photonic-crystal cavity leads to ultralow-threshold lasing.

Vinod Menon

Nanolasers offer the possibility of reaching the quantum limit of a single emitter, and are essential for reducing power consumption in optical interconnects, high-resolution imaging and sensing. As the physics governing the operation of lasers — in essence, stimulated emission by a two-level system — became established, research shifted to their technological characteristics: emission at different frequencies, exploitation of different materials, and reduction of their size. Now, Xiaodong Xu, Arka Majumdar and co-workers report in *Nature* that lasing can arise from a monolayer of tungsten diselenide (WSe_2) — a two-dimensional (2D) semiconductor — when coupled to an underlying photonic-crystal cavity¹. The

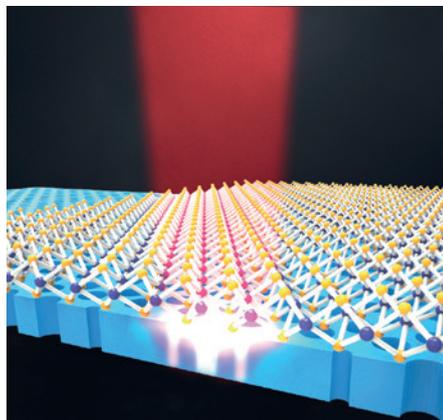


Figure 1 | Schematic of a 2D semiconductor nanolaser, consisting of a monolayer of WSe_2 on top of a photonic crystal. Image courtesy of Tal Galfsky.

researchers achieve continuous-wave lasing under optical pumping with a very low threshold of 27 nW at 130 K.

Among 2D atomic crystals, monolayers of transition metal dichalcogenides have emerged as the most attractive candidates for photonic and optoelectronic applications. Transition metal dichalcogenides exhibit bandgaps ranging from the visible to near-infrared frequencies, and the crystals’ interaction with light can be controlled when they are incorporated into photonic structures such as microcavities. This can lead to enhanced spontaneous emission^{2–4}, strong coupling and the formation of exciton polaritons⁵.

By using a polymer-transfer process, Xu and co-authors placed a mechanically exfoliated monolayer of WSe_2 — which plays the role of the gain medium — on top of a GaP photonic-crystal cavity, where light is localized (Fig. 1). The photonic crystal was made from GaP because of its high refractive index and transparency to the emission wavelength of WSe_2 . Although contrary to conventional laser designs, placing the gain medium outside the cavity is feasible because the atomically thin WSe_2 crystal is confined within 1 nm of the surface of the photonic-crystal cavity. Hence, the crystal still has considerable overlap with the optical field. Such an architecture opens up the possibility of placing gain medium at desired locations after the fabrication of the photonic crystal or even larger photonic circuits. Additionally, this approach also alleviates restrictions imposed by traditional semiconductor-fabrication technologies, such as surface

recombination arising from the etching of the embedded gain medium.

In contrast to previous attempts with monolayer semiconductors, Xu and colleagues used cavities with a high quality factor, which ensures that photons will stay within the cavity long enough and interact with the 2D gain medium. In their devices, lasing is manifested by a distinct nonlinear threshold (a ‘kink’; Fig. 2) in the light output at an incident pump power of 27 nW, accompanied by a collapse of the spectral linewidth (Fig. 2). These signatures are indicative of a phase transition from spontaneous to stimulated emission occurring in the device. The ratio

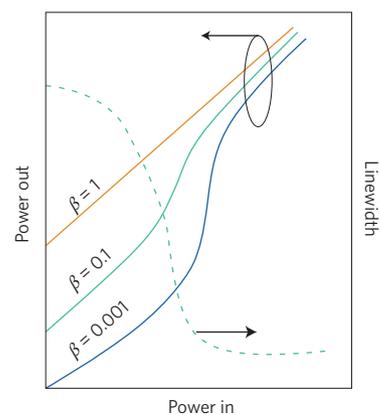


Figure 2 | Characteristics of a 2D semiconductor nanolaser. The dependence of power-out versus power-in for different β values shows the appearance of a nonlinear ‘kink’ along with the collapse in linewidth (as seen by Xu and colleagues).