Molecular J-aggregates provide a classic example of GOST; indeed, it is their exceptionally sharp absorption spectrum and absorption strength that cemented these somewhat complex structures as premium dyes for photographic media. It has been found that their radiative lifetime is short, and exhibits a characteristic temperature dependence[10]. As in the case of nanoplatelets, that unusual temperature dependence is related to the structures' dimensionality. The nanoplatelets are formed by the aggregation of magic-sized nanocrystals. Is that a clue to the physical origin of the GOST? Can dielectric screening be defeated by coherent superpositions of excitation throughout an array of intimately connected nanocrystals? Such coupling of nanocrystals might also provide a way to reverse the ordering of bright and dark exciton states, which is hinted at by the observation that photoluminescence decay time decreases with temperature. Mirafzal and Kelley proposed such a bright–dark exciton reversal for coupled gallium selenide nanoparticle aggregates[11]. The essential idea is that if long-range exchange from the coupling between nanoparticles is larger than the exchange interaction, then the bright state can lie below the dark state. Long-range exchange is the same kind of electronic coupling that gives molecular exciton splitting or promotes Förster energy transfer. It can have a magnitude of a few tens of millielectron volts (meV). The exchange interaction is half the singlet–triplet splitting in molecules and has a value of a few meV in nanocrystals. Reversal of the bright–dark splitting would have substantial consequences for the photoluminescence properties and it may well be at play in the nanoplatelets. As one example, a key difference between poly(phenylenevinylene)-based conjugated polymers, which are excellent fluorophores, and non-fluorescent polyenes is the ordering of their lowest, bright and dark singlet excited states.

Size and shape are well recognized ways to tune the optical properties of nanoscale excitons. However, evidently, there is a richer variety of tuning knobs for adjustment of optical properties connected to the dimensionality, structure and organization of the building blocks. ❐

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THIN FILMS

Folded in hierarchy

Elastic thin films attached to a foundation under compression develop wrinkles, which in turn can generate invaginated folds. Hierarchical patterns of localized folds have now been observed in thin films under biaxial compression, which show intriguing resemblance to fracture patterns in drying pastes and to venation networks in leaves.

Pedro M. Reis

Wrinkles in ageing skin, drying fruit and wetted fingertips have a common origin: they emerge as a result of the compression of a stiff thin film (the skin of the fingers and fruits) that is attached to a soft foundation (the subcutaneous tissue and the fruits' pulp). Wrinkles are realizations of buckling — a mechanical instability whereby, above a critical applied load, a flat film develops out-of-plane undulations — and are ubiquitous in biological systems (for instance, the inner arterial walls[1] and the lipid monolayers in lung surfactant[2]) and in man-made structures (such as road pavements, sandwich panels[3] and stretchable electronics[4]). Undulations of wrinkles are typically regular, yet with increasing compressive stress they become spatially heterogeneous, eventually evolving into sharp, localized folds (that is, invaginations into the foundation). Such a wrinkle-to-fold transition, as well as the onset and morphology of the resulting two-dimensional wrinkling patterns[5], have been studied primarily in conditions of uniaxial compression[2] (on elastic, or Winkler, foundations in structural mechanics, for example), and thus little is known about how these evolve into spatially extended networks of sharp, localized folds. Writing in *Nature Materials,* Kim, Abkarian and Stone[6] report that repetitive and successive wrinkle-to-fold transitions in a thin film under biaxial compression result in hierarchical patterns of localized folds, and provide insights into their nucleation and evolution.

Kim *et al.* used a film consisting of a stiff, thin polymer crust floating on a viscoelastic foundation (Fig. 1a). When irradiated with plasma, the crust expands isotropically, and the resulting confinement-induced equibiaxial compression leads to the development of a regular wrinkling field (Fig. 1b). Under further compression the field of wrinkles evolves into a complex reticulated network of sharp folds (Fig. 1c–e). The authors found that the patterns in the network of folds are hierarchical: consecutive generations of small-scale structures form progressively under increased compression, creating increasingly smaller domains (see supplementary movies in ref. 6).They also systematically studied the evolution and morphology of the patterns, and related the observed disclinations in the precursor wrinkling field to the nucleation and growth of networks of localized folds. Another interesting aspect of the study is that folds are found to communicate and affect each other through the interstitial inhomogeneous field of wrinkles in a manner that is non-local and that affects the propagation mode. In fact, the authors show that by varying the initial and boundary conditions, one can have some control of the morphology of the final patterns. This interplay between geometry and the networks of localized folds could offer opportunities for the rational design of folded structures.

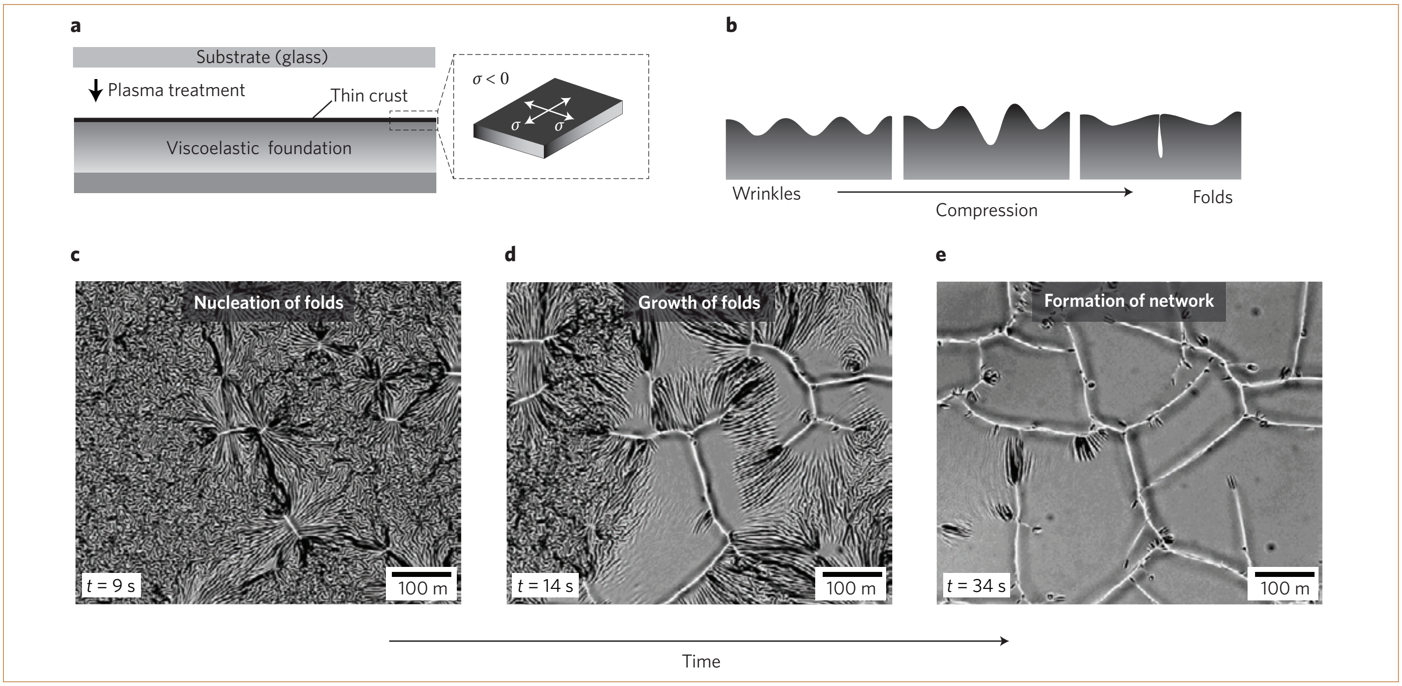

Figure 1 | Hierarchical folding of a thin film. **a**, Scheme of the crust-foundation system used by Kim and colleagues[6]. Plasma irradiation of the thin polymer crust floating on a viscoelastic foundation induces expansion, and therefore equibiaxal compressive stress (σ), of the film. **b**–**e**, On continuous irradiation and therefore increasing compression of the crust, a field of wrinkles first develops (**b**), from which localized folds start to nucleate (**c**) and grow (**d**), leading to a hierarchical network of localized folds (**e**).

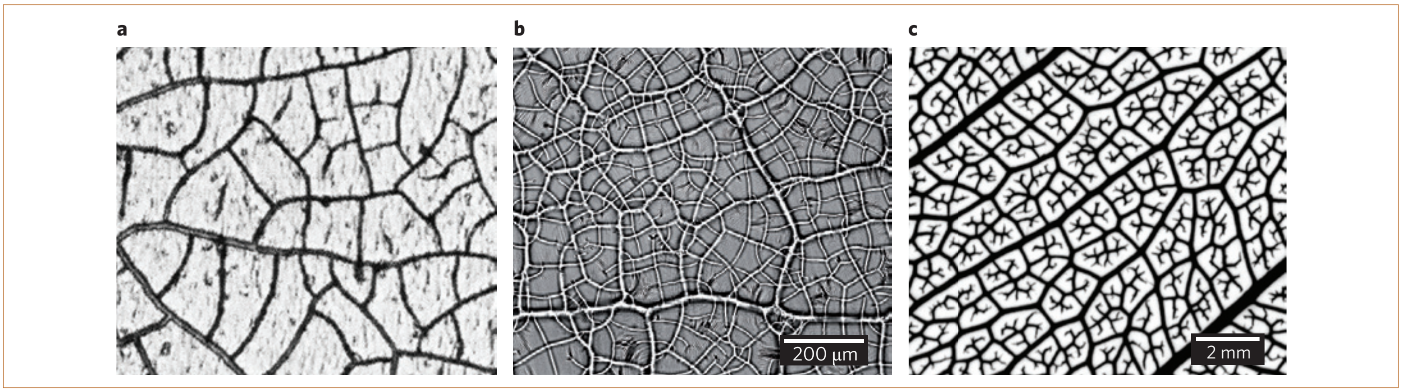

Figure 2 | Hierarchical patterns of **a**, fractures in drying pastes (typical spacing of 80 μm between cracks)[11,13], **b**, localized folds in the thin films of Kim *et al.*[6] and **c**, veins in the mature dicotyledon leaf[11] exhibit remarkable resemblance. Panel **a** reproduced with permission from ref. 11, © 2002 Springer.

Localized folds look similar to creases, yet they are not to be confused. Creases are points of discontinuity or cusps on the surface of compressed soft solids that do not have a thin film bound to its surface. For the formation of a crease, the surface undergoes a discontinuous transition from a flat to a sharp surface cusp, bypassing the wrinkled state[7]. Therefore, the mechanics of localized folds and creases is remarkably different; for instance, whereas wrinkles and folds are stable and robust[2], creases are highly sensitive to surface defects and perturbations[8].

Folds and creases are examples of a wider class of problems that involve spontaneous localization through the focusing of energy and stress, for which singularities in crumpled thin sheets[9] have become the canonical example. Owing to the challenges imposed by the strong geometric nonlinearities involved, developing predictive understanding of stress-focusing in systems far from the wrinkling threshold is a formidable challenge that will require combined efforts in the fields of continuum and structural mechanics, nonlinear physics and pattern formation. The intriguing hierarchical patterns of networked folds reported by Kim *et al.* are bound to generate a spark of interest in the development of predictive analytical and numerical frameworks for stress localization under biaxial compression. Also, the authors' fundamental insight into localized surface modes of deformation resulting from surface instabilities is relevant to applications. For instance, the emergence of localized deformation in surface films under compression can lead to damage and functional failure in stretchable electronics, microfluidic devices and anti-fouling coatings on ship hulls.

Moreover, a better understanding of localization patterns under biaxial compression may provide insight into the formation of some biological patterns. For example, folding processes are intrinsic to morphogenesis in the early development of the embryo[10]. Also, another study has hypothesized that venation networks in leaves may reflect a coupling between the underlying stress field and other biochemical and gene expression processes[11]. This is in tune with recent findings that mechanical stress can influence the differentiation of mammalian cells[12] (yet there is no such evidence for plant cells). More generally, the striking resemblance of the hierarchical network of localized folds[6] (Fig. 2b), the fracture patterns in drying pastes[13] (Fig. 2a) and the venation networks in leaves (Fig. 2c), raises the possibility that there may be a universal class of localization patterns under biaxial stress (compression or tension). In this regard, the hierarchical folding patterns and the ingenious and elegant experimental system reported[6] by Kim *et al.* are truly motivating. ❒

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Correction

In the News & Views 'Electron microscopy: The challenges of graphene' (*Nature Mater.* **10**, 165–166; 2011), the sentence introducing reference 4 was potentially misleading, and should have read: 'The structure of graphene has only recently been imaged with atomic resolution. A textbook example is the work by Jinsheck *et al.*[4], in which the authors employed the wavefunction reconstruction technique in an aberration-corrected, state-of-the art instrument (see Fig. 1).' This has now been amended in the HTML and PDF versions, after print: 23 November 2011.

MATERIAL WITNESS

A LIGHT COMPASS?

The idea that the Vikings navigated across the Atlantic using birefringent Iceland spar (calcite) to locate the Sun's position on cloudy days is surely one of the most ingenious and captivating recent hypotheses about ancient materials use. The suggestion itself is an old one[1], but has been given strong support in new experiments by Ropars and colleagues[2].

The claim, which has understandably enjoyed much media interest, has a lot going for it. References in Viking sagas to a 'sunstone' used in seafaring sound akin to magic, but there is now a good physical basis for thinking that Iceland spar — abundant in the Viking homelands, as the name implies — might be used in this way with sufficient accuracy.

A narrow beam of polarized light passing into the mineral is split into two by the optical anisotropy that causes birefringence. The 'ordinary' beam behaves as it would in glass; the 'extraordinary' beam is parallel but displaced from it, defying Snell's law. Light passing through a hole in a screen over a calcite crystal therefore forms two images on the far side. When the crystal is oriented to equalize their brightness, it completely depolarizes the light.

Sunlight acquires a slight polarization as it is scattered by the atmosphere. The researchers demonstrate how, with calibration on a clear day, the depolarization point at which the split images are equally bright could be used to locate the Sun when it is obscured by cloud, from the light arriving from a patch of blue sky. They have constructed a wooden device containing a calcite crystal that could have been used by Viking sailors to pinpoint the Sun even at twilight.

They say that this proposal is made all the more plausible by the recovery of a piece of Iceland spar from an Elizabethan ship wrecked off the coast of the Channel Island of Alderney in 1592[3]. It may have been carried as an alternative to the compass, they say, which was vulnerable to disturbance from the iron cannons.

The idea that birefringence of Iceland spar might have been used by navigators from the Dark Ages until at least Elizabethan times is, however, problematic. It is hard to see how this would have been common practice without it ever having been recorded or coming to the attention of natural philosophers. It is just the kind of trick Giambattista della Porta, a specialist in optics who conceived of the telescope before its invention, would have revelled in discussing in his

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1558 book *Natural Magic*, had it been known. When Rasmus Bartholin wrote the first experimental account of birefringence in Iceland spar in 1669, he made no mention of such uses; neither did the eminently practical Christiaan Huygens when he offered the first explanation of birefringence 21 years later.

This is not to say that the hypothesis of Ropars *et al.* is wrong. Rather, it underscores the need for studies of historical materials usage to integrate the scientific arguments with careful consideration of historical sources and context. ❒

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