

SEMICONDUCTOR NANOSTRUCTURES

Two dimensions are brighter

The synthesis of a family of plate-like semiconductor nanocrystals yields solutions of small quantum wells with excellent optical properties.

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When it comes to the optical properties of semiconductors, smaller is often bigger. For example, semiconductors are brighter emitters of light when they are fabricated to be only tens to hundreds of atoms thick in one or more dimensions. Two-dimensional materials of this type, called quantum wells, make excellent lasers. Brightness requires two factors: strong absorption of energy in the form of light resulting in the creation of electron–hole pairs, or excitons, and efficient conversion of the exciton energy to emitted light (photoluminescence). These factors are optimized by first forcing the absorption strength into one electronic state, rather than spreading it over a band as in a bulk semiconductor, and second, by preventing the absorbed energy — the exciton — from dissociating into charge carriers or heat before it has a chance to radiate photoluminescence. Therefore, dimensionality and time are of the essence.

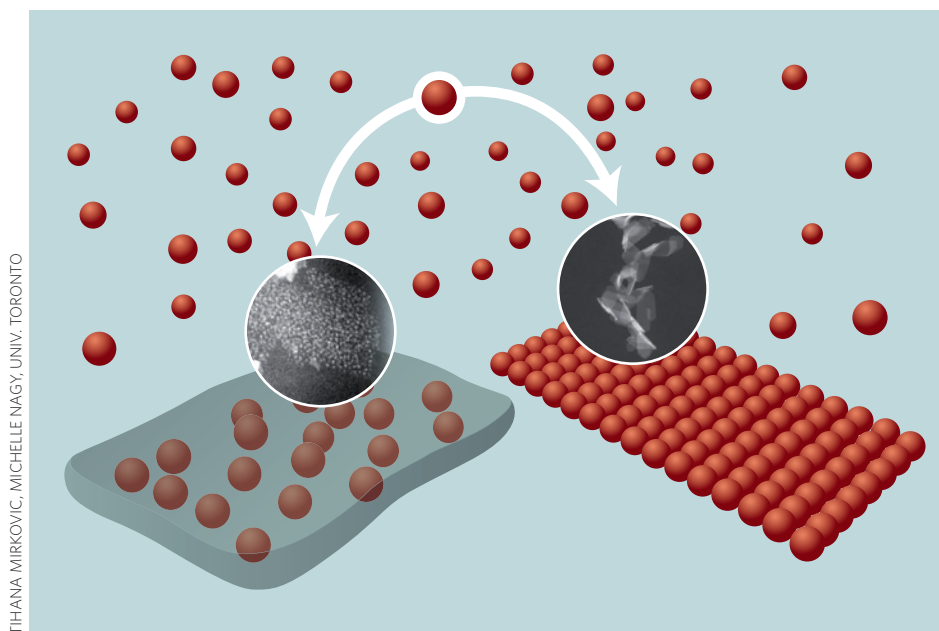
It was thought that zero-dimensional semiconductors called quantum dots were optimal bright emitters. However, writing in *Nature Materials*, Ithurria and colleagues now report¹ that nanoplatelets reminiscent of quantum wells are potentially better emitters because more atoms are recruited to capture and radiate light coherently.

Nanoplatelets of semiconductors such as cadmium selenide are formed in solution by an unusual process whereby seed nanocrystals aggregate into rafts that eventually fuse into a two-dimensional sheet^{2,3} (Fig. 1). The seed nanocrystals are known as ‘magic-sized’ clusters because they are monodisperse⁴ — in marked contrast to typical nanocrystalline colloids where the size dispersion hides details of electronic transitions from spectroscopists. Key advances reported by Ithurria *et al.*¹ include, first, a compelling assignment of the electronic transitions — that is, the exciton energies. That theoretical model also helped

confirm that the nanoplatelets are atomically flat and their thickness determines the photoluminescence energy. Second, the characterization of the surprisingly short photoluminescence lifetime leads to the conclusion that these nanoplatelets possess giant light-absorbing power.

The high propensity to absorb, and emit light — termed giant oscillator strength (GOST) — is related to the interaction between electrons and light in matter. Light is absorbed or emitted because electrons oscillate in resonance with the electric field of light. The strength of the electronic transition accompanying that resonance, called oscillator strength, depends on how far an electron is driven coherently backwards and forwards. In low dielectric systems the coherence can be long-range, leading to a phenomenon called superradiance⁵. In that case, many small oscillations are coordinated in step by electronic interactions among molecules or atoms. In semiconductors, the limitation to the size of the dipole transition moment is screening by the many other electrons in the system. Structures that overcome scaling laws dictated by screening have a GOST. By monitoring how rapidly photoluminescence radiated from the nanoplatelets compared with the photoluminescence lifetime of quantum dots, Ithurria *et al.*¹ showed that nanoplatelets are exceptional emitters.

Properties found in one nanoscale system often have analogues in other systems, as well as in molecules⁶. Some perspective on GOST and nanoplatelets can therefore be gained by realizing that many small molecules with exceptional brightness have been prepared. Dyes based on the boron dipyrromethene (BODIPY) motif are a spectacular example⁷, especially considering their small size. On the nanoscale, semiconductor carbon nanotubes also have picosecond radiative lifetimes⁸, although their fluorescence properties are complicated by dark states lying below the light-absorbing excitons. Similarly, it is the small energy gap between bright and dark exciton states in cadmium selenide nanocrystals that strongly influences their photoluminescence process⁹ as a function of temperature.



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Figure 1 | Aggregation of magic-sized cadmium selenide nanocrystals. Self-assembly of semiconductor nanocrystals in solution can lead to atomically flat nanoplatelets (right), as described by Ithurria and colleagues¹. We have also observed the formation of less ordered, ‘loose’ aggregate architectures that are supported by an organic matrix of ligand molecules (left). The insets show representative transmission electron microscopy images.

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 dependence¹⁰. 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 aggregates¹¹. 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.

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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 walls¹ and the lipid monolayers in lung surfactant²) and in man-made structures (such as road pavements, sandwich panels³ and stretchable electronics⁴). 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 patterns⁵, have been studied primarily in conditions of uniaxial compression² (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 Stone⁶ 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.