

Spontaneous Superalignment of Nanotubes in a Dilute Solution

A new concept produces highly ordered nanotubes with controllable separations in a dilute and spacer-free system via the synergistic effects of the solvation and the rotational constraints.

One application of interest in the precisely controlled self-assembly of ordered nanomaterials is its full potential in nanolithography technology.¹ In general, ordered colloidal arrays can be easier to produce either with repulsive colloids at large concentrations (e.g., 68 vol% for a body-centered cubic system) or on introducing spacer molecules for attractive colloids at moderate concentrations. Here, the spacer molecules (e.g., surfactants or acids or polymers) play a critical role in preventing coagulation, suppressing Brownian motion and organizing nano-objects to form an ordered structure. How to achieve highly ordered superstructures or colloidal crystals in a dilute solution without spacer molecules is, however, a great challenge.

Chi-Chung Hua (National Chung Cheng University) and his co-workers hypothesized that preserving the inter-particle repulsion while also suppressing the Brownian motion of particles is the key to achieve ordered colloidal crystals in dilute and spacer-free solutions.² As shown in **Fig. 1(a)**, the agglomeration can be avoided with effective solvation effects, which leads to the stabilization of the nanoparticles in the solution, but forming an ordered phase in the dilute solution cannot be achieved by the solvation effects alone. It is conceivable that, because of the small density of the particles (corresponding to a "gas"), the particles can move freely according to Brownian diffusion; the entropy favors a disordered state. To overcome this limitation, they had an excellent idea to diminish the degrees of freedom of the particle motion, *i.e.*, the additional rotational constraints through the asymmetric shape of objects, as shown in **Fig. 1(b)**. For nanotubes with effective solvation, a loss of solvation shell when adjacent tubes become too near can introduce inter-tubular repulsive forces, constrain the rotational motion of the nanotubes and subsequently lead to an ordered colloidal phase.

Hua's group used a simple system comprising only highly hydrophilic aluminosilicate nanotubes (AlSiNT, also known as synthetic imogolite) and water, with no spacer molecule nor external force, to demonstrate their idea. At this point, small-angle X-ray scattering (SAXS) at **TLS 23A1** provides a powerful tool to study the self-assembly

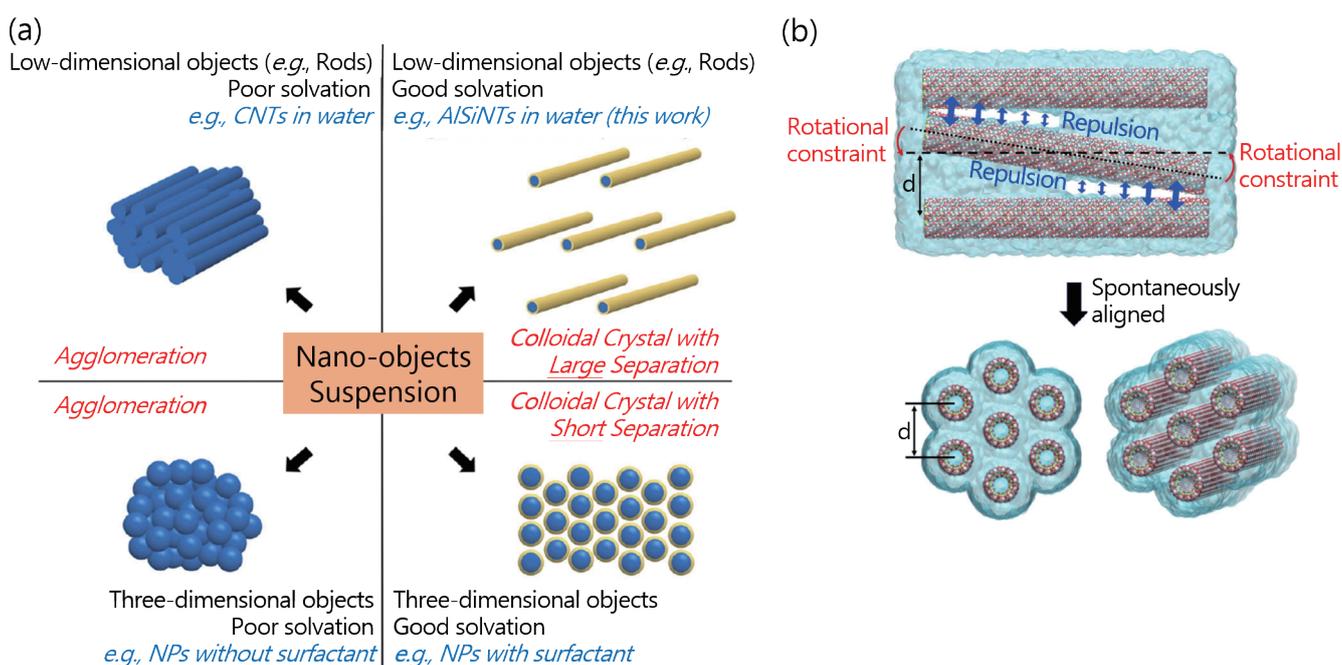


Fig. 1: (a) Illustration of possible solution phases for nano-object suspensions via varied solvation degree and dimensionality of the objects. (b) Schematic of spontaneously ordered nanotubes via synergistic solvation effects and rotational constraints. [Reproduced from Ref. 2]

bly of ordered nanomaterials. As shown in **Fig. 2(a)**, the SAXS data reveal the formation of highly ordered hexagonal packing in a dilute aqueous solution of AlSiNT (1.0 wt%). The tube diameter of AlSiNT is about 2 nm; the inter-tubular distance of the hexagonal structure is ~ 20 nm. The scattering structure factors, as shown in **Fig. 2(b)**, demonstrate that such an inter-tubular distance of the hexagonal structure is tunable *via* control of the concentration and the length of the nanotubes. The stature of all four Bragg signals decreases with decreasing concentrations and disappears abruptly below concentration 0.85 wt%, indicating a sharp transition from the hexagonal structure to the nematic phase (**Fig. 2(b) inset**). There is hence a critical inter-tubular distance associated with the geometry of the nanotubes. Moreover, the group used a cryo-TEM to visualize directly the ordered phase and undertook a simulation of the molecular dynamics (all-atom MD and coarse-grained MD) to achieve an atomistic understanding.

In conclusion, Hua's group proposed that constraining the rotational motion of low-dimensional

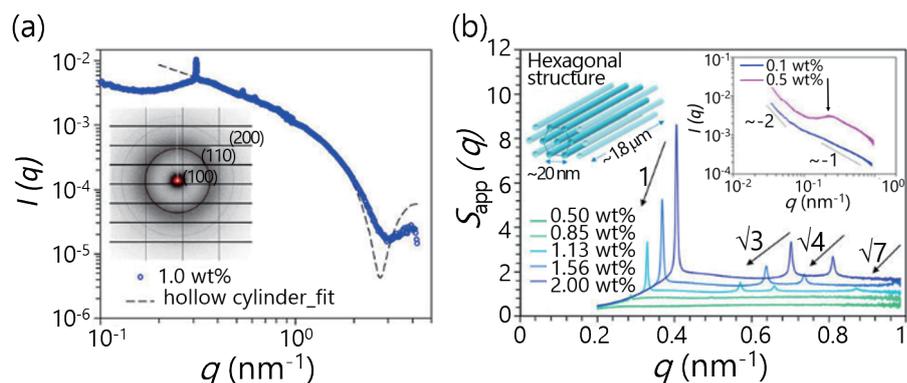


Fig. 2: (a) SAXS scattering data of an AlSiNT solution (1.0 wt%). The sharp features correspond to nanotubes in a hexagonal packing. (b) Structure factors of various tube concentrations show a tunable inter-tubular distance. The inset shows small concentrations that produce only either a nematic phase (0.5 wt%) or a disordered network (0.1 wt%). [Reproduced from Ref. 2]

nanotubes utilizing solvation-induced repulsive forces can achieve a spontaneously well-aligned colloidal superstructure with tunable inter-tubular distances in dilute and spacer-free solutions. They produced a novel method to manipulate an ordered superstructure and to challenge the existing 5-nm node lithography and nanorobotics. (Reported by Che-Min Chou, National Taiwan University)

This report features the work of Chi-Chung Hua and his co-workers published in Phys. Rev. Lett. 123, 238002 (2019).

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- SAXS
- Materials Science, Self-assembling Nanotubes

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High Performance of Organic Solar Cells Based on Matching Donor-Acceptor Pairs

A fluorinated heptacyclic dithienocyclopentacarbazole non-fullerene acceptor was synthesized to be blended with donor polymers with complementary absorption and energy levels well matched. Control of molecular orientation in donor/acceptor solar cells exhibited higher power-conversion efficiencies.

Solution-processable organic solar cells (OSC) with a treatment of bulk heterojunctions can achieve large power-conversion efficiencies (PCE) and resolve an increasing demand for renewable energy. Being a function of open-circuit voltage (V_{oc}), short-circuit

current (J_{sc}), and fill factor (FF), PCE values above 11% were obtained on utilizing fullerene derivatives (e.g., PC₆₁BM and PC₇₁BM) as electron acceptors owing to their superior electron mobility and isotropic charge transport, when paired with *p*-type polymers featur-