Dynamic Self-Assembly of Nanocomposite Ring Structures

- a Cooperative Interplay of Thermodynamics and Energy-dissipation

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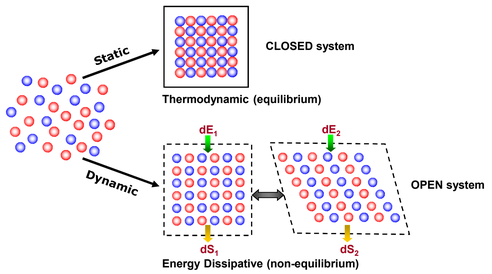
SAND2007-8137P

INTRODUCTION

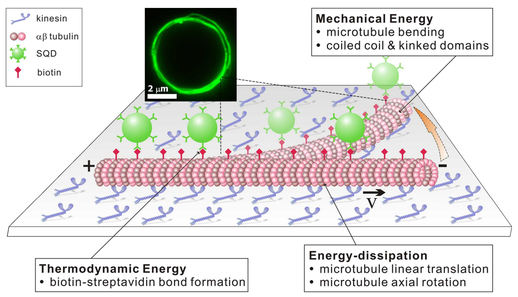
The most significant quality of an open system is that it can perform work in order to continuously renew itself and to avoid a transition into thermodynamic equilibrium. Orders of a dissipative structure in an open system can be maintained only in a non-equilibrium condition, which needs continuous exchange of energy, matter or entropy with the environment.



Thermodynamic relaxation can generate complex nanostructured materials via self-assembly when reaching equilibrium; these structures, however, are ultimately limited by chemical equilibria and diffusional transport processes. Conversely, biological systems (open systems) use a concerted combination of energy-dissipating and thermodynamic processes to remove these functional limitations, and generate structured materials with a wide range of complex, adaptive, or emergent behaviors.

Here we describe a unique biomimetic self-assembly scheme, in which the dynamic and cooperative interaction of energy-dissipation (biomolecular transport) and thermodynamics (non-covalent bond formation) drive the formation of nanocomposite ring structures.

• Experimental Scheme

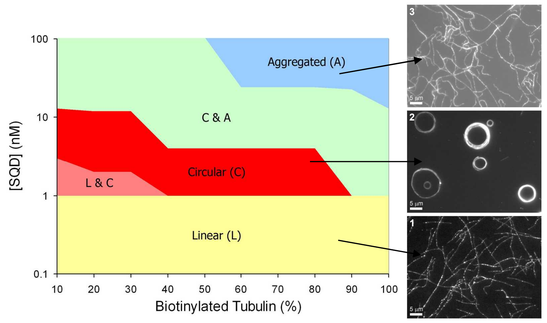


- Surface-adhered kinesin motors translate biotinylated microtubule filaments laden with streptavidin-coated quantum dots (SQDs), across a surface.
- The kinesin motors dissipate the energy produced by ATP hydrolysis, which is coupled to the linear translation and axial rotation of microtubules.
- Thermodynamic energy comes from the formation of biotin-streptavidin non-covalent bonds between SQDs and microtubules.
- Mechanical energy is stored in the bending of the microtubules, as well as the formation of coiled coil and kinked domains.

This model system demonstrate a dynamic self-assembly process in which energy dissipation, thermodynamics, and mechanical strain energy drive the formation of non-equilibrium nanocomposites.

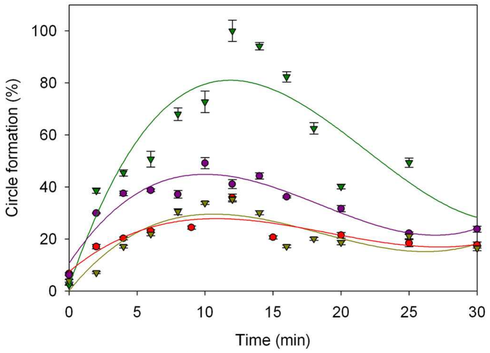
EXPERIMENTS and RESULTS

• Phase diagram of nanocomposite assembly



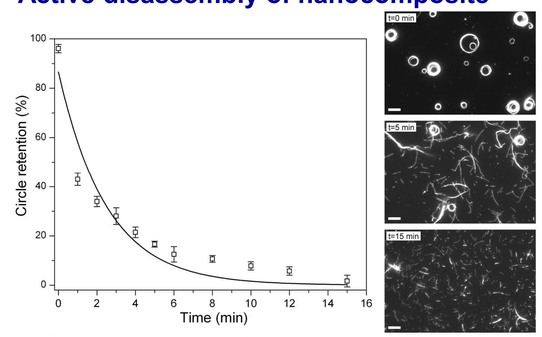
- Three distinct structures are assembled upon introduction of SQDs: (1) mobile linear, (2) rotating circular, and (3) immobile aggregate.
- Because the dissipative energy remained virtually constant throughout the whole process, the formation of different structures is controlled by the level of thermodynamic input.
- The circular nanocomposites are formed only in a delicately balanced regime in which energy-dissipation and thermodynamics interact cooperatively.

• Kinetics of nanocomposite assembly



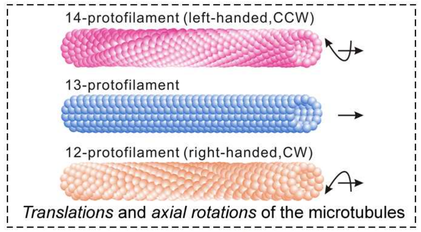
- A nonlinear cyclic assembly/disassembly process.
- The process follows a cubic polynomial curve, and is dependent on the level of biotinylated tubulin: 20%(●), R^2=0.76, P<0.03; 50%(●), R^2=0.89, P<0.01; 70%(▼), R^2=0.80, P<0.01; 90%(▼), R^2=0.79, P<0.01.
- The size of the rings (n = 86 ring structures) range between 2.5 μm and 11 μm, with an average inner and outer diameter of 3.4 ± 0.2 μm and 5.2 ± 0.2 μm, respectively.

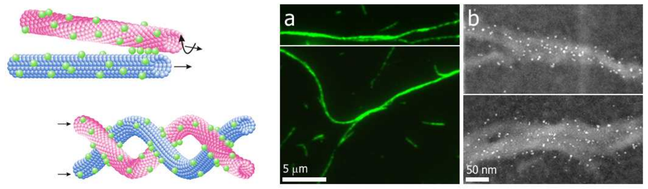
• Active disassembly of nanocomposite



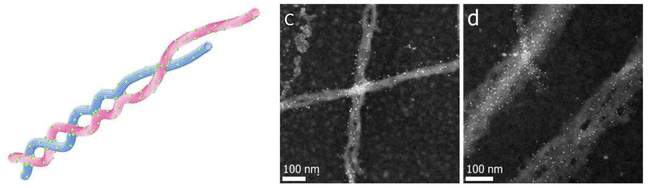
- Addition of excess biotin to rotating circular nanocomposites reduces the thermodynamic input (i.e., reduced the number of biotin-streptavidin bonds holding the composite together), and induces the disassembly of the composites.
- The disassembly follows an exponential rate, reaching complete disassembly within 15 min.
- Excess biotin alone, however, is not sufficient to drive disassembly. The circular structure maintains when excess biotin is added to AMP-PNP immobilized circles, demonstrating the necessity of the energy-dissipating component in disassembly process.

• Evolution of circular composite assembly

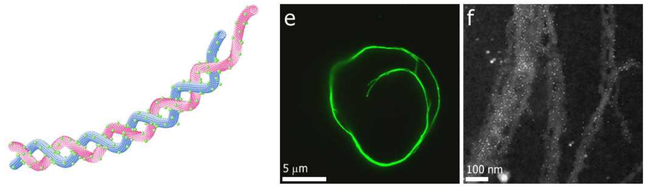




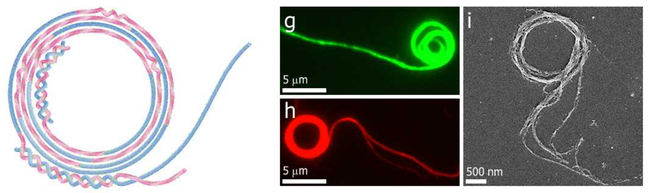
i. **Formation of oligomeric structures** is due to the "gluing" effect (thermodynamic interaction). The oligomers continue to be transported and rotated (energy dissipation).



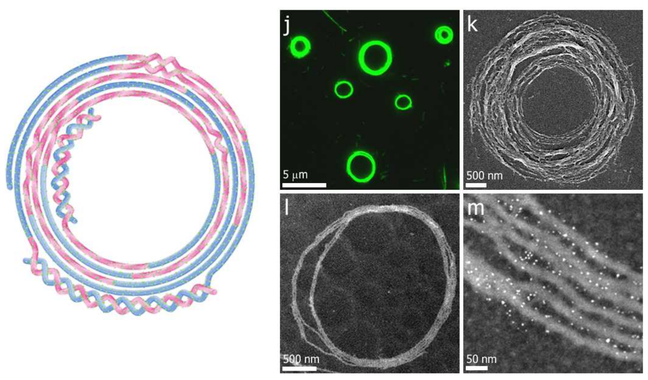
ii. **Coiled coil and kinked domain formation** is a result of the rotation of the oligomers.



iii. **Bending of oligomers** is induced by the strain energy, while much of the mechanical strain is compensated by the biotin-streptavidin bonds.



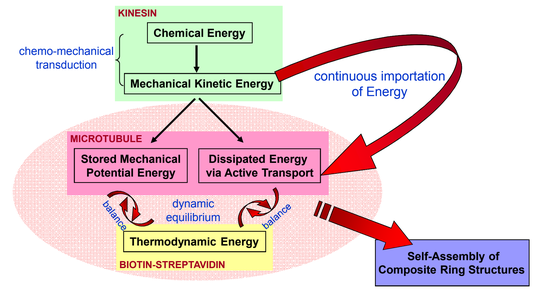
iv. **Circle winding direction** is dictated by the axial rotation in the oligomers, which ultimately dictates the rotational direction of the circular compostites.



v. **Circular composites** reach a metastable state around 15 min after addition of SQD. The rotation of the composites enables the incorporation of microtubules upon contact.

CONCLUDING REMARKS

• Dissection of Energetics



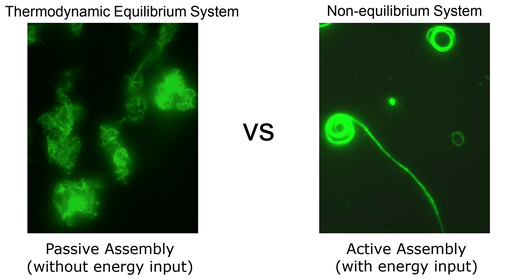
• Conclusion

Our work has established a unique nanocomposite dynamic self-assembly system that involves the cooperative interaction of thermodynamics and energy-dissipation. Together with the mechanical strain, these three components drive the formation of non-equilibrium nanocomposite ring structures.

- Collisions induced by the kinesin-driven transport of biotinylated microtubules laden with SQDs induce the assembly of highly constrained circular nanocomposites.
- Circular nanocomposites are formed on in a delicately balanced regime in which energy-dissipation and thermodynamics interact cooperatively. An imbalance in this relationship results in the formation of either linear composites (thermodynamic input too low) or disordered aggregates (thermodynamic input too high).
- Linear translation and axial rotation of microtubules (energy-dissipating process) drive the formation of mechanical strain within the assembled structures, which ultimately defines the structural shape and rotational direction. The strain energy is counter-balanced by thermodynamic input.
- Energy dissipation is required for both assembly and disassembly.

• Significance

This works serves as an excellent example of biomimetic dissipative structures. The open system has the capability to continuously import energy from the environment and, at the same time, export entropy to create order.



Our system provides an enabling model of how the collective behavior of energy-dissipating and thermodynamic processes may be used to drive the dynamic assembly of nanostructured composites. Exploitation of such dynamic self-assembly processes promises developing novel nanostructured materials that exhibit dynamic functionalities (e.g. color change) that are unconstrained by the energetic limitations of passive self-assembly processes.

Acknowledgement :

1. Division of Materials Sciences and Engineering in the Department of Energy Office of Basic Energy Sciences (BES).
2. Sandia's Laboratory Directed Research and Development Office (LDRD).