In the present study, gold nanorods (47 nm long by 14 nm wide) stabilized by cationic surfactants are flowed into a Si$_3$N$_4$-windowed microchannel and imaged via TEM at rates of about four frames per second. By tracking the relative positions of the rods’ centers, the authors construct the radial distribution function $g(r)$, which measures the average particle density at a distance $r$ from any given particle. Their analysis

reveals a low density “halo” surrounding each particle indicating the presence of repulsive forces between neighboring rods. At equilibrium, these forces can be expressed as gradients of the potential, $u(r) = -k_B T \ln g(r)$, which quantifies the effective interaction between two particles. Calculating $u(r)$ in this manner, the authors find that nanorods interact through a repulsive potential that decays exponentially with distance, $u(r) \propto e^{-r / \kappa}$, over a length $\kappa^{-1} = 16 \text{ nm}$. This observation is consistent with the screened electrostatic interactions predicted by DLVO theory, in which $\kappa^{-1}$ is identified as the Debye screening length. The measured value of $\kappa^{-1}$ corresponds to a salt concentration of ca. 0.4 mM, which unfortunately cannot be independently controlled due the generation of charge carriers by the electron beam.

The authors show that neighboring rods tend to align parallel to one another before attaching irreversibly at their respective ends.

Despite repulsive electrostatic interactions, the charged nanorods are stable against aggregation only in a kinetic sense. Their Brownian motion can “kick” them over an energy barrier and into a deeper, thermodynamically favored potential well due to short-ranged attractive forces between the particle surfaces. Here, this classic view of colloidal stability takes an interesting twist. Owing to the anisotropic shape of the particles and their nanoscale dimensions comparable to the screening length, the energy barriers that inhibit colloidal aggregation are not spherically symmetric. As a result, it is more probable for charged rods to “collide” end-to-end than side-to-side, although the latter is favored
thermodynamically due to the higher contact area. Alivisatos and co-workers capture the dynamics of such end-to-end attachments in real time to confirm this intuitive but unexpected assembly mechanism (Figure 1). The authors show that neighboring rods tend to align parallel to one another before attaching irreversibly at their respective ends. This simple kinetic mechanism is distinct from that of previous studies on linear nanorod assemblies, which rely on heterogeneous surface chemistries to encourage end-to-end attachment.6

Beyond this pioneering demonstration, in situ TEM promises to reveal a wealth of quantitative information on the forces acting between nanoscale objects as well as the dynamic processes by which they assemble. To this end, previous studies of micron-scale colloids by optical video microscopy over the past two decades can provide useful guidance in extracting such information. Of course, current capabilities of in situ TEM are not without limitations. Samples are confined to quasi-two-dimensional domains, which may lead to apparent particle–particle interactions that differ from those found in bulk dispersions.7 Another challenge is controlling the beam-induced generation of charged species (e.g., solvated electrons), which can alter the ionic strength and/or surface charge thereby modifying electrostatic interactions in situ. As shown here, however, this effect can also be used as an external stimulus to induce the self-assembly of charge stabilized components. Finally, it is important to note that the diffusive dynamics of colloidal objects accelerates with decreasing size—a 10 nm particle diffuses one particle diameter in ~1 µs.

No longer must nanoscale colloids be viewed only as relics dried on the desert of a TEM grid or frozen in a tomb of amorphous ice.