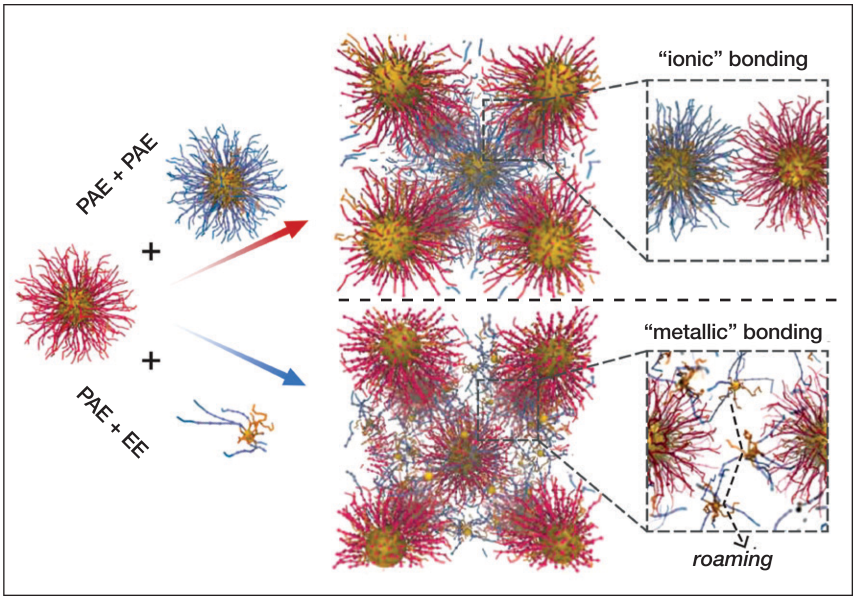
DNA-enveloped particles show electron-like behavior in colloidal crystals

The "sea" of free-floating delocalized electrons is, of course, the origin of several key properties of metals, especially good electrical conductivity. Recently, strategies have been developed to create superlattices from inorganic nanoparticles. Much like crystals of ions or molecules, these versatile materials have long-range ordering and a regular, repeating structure, where the "atom" in the material is substituted by a nanoparticle. The most common representation of this atom equivalent is a nanoparticle that is enveloped by a monolayer of organic molecules. However, while the structure is analogous to that of traditional metal crystals, to date there has been no equivalent of the delocalized, free-roaming electrons.



Researchers were able to control the structure, crystallinity, and metallicity of colloidal crystals by inserting electron equivalent (EE) particles into networks of particle atom equivalents (PAEs). While structures composed of only PAEs that relied on dense DNA grafting repelled neighboring units and resembled ionic crystals, lightly grafted EEs dissolved into the PAE matrix and facilitated metallic behavior. Credit: *Science*.

A particularly powerful approach to create such nanoparticle superlattices uses nanoparticles functionalized with DNA molecules. Indeed, this approach has been used to design over 50 different crystal symmetries. DNA functionalization programs the assembly of complementary DNA-particle conjugates into ionic-like compounds of programmable atom equivalents (PAEs). Researchers from Northwestern University, in collaboration with scientists at Argonne National Laboratory, have been able to create structures in which PAEs exhibit mobility throughout the structure, as do electrons in a classic metal. When small metal nanoclusters functionalized with just a few (6 or fewer) DNA strands are combined with PAEs that are coated with densely packed DNA strands (140 or more), the mixture forms a metallic-like crystal structure. The researchers published their findings in a recent issue of *Science* (doi:10.1126/science.aaw8237).

"By tracking the trajectories of the small particles in the crystal, we defined and characterized a new property of matter, colloidal crystal metallicity, which measures the ability of delocalized small particles to maintain large particles in crystal lattice sites, akin to electrons holding metallic ions in atomic crystal lattices. The resemblance of the behavior of the metallicity we predicted to the behavior of the conductivity in metals [is] remarkable," says Monica Olvera de la Cruz from Northwestern, the lead theorist in the team.

"The discovery that particles can act like electron equivalents in addition to atom equivalents will open the door to designing many new crystal types with properties defined both by structure and potentially particle mobility," says Chad Mirkin of Northwestern, the experimental lead researcher and pioneer in the field of colloidal crystal engineering incorporating DNA.

The structure and properties of the engineered colloidal crystals depended on the interactions between the smaller, lightly DNA-grafted electron equivalent particles and the enveloping densely grafted atom equivalent particles. Changes in the grafting density of the electron equivalents facilitated different crystal structures (such as face-centered or body-centered-cubic phases) and affected the particle diffusion through the resulting colloidal crystals. Diffusion could also be tuned by varying the ratio of small to large particles. Simulations showed that a reduction in the ratio of small to large particles also non-monotonically decreased metallicity, akin to electronic conductivity trends in regular metals, semiconductors, and insulators. One of the lead authors of the publication—Martin Girard—performed the simulations and describes the novelty of this electron equivalent particle component of colloidal crystals: it "could provide insights into fundamental aspects of matter, especially if we can reproduce other metallic structures such as colloidal metallic alloys."

This discovery unlocks many novel capabilities for this emerging class of highly versatile materials. The controllable metallicity and crystallinity of the resulting solids provides new routes to metallic, intermetallic, and compound phases, affects molecular and charge transfer through these structures, and influences their ability to refract or transmit light. As a result, these unique colloidal structures may lay foundations for novel catalytic reactors, photonic crystals, and optical sensors.

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