How Nanoparticles Go with the Flow

Nanoparticle studies are leading to a better understanding of the environmental and health effects of the manufactured nanomaterials used in common products such as lotions and skin creams.

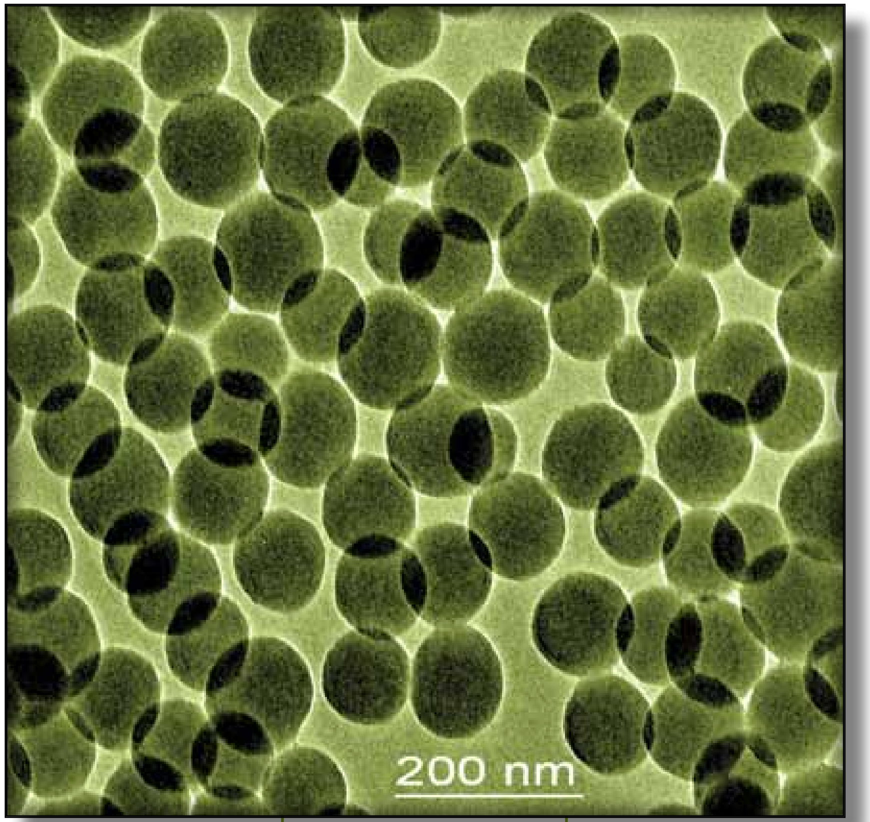
Sunscreen and facial makeup sold at the local drug store consist of particles as small as 30 billionths of a meter, or 30 nanometers. These "engineered nanoparticles"—made of titanium oxide (TiO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3), silicon oxide (SiO_2), and other nanomaterials—are being produced in growing quantities by industrial firms and research laboratories. Concerns are mounting about the effects of these nanoparticles on human health and the environment. The U.S. Environmental Protection Agency is particularly interested in the "fate, transport, and transformation of nanoparticles" to better estimate the environmental and health effects of exposure to manufactured nanomaterials.

Studies indicate that TiO_2 nanoparticles—used in sunscreen to protect skin from ultraviolet light—can penetrate the skin. In some experiments with mice, TiO_2 nanoparticles trigger rapid and long-lasting defensive responses. Other studies show that nanosized TiO_2, SiO_2, and ZnO in water are somewhat toxic to *Escherichia coli*, the kind of bacteria that perform a useful function in the human stomach. Nanoparticles may also act as important carriers of pathogens and environmental contaminants.

Baohua Gu and Wei Wang, both of ORNL's Environmental Sciences Division, are teaming with Ken Littrell, Hassina Bilheux, and Xun-Li Wang, NSSD, to study the behavior of these engineered nanoparticles under environmental conditions. Changes in water chemistry profoundly influence the surface chemistry of these particles, which in turn will affect whether nanoparticles flow as individual particles, or as aggregates that attach to subsurface sediment materials such as quartz sands. The researchers have made the first-ever proof-of-principle measurements of the transport and deposition of nanoparticles in packed sand beds in real time and space. Neutrons made it possible to peek into nanoparticle behavior inside the sand bed.

The data being gathered using neutron radiography at the Technische Universität München, Garching, Germany, and SANS at HFIR will help researchers predict the fate and mobility of nanoparticles in the environment. Specifically, the ORNL team is focusing on the behavior of nanoparticles that Gu and Wang synthesized to ensure that particle size and shape are uniform. For the first experiments, they selected TiO_2 and SiO_2 nanoparticles because of their chemical stability in solution (i.e., they do not dissolve in water) and their surface charge dependence on solution chemistry. Also, these nanoparticles are among the most commonly manufactured nanomaterials.

During SANS experiments at HFIR, the TiO_2 nanoparticles suspended in a solution are pumped into a glass column of packed quartz sand, and a beam of neutrons with a defined width is directed at the nanoparticles in the flow-through system. SANS research can be particularly useful for tracing the fate and behavior of the nanoparticles inside the sand bed. The quartz sand surface normally carries negative charges at neutral pH. When the acidity levels increase, nanoparticles such as TiO_2 will flip their surface charge from negative to positive and start sticking to the negatively charged sand surfaces that previously repelled the nanoparticles. Silica particles cannot be used in this experiment because of their similarity to quartz sand. Some nanoparticles remain as single particles and flow freely through the sand bed, but others attach to each other or to the larger sand particles, eventually clogging the flow through the sand. Aggregates of nanoparticles are formed where coagulation occurs. The neutrons in the low-energy, long-wavelength cold beam "see" only nanoparticles at a given spot. The larger sand particles in the packed column do not interfere with the analysis because of their greater length scale.

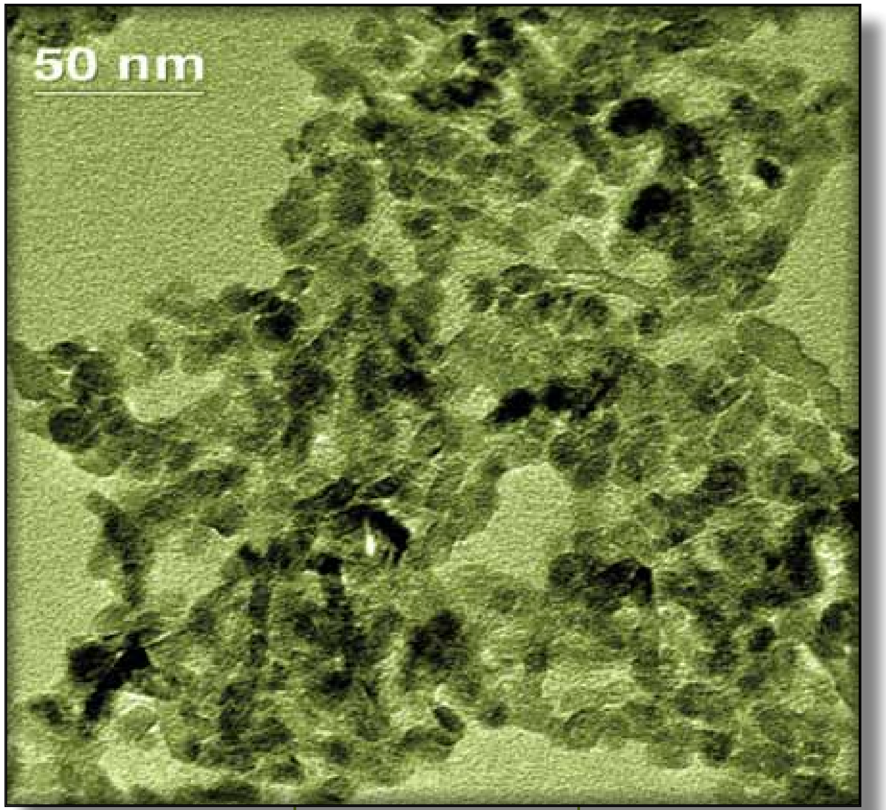


SiO_2 nanoparticles.

In neutron radiography experiments at Garching, the nanoparticles are labeled with a neutron-absorbing element such as gadolinium (as Gd_2O_3). A collimated neutron beam passes through the sand bed to the neutron detector. Because some neutrons will be absorbed by the labeled nanoparticles, they will not reach the neutron detector. The pixilated neutron detector, which has a charge coupled device camera, enables researchers to determine the bulk of nanoparticles as they pass through the packed sand column in real time and space.

"Whether the nanoparticles flow out, attach to each other, or deposit onto larger sand particles depends on the surface and the solution chemistry," Gu says. "Nanoparticles will attach to one another if the repulsion forces are weak between them. For our system, this attachment occurs if the water has higher salt levels. The nanoparticles will coagulate and form aggregates that scatter the neutron beam more effectively."

"What we learn from these experiments," Gu says, "will help scientists better understand and predict how nanoparticles will behave in the environment under different conditions and how they might affect human health."



TiO_2 nanoparticles.