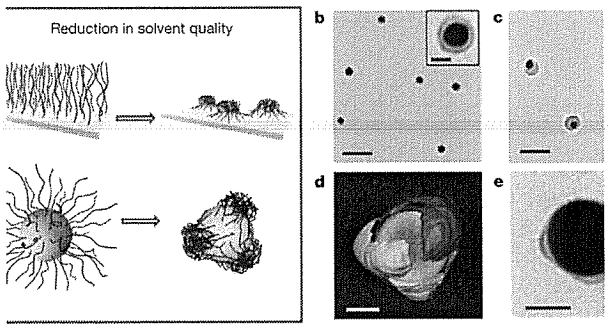
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Surface-patterned colloidal particles

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Surface patterning of nanoparticles with polymer patches. Credit: (c) *Nature* (2016) doi:10.1038/nature19089

(Phys.org)—A group of researchers from several institutions have attached thiol-terminated polymers to gold nanoparticles and created surface micelles by changing the solvent from one that is favorable for the polymer to one that is less favorable.

Rachelle M. Choueiri, et al. have demonstrated that nanoparticle surface patterning, from the surface aggregation of polymers into "patches," can be thermodynamically controlled via changing polymer characteristics and solvent properties. Furthermore, the surface pattern can be locked into place by crosslinking the polymer. Their work appears in *Nature*.

Three-dimensional surface-patterned particles have proved helpful as models for colloidal analogs of reactive materials and phase transitions in liquid systems, as well as colloidal surfactants and templates for synthesizing hybrid particles. Prior research has shown few examples of colloidal patchy particles at the nanometer level. Even when patches can be formed at this level, there are typically no more than two patches per nanoparticle.

In the current research polymer molecules tethered to gold nanoparticles can change from a uniform distribution (i.e., a polymer brush) to surface pinned micelles via thermodynamic processes. Specifically, one can control the size of the patches by changing the polymer dimensions and grafting density. One can control the number of patches per nanoparticle by tuning the ratio of nanoparticle diameter and polymer size.

The first step was to see if changing the solvent can drive polymer patch formation. Choueiri, et al. made gold nanoparticles with diameters in the range of 20 ± 1.0nm and 80 ± 1.5nm with thiol-terminated polystyrenes. The polystyrenes had either a molecular mass of 29,000 Daltons or 50,000 Daltons to see if molecular weight played a role in patch formation. The nanoparticles dispersed in DMF, which is a good solvent for polystyrene, were coated with a uniformly thick layer. They exhibited uniformly thick polymer dispersion. When water, a poor solvent, was added, the polymer layer turned into patches, which was reversible upon addition of DMF. Patch size and number per nanoparticle could be controlled by polymer molecular weight.

Given these results, Choueiri, et al. then explored what would happen if they changed the nanoparticle diameter, the polystyrene length, and the density of polystyrene polymers tethered to the surface. In general, their studies showed that the patch size can be controlled by the polymer length and surface density while the number of patches per nanoparticle can be controlled by changing the nanoparticle diameter and the length of the polymer. Theoretical studies confirmed that the thermodynamic component of the surface patterns were due to polymer and solvent interactions and how much the polymer can stretch from its tethered position to the surface patch.

The next step was to see if surface shape changed the surface pattern. Choueiri, et al. looked at polymer segregation on nanorods, nanocubes, and triangular nanoprisms. They found that patches

tended to form at the tips of the nanoraods and on the edges of the nanocube and triangular nanoprisms. Additionally, they tested polymers other than polystyrene and found that some of these polymers formed patches on gold nanospheres after changing certain solvent properties, such as pH or hydrophobicity.

Finally, they tested the self-assembly of patchy nanoparticles in a poor solvent. They found that after sufficient time, the patterned nanoparticles exhibited new binding modalities in DMF mixed with water.

The nanocubes, in particular, showed a unique "checkerboard" self-assembled structure. This is different from when the nanocubes were evenly coated with polystyrene and then solvent changes were made. In this case, the pattern was "face-to-face" rather than checkerboard.

This research provides a new way to pattern nanoparticle surfaces that is versatile and tunable to the desired number of patches and nanoparticle shapes. Future research will involve exploring more nanoparticle shapes and polymer systems to see how this strategy can produce unique self-assembled structures and tailor new functionalities to patchy nanoparticles.

More information: Rachelle M. Choueiri et al. Surface patterning of nanoparticles with polymer patches, *Nature*