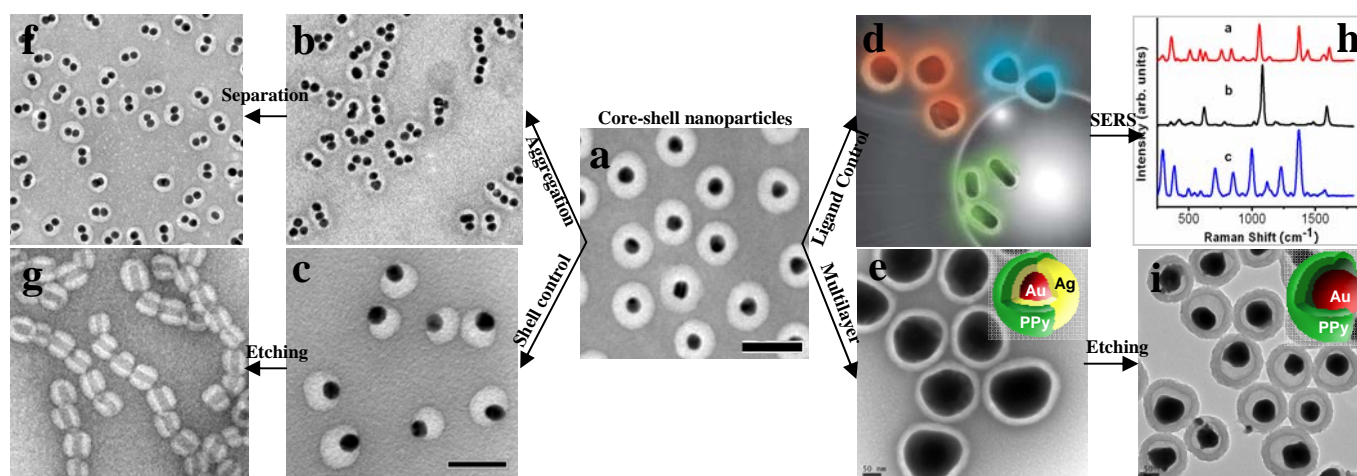


Fabrication of Complex Nanostructures by Solution Chemistry

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Controlling the composition, morphology and structural order of nanoparticles is of paramount significance in tailoring the properties of nanomaterials. Our group focuses on the manipulation of core-shell nanoparticles to impart specific functionalities. The long-term goal is to develop a synthetic system like organic chemistry: nano-devices will be assembled from components in solution, stabilized, and then purified. Solution methods are generally facile, scalable, and more reproducible compared to surface-based fabrication methods.

It has been demonstrated that amphiphilic diblock copolymers, such as polystyrene-*b*-poly(acrylic acid) (PSPAA), could self-assemble to form uniform shells on gold nanoparticles (Fig. a). Since one block of the polymer is extremely hydrophobic and the other extremely hydrophilic, the poly-



mer formed micelles that include hydrophobically functionalized nanoparticles. The micelles are covered with long ionic PAA chains in extended conformation, which introduce charge and steric repulsion against aggregation.

Gold nanoparticles could be induced to aggregate, before polymer was added to encapsulate and stabilize the resulting clusters (Fig. b). Previously, direct observation of nanoparticle aggregates has been difficult, since the preparation of TEM/SEM samples would cause the nanoclusters to further aggregate. The presence of polymer shell maintained the structural integrity of nanoclusters and allowed them to be isolated, enriched and then characterized. Most recently, we developed a new method to separate dimers (Fig. f) and trimers of gold nanoparticles from the synthetic mixture, by differential centrifugation in CsCl solutions. The dimers were enriched to unprecedented purity (95% out of 1435 particles surveyed).

In addition to the concentric shells (Fig a), anisotropic polymer coating was also generated by using both hydrophobic and hydrophilic ligands for the encapsulation (Fig. c). The competitive binding of the two ligands on gold surface led to selective attachment of PSPAA on one side of the nanoparticles. The facile fabrication gave large quantities of Janus (two-sided) nanoparticles amenable for selective functionalization and controlled assembly. Using this approach, gold nanorods were also partially encapsulated, leaving only the two ends exposed. After etching to remove the gold, the remaining polymer shells formed cavities that have openings on both ends (Fig. g); the size and shape of the cavities could be readily tailored by the choice of the initial sacrificial cores.

A variety of hydrophobic ligands (e.g. 2-naphthalene-thiol) could be used for the encapsulation of metal nanoparticles, which enhance the Raman signal of the surface ligands. Thus, these core-shell nanoparticles act as multiplexed nanoprobbers based on surface-enhanced Raman scattering (SERS). Upon laser excitation, the nanoparticles of different synthetic origin emit characteristic Raman fingerprints (Fig. d and h), showing potentials for labeling applications.

Other than the above systems based on block copolymers, metal nanoparticles were also coated with conductive polymers, such as polyaniline (PANI) and polypyrrole (PPy). In the presence of sodium dodecylsulfate (SDS), the adsorption and *in situ* polymerization of aniline or pyrrole on the surface of gold nanoparticles give uniform polymer shells. A similar approach was developed to give 3-layer nanopar-

ticles Au@Ag@PPy in one step (Fig. e). After etching the Ag layer, yolk-shell nanoparticles were prepared (Fig. i). The aspects of these triple-layer NPs could be readily tailored and further structural complexity could be introduced.

Structural control and assembly of nanocomponents are important steps toward scalable fabrication of nano-devices. The detailed studies in these fundamental steps have allowed insights in the underlying mechanisms, which could be extended to similar systems. Using this knowledge, we are now designing and fabricating nanodevices with simple functions.

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