Metal at the Nanoscale: Manipulating Matter to Control Light

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Metal nanoparticles find use in a wide range of technologies — from catalysis to sensing biological molecules. An important consideration for almost all applications is the size and shape of the particles; for example, small nanometer-sized particles are used for catalysis,[1,2] whereas larger particles are used for surface-enhanced spectroscopies, such as surface-enhanced raman spectroscopy (SERS).[3−6] Thus, controlling the size and shape of the particles and understanding how size and shape affects properties is a major area of research in physical science.[7] The Perspectives in this issue of *The Journal of Physical Chemistry Letters* describe recent advances in the synthesis of metal nanoparticles and their applications to different optical spectroscopies.

The Perspective by Zan et al.[8] gives the current understanding of how metals interact with graphene to form supported nanoparticles. Graphene-supported metal nanoparticles are becoming widely used in catalysis[9] and SERS,[10,11] and contact between graphene and metals is also important for device applications.[12] The authors discuss transmission electron microscopy studies, which give information about the size distribution of the particles and show that evaporation-deposited metals form nanoparticles on hydrocarbon contamination sites, rather than pristine graphene surfaces. These measurements also show differences in reactivity for few-layer compared to monolayer graphene and, in combination with density functional theory (DFT) calculations, provide insight into the role of vacancies in the formation of nanoparticles of metals such as Al, Ti, and Pd.[13]

In contrast to supported nanoparticles, the Perspective by Jose et al.[14] discusses the synthesis of monolayer protected metal nanoparticles in solution, in particular, the issue of thermodynamic versus kinetic control.[15] The authors show that when digestive ripening is used to focus the size distribution, similar sizes are created for a given thiol ligand, indicating thermodynamic control of the size distribution. In this reaction system, the small particles grow by Ostwald ripening, and the larger particles are etched by atom transfer.[16] This occurs because of the ability of thiols to both oxidize and reduce gold.[17]

From focusing size distributions to focusing light, the Perspective by Raschke and co-workers discusses the use of metal nanostructures as antennas for near-field optical experiments.[18] In particular, the authors describe the use of conical metal tips to focus surface plasmon polaritons to nanometer-scale dimensions. The concentrated electric field at the tip of the cone interacts with molecules via dipole−dipole coupling[19] and can induce linear and nonlinear optical signals from a sample.[20] Using these systems, the authors have demonstrated ∼20 nm spatial resolution, which allows the study of a variety of nanoscale pehenomena, such as domain formation in crystals and inhomogeneities in polymer blends.[21] They have also shown that ultrafast laser sources can be focused to nanometer-sized dimensions without dispersion of the pulse. This achievement opens the door to exciting possibilities for exploring the ultrafast dynamics of single chromophores.[22]

Finally, the Perspective by Alvarez-Pueblo provides an overview of the different effects that determine the spectral enhancements in SERS.[23] This article covers the technical aspect of these experiments (choice of excitation sources and objectives), as well as the chemical and photochemical aspects. An important consideration in SERS experiments is the position of the localized plasmon resonances of the nanoparticles used as the SERS substrate[24] and the presence of hot-spots.[25,26] The article also discusses common problems in SERS experiments, such as photodegradation of the sample and thermal heating,[27] and the strategies to overcome them.

These Perspectives show that metal nanoparticles play an important role in many aspects of physical science and that both their synthesis and applications are active areas of research. In particular, the optical applications of metal nanostructures were recently highlighted in *The Journal of Physical Chemistry* Virtual Issue,[7] and the Perspectives in this issue of *The Journal of Physical Chemistry Letters* provide an overview of recent advances in this field.

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