Spectroscopy, Imaging, and Solar Energy Conversion with Plasmons

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The interaction of light with matter is an important topic in Physical Chemistry. This interaction can be amplified by using the surface plasmon resonances of metal nanoparticles to enhance local electromagnetic fields.[1] The current issue of *The Journal of Physical Chemistry Letters* has several articles that describe new results in this area of research. In the Perspective article by Hägglund and Apell, the use of metal nanostructures to improve the performance of thin-film solar cells is discussed.[2] The enhanced electric field at the surface of the particles increases the optical absorption of the sample,[3] although this interface can also cause quenching.[4] The authors show that a balance between enhancement and quenching can be achieved through careful design, and that solar cells with extremely thin active layers are possible.

The Raman effect can also be enhanced by interactions with the plasmon resonances of metal nanoparticles.[5] This is known as surface enhanced Raman spectroscopy (SERS), and even though this effect has been known for several decades, it is still a very active area of research.[6] The largest enhancements are seen for aggregates of metal nanoparticles, which generate SERS "hot-spots". The Perspective article by Willets and co-workers discusses recent advances in understanding these hot-spots achieved through super-resolution imaging (spatial resolution less than the diffraction limit).[7] These experiments give information about the size and shape of the hot-spots, and also show that molecules are mobile within the hot-spots. In the Perspective article by Saito and Verma, a different aspect of SERS, polarization analysis, is described.[8] These authors discuss how to use spatial light modulators and high numerical aperture objects to create *z*-polarized light, which is light with its polarization vector pointing in the direction of propagation. This type of light field is extremely useful in tip-enhanced Raman spectroscopy (TERS),[9] where the enhanced field from a metal nanoparticle attached to the cantilever of an atomic force microscope (AFM) is used to achieve high spatial resolution (tens of nanometers) in Raman images. Although both these Perspective articles deal with super-resolution Raman imaging, the way this is achieved is very different.

The electromagnetic field enhancements associated with plasmon resonances also make metal nanoparticles strong absorbers.[1] The articles by the Link and Lounis groups describe advances in imaging metal particles through absorption using photothermal heterodyne imaging (PHI).[10,11] In PHI, the change in refractive index of the surroundings caused by local heating is used to detect absorption.[12] When implemented with high frequency modulation, PHI can be extremely sensitive.[13] The signal depends on the absorption cross-section of the nano-object and the way the refractive index of the surroundings changes with temperature.[14] There has been considerable effort in finding materials that enhance the PHI signal.[15] The articles by the Link and Lounis groups report experiments on Au nanoparticles in a thermotropic liquid crystal: 4-cyano-4′-pentylbiphenyl (5CB).[10,11] This material undergoes a nematic to isotropic phase transition at just above room temperature, and its refractive index is very sensitive to temperature. Using 5CB in PHI experiments creates a ca. 20× enhancement in the signal. The authors also show that the PHI signal can be used as a sensitive probe of structural order in the liquid crystal.[10,11]

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REFERENCES

(1) Alvarez-Puebla, R.; Liz-Marzan, L. M.; Garcia de Abajo, F. J. Light Concentration at the Nanometer Scale. *J. Phys. Chem. Lett.* **2010**, *1*, 2428−2434.

(2) Hägglund, C.; Apell, S. P. Plasmonic Near-Field Absorbers for Ultrathin Solar Cells. *J. Phys. Chem. Lett.* **2012**, *3*, 1275−1285.

(3) Atwater, H. A.; Polman, A. Plasmonics for Improved Photovoltaic Devices. *Nat. Mater.* **2010**, *9*, 205−213.

(4) Viste, P.; Plain, J.; Jaffiol, R.; Vial, A.; Adam, P. M.; Royer, P. Enhancement and Quenching Regimes in Metal−Semiconductor Hybrid Optical Nanosources. *ACS Nano* **2010**, *4*, 759−764.

(5) Stiles, P. L.; Dieringer, J. A.; Shah, N. C.; Van Duyne, R. R. Surface-Enhanced Raman Spectroscopy. *Annu. Rev. Anal. Chem.* **2008**, *1*, 601−626.

(6) Etchegoin, P. G.; Le Ru, E. C. A Perspective on Single Molecule SERS: Current Status and Future Challenges. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6079−6089.

(7) Willets, K. A.; Stranahan, S. M.; Weber, M. L. Shedding Light on Surface-Enhanced Raman Scattering Hot Spots through Single-Molecule Super-Resolution Imaging. *J. Phys. Chem. Lett.* **2012**, *3*, 1286−1294.

(8) Saito, Y.; Verma, P. Polarization-Controlled Raman Microscopy and Nanoscopy. *J. Phys. Chem. Lett.* **2012**, *3*, 1295−1300.

(9) Bailo, E.; Deckert, V. Tip-Enhanced Raman Scattering. *Chem. Soc. Rev.* **2008**, *37*, 921−930.

(10) Chang, W. S.; Link, S. Enhancing the Sensitivity of Single-Particle Photothermal Imaging with Thermotropic Liquid Crystals. *J. Phys. Chem. Lett.* **2012**, *3*, 1393−1399.

(11) Parra-Vasquez, A. N. G.; Oudjedi, L.; Cognet, L.; Lounis, B. Nanoscale Thermotropic Phase Transitions Enhancing Photothermal Microscopy Signals. *J. Phys. Chem. Lett.* **2012**, *3*, 1400−1403.

(12) van Dijk, M. A.; Tchebotareva, A. L.; Orrit, M.; Lippitz, M.; Berciaud, S.; Lasne, D.; Cognet, L.; Lounis, B. Absorption and Scattering Microscopy of Single Metal Nanoparticles. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3486−3495.

(13) Gaiduk, A.; Yorulmaz, M.; Ruijgrok, P. V; Orrit, M. Room-Temperature Detection of a Single Molecule's Absorption by Photothermal Contrast. *Science* **2010**, *330*, 353−356.

(14) Selmke, M.; Braun, M.; Cichos, F. Photothermal Single-Particle Microscopy: Detection of a Nanolens. *ACS Nano* **2012**, *6*, 2741−2749.

(15) Gaiduk, A.; Ruijgrok, P. V.; Yorulmaz, M.; Orrit, M. Detection Limits in Photothermal Microscopy. *Chem. Sci.* **2010**, *1*, 343−350.

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