Communication

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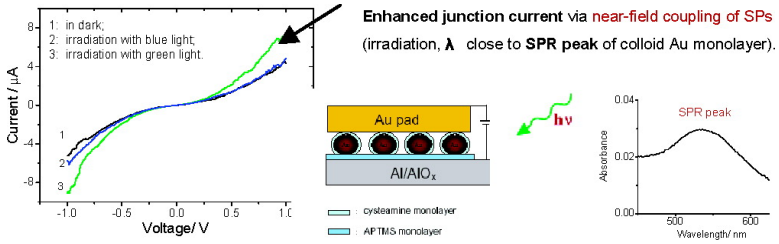

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Surface Plasmon Resonance-Mediated Colloid Gold Monolayer Junctions

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Surface plasmon resonances in metallic nanoparticles are being exploited for a variety of applications, including molecular sensing[1−3] and tagging,[4,5] focusing or guiding light,[6,7] near-field optical microscopy,[8] and other subwavelength photonics.[9] The strong interactions of metallic nanoparticles with visible light originate from the excitation of collective oscillations of conduction electrons within these particles, an elementary excitation termed "surface plasmon" (SP).[10] SPs are of interest for applications, such as those mentioned above, because they lead to large electromagnetic field enhancement near the metal surface, peaking at a resonance wavelength that depends on the size, shape, and local dielectric environment of the nanoparticles. Because of the localized field amplification that occurs, excitation of SPs in metal nanoparticles-based, current-carrying devices can be expected to lead to new and interesting optoelectronic phenomena and applications.

Surface plasmons, optically excited on a Ag film, were shown previously to induce an additional current of electrons from a scanning tunneling microscope (STM) tip to the Ag sample.[11] Excitation of surface plasmon resonances (SPRs) in spherical Au nanoparticles, deposited on a semiconductor surface, enhanced the optical absorption and photocurrent generated in a semiconductor.[12] Here, we report a simple wet chemical way to prepare colloid Au monolayer junctions that show SPR-enhanced photocurrents. The junctions are prepared by soft deposition of Au pad electrodes on the monolayer. The SPR-enhanced current was observed upon illumination with light in the wavelength range that corresponds to the nanoparticle plasmon resonance. This current is superimposed on the tunneling current observed in the absence of SP excitation.

The citrate-stabilized, Au nanoparticles (~3 ± 1 nm diameter) were synthesized as described elsewhere.[13,14] Formation of monodispersed Au colloidal particles is indicated by a sharp absorbance peak at ~513 nm (Figure 1, inset), which corresponds to the Mie resonance for isolated small Au particles.[15] The particles were then deposited onto an Al substrate (~50 nm thick Al film, vacuum evaporated on quartz) covered with a natural oxide layer (which we will denote as "AlO_x"). The suspended Au nanoparticles (pH ~ 5) were bound to the AlO_x surface via the exposed APTMS amino groups.[16a] After formation of a saturated colloidal Au monolayer (incubation time >6 h; monolayer formation was confirmed by atomic force microscopy), the Au-covered surface was treated with 20 mM aqueous cysteamine for ~30 min to passivate the colloid surface. Junctions were prepared by depositing preformed Au pads (60 nm thick Au dots, 0.5 mm in diameter) on the cysteamine-capped colloid Au monolayer in a nondestructive manner, using the "lift-off, float-on" technique (LOFO).[17] The basic junction structure is shown schematically in Figure 1.

After formation of a saturated Au colloidal monolayer on the APTMS-coated glass slide, the SP absorption peak shifts slightly to ~535 nm and broadens (Figure 1), due to a collective particle SPR.[18] Atomic force microscopy (AFM) measurements showed a densely packed monolayer of Au colloids with an average density of about ~8 × 10^{11} particles/cm^2,[19] as can be seen in Figure 2.

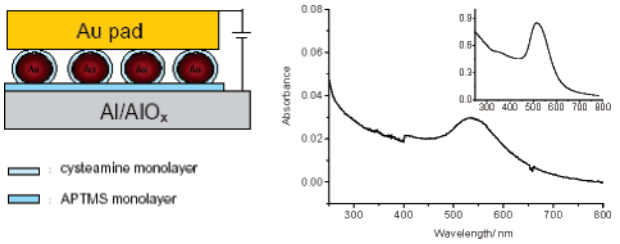

Figure 1. Schematic diagram of colloid Au monolayer junction device structure. The SPR-enhanced junction current flows through the junction upon illumination with light of energies that correspond closely to the nanoparticle plasmon resonance wavelengths. (Right) UV−vis spectra of as-prepared colloid Au suspension (inset) and of monolayer on APTMS-modified glass slide.

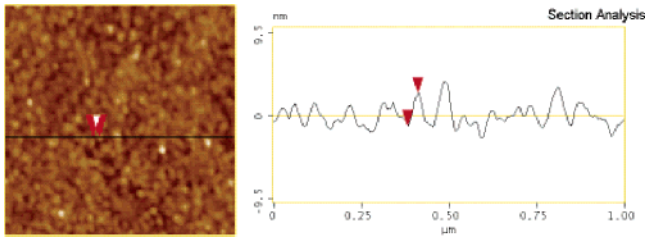

Figure 2. Representative AFM image (1 × 1 μm) of a saturated colloid Au monolayer on APTMS-modified Al/AlO_x substrate, formed by self-assembly. Line scans show that the average height of the Au particles is about 2−4 nm.

The average interparticle spacing is dictated during the self-assembly process by the interparticle electrostatic repulsion of the negatively charged citrate-stabilized Au nanoparticles.[20] The AFM image is a tip−sample convolution, and therefore, the images of individual small colloid particles are enlarged by the AFM tip (typical size > 10 nm).[14] However, section analysis shows that the height of the feature (typical 2−4 nm) is consistent with the known size of the Au nanoparticles. Typical root mean square roughness of the Au particle monolayer surface is ~1.2 nm, while the original APTMS-modified Al/AlO_x surface is quite smooth with a root mean square roughness of ~0.65 nm.

Typical room temperature current−voltage (I−V) characteristics of the resulting colloid Au monolayer junctions are shown in Figure 3. The curves were recorded in the dark and then with blue or green light illumination. Because the cysteamine-capped small Au particles are nonmetallic,[16b] a monolayer of such particles will not short two metal contacts.[16a] The nonlinear characteristics are similar to those of a 15 nm Au particle monolayer.[20] The exponential increase of I with the increase of V indicates that the conduction was contributed by the tunneling of electrons through the colloid Au monolayer. The dark current is approximately 4.4 μA at 1 V applied bias. Upon illumination with green (λ > 550 nm) light, close to the nanoparticle plasmon resonance wavelengths, the current increases to ~7.3 μA (~65% increase in magnitude) at 1 V applied bias, while a much smaller increase was seen (~4.8 μA

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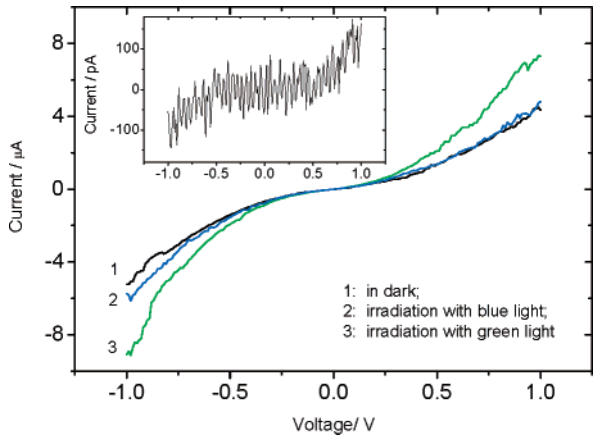

Figure 3. Representative $I-V$ curves of the colloid Au monolayer junction measured at ambient (40% RH, 22 °C) condition, in dark, or illuminated with blue or green light. Inset shows typical $I-V$ characteristic of a control junction gapped by ~5 nm thick insulator (without photoeffect).

at 1 V) upon illumination with blue (380 nm $< \lambda <$ 440 nm) light (energies far away from the nanoparticle plasmon resonance wavelengths). Figure S1 (Supporting Information) shows similar $I-V$ responses of another junction. Although the currents vary slightly from junction to junction, the $I-V$ measurements are reproducible with respect to current magnitude. Out of a group of six independent junctions, made from two independent sample preparations, five junctions were functional and all yielded similar photoeffect. One junction broke down mechanically immediately upon approaching the Au pad with the W needle. We can rule out thermal effects of the junction current because the green and blue light intensities that were used are roughly the same. The close correspondence between the colloid Au plasmon peaks and the illumination wavelength is clear evidence for the role of the nanoparticle plasmon resonances in the observed photocurrent. The enhanced photocurrent—originating from the near-field coupling of photoexcited SPs to junction dark current—is superimposed on the tunneling current observed in the absence of SPs.

Although light can excite SPs on a flat Au thin film (~50 nm)[14] or on a thin Al film (~20 nm)[21] using prism coupling to enhance the momentum of the incident light, generally, light cannot excite SPs on a flat metal surface directly because of the momentum mismatch between the light waves and the waves of the SPs.[22] It is not possible to directly check for possible photocurrents from the Au electrode/APTMS−AlO_x−Al junctions because such junctions will be shorted. Therefore, we sandwiched a ~5 nm thick molecular insulator[23] instead of the colloid Au monolayer between the two metal electrodes. We chose a 5 nm thick film because this distance is still within efficient propagation length of surface plasmon polaritons, while tunneling should be negligible in the absence of SPs.[11,24] As shown by in the inset in Figure 3, the current flowing through this 5 nm thick control gap is indeed negligible. The pA current was very noisy, and no photoeffect was detectable, indicating that direct light irradiation cannot excite SPs between the metal thin film electrodes.

In conclusion, we report a simple way to prepare SPR-mediated colloid Au monolayer junctions by wet chemistry and soft top electrode deposition. The SPR-enhanced junction current was observed upon illumination with light over wavelength ranges that correspond closely to the nanoparticle plasmon resonance wavelengths. The coupling of light into the tunneling gap by means of metal nanoparticle-based surface plasmons opens up a new field of optoelectronic nanodevices and sensors by near-field enhancement effects.[25]

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Supporting Information Available: Another set of $I-V$ curves of another colloid Au monolayer junction. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
(2) Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, T.; Itzkan, I.; Dasari, R. R.; Feld, M. S. *Phys. Rev. Lett.* **1997**, *78*, 1667.
(3) Nie, S. M.; Emery, S. R. *Science* **1997**, *275*, 1102.
(4) Schultz, S.; Smith, D. R.; Mock, J. J.; Schultz, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 996.
(5) Taton, T. A.; Mirkin, C. A.; Letsinger, R. L. *Science* **2000**, *289*, 1757.
(6) Li, K.; Stockman, M. I.; Bergman, D. J. *Phys. Rev. Lett.* **2003**, *91*, 227402−1.
(7) Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Meltzer, S.; Requicha, A. A. G.; Atwater, H. A. *Adv. Mater.* **2001**, *13*, 1501.
(8) Kalkbrenner, T.; Ramstein, M.; Mlynek, J.; Sandoghdar, V. *J. Microsc.* **2001**, *202*, 72.
(9) Ditlbacher, H.; Krenn, J. R.; Schider, G.; Leitner, A.; Aussenegg, F. R. *Appl. Phys. Lett.* **2002**, *81*, 1762.
(10) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters;* Springer-Verlag: Berlin, 1995.
(11) Möller, R.; Albrecht, U.; Boneberg, J.; Koslowski, B.; Leiderer, P.; Dransfeld, K. *J. Vac. Sci. Technol. B* **1991**, *9*, 506.
(12) Schaadt, D. M.; Feng, B.; Yu, E. T. *Appl. Phys. Lett.* **2005**, *86*, 063106.
(13) Grabar, K. C.; Allison, K. J.; Baker, B. E.; Bright, R. M.; Brown, K. R.; Freeman, R. G.; Fox, A. P.; Keating, C. D.; Musick, M. D.; Natan, M J. *Langmuir* **1996**, *12*, 2353.
(14) Jin, Y. D.; Kang, X. F.; Song, Y. H.; Zhang, B. L.; Cheng, G. J.; Dong, S. J. *Anal. Chem.* **2001**, *73*, 2843.
(15) Bohren, C.; Huffman, D. R. *Absorption and Scattering of Light by Small Particles;* Wiley: New York, 1983.
(16) (a) Geng, J. F.; Thomas, M. D. R.; Shephard, D. S.; Johnson, B. F. G. *Chem. Commun.* **2005**, 1895. (b) Brust, M.; Bethell, D.; Kiely, C. J.; Schiffrin, D. J. *Langmuir* **1998**, *14*, 5425.
(17) Vilan, A.; Shanzer, A.; Cahen, D. *Nature* **2000**, *404*, 166.
(18) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.
(19) Jin, Y. D.; Shen, Y.; Dong, S. J. *J. Phys. Chem. B* **2004**, *108*, 8142.
(20) Schmid, G.; Simon, U. *Chem. Commun.* **2005**, 697.
(21) Gryczynski, I.; Malicka, J.; Gryczynski, Z.; Nowaczyk, K.; Lakowicz, J. R. *Anal. Chem.* **2004**, *76*, 4076.
(22) Srituravanich, W.; Fang, N.; Sun, C.; Luo, Q.; Zhang, X. *Nano Lett.* **2004**, *4*, 1085.
(23) Jin, Y. D.; Friedmann, N.; Sheves, M.; He, T.; Cahen, D. Unpublished work. The ~5 nm thick molecular insulator is made up of the apoprotein bacterioopsin (BO) and lipid bilayers. The use of the apoprotein, which has negative surface charge, enhances the electrostatic adhesion and stiffness of the lipid bilayers on the positively charged surface (by the amino group of APTMS, which is charged in the 0.1 N HCl solution used here) for robust $I-V$ measurements (to prevent shorting).
(24) Andrew, P.; Barnes, W. L. *Science* **2004**, *306*, 1002.
(25) Barnes, W. L.; Dereux, A.; Ebbesen, T. W. *Nature* **2003**, *424*, 824.

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