

Plasmon scattering from a single gold nanoparticle collected through an optical fiber

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A single gold nanoparticle is attached to the end of a chemically etched fiber axicon microlens tip by modifying the tip surface with linker molecules. The high collection efficiency of the fiber axicon microlens allows plasmon scattering of a single nanoparticle to be measured directly through the optical fiber. The portable nature of this probe allows direct optical sensing of environmental changes using a single nanoparticle. © 2005 American Institute of Physics. [DOI: 10.1063/1.1851011]

Optical responses from a single nanoparticle, such as scattering and fluorescence, depend not only on the intrinsic electronic states of the particle,^{1,2} but also on its surrounding environment.³ Understanding and manipulating optical signals on the single particle level could lead to tremendous applications in the field of surface enhanced Raman scattering,⁴ chemical sensors,⁵ and biological sensors.⁶ Experimentally, single particle spectroscopy is typically carried out using either dark field (DF) imaging⁷ or near-field scanning optical microscopy (NSOM).^{8–10} Aside from the drawback of low signal to noise ratio in both techniques, DF imaging also requires a very low particle density, whereas many NSOM schemes suffer from the ambiguity caused by the interaction between the particle and the probe. Furthermore, both techniques are intrinsically difficult to modify for practical sensor applications.

An alternative approach is to create an active probe, where a single particle is directly attached to a bare optical fiber tip. The close proximity between the nanoparticle and the optical detection path can significantly increase the detection sensitivity. Such an active probe can also be used as a local near-field optical source or detector, which can significantly reduce the artifacts caused by the far field interference. Its portability will allow studying the same nanoparticle in different environments, which is potentially very useful for many applications such as sensing and *in vivo* imaging of biological samples. Kalkbrenner *et al.*¹¹ have previously reported an active probe based on this principle. However, the detection of the optical signals through the optical fiber was not demonstrated. The difficulty could lie in the fact that the mechanical process used to create such tapered fiber probes might significantly narrow the optical passage at the end of the tip. To make matters worse, the physi-

cal axis could sometimes become misaligned with the optical axis of the fiber. Both can cause a large reduction of fiber collection efficiency. This letter demonstrates an active probe using a chemically etched fiber axicon microlens. We show that the scattering from a single nanoparticle (50–100 nm) can be detected through the fiber in various solvent environments, and that the resonance is sensitive to the different dielectric constant of the solvents.

The fiber axicon microlens tip was fabricated by selective chemical etching of a single mode optical fiber (Newport F-SA) using a solution of hydrofluoric acid (HF) and ammonium fluoride (NH₄F).¹² The inset of Fig. 1 shows a scanning electron micrograph (SEM) image of a tip made using this technique. The germanium doped core etches more slowly than the cladding, resulting in the formation of a cone at the flat end of the fiber. By adjusting the relative concentration of HF and NH₄F, the angle of the cone shape tip can be controlled. Tips with a cone base diameter of roughly 3 μm and tip diameter less than 50 nm are routinely fabricated. The surface of this fiber tip was further modified to increase its affinity for gold nanoparticles. This was achieved by im-

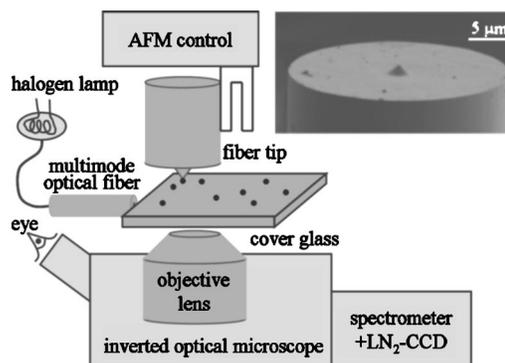


FIG. 1. Experimental setup for picking up a single nanoparticle from the surface. Nikon TE200 inverted optical microscope has a 60× objective lens with a numerical aperture of 0.85, and it is coupled to a Jobin Yvon TRIAX 190 monochromator equipped with a liquid nitrogen cooled CCD. The inset shows a SEM image of the etched fiber axicon microlens tip.

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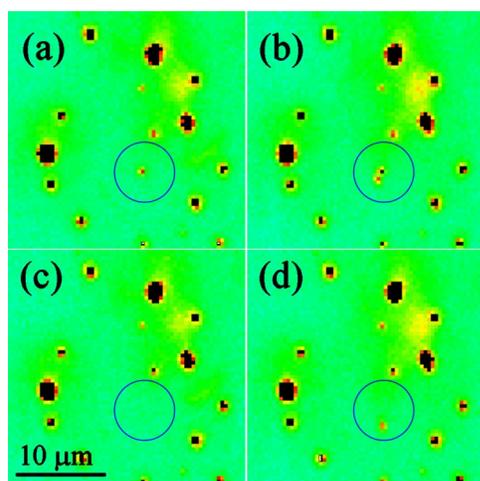


FIG. 2. Images from scattered light collected through the objective lens during the pick-up process of a single nanoparticle from the surface by a modified fiber tip. Circled area is a target region with a single nanoparticle. (a) Before the tip approaches the surface. (b) When the tip is in shear-force feedback with the surface. (c) After the tip scans the target region and is retracted from the surface. (d) After the tip reapproaches the surface with a nanoparticle attached, both the particle and the tip scatter the evanescent field.

mersing the fiber tip in (3-mercaptopropyl)methyltrimethoxysilane vapor. The vapor deposition process consistently yields smooth coverage on the fiber surface as determined by SEM. A tuning fork was then glued to the chemically modified optical fiber, allowing it to be used as a NSOM scanning probe.

The attachment of a single particle to the end of the fiber tip was achieved using a homebuilt (NSOM) system, shown schematically in Fig. 1. Gold nanoparticles with a size range from 50 to 100 nm were synthesized by citrate reduction of Au salt in an aqueous solution, using the seed and growth technique.¹³ A low density of the particles was then deposited onto a thin cover glass slide (Fig. 2). A multimode optical fiber coupled with a 150 W halogen lamp was used as an illumination source. A total internal reflection of the illumination source was created at the glass-air interface by coupling the multimode optical fiber to the side of the glass slide. The scattering from the particles in the evanescent field was collected by the objective lens and analyzed by the spectrometer and liquid nitrogen cooled charge coupled detector (CCD). The target single particle was selected by analyzing the shape of the plasmon peak. Aggregates typically give a nonsymmetric plasmon response, due to simultaneous excitation of multiple modes at different wavelengths. Once an isolated nanoparticle was identified, the NSOM tip was engaged to the targeted region to pick up the nanoparticle by scanning near the surface. Figure 2 shows the entire pick-up process monitored through the objective lens. SEM was used to confirm the attachment of a single particle to the fiber tip (Fig. 3 inset).

The fiber axicon microlens has a large solid angle for light collection and a well-aligned optical path; both contribute to the high collecting efficiency. The portable nature of this single particle active probe also allows measuring the optical signal of the same particle in different environments. Figure 3 shows a scheme to measure surface plasmon scattering of the attached Au nanoparticle in various organic solvents. The illumination was provided by a white light halo-

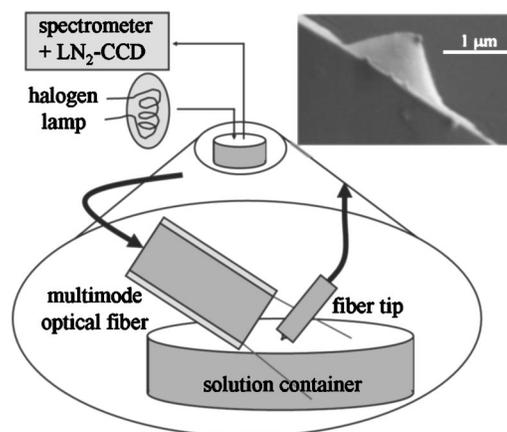


FIG. 3. Schematic diagram for measuring the scattering of a single nanoparticle in various solvents through the optical fiber. The inset shows a SEM image of a nanoparticle attached to the fiber tip.

gen lamp through a separate multimode optical fiber. During the measurement, the angle between the illumination and the detection optical path was fixed at an angle between 68° and 135° . The modified optical fiber tip was immersed into the solution, and the scattering signal was measured by coupling the active probe fiber to the spectrometer and liquid nitrogen cooled CCD detector. After each measurement, the tip was dried in air before immersion into another solution. The position of the illumination and collection optics were kept intact during the solvent exchange.

Figure 4 shows the single particle plasmon scattering signals measured in different solvents. Compared with extinction spectra, the plasmon scattering signal is quite symmetric, without the contribution from the Au interband transition at the short wavelengths. The position of the peak is

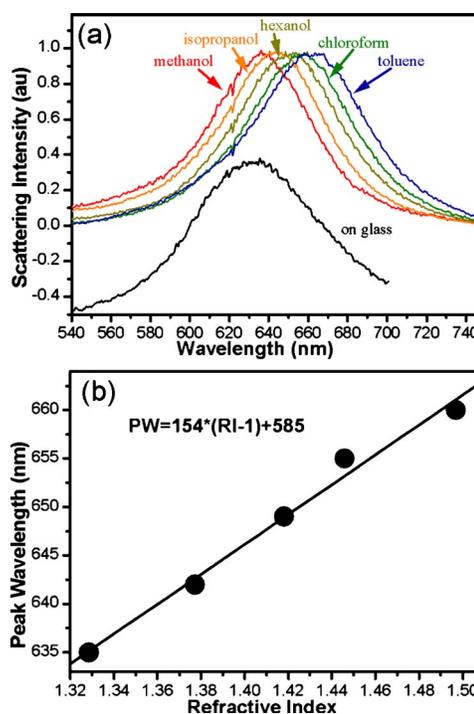


FIG. 4. (a) Normalized plasmon scattering from a single gold nanoparticle in various solvents measured through the optical fiber. The offset curve is the plasmon scattering measured on a glass slide before being picked up by the modified NSOM tip. (b) Dependence of the surface plasmon peak position on the index of refraction of the solvents.

redshifted from the typical bulk extinction measurements as well, which may result from a nonspherical shaped particle^{5,14} as well as its close proximity with the moderate index of refraction glass fiber. The plasmon peak shifts linearly to longer wavelength with increasing solvent index of refraction, from methanol (1.33) to toluene (1.50). The amount of shift obtained from the linear fitting is about 1.54 nm per 0.01 change in index of refraction. This number is similar to the DF measurement of silver nanoparticles on a glass slide.¹⁵ In the quasistatic model, the plasmon resonance occurs when $\epsilon_m + L[\epsilon_1(\omega) - \epsilon_m] = 0$, where L is a geometric factor associated with particle shape. For a spherical particle, $L = 1/3$. ϵ_1 is the real dielectric constant of gold and ϵ_m is the dielectric constant of the adjacent medium (i.e., solvent). For a small change of the solvent index of refraction, Δn_m , the shift of the resonance is

$$\Delta\lambda = -2n_m\Delta n_m \left(\frac{1-L}{L} \right) \bigg/ \frac{d\epsilon_1}{d\lambda}. \quad (1)$$

The measured plasmon shifting rate and the published dielectric constant of Au¹⁶ yield a the geometric factor of $L \approx 0.21$. This is not too far from the value for a spherical particle, indicating that particle shape may slightly contribute to the large shift observed in the experiment. SEM of the sample typically showed faceted particle shapes, which corroborates the aforementioned analysis.

In conclusion, a process to attach a single Au nanoparticle to a chemically etched fiber tip has been demonstrated. The high optical signal collection efficiency allows measuring the same particle response in different solvent environments. This simple detection scheme opens up potential applications using a single particle as chemical and biological sensor on a nanometer scale.

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¹U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).

²S. Empedocles and M. Bawendi, *Acc. Chem. Res.* **32**, 389 (1999).

³K. T. Shimizu, W. K. Woo, B. R. Fisher, H. J. Eisler, and M. G. Bawendi, *Phys. Rev. Lett.* **89**, 117401 (2002).

⁴K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari, and M. S. Feld, *J. Phys.: Condens. Matter* **14**, R597 (2002).

⁵A. D. McFarland and R. P. Van Duyne, *Nano Lett.* **3**, 1057 (2003).

⁶S. Schultz, D. R. Smith, J. J. Mock, and D. A. Schultz, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 996 (2000).

⁷C. Sönnichsen, S. Geier, N. E. Hecker, G. von Plessen, J. Feldmann, H. Ditlbacher, B. Lamprecht, J. R. Krenn, F. R. Aussenegg, V. Z.-H. Chan, J. P. Spatz, and M. Möller, *Appl. Phys. Lett.* **77**, 2949 (2000).

⁸T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkel, and J. Feldmann, *Phys. Rev. Lett.* **80**, 4249 (1998).

⁹A. A. Mikhailovsky, M. A. Petruska, M. I. Stockman, and V. I. Klimov, *Opt. Lett.* **28**, 1686 (2003).

¹⁰G. A. Wurtz, J. S. Im, S. K. Gray, and G. P. Wiederrecht, *J. Phys. Chem. B* **107**, 14191 (2003).

¹¹T. Kalkbrenner, M. Ramstein, J. Mlynek, and V. Sandoghdar, *J. Microsc.* **202**, 72 (2001).

¹²S.-K. Eah, W. Jhe, and Y. Arakawa, *Rev. Sci. Instrum.* **74**, 4969 (2003).

¹³N. R. Jana, L. Gearheart, and C. J. Murphy, *Chem. Mater.* **13**, 2313 (2001).

¹⁴J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, *J. Chem. Phys.* **116**, 6755 (2002).

¹⁵J. J. Mock, D. R. Smith, and S. Schultz, *Nano Lett.* **3**, 485 (2003).

¹⁶P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**, 4370 (1972).