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# Near-field optical studies of local photomodification in nanostructured materials

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## Summary

Fractal aggregates of silver nanoparticles are studied experimentally using atomic force microscopy and photon scanning tunnelling microscopy. Large changes in the near-field optical response of fractal aggregates are observed after the irradiation of samples with nanosecond laser pulses. The threshold energy density for photomodification using a 532 nm laser is measured to be 9 mJ $cm^{-2}$. It is shown that photomodification-induced changes in the local optical response can be two orders of magnitude larger than changes in far-field absorption.

## Introduction

Fractal structures exhibit dilation symmetry rather than the translation symmetry found in crystalline materials. This unique symmetry often results in localization of dynamic excitations in fractals (Alexander & Orbach, 1982; Markel *et al.*, 1991; Shalaev, 1996). Theoretical analysis predicts that the electric field at optical frequencies near a fractal material is highly nonuniform. There exist areas of nanometre dimensions (called hot spots) where the local electric field exceeds the applied field by several orders of magnitude (Shalaev & Stockman, 1987; Markel *et al.*, 1991; Shalaev, 1996; Stockman *et al.*, 1996). Owing to the fractal's scale-invariant geometry, the highly localized electric field or hot spots exist over a spectral range much broader than the absorption bandwidth of an individual nanoparticle. The presence of hot spots on silver fractal aggregates has been observed directly using near-field optical microscopy (Tsai *et al.*, 1994; Bozhelvolnyi *et al.*, 1998). Utilizing the huge local enhancement of Stokes fields (up to a factor of $10^{15}$; Gadenne *et al.*, 1998), surface-enhanced Raman scattering from single molecules can be achieved (Kneipp *et al.*, 1997; Nie & Emory, 1997).

Irradiation of silver fractal aggregates by a laser pulse with energy above a threshold leads to 'photoburning' of a spectral hole in the absorption spectrum of the aggregates near the laser wavelength (Karpov *et al.*, 1988; Plekhanov *et al.*, 1991). Electron microscopic study of the aggregates before and after irradiation shows that the aggregate structure as a whole remains the same after irradiation, but that nanoparticles within some nanometre-scale regions change their shape and local arrangement (Safonov *et al.*, 1998). The diameters of the selectively photomodified regions are of the order of 10 nm and decrease as the photomodification laser wavelength increases, in agreement with theoretical predictions (Shalaev & Stockman, 1987; Markel *et al.*, 1991; Shalaev, 1996; Stockman *et al.*, 1996). After photomodification with a laser energy slightly above the threshold, the absorption coefficient of a macroscopic fractal sample, measured in the far field, changes by $\approx 1\%$ (Safonov *et al.*, 1998).

In this paper, we report experimental investigations of local changes in the optical near-field of metal fractal aggregates carried out using photon scanning tunnelling microscopy (PSTM) and atomic force microscopy (AFM).

## Experimental

Fractal samples were studied using a microscope constructed from a modified commercial atomic force microscope (Quesant Q250) for simultaneous acquisition of AFM and PSTM images. As illustrated in Fig. 1, samples were mounted on the hypotenuse face of a 90° prism with index-matching fluid and illuminated by the evanescent field in the total internal reflection geometry. The illumination source was a He–Ne laser operating at 532 or 633 nm and *s*-polarized. The local optical signal was collected through an uncoated optical fibre, which was sharpened to $\approx 50$ nm

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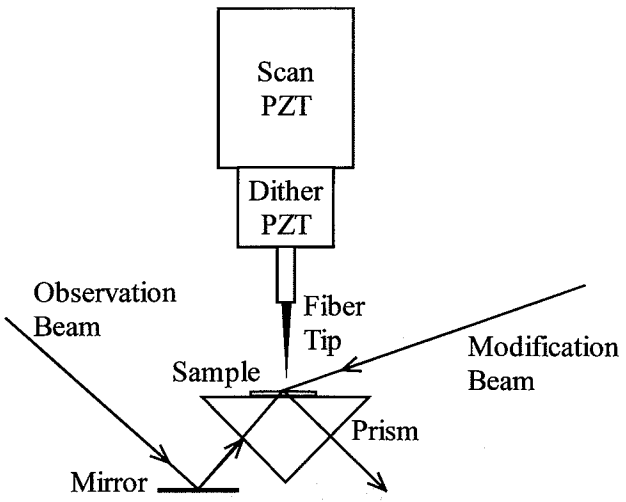


**Fig. 1.** Illumination geometry used in the photomodification experiments. Both modification and observation beams are *s*-polarized at the sample surface.

in radius at the tip using a fibre puller (Sutter Instruments P-2000). The separation between the tip and a sample was regulated using nonoptical shear-force feedback as suggested by Lee *et al.* (1996). In contrast to conventional optical methods (Betzig *et al.*, 1992), this method of feedback control eliminates the need for the complicated alignment of a feedback laser and a photodetector to the fibre tip and for filtering the detected light to remove unwanted signals from the feedback laser. Photomodification was achieved by irradiating the sample, *in situ*, using 5 ns pulses of the second harmonic output of a Nd:YAG laser (Quantel Brilliant). The modification beam was incident on the sample, from above, at an incident angle of 70° from the surface normal.

The fractal films used in our experiments were synthesized by two different methods. In the first (Safonov *et al.*, 1998), fractal aggregates of silver nanoparticles were grown in a colloidal solution prepared from ethylenediamine tetraacetic acid (Heard *et al.*, 1993) and deposited on a glass substrate. This type of silver colloidal aggregate has been characterized using electron microscopy and was used in our previous far-field measurements (Markel *et al.*, 1996; Safonov *et al.*, 1998). Fractal aggregates were also prepared by laser ablation of a silver target placed in a vacuum chamber back-filled with a buffer gas (Plekhanov *et al.*, 1991). An Nd:YAG laser (Quanta-Ray DCR), which provided 8 ns, 1064 nm pulses at a 10 Hz repetition rate, was focused onto the silver target. Silver nanoparticles formed during laser ablation were aggregated together in the buffer gas during a diffusion-limited process and became fractal clusters (Plekhanov *et al.*, 1991). The fractal clusters eventually settled down on a glass substrate placed at the bottom of the chamber, forming a thin film of fractal material. Our electron microscopic study showed that fractal clusters of this type consisted of hundreds to thousands of nanoparticles.

## Results

Figure 2 shows atomic force and near-field optical images of silver colloidal aggregates. The PSTM images show a very inhomogeneous distribution of optical intensity, as predicted theoretically (Shalaev, 1996) and observed in previous experiments (Tsai *et al.*, 1994). The minimum feature size is $\approx 200$ nm, corresponding to the lateral resolution of our PSTM. The theoretical minimum feature size is smaller by an order of magnitude (Shalaev, 1996). The contrast of the observed intensity fluctuations is lower than the theories predict; this is probably due to the limited resolution of uncoated fibre tips. We feel, however, that it is important to use uncoated tips for this type of measurement, in order to minimize the tip's perturbation of the local field (Tsai *et al.*, 1994; Bozhelvolnyi *et al.*, 1996).

The three images on the left of Fig. 2 were recorded on a freshly prepared sample. The fractal film was then irradiated with 10, *s*-polarized, 20 mJ cm$^{-2}$ pulses from the Nd:YAG laser. Another set of images was recorded after irradiation and is shown on the right of Fig. 2. The AFM images verify that we are observing the same area of the sample during each scan. The PSTM images after irradiation exhibit significant differences from those taken before irradiation. The local intensity at some hot spots decreases by as much as a factor of two after irradiation. Other hot spots increase in intensity as a result of photomodification. For example, in the images recorded using the 543 nm observation wavelength, the excitation initially at $x = 1{\cdot}5\ \mu$m and $y = 3{\cdot}2\ \mu$m is diminished after irradiation. In the images recorded using a 633-nm beam, the excitation initially at $x = 2{\cdot}9\ \mu$m and $y = 3{\cdot}8\ \mu$m reduces in intensity after irradiation and a hot spot at $x = 0{\cdot}5\ \mu$m and $y = 2{\cdot}7\ \mu$m doubles in intensity. Occasionally, a hot spot will appear or disappear entirely.

When the fractal film is irradiated at 532 nm, resonance modes with wavelengths around 532 nm are excited and nanoparticles in the corresponding hot spots are restructured. This explains why photomodification is observed when the modification beam is at 532 nm and the observation beam is at 543 nm; these beams have similar wavelengths. Because the restructured nanoparticles also participate in the excitation of other resonance modes at various wavelengths, photomodification can also occur when observed at wavelengths far from that of the modification source. Therefore, significant differences in the PSTM images are still observed at 633 nm, even though this is at the long-wavelength edge of the spectral hole burned by laser pulses at 532 nm.

In a previous paper, we observed irradiation-induced restructuring, or sintering, of a small number of nanoparticles using electron microscopy (Safonov *et al.*, 1998).

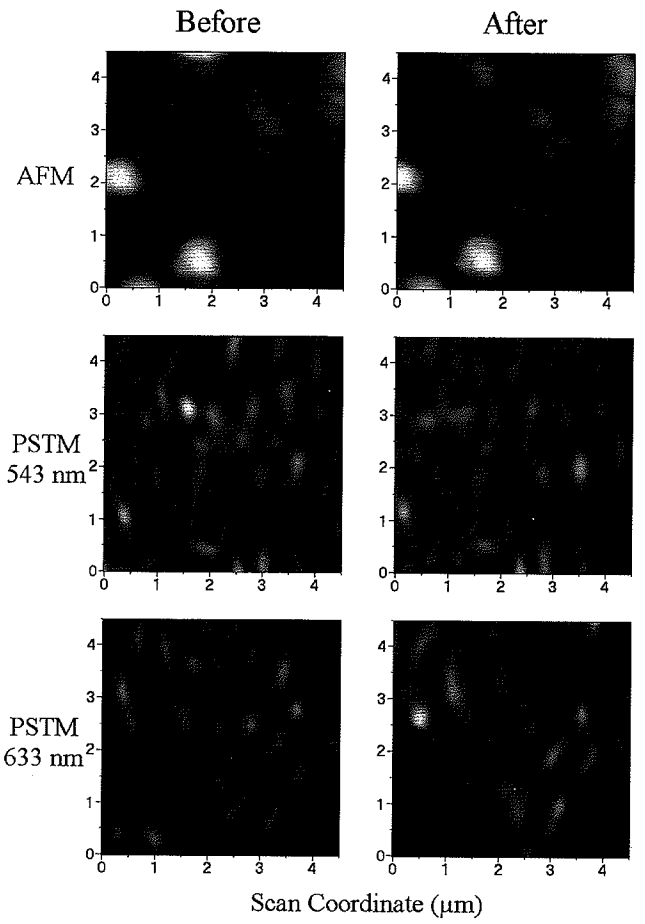


**Fig. 2.** AFM and PSTM images of a silver fractal film before and after photomodification of the sample using nanosecond laser pulses at 532 nm. The PSTM images were recorded using observation wavelengths of 543 and 633 nm.

The experiments reported in the current paper provide direct evidence that such a small structural change can result in significant modification of local optical intensity.

The threshold nature of the photomodification process is revealed in Fig. 3, which shows PSTM images from three consecutive scans of the same area of a fractal film. Between the scans shown in the figure, the tip was retracted from the sample and the fractal surface was irradiated with 10 pulses at 532 nm. The energy density incident on the sample surface was $8{\cdot}5\,\mathrm{mJ\,cm^{-2}}$ between the first two scans and $9{\cdot}5\,\mathrm{mJ\,cm^{-2}}$ between the second and third scans. The first two PSTM images are nearly identical, whereas the second and third images show individual hot spots that change dramatically. A spot near $x = 2{\cdot}2\,\mu\mathrm{m}$ and $y = 3{\cdot}0\,\mu\mathrm{m}$, for example, decreases in intensity by a factor of two after irradiation with an energy density of $9{\cdot}5\,\mathrm{mJ\,cm^{-2}}$. These observations indicate a threshold energy density of $\approx 9\,\mathrm{mJ\,cm^{-2}}$, which is in general agreement with our previous work, where a threshold of $12\,\mathrm{mJ\,cm^{-2}}$ was measured from small spectral holes in the far-field optical absorption (Safonov *et al.*, 1998). Near the threshold, the relative intensity changes at some local areas are of the order of 100% (Figs 2 and 3), whereas the far-field-absorption change was only $\approx 1\%$ (Safonov *et al.*, 1998).

Experiments on fractal clusters prepared using the laser ablation technique showed similar results. The threshold energy density is $\approx 8\,\mathrm{mJ\,cm^{-2}}$ for photomodification of the laser-ablated samples.

## Conclusion

Near-field optical images of the selective photomodification of silver fractal aggregates were obtained. Experimental data

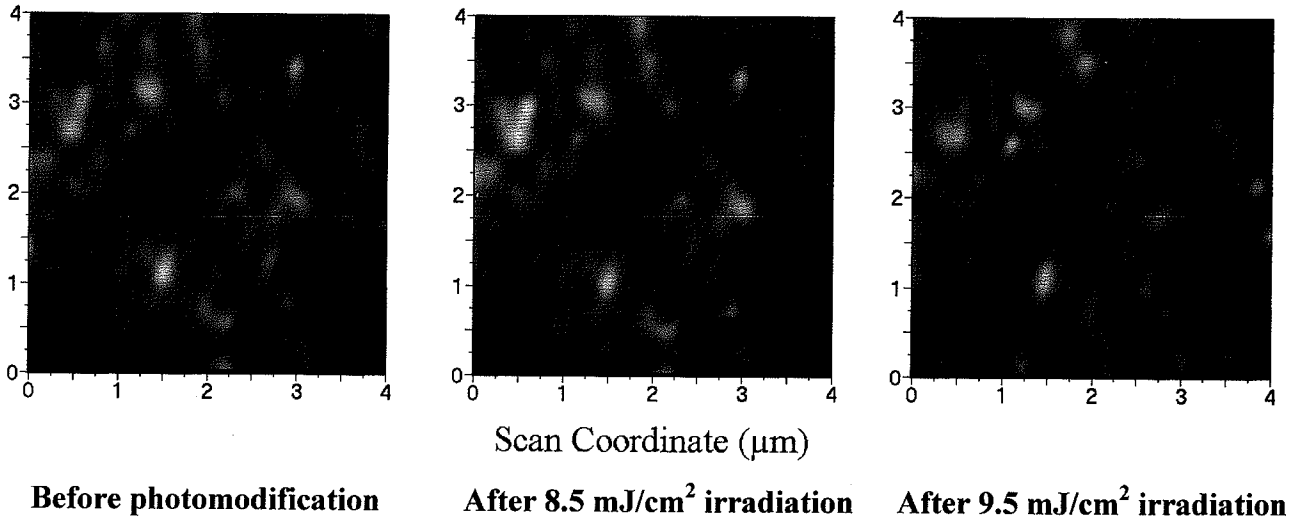


**Fig. 3.** Three successive PSTM images of a silver fractal film showing the onset of photomodification. The modification beam had energy densities of $8{\cdot}5\,\mathrm{mJ\,cm^{-2}}$ between the first two scans and $9{\cdot}5\,\mathrm{mJ\,cm^{-2}}$ between the second and third scans.

show that the local structure of hot spots, corresponding to localized optical excitations, changes as a result of the selective photomodification. The scale of the observed near-field restructuring is less than the laser wavelength. Photomodification-induced changes in the local near-field response can be two orders of magnitude larger than changes in far-field optical absorption. Selective local writing and reading, as demonstrated in this study, suggests possible applications in dense optical data recording.

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