

## TOWARDS NANOMETRIC OPTICAL TWEEZERS THROUGH NEAR-FIELD PHOTOCHEMISTRY

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Photoexcitation of chemical reaction with resolution below the diffraction limit can be achieved in the far-field using a two-photon reaction activated by diffraction-limited laser-spot [1], or in the near-field using a sub-wavelength aperture [2]. We present an alternative method based on interaction of light with a conductive nano-object [3]. In combination with appropriate materials, which show molecular migration under the influence of light intensity gradient, the method allows to trap in the near-field of illuminated metallic nano-tip a few photosensitive polymer molecules, and to transfer theirs on other place of the surface.

The illumination of metallic nano-particle causes a strongly localized electromagnetic field close to the particle (i.e. near-field).[4] Depending on the light wavelength and on the material and shape of the particle, the intensity of the near-field can be  $10^5$  higher than the irradiating light intensity.[5] The photoexcitation of organic molecules by such an extremely enhanced near-field have been experimentally observed through surface-enhanced Raman scattering, luminescence and second harmonic generation. As the photoexcitation is the first step of any photochemical reaction, one might expect that the subsequent interstate crossing of suitable molecules in the vicinity of illuminated metallic nano-object would be also enhanced. In other words, the enhanced near-field could be used to achieve a strongly localized photochemical reaction.

To verify this assumption we used azobenzene-containing polymers, which can undergo reversible isomerization under illumination of specific spectral band. During photoisomerization an electron density redistribution takes place causing a change in both the magnitude and direction of the molecular dipole moment. Since in the sample the azogroups were noncentrosymmetrically oriented along the normal to the substrate, the changing normal component of the dipole moment caused a change of the surface potential, which was detected by Scanning Kelvin Microscope (SKM) [6].

It was found, that a strongly localized change of the surface potential occurred when a conductive SKM tip was scanned a fixed distance from the surface (noncontact mode) while simultaneously irradiating the sample with light of low intensity at definite wavelength [3]. The magnitude of the photoinduced change of the surface potential had a significant maximum at ca. 11 nm tip-surface distance. No alterations in topography were observed.

We rank the experiment described above to the first example of artificially enhanced photo-isomerization in the vicinity of illuminated metallic nano-object.

The further development of this method is excitation of photoprocess taking place solely in the near-field of the illuminated object. Light-induced mass-transport effect [7] (molecular migration), which occurs in some azobenzene-containing systems under the influence of light intensity gradient, was used for this purpose. The substances were used show a positive molecular migration at intensity gradient. That means, the molecules mowed from arias with low to arias with high intensity, as is clear from the AFM pictures of the sample modified by scanning laser illumination.

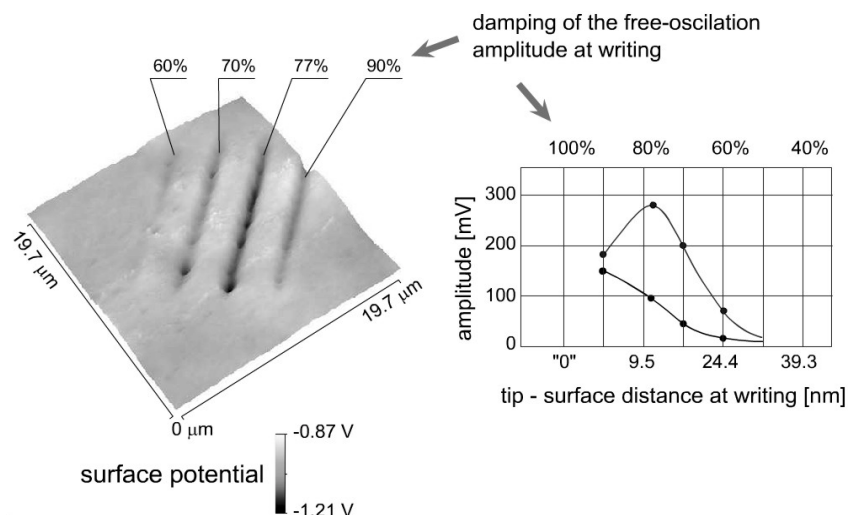


Fig. 1. Dependence of the photoisomerization rate on the tip-surface distance.

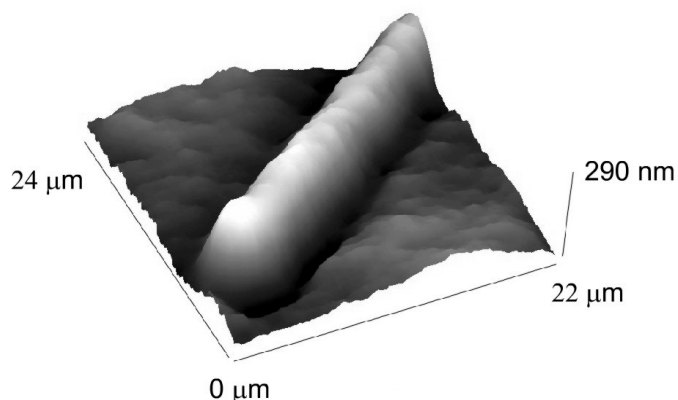


Fig. 2.

AFM image of the surface of azobenzene containing film modified by scanning laser illumination.

Since at uniform illumination of a surface with deposited metallic nano-particles, the light intensity gradient exists only near to the particles, one might expect that azo-molecules will migrate solely in the vicinity of the particles. It was found, that after illumination, a knolls arise around gold nano-particles deposited on the surface of azobenzene-containing film. The angular distribution of the matter in the circular knolls depends on the polarization of the light, as well as on the distance between the particles. Presumably the coupling of the plasmons in nearby particles influences the knolls shape.

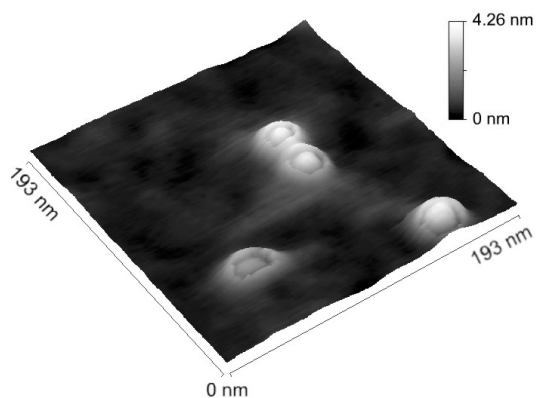


Fig 3.

The surface of azobenzene containing film with deposited gold nanoparticles after illumination with visible light.

The potential application of optical near-field for high-resolved trapping of nano-objects has been discussed in theoretical works. [8] The realizing “nanometric optical tweezers” encounters however with the necessity of relatively high illuminating light intensity to produce a force able to trap in the near-field any free-state dielectric nano-object. The azobenzene derivatives leave to avoid this complexity due to their high sensitivity to light intensity gradient.

On the Fig. 4 are presented five hillocks produced by irradiation of platinum AFM tip while it approaches, but not contact to the surface of azobenzene-containing film (noncontact operation mode). The width of one single-structure is about 33 nanometers (including the AFM tip radius) and the corresponding volume is commensurable with the volume of polymer single-molecule.

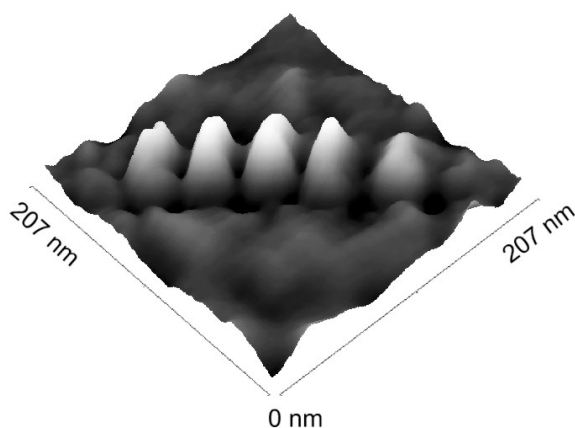


Fig. 4

Light induced nano-modification produced in noncontact operating mode. The gray scale correspond to 0...3.6 nm.

Though the molecules, driven by light intensity gradient aspire to the tip, they cannot leave the surface if the AFM operates in noncontact mode because of the dominating of the surface tension force, which keeps the molecules on the surface. This limitation could be obviated if the tip contacts the surface during illumination. We were able in that way to trap a nano-sized part of the surface with the AFM tip and to transfer it on a new place.

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