**Detecting Intruders on the Nanoscale**
Carsten Sönnichsen
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PHYSICS

# Detecting Intruders on the Nanoscale

Changes in position within a complex stack of gold nanorods can be detected optically and may enable more precise position sensing of biomolecules.

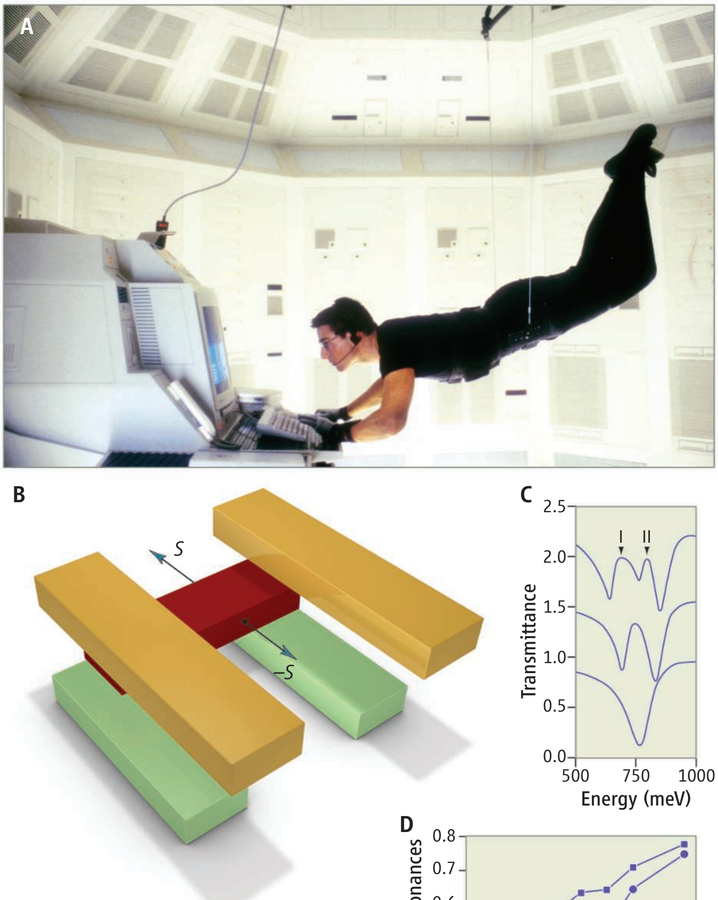
**Carsten Sönnichsen**

Intruder detectors work because they contain proximity sensors; for example, a person entering a room triggers a change in distance (see the figure, panel A). At the molecular scale, small metal objects, such as gold nanoparticles, can be attached to biomolecules and used as proximity sensors. The nanoparticles act as dipolar "antennas" for visible and near-infrared light waves and create plasmon resonances that strongly absorb or scatter light at specific frequencies. They act as one-dimensional (1D) plasmon rulers because the specific resonance frequency depends strongly on the proximity of other objects (*1*). More elaborate metal nanostructures, or metamaterials, show complex optical responses, with resonance modes corresponding to electric dipole and higher-order multiple oscillations (*2*). On page 1407 of this issue, Liu *et al*. (*3*) have used a stack of five gold nanorods that can report not just a single distance but the precise position of one central rod with respect to the others, creating a 3D plasmon ruler.

Plasmon rulers are useful for investigating dynamic processes of biomolecules in physiological environments because they report local distance changes on subnanometer scales continuously, with high temporal resolution over long times. Relative to other structural analysis techniques such as nuclear magnetic resonance or x-ray crystallography, plasmon rulers are more compatible with liquid environments and are more useful for studies of single molecules; relative to other single-molecule techniques such as Förster resonance energy transfers (FRET) between organic dyes, plasmon rulers are considerably more photostable, cover larger distances, and provide very strong optical signals. Nanometer-sized metallic objects interact so strongly with light that gold nanoparticles were probably the first submicroscopic or "nano" objects observed individually (*4*).

In Liu *et al*.'s 3D plasmon ruler, the central rod was sandwiched between two pairs of parallel rods arranged in a configuration as in the letter H (where the central rod is the horizontal bar; see the figure, panel B). The two pairs of parallel rods were chosen such that they acted as quadrupolar antennas at slightly shifted frequencies. Any movement of the central rod relative to those two quadrupole antennas showed up in a characteristic way as shifts in the plasmon resonances of the system (see the figure, panels C and D). Liu *et al*. fabricated nearly identical stacks of gold rods (varying only the position of the central rod) with an impressive use of high-precision electron beam lithography.

Harnessing such 3D rulers to study the dynamics of biomolecules will likely require simpler fabrication methods. In the past decade, there has been a renaissance of optical applications of metallic nanoparticles involving the direction and concentration of light on the subwavelength scale (*5*). These efforts were driven by rapid progress in the chemical fabrication of metal nanoparticles of precisely controlled shape, as well as the development of directed self-assembly methods (*6*). However, classical top-down lithography is often superior to the wet-chemical approach for complex objects such as 3D plasmon rul-




**A nanoscopic motion sensor.** (**A**) In the macroscopic world, capacitive or inductive motion sensors are used for intruder alarms or simple motion-sensitive light switches. They react to changes in the environment around an antenna near field, resulting in a change of the antenna characteristics (unless defeated by clever exploits). (**B**) The 3D plasmon ruler fabricated by Liu *et al*. is a nanoscopic version of position sensing with optical readout; changes in displacement of the red bar vertically or laterally (*S*) can be detected. (**C**) A theoretical analysis shows how lateral displacement of the red bar shifts the plasmon resonances created by its nonequivalent interactions with the fixed yellow (I) and green (II) bars. (**D**) The frequency of these resonances (and the optical transmission at the resonances) shifts up or down, depending on the direction and magnitude of displacement.

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ers. Complex templates would be needed to direct self-assembly from solution. Such complexity does exist, for example, in DNA origami structures (*7*), but these molecules have not been harnessed as templates.

Optical techniques to study the plasmon resonances of individual objects also need further development if 3D plasmon rulers are to be fully exploited. Fluorescence microscopy has long been used because the excitation light does not interfere with the signal (it is at shorter wavelengths and is readily filtered out), but its use is limited to investigation of fluorescent molecules. More complicated methods will be needed to generate the contrast necessary to detect individual nanoscale plasmonic objects (that show no fluorescence) and to monitor their spectral response over a relatively large range. The efforts of Zsigmondy and Siedentopf in the early 20th century to study individual gold colloids have been reinvigorated with the advent of modern spectrometers capable of quantitative analysis (*8*), although more advanced optical techniques continue to be developed (*9–11*).

Plasmon rulers excel at the dynamic monitoring of molecular distance changes on a single-molecule level. Just as with FRET distance rulers, absolute distances are not as easily obtained with plasmon rulers, because the calibration of an individual ruler is a challenging task on the single-molecule level; however, absolute distances are routinely deduced (on static objects) by imaging techniques, mainly electron microscopy. Monitoring the structural dynamics of single molecules is central to the understanding of biological function and, more fundamentally, to the general understanding of nonequilibrium processes on a molecular level (*12*, *13*). The 3D ruler concept of Liu *et al*. provides a novel twist by introducing multiple coupled plasmon modes that interact in a way that provides rich structure in spectra that are otherwise often featureless. It should be feasible to extend this idea toward even more complicated plasmon structures that may respond to local changes in a very complex way.

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GEOPHYSICS

# A Tale of Two Earthquakes

**Networks of GPS detectors can provide a detailed picture of the dynamics of earthquakes before, during, and after the event.**

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Thousands of lives were saved by the "Large Tsunami Warning" announcements of the Japan Meteorological Agency that followed the Tohoku-Oki earthquake of 11 March 2011. A similar alert followed the Central Chile (Maule) earthquake on 27 February 2010. Understanding better how such earthquakes develop might provide even more effective early-warning systems to help mitigate their devastating power. Four papers in this issue—by Sato *et al*. on page 1395 (*1*), Simons *et al*. on page 1421 (*2*), Ide *et al*. on page 1426 (*3*), and Vigny *et al*. on page 1417 (*4*)—report on both of these magnitude 9 (*M*9) earthquakes, illustrating the use of networks of Global Positioning System (GPS) detectors to reveal how the Earth's surface deformed during and after the events.

Four *M*9 earthquakes hit Kamchatka, Aleutian Islands, Chile, and Alaska in a relatively short period between 1952 and 1964. After remaining silent for more than 40 years, *M*9 earthquakes have resumed: the 2004 Sumatra-Andaman (*M*9.2) (*5*), 2010 Maule (*M*8.8), and 2011 Tohoku-Oki (*M*9.0) earthquakes. The last two are the first *M*9 events to be studied by dense networks of continuous GPS observing stations. The region of the Chilean subduction zone reported on by Vigny *et al*. is known as the Concepción-Constitución seismic gap (*6*), because it fits the "seismic gap" hypothesis—that the recurrence history of past earthquakes suggests imminent rupture. Thus, multiple international teams deployed GPS stations in the area, resulting in a dense network of seismic detectors.

Tsunamis are caused by coseismic vertical movements of the sea floor. Coseismic crustal movements in the 2010 Maule earthquake were observed at ~90 GPS stations and observed continuously at ~60 sites (*4*) (see the figure). The earthquake released east-west compressional strain accumulated in South America by the eastward subducting Nazca Plate. Meters of westward displacements occurred along the Chilean coast with smaller displacements extending across the continent to the Atlantic coast. In the 2011 Tohoku-Oki earthquake, eastward displacements extended as far as Kyushu in southwest Japan. In Chile, because the boundary between coseismic uplift and subsidence roughly coincides with the coastline, coastal towns experienced relatively small vertical movements. However, the northeastern Japan shoreline was farther away from the trench, and coastal lowlands already suffer from inundation at high tide caused by the coseismic subsidence of this earthquake. This subsidence will not be compensated by future interseismic uplift (*7*).

The largest displacement of a GPS station on land was about 5 m in both earthquakes (southwest of Concepción in Chile, and in the Oshika Peninsula in northeast Japan). In Japan, measurements of sea-floor positioning revealed eastward coseismic movement of 24 m near the epicenter, ~100 km off the coast (*1*). This, together with the 31-m displacement east-southeast (not included in the figure), measured by the Tohoku University group at a submarine benchmark ~175 km offshore, would be the world record for measured coseismic displacement .

Large interplate earthquakes are often followed by silent fault slip (afterslip), and this causes postseismic crustal movement in the same direction as that of coseismic jumps (*8*). Postseismic movement of ~15 cm was recorded in Concepción in the first 12 days after the Maule earthquake (*4*). In

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