

Nanoantenna-enhanced gas sensing in a single tailored nanofocus

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Abstract

We demonstrate antenna-enhanced hydrogen sensing at the single-particle level. We place a single palladium nanoparticle near the tip region of a gold nanoantenna and detect the changing optical properties of the system upon hydrogen exposure.

1. Introduction

Metallic nanostructures exhibit plasmonic resonances which spatially confine light on the nanometer scale [1]. In the ultimate limit of a single nanostructure, the electromagnetic field can be strongly concentrated in a volume of only a few hundred nm³ or less. This optical nanofocus is ideal for plasmonic sensing. Any object that is brought into this single spot will influence the optical nanostructure resonance with its dielectric properties. Here, we demonstrate antenna-enhanced hydrogen sensing at the single particle level. We place a single palladium nanoparticle at distance d near the tip region of a gold nanoantenna (Fig. 1a) and detect the changing optical properties of the system upon hydrogen exposure (Fig. 1b) by dark-field microscopy. Our method avoids any inhomogeneous broadening and statistical effects that would occur in sensors based on nanoparticle ensembles [2]. Our concept paves the road towards the observation of single catalytic processes in nanoreactors.

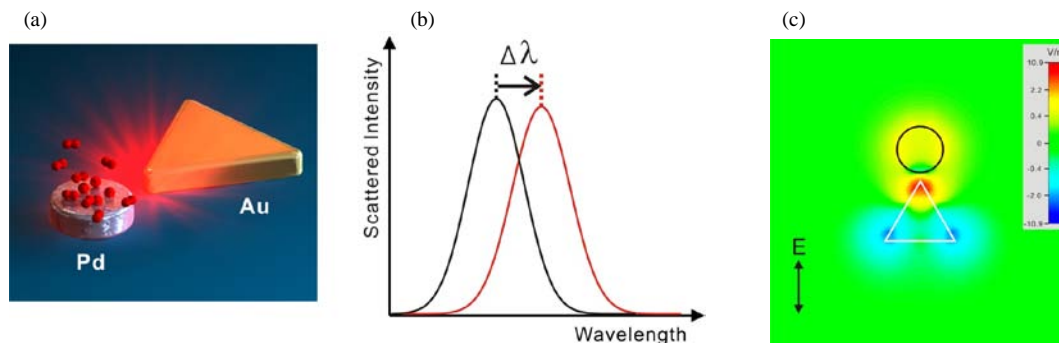


Fig. 1. (a) Hydrogen sensing using a resonant antenna-enhanced scheme. The palladium nanoparticle is placed at the nanofocus of a gold antenna, which scatters strongly. (b) Hydrogen absorption in the palladium particle changes its complex dielectric function, which causes a resonance shift ($\Delta\lambda$) of the gold antenna that can be optically detected. (c) Electromagnetic FDTD simulation of the local electric fields. The polarization is along the vertical direction. Near the tip of the gold triangle antenna, the electromagnetic fields are highly localized and strongly enhanced.

2. Results and discussions

Fig. 1c displays the simulated electric-field distribution of the gold triangle antenna sensor at resonance. The incident light is polarized parallel to the longer axis of the individual system. It is evident

that when the gold antenna is resonantly excited, collective dipolar-like particle plasmons lead to greatly enhanced fields at the tips of the gold triangle. Specifically, due to the sharp tip feature of the gold triangle, the near-fields are spatially concentrated in a single spot right next to the palladium particle.

Fig. 2 presents the scattering spectra of the gold triangle sensor in response to hydrogen/nitrogen exposure. The optical scattering measurement of the gold triangle sensor, in which d is as small as 10 nm, is shown in Fig. 2a. The spectral peak positions were extracted from the experimental spectra. The smoothed curves are represented by black solid lines in the same figure. In order to highlight the spectral shift in dependence on the hydrogen concentration, the extracted spectral peak positions are displayed in the right column of Fig. 2a. When the hydrogen pressure is 0 Torr, i.e., pure nitrogen, a plasmonic resonance is visible around 638 nm, which is represented by the lowest spectrum in Fig. 2a. This resonance is associated with the resonant excitation of dipolar-like particle plasmons in the gold triangle (see Fig. 1c). When the hydrogen pressure is increased to 8 Torr ($\sim 1\%$ concentration), a clear resonance red-shift (~ 5 nm) is observable and simultaneously the resonance intensity is dramatically suppressed (see the second lowest spectrum in Fig. 2a). As a result, the hydrogen absorption event in the palladium particle is indirectly detected by monitoring the gold antenna particle plasmon response. This relies on the fact that the dielectric permittivity of the palladium is modified upon Fermi level shifting due to incorporation of free electrons from the adsorbed hydrogen. A subsequent pressure increase of hydrogen (16 Torr, $\sim 2\%$) leads to a further resonance red-shift (~ 9 nm) as shown in Fig. 2a. In order to probe the hydrogen adsorption/desorption response, the hydrogen pressure is driven back in a second cycle. As shown in Fig. 2a, the resonance peak does not return to the original position at 0 Torr in the first cycle. It exhibits a net red-shift around 4 nm, showing hysteresis [3]. As a sidemark, this is the first *optical* observation of net hysteresis effects in a single palladium nanoparticle.

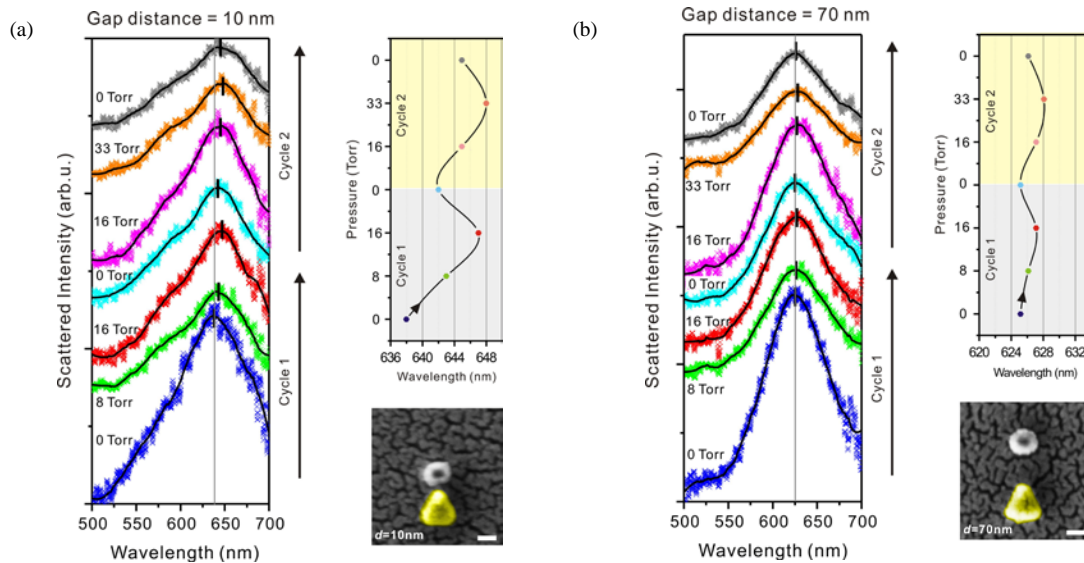


Fig. 2. Optical scattering measurements of a single palladium-based gold triangle antenna upon hydrogen exposure in dependence on the separation d between the gold antenna and the palladium nanoparticle. (a) $d = 10$ nm; (b) $d = 70$ nm. In each figure, the hydrogen partial pressure is raised from 0 Torr to higher pressures and driven back to 0 Torr. Two cycles are displayed. 33 Torr corresponds approximately to a 4% H_2/N_2 concentration. The right diagram in each figure shows the behavior of the resonance peak upon hydrogen cycles one and two. The lines connecting the data points are guides to the eye. The arrow indicates the direction of measurements. The SEM image of the nanostructure is shown in each figure accordingly. The scale bar is 50 nm. At larger distances, the spectral shift substantially decreases. The spectral shift does not go back to its original value due to hysteresis effects of the hydrogen uptake.

In order to investigate the influence of the local field enhancement on the sensor activity, the gap distance d between the gold antenna and the palladium particle is systematically increased. Fig. 2b displays the optical scattering spectra of the gold triangle sensor in response to hydrogen exposure, in which d is increased to 70 nm. Just like in the case of $d = 10$ nm, the sensor follows an overall similar trail upon hydrogen absorption or desorption, however, with much smaller spectral shifts. This is due to the fact that plasmon-induced electromagnetic fields decay exponentially away from the gold antenna surface. As a result, the particle plasmon resonance of the nanoantenna shows a substantially reduced response to the dielectric change in a spot away from the nanofocus.

Antenna-enhanced single-particle sensing pushes the sensitivity of plasmonic gas sensors to an ultimate limit and opens up myriad possibilities for detecting optically inactive species in a controlled fashion. The single-particle sensing strategy will have profound significance for the optical observation of chemical reactions and catalytic activities on a single platform in nanoreactors, and has the potential to be extended to biochemical systems in the future. Moreover, antenna-enhanced sensing comprises a noninvasive and generalizable scheme that is applicable to a variety of physical and biochemical materials.

3. Acknowledgements

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