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Differential Plasmon Spectroscopy as a Tool for Monitoring Molecular Binding to Ultrathin Gold Films

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A novel scheme for sensing molecular binding to gold is presented. The method is based on ultrathin, island-type gold films and differential plasmon spectroscopy (DPS) in the transmission UV/vis mode. It is submonolayer sensitive and simple to apply.

Ultrathin (less than 10 nm) Au films evaporated on transparent substrates such as mica or quartz are easy to prepare, showing a well-defined island structure that may be controlled by the evaporation parameters.[1] Such films show unusual optical properties, strikingly different from those of bulk Au.[2] Thicker films were used as optically transparent electrodes in spectroelectrochemistry.[3] Ultrathin Au films can be used as substrates for monolayer self-assembly, and in the case of monolayers containing chromophores (e.g., metalloporphyrins or metallophthalocyanines) their transparency allows monolayer characterization by transmission UV/vis spectroscopy.[1b,c,4]

The notable sensitivity of surface plasmon excitation to the presence of adsorbates provides an effective route for monitoring molecular binding to Au surfaces. This has been widely used in surface plasmon resonance (SPR) sensors for characterization of surface-confined processes.[5] Other arrangements that use thin Au films have been suggested,[6] such as a fiber optic surface plasmon based sensor[6a,b] and an Au film evaporated on a monolayer of polystyrene spheres attached to a continuous Au layer.[6c] Systems containing Au nanoparticles have also been tested for use as optical sensors,[6c,7] as the position and intensity of the maximum observed in the surface plasmon absorption of Au colloids depends strongly on the dielectric constant of the contacting medium.[8] The similarity in the optical properties of Au colloids and island-type films suggests that the latter might also be used as optical sensors.

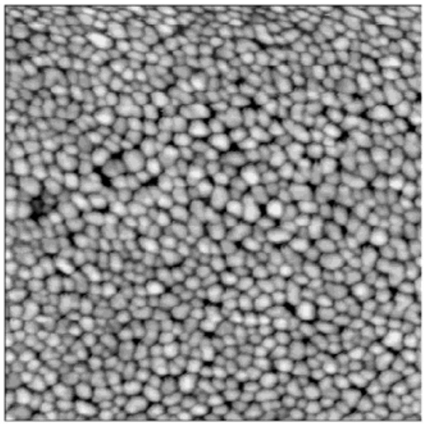

Figure 1. Noncontact AFM topographic image (500 nm scan) of unannealed ultrathin (2.5 nm nominal thickness) Au film, evaporated on quartz at 0.005 nm/s.

Here we demonstrate the use of ultrathin, island-type Au films, evaporated on transparent substrates, as optical sensors whose sensitivity to changes in the contacting phase is similar to that of SPR or colloid systems, while their application is exceedingly simple. Changes in the surface plasmon intensity, obtained directly from difference (transmission UV/vis) spectra, are shown to linearly correlate with the amount of adsorbed molecules, thereby fulfilling the basic requirement for quantitative monitoring and sensing.

Figure 1 shows an atomic force microscope (AFM) image of an unannealed, 2.5 nm (nominal thickness) Au film evaporated on quartz. As with previously reported ultrathin Au films on mica,[1c] the film in Figure 1 appears rather continuous, with a narrow island size distribution. The same is observed for films with other thicknesses in the range ≤10 nm, both annealed (3−4 h at 250 °C) and unannealed.[9] Previously reported films of a similar kind[6b,10] showed Au islands separated by distances comparable to their size; the different morphology observed here may be due to the slow evaporation rate (0.005 nm/s).

The molecule **1** (Figure 2b, inset), used here to demonstrate the method, possesses a cyclic disulfide for attachment to a gold surface, and two pyrene residues showing three intense absorption bands in the UV region, while in the visible range the molecule is nearly transparent (Figure 2b, dashed line). It enables one to determine directly the amount of adsorbed molecules by the intensity of these three UV absorption bands, while simultaneously following changes in the Au surface plasmon absorption accompanying molecular binding to the Au.[1c]

The series of transmission UV/vis absolute (Figure 2a) and difference (Figure 2b) spectra of a 2.5 nm Au island film show the changes observed during formation of a monolayer of **1.** The self-assembly process (Figure 2a) is accompanied by an increase of the chromophore absorption bands in the UV range, and an increase and a red shift of the Au surface plasmon absorption band around 600 nm.[11]

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(11) The maxima around 245 and 360 nm in the background spectrum (0 s) are quartz and Au absorptions, not related to the chromophore.

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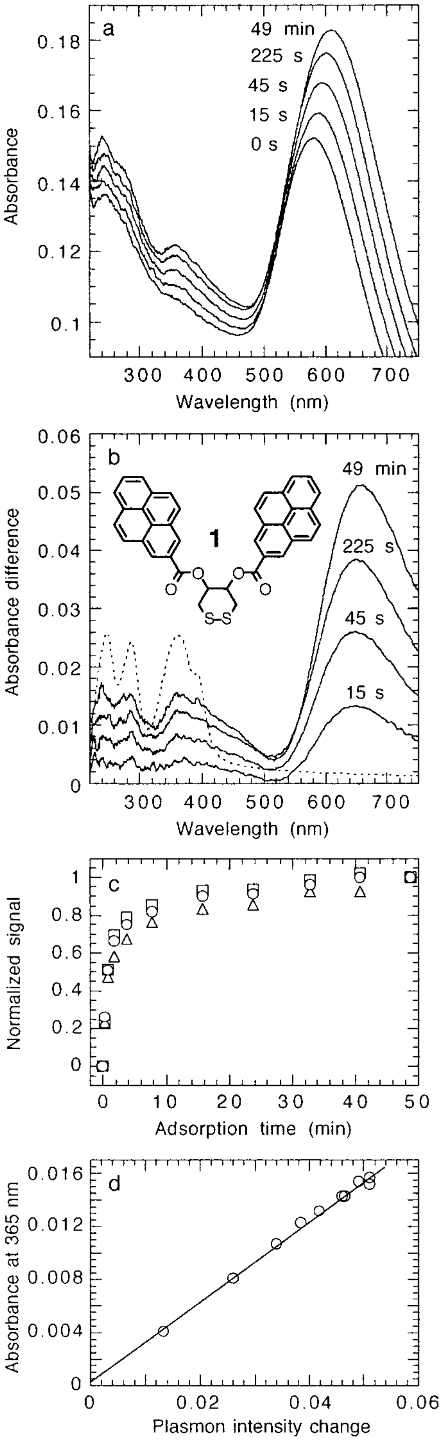

Figure 2. Transmission UV/vis spectroscopy for the formation of a monolayer of **1** (see inset in b) on an unannealed Au substrate (2.5 nm nominal thickness, evaporated on quartz), adsorbed from a 2 mM solution of **1** in chloroform: (a) absolute spectra; (b) difference spectra (obtained by subtraction of the 0 s spectrum from the other spectra in a), where the dashed line corresponds to the spectrum of a thick layer of **1,** obtained by evaporation of a drop on quartz (original spectrum divided by 6); (c) normalized quantities of the plasmon absorbance vs. adsorption time (triangles, shift of the wavelength of maximum absorbance (from a); squares, change in the intensity at maximum absorbance (from a); circles, intensity of the maximum difference peak (from b)); and (d) correlation between the plasmon intensity change and the maximum absorbance of **1** at 365 nm (both from b). All UV/vis spectra were taken ex situ, after rinsing the sample with chloroform and ethanol and drying under a nitrogen stream.

Table 1. DPS Response for Various Adsorbing Molecules

adsorbing molecule	direct/ indirect binding	adsorption medium	typical time to reach 95% coverage (s)	linear response shown
1	direct	solution	2400	yes
benzene[9]	direct	gas	100	
pyridine[9]	direct	gas	200	
$CH_3(CH_2)_9SH$[9]	direct	solution, gas	300, 150	
DIB/CoTPP[1c]	indirect	solution	450	yes

The concurrent development of the pyrene bands and the Au surface plasmon absorption is seen more clearly in the DPS presentation (Figure 2b), obtained by subtracting the background spectrum (0 s in Figure 2a). As shown in Figure 2c, the absolute plasmon intensity and position (Figure 2a) as well as the plasmon intensity change (PIC) (Figure 2b) can be used to monitor the binding of the molecule to the Au, showing essentially identical behavior. Quantitative determination of the intensity change is more accurate than that of either the absolute intensity or the position of the plasmon band.

Figure 2d shows an excellent linear relationship between the PIC and the intensity of the pyrene band, indicating that the PIC is linearly correlated with the amount of molecules bound to the Au surface.[12] This relationship, not previously shown, forms the basis for application of Au island films as optical sensors using Au surface plasmon absorption measurements. As seen in Figure 2, the sensitivity of the method is ca. 2% of a monolayer.[13] A similar sensitivity was observed with other molecules studied by this method,[9] some of which are given in Table 1. As seen from these examples, the method is applicable to different types of molecules and adsorption modes, i.e., chemical, physical, and indirect binding to the gold, both in liquid and in gas phase.

In conclusion, the use of ultrathin Au island films on transparent substrates and measurement of changes in the Au surface plasmon absorption in transmission UV/vis spectroscopy (DPS mode) provide a novel scheme for quantitative determination of molecular binding to Au surfaces. A linear relationship was shown between the PIC and the Au surface coverage, suggesting possible use in sensing applications. The method is widely applicable,[9] submonolayer sensitive, and exceedingly simple, requiring just a conventional spectrophotometer. Compared with related techniques, the present method does not require complicated and expensive instrumentation (as in SPR) or highly specialized sample preparation (as in colloid films). DPS is inherently nonselective; however, we have shown that binding to a monolayer on the Au island film can be detected,[1c] hence, selectivity may be induced by applying a selective monolayer on the Au film and using DPS to follow molecular binding to the monolayer. Application of the method to a wide range of chemical and biological sensors can be envisioned.

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(12) The same relationship is observed for the other two pyrene absorption bands.

(13) The value of the surface plasmon intensity change for a full monolayer was taken as 0.05 (Figure 2b), while the minimal detectable absorbance for the Jasco 570 UV/vis spectrometer used here is 0.001.