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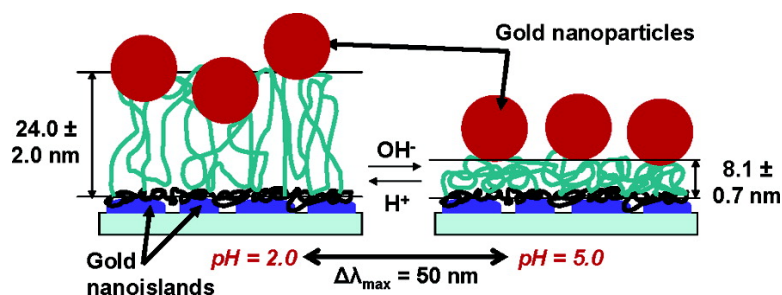
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Nanosensors Based on Responsive Polymer Brushes and Gold Nanoparticle Enhanced Transmission Surface Plasmon Resonance Spectroscopy

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In the present communication, we describe the construction of a novel nanosensor. The nanosensor is based on the real-time determination of swelling (and shrinking) of responsive ultrathin polymer brushes by an inexpensive, simple, efficient, and highly sensitive technique: gold nanoparticle enhanced transmission surface plasmon resonance (T-SPR) spectroscopy. The approach is illustrated by the observed 50 nm shift (to lower wavelength) of the T-SPR absorption maximum by the swelling of poly(2-vinylpyridine) (P2VP) polymer brushes caused by changing the pH from 5.0 to 2.0. The process was found to be reversible (Figure 1).

Polymer chains anchored by one end to substrates, referred to as polymer brushes,[1] have been shown to provide an entry to the fabrication of versatile adaptive surfaces capable of responding to changes of temperature, solvent polarity, pH, and other stimuli, generally by reversible swelling.[2] Recently, highly responsive pH-dependent reversible swelling has been described for polymer brushes, prepared from weak polyelectrolytes (PE).[3] The charge density of a weak PE brush is a function of the local concentration of protons. Changes in pH (a decrease or an increase for basic or an acidic PE, respectively) generates more charges in the interior of the polymer brushes, which are then forced by electrostatic repulsions to stretch out and, hence, to swell to a thickness several times greater than that for the uncharged polymer.[3,4]

T-SPR spectroscopy is based on the exploitation of localized surface plasmon resonance.[5] Localized surface plasmons (LSPs) are charge density oscillations confined to coinage metal nanoparticles and nanoislands. Excitation of LSPs by light at an incident wavelength where resonance occurs results in the appearance of intense surface plasmon (SP) absorption bands. The intensity and position of the SP absorption bands are characteristic of the type of material (typically, gold, silver, or platinum), the size, size distribution, and shape of the nanostructures and are highly sensitive to the changes of the surrounding environments. This sensitivity is exploited in T-SPR spectroscopy.[6] Recently, we reported that the T-SPR shift caused by the adsorption of double-stranded DNA onto gold nanoislands is considerably enhanced by attaching 12 nm diameter gold nanoparticles onto the complementary single-stranded DNA used in the hybridization.[7]

Three different samples of P2VP brushes of almost the same brush thickness were fabricated on the surfaces of three different substrates. Gold nanoislands, evaporated on transparent glass slides[8] (nominal thickness of ~4 nm and annealed overnight in a vacuum oven at 140 °C), were used as substrates for T-SPR. Highly polished Si wafers were used as substrates for ellipsometry. Thin continuous gold film deposited on the surface of a glass slide was used as a substrate for surface plasmon resonance (SPR) experiments. On these substrates, a thin layer of polyglycidyl methacrylate, PGMA (2.3 ± 0.5 nm thick), was deposited by spin-coating from a 0.01% solution in tetrahydrofurane and cross-linked overnight at room temperature to form a stable and strongly adhered macromolecular anchoring layer. Afterward, a carboxyl group-terminated poly(2-
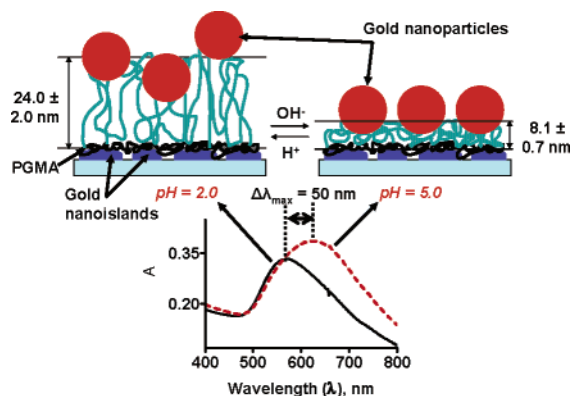

Figure 1. Top: Schematics of the reversible pH change-induced swelling of gold nanoparticle-coated poly(2-vinylpyridine) (P2VP) polymer brushes. Bottom: T-SPR spectra of gold nanoislands (containing adsorbed PGMA, P2VP polymer brushes, and gold nanoparticles) at pH 2.0 and 5.0.

vinylpyridine) (P2VP−COOH, M_n = 39 200 g/mol, M_w = 41 500 g/mol) film was spin-coated from a 2% solution in chloroform onto the cross-linked PGMA anchoring layer and was annealed, once again, for 8 h in a vacuum oven at 140 °C. The epoxy groups of the PGMA anchoring layer reacted with the end carboxyl groups of the polymer, yielding a layer of tethered chains (polymer brushes) of P2VP.[8−10] The film was rinsed several times in chloroform and water (pH 2.0) to remove the ungrafted polymer. The thickness of the unswelled (dry) P2VP polymer brush was determined to be 8.9 and 8.1 ± 0.7 nm by ellipsometry[4] and SPR technique,[11] respectively (see Supporting Information). An AFM scratch test gave the thickness of 8.0 ± 2.0 nm for the brush prepared for T-SPR. This brush thickness corresponds to the grafting density value of ~0.12 nm^{-2} and the distance between grafting points of ~3.0 nm. The mean square root end-to-end distance of the swollen P2VP chains is about 10.0 nm in Θ-solvent and much larger in acidic water, confirming the presence of a true brush regime. In water, when the pH was changed from 5.0 to 2.0, the polymer brush swelled to a thickness three times the original (from 8.1 ± 0.7 to 24.0 ± 2.0 nm). Finally, citrate ion-stabilized 12.8 ± 1.9 nm diameter gold nanoparticles[7] were adsorbed onto the polymer brush from their aqueous solution (Figure 1). Depositions of PGMA, P2VP, and gold nanoparticle layers were monitored by T-SPR (Figure 2), AFM scratch test, and SPR (see Supporting Information). The gold nanoparticles formed a fairly closed-packed uniform coverage on the polymer brushes, as evidenced by AFM (see Supporting Information).

The absorption maximum of the T-SPR spectrum of the gold nanoislands, in the presence of attached PGMA and P2VP polymer brushes, was found to shift by 6 nm between pH 5.0 and 2.0 (from 568 to 562 nm, in a typical example; see Figure 3A). This shift is caused by the protonation of P2VP (p$K_a \approx 2.3$) and the consequent increase of the electrostatic repulsions between the positively
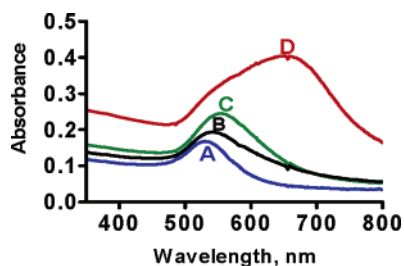
Figure 2. T-SPR spectra of bare Au nanoislands (A), Au nanoislands and PGMA (B), Au nanoislands with PGMA and P2VP (C), and Au nanoislands with PGMA, P2VP, and Au nanoparticles (D). All T-SPR spectra were taken in air.
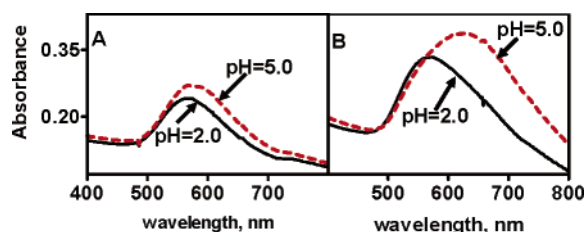

Figure 3. T-SPR spectra of Au nanoislands with PGMA and P2VP in the absence (A) and in the presence (B) of adsorbed 11.7 ± 1.9 nm diameter citrate-capped gold nanoparticles at pH 2.0 and 5.0.

charged PE, osmotic pressure, and in the swelling of the P2VP polymer brushes (Figure 1).

A dramatically enhanced shift of this pH-induced T-SPR absorption spectrum was observed if gold nanoparticles were adsorbed on the P2VP polymer brush. The absorption maximum of the T-SPR spectrum of the gold nanoislands, in the presence of the P2VP brush and gold nanoparticles, was found to shift by 50 nm between pH 5.0 and 2.0 (from 624 to 574 nm), corresponding to a shrinking of the polymer brushes from 24.0 to 8.1 nm, in a typical example (Figures 1 and 3B). Since a shift of 2 nm in the absorption maximum is readily observable, a change as small as 0.5 nm in swelling (or shrinking) of the polymer brushes is easily detectable by T-SPR spectroscopy. This sensitivity is of the same level as that measurable by more complex techniques (in terms of instruments and data processing), such as ellipsometry, SPR, or fluorescence labeling.

The pH-induced shrinkage of the polymer brush was found to be completely reversible. Changing the pH from 2.0 to 5.0 shifted the T-SPR spectrum of the gold nanoislands (in the presence of attached PGMA, P2VP, and gold nanoparticles) from 574 to 624 nm (corresponding to a shrinking from 22.1 to 7.2 nm). We repeated changing the pH from 5.0 to 2.0 and back five times and obtained identical optical results. We note, however, that the pH-induced shift of the absorption maximum of the Au nanoislands (in the presence of Au nanoparticles) suffers from hysteresis: a larger initial shift is followed by highly reproducible values (see Supporting Information).

Measurements of the T-SPR spectra at different pH values produced a titration curve, with a pH values of 3.82, which represented 50% protonation of the P2VP brush polymer (Figure 4). This corresponded to 50% swelling of the polymer chain, as independently determined by SPR measurements.
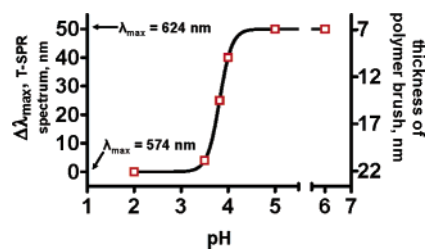
Figure 4. Shift of the absorption maximum of the T-SPR and the thickness of the polymer brush determined by SPR as a function of pH.

Similar optical measurements were performed in the absence of the gold island film (on glass slides). We found that the spectrum of gold nanoparticles deposited on the P2VP layer is composed of two peaks: one at 542 nm (representing the separate particles) and another around 625 nm (characteristic for aggregated particles). Shrinking and swelling of the thin polymer layer resulted in changing the ratio of these two peaks (Supporting Information). Obviously, these changes are too complex and less sensitive than those obtained in the presence of the gold nanoislands.

Demonstration of an extremely straightforward but highly sensitive nanosensor, based on gold nanoparticle enhanced T-SPR spectroscopy, is the most significant result reported here. Additionally, to the best of our knowledge, no previous work appeared on the construction of such an ultrathin reversibly swelling polymer brush. Ultrathin reversibly swelling polymer brushes, of course, minimize the diffusion of the analyte to the sensor and, hence, shorten the response time.

Supporting Information Available: Ellipsometry, SPR, AFM, and T-SPR, and stability data. This material is available free of charge via the Internet at http://pubs.acs.org.

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