METAL NANOWRINKLES AND NANOPETALS FOR ENHANCED FLUORESCENCE

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ABSTRACT

A simple two-step (metal deposition and subsequent heating) approach to fabricate controllable biaxial and uniaxial nanowrinkles and nanopetals based on shape memory polymer (pre-stressed polystyrene) sheets is presented. Wavelengths of wrinkles can be tuned from 300nm to 800nm by controlling the thickness of deposited metal. We demonstrate utility of these nano structures with ready integration into microchannels and effectiveness in surface enhanced sensing.

KEYWORDS: biaxial, uniaxial, microchannels, surface enhanced fluorescence

Recently, there has been a resurgence of interest in emulating and leveraging wrinkles for various applications.[1] Previous demonstrations of wrinkles exhibited relatively large wrinkle wavelengths. Here, by just leveraging the stiffness mismatch of materials, we present a simple and ultra-rapid method to controllably create nanoscale metal wrinkles. First, 10nm thickness of gold film is deposited on the Shrinky-Dinks sheets. Heating at 160°C causes substrates to retract to less than half of its original size and therefore induces the stiffer, non-shrinkable metal film to buckle (Fig. 1a, left). [2] Scanning electron microscope (SEM) images (Fig. 1b) show that uniform biaxial nanowrinkles with a peak wavelength near 400nm (black dash line of Figure 2a) can be produced. To verify the theoretical predictions (detals in our recent publication, ref. 3), we varied the thickness of deposited gold from 10 nm to 50 nm. This caused a shift of hundreds of nanometers in the wavelength distributions and scaling of the peak wavelength with film thickness (the black dots of Fig 2a, bottom) has a slope of 8.4, which agrees well with our theorized slope for the scaling of the coherence length $\eta^{2/3} \approx 7.9$ (the black dash line of Fig 2b, bottom). This suggests that a loss of coherence is the dominant effect in determining the morphology in the biaxial case.

Uniaxial wrinkles can be easily created as well (Fig. 1a, right). We modify the fabrication process by introducing boundary conditions via clamping two edges of a gold-coated PS sheet during the heating process. Well aligned linear-wrinkles can be produced (Fig. 1c). For the 10nm thickness sample, these wrinkles exhibit two distinct populations with peaks at 300nm and 800nm (green line of Fig. 2a, top). Similar to what we found for the biaxial case, the peak wavelengths of both populations are proportional to the thickness of deposited gold and can thus be controllably tuned by adjusting the thickness of deposited gold (Fig 2a, bottom). The scaling of

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the dominant wavelengths with film thickness for both first and second generations is linear, with slopes of 2.1 and 2.4, respectively (blue and red dots of Fig 2a, bottom). The consistency between experimental results and the anticipated value for the bare metal film ($\eta^{1/3} \approx 2.8$, blue and red lines in Fig 2a, bottom) indicates that the loss of coherence is not the dominant issue allowing us to clearly see features of the underlying wrinkle distribution. [3]

Silver wrinkles can be fabricated and easily integrated into Shrinky-Dinks microfluidic based devices as well. Besides the simple biaxial wrinkles, uniaxial wrinkles can be aligned inside the microchannel.[2,3] Figure 2b shows that these wrinkles are perpendicular aligned within a channel with width of 280 μm. Thermal bonding can be achieved easily as described in our previous papers. [2] In addition, we demonstrated that our wrinkles can be easily patterned by using a TEM grid as a shadow mask. In Figure 2c, spotted wrinkled-flowers with diameter around 50μm are well aligned. One potential application is to improve the sensitivity of DNA microarrays, in which high density fluorescent probes with spot sizes from 10 to 500 μm are immobilized on substrates. Utility of metal enhanced fluorescence (MEF) to lower the detection limit is desirable to broaden its applications. [3]

We demonstrate that our continuous gold wrinkled substrate is useful for MEF. Figure 3a and 3b (left) show fluorescence images along with the corresponding intensity profiles of dyes, dissolved in polymer solution, spin-coated on a bare glass plate and on uniaxial gold wrinkles, respectively. An average fluorescence intensity increase of approximately 3-fold over a relatively large area was observed when dyes were deposited on the wrinkles as compared to the glass. Many bright lines parallel to the direction of wrinkles indicates that there are many continuous hot-spots along the wrinkles, with enhancements of 5- to 7- fold. To confirm enhancement resulted from plasmon effects rather than aggregation of dyes, fluorescence lifetime measurements were performed with a homemade confocal microscope with a time correlated single-photon counting module. Figure 3b (right) shows that the average fluorescence lifetime of dyes on a glass plate is 3.5 ns, and after deposited on wrinkles, their average lifetime dramatically decreases to 0.4 ns. This ~ 9-fold decrease in average lifetime suggests that enhancement results from strong interactions between fluorophore and surface plasmons. To extend the penetration depth of surface plasmon, bimetallic perals are fabricated (Fig. 4a). When the thickness of each film larger then 80nm, wrinkling induced cracks make it possible to fabricate biaxial and uniaxial nanopetals as shown in Fig. 4b and 4c..

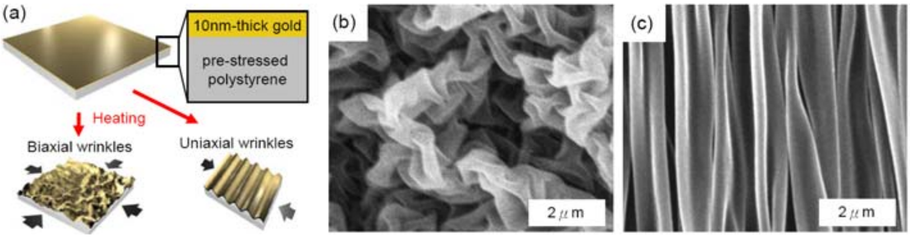

Figure 1. (a) Schematic of fabricating biaxial (left) and uniaxial (right) wrinkles. SEM images of biaxial (b) and uniaxial (c) wrinkles

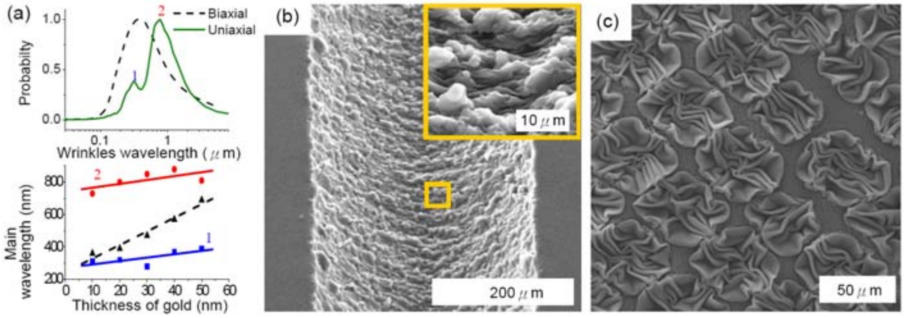

Figure 2. (a)Wavelength distributions of biaxial and uniaxial wrinkles with 10nm thickness of gold (top) and plot of main wavelength of biaxial (black dash line) and uniaxial (red and blue line) wrinkle as a function of gold layer thickness. Note that "1" and "2" indicates the first and the second population of uniaxial wrinkles wavelength, respectively. (b) The SEM image of uniaxial wrinkles, with 45-nm-thick silver layer, inside a channel. Insets: enlarged view of corresponding images. (c) The SEM image of discrete wrinkled flowers.

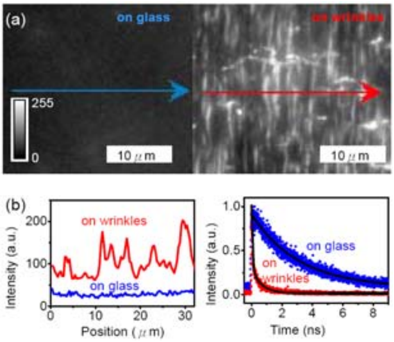

Figure 3. (a) The wide-field epifluorescence image of dyes on a glass plate (left) and on uni-axial wrinkles (right). (b) Left, the corresponding intensity profiles along the arrows in (a). Right, fluorescence lifetime measurements of dyes on a glass plate (blue) and on wrinkles (red).

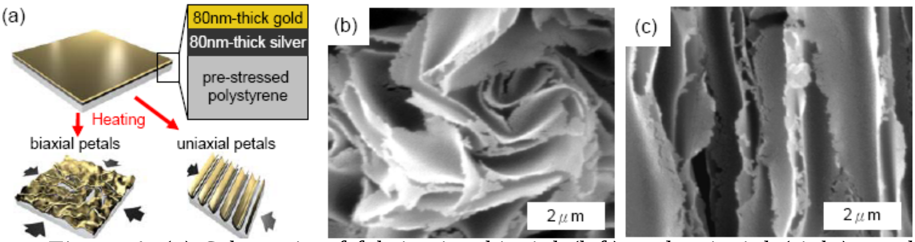

Figure 4. (a) Schematic of fabricating biaxial (left) and uniaxial (right) petals. SEM images of biaxial (b) and uniaxial (c) wrinkles

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