

## Micropatterns constructed from Au nanoparticles

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Covalently linked Au–NPs micropatterns have been successfully fabricated from the self-assembly film composed of 4-mercaptophenol-capped Au nanoparticles (Au–NPs) and  $-N_2^+$  containing polymers of nitro-diazo-resin (NDR) by selective exposure to UV light and development in sodium dodecyl sulfate (SDS) aqueous solution. The resultant well-defined micropatterns were characterized with AFM and XPS.

Realization of the micro-pattern composed of metallic nanoparticles is an increasingly fascinating research field. It is greatly motivated by the unique size-tuned optical and electronic properties of metallic NPs. In particular, Au nanoparticles (Au–NPs) are more attractive to pursue the wide potential applications in the areas of advanced microelectronic devices, non-linear optics, electrochemical sensor and bio-analysis.<sup>1</sup> So far, many techniques have been developed to fabricate the metallic micropatterns or the templates used to direct the selective deposition of metallic NPs, such as microcutting, soft lithography, nanolithography, electron beam, photolithography and so on.<sup>2</sup>

In this paper, we report the construction of a covalently linked Au–NPs micropattern from the self-assembly multilayer film composed of nitro-diazo-resin (NDR)<sup>3</sup> and 4-mercaptophenol-capped Au–NPs ( $\phi \sim 3\text{nm}$ ).<sup>4</sup> The micropattern formation contains the following two steps. Firstly, the photosensitive composite film was fabricated by layer-by-layer self-assembly via H-bond formation between the diazonium group ( $-N_2^+$ ) of NDR and the phenolic hydroxy ( $-OH$ ) of 4-mercaptophenol-capped Au–NPs.<sup>5</sup> The introduction of self-assembly endows the enormous flexibility to tune the thickness and the structure of the metallic films in comparison with other methods.<sup>6</sup> Subsequently, the assembled film was selectively exposed to UV light through a photomask with sodium dodecyl sulfate (SDS) aqueous solution as the developer.<sup>7</sup> It has been reported that the conversion of covalent bonds from H-bonding between the layers of the film takes place following the photo-decomposition of diazonium group and the irradiated parts of the film become excessively stable towards polar solvents or salt solutions.<sup>8</sup> Whereas the un-irradiated parts linked by H-bonding were unstable and thoroughly removed from the surface of the substrate in SDS solution, in which the diazo-resin based complexes, including from electrostatic and H-bonding, can be dissolved.<sup>9</sup> As a result, the covalently attached micropatterns were constructed by taking advantage of the remarkable difference for the stability of irradiated and un-irradiated film in SDS solution.

The UV-vis spectra were used to monitor the evolution of the absorbance for NDR/Au–NPs photosensitive film with an increase of the bilayer on quartz wafer (Fig. 1). The absorbance at 386 nm is assigned to the  $\pi-\pi^*$  transition absorption of  $-N_2^+$  group of NDR. The linear increase of the absorbance with the bilayers (inset plot) reveals that the self-assembly is a uniform deposition process. Considering that NDR and 4-mercaptophenol-capped Au–NPs do not dissociate in methanol solution, the main driving force of NDR/Au–NPs assembly should be attributed to the H-bond formation rather than electrostatic interactions (Scheme 1, left). The H-bond formation between

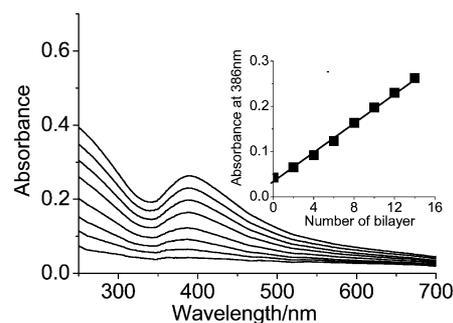
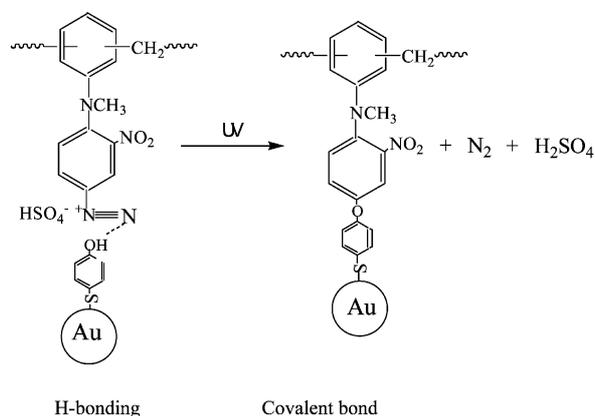


Fig. 1 The UV-vis spectra of NDR/Au–NPs ultrathin film with different bilayers. Bilayers (from bottom to top): 0, 2, 4, 6, 8, 10, 12, 14.

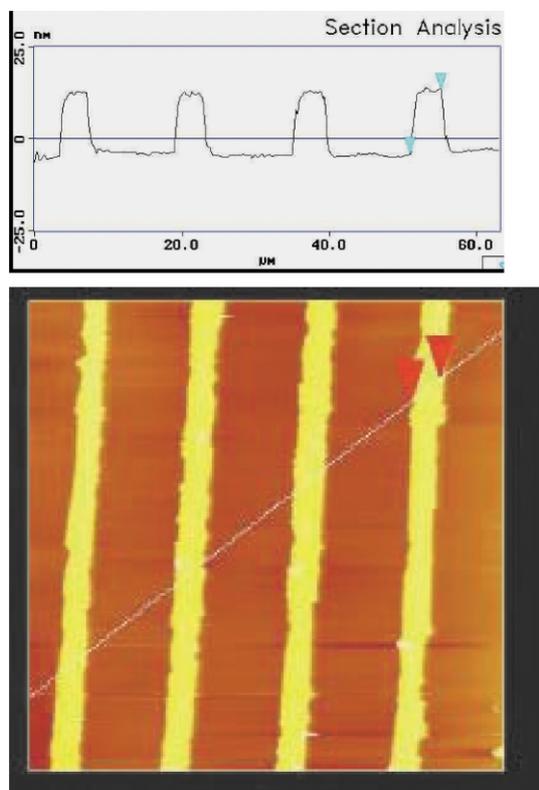
$-N_2^+$  and the phenolic hydroxy group has been previously characterized.<sup>8</sup> The conversion of H-bond to the covalent bond between the layers of NDR/Au–NPs film under the exposure to UV light, referring to our previous study, can be illustrated in Scheme 1.

The micropatterned NDR/Au–NPs multilayer film constructed on the silicon substrate was characterized with AFM in tapping mode and shown in Fig. 2. The well-defined pattern has stripes and grooves with  $\sim 2.5\ \mu\text{m}$  and  $\sim 8\ \mu\text{m}$  width respectively. The average depth of the grooves is about  $18\ \mu\text{m}$  determined by the section analysis of AFM. From this data we can estimate the contribution of each deposition cycle for the film thickness is  $\sim 3\ \text{nm}$ , less than expected from the individual thickness of each layer (NDR layer  $\sim 2\ \text{nm}$  thick<sup>10</sup> and the Au–NPs layer  $\sim 3\ \text{nm}$  thick<sup>4</sup>). This difference should arise from the interpenetration between the layers, which commonly exists in self-assembly films.<sup>11</sup>

The well-defined micropattern of (NDR/Au–NPs)<sub>6</sub> film prepared using another photomask was investigated by X-ray photoelectron spectroscopy (XPS) (Fig. 3). The existence of the typical Au 4f peaks, as well as O1s, C1s and N1s peaks, indicates that the NDR and 4-mercaptophenol-capped Au–NPs



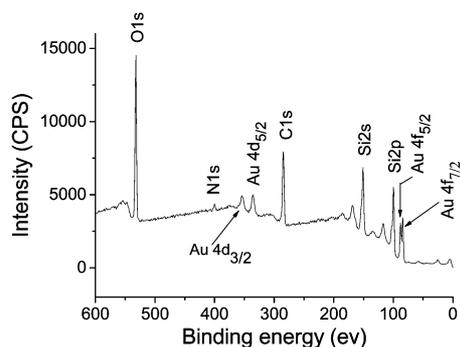
Scheme 1 The schematic illustration for the conversion of the bond nature from H-bonding to covalent between the layers of NDR/Au–NPs film under UV irradiation.



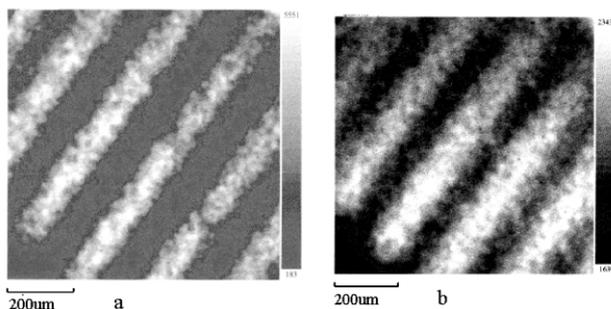
**Fig. 2** 50 μm × 50 μm AFM image of the micropatterned (NDR/Au-NPs)<sub>6</sub> film fabricated on silicon wafer.

have been deposited on the film. The Si peaks in the binding energy range 99–160 eV belong to the signals of the exposed silicon wafer. In addition, the corresponding elemental distribution images with the signals of Au 4f<sub>7/2</sub> at 84.3 eV and Si2p<sub>3/2</sub> at 99 eV were given in Fig. 4 (a) and (b) respectively. The distribution of Au matches well with that of Si, revealing that the un-irradiated regions of the film are thoroughly removed, whereas the irradiated regions are reserved on the silicon surface.

In conclusion, well-defined and covalently attached micropatterns have been obtained by layer-by-layer self-assembly of NDR and 4-mercaptophenol-capped Au-NPs, followed by selective exposure to UV light through the photomask, and then developed in SDS aqueous solution. The resultant micropatterns were characterized with AFM and XPS. All results



**Fig. 3** Survey-scan X-ray photoelectron spectra of the micropatterned (NDR/Au-NPs)<sub>6</sub> film fabricated on silicon wafer.



**Fig. 4** The XPS elemental distribution images of (NDR/Au-NPs)<sub>6</sub> micropattern. (a): Au 4f<sub>7/2</sub>; (b) : Si2p<sub>3/2</sub>.

suggest that the self-assembly technique coupling photolithography is a potential approach to fabricate the covalently linked metallic micropatterns.

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