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COMMUNICATION

Direct photopatterning of light-activated gold nanoparticles†

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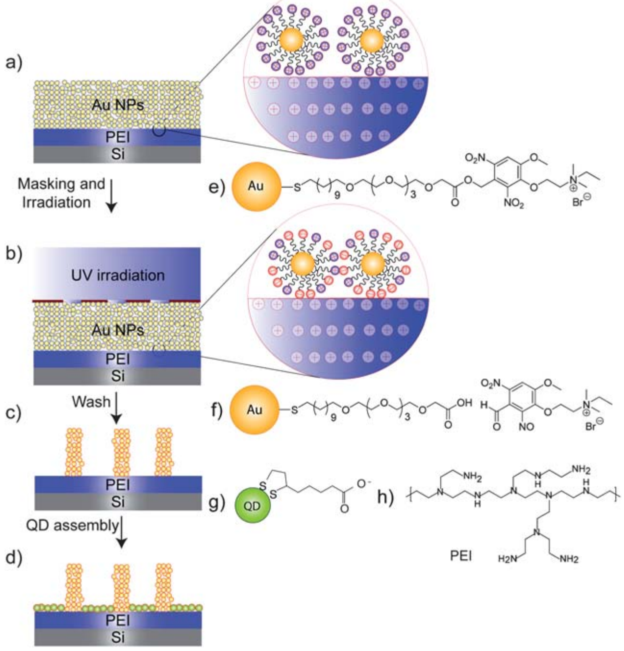
Photoactivatable gold NPs were patterned *via* photolithography. In this approach, charge reversal of the ligands on NPs upon UV irradiation induces crosslinking to generate stable NP patterns.

Fabrication of functional structures using spatial organization of nanometre-scale building blocks including nanoparticles, carbon nanotubes, proteins, organic molecules and polymers is important for various applications such as electronics,[1] optics,[2] biological,[3] and sensing systems.[4] Recently, ligand protected metallic and semiconducting nanoparticles (NPs) have been widely used in the fabrication of functional structures. The tunable size and surface properties of NPs provide potential applications in nanostructured conductors, novel resists, and templates for electronics,[5] sensors,[6] and biological recognition.[7]

Templated assembly method and direct patterning are two major techniques that have been widely used to pattern NPs onto surfaces. In the templated assembly method, the template is created using lithographic techniques including photo-passivation,[8,9] nanoscale phase-separated block copolymer,[10] electron beam lithography,[11] nanoshaving,[12] nanoimprinting,[13] electro-oxidation nanolithography[14] and scanning probe lithographies.[15] While NP patterning through templates is useful for many applications, direct patterning[16] provides a facile way to create features of arbitrary thickness that are substrate independent. Moreover, direct patterning of charged NPs provides a platform for the fabrication bio-sensors[17] and optoelectronic devices.[18]

Herein, we present a direct approach to pattern NPs *via* photolithography using NPs featuring photocleavable ligands.[19] Our strategy differs from previous methods by using partial charge reversal to effect patterning of charged NPs, providing patterns of arbitrary thickness, an important criterion for the fabrication of nanoparticle based devices. Using this strategy, photopatterning of charge switchable gold NPs provided stable features. NP patterning on crosslinked polyethyleneimine (PEI) substrates provided access to orthogonally functionalized surfaces through electrostatic deposition of quantum dots (Scheme 1).

In our initial studies, we determined the time course of the photoactivation using UV-vis spectroscopy. We investigated the photocleaving behavior of the free photocleavable thiol ligand and the NP using 365 nm UV radiation. A decrease of absorbance was observed at 250 nm, along with an increase at 320 nm, indicating the breakage of the photolabile ester bond and the formation of *o*-nitrobenzaldehyde with concomitant charge conversion on the ligand. These results confirm that the photolytic reaction of the NP proceeds in an analogous fashion to that of the free photocleavable thiol ligand



Scheme 1 Fabrication of NP pattern *via* photolithography of photoactivable gold NPs. (a) Spin-coating NPs onto PEI coated silicon substrate, (b) light activation of NPs under a mask using UV lamp 365 nm wavelength; zoomed image shows the reversal of charge on NPs, (c) developing NP patterns using a methanol wash, (d) electrostatic assembly quantum dots onto PEI surface, (e) chemical structure of NP before light activation, (f) chemical structure of NP after light activation, (g) chemical structure of quantum dot, and (h) chemical structure of polyethyleneimine.

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(Fig. 1). After 365 nm UV exposure, there is no change in absorbance at 525 nm in UV-vis spectra (Fig. 1) which clearly demonstrates that 365 nm light activation retains the optical properties of the starting NPS.

For our patterning studies, the particles were deposited onto crosslinked PEI. To provide the PEI layer, PEI and 5% wt of diglycidyl ether of bisphenol-A (DGEBA) were spin-coated onto a silicon substrate and thermally crosslinked at 100 °C for 5 h. This process provides a surface with a sufficient amount of amine functional groups still available for subsequent electrostatic interactions on the surface. A thin layer (~100 nm) of photo-switchable 6 nm core NPs was then spin-coated on top of the PEI. Photolithography was performed for 30 minutes, resulting in transfer of the mask pattern into the NP layer. Next, the pattern was developed onto the PEI film by washing it with methanol providing patterned NP features (Fig. 2a). AFM shows there is no significant change in the thickness of the film after photo-irradiation and methanol washing (ESI†).

Scanning electron microscope (SEM) was used to image the NP patterns (Fig. 2b). The magnified SEM image showed the discrete NP structure in the patterns. We next carried out atomic force microscopy measurements to find out the pattern thickness. The feature height of 100 nm was observed by AFM imaging (Fig. 2c), consistent with the spin coating thickness, indicating multiple layers of particles (NP core diameters ~6 nm). No NP deposition was detected in the trench regions between features, indicating the high specificity of the particles photocrosslinking.

We next investigated the possibility of co-assembling metallic and semiconducting nanoparticles (QDs) onto the substrate.[20] To provide orthogonal assembly, we utilized the electrostatic assembly of negatively charged carboxylate functionalized QDs onto the positively charged exposed PEI surface. Exposure of the pattern to negatively charged QDs at a pH of 7.5 for 30 min, followed by thorough washing resulted in specific deposition of the QDs onto the surface (Fig. 2). The increase in fluorescence demonstrates the successful assembly of QDs onto the PEI surface where gold NPs were not photoswitched (Fig. 3).

To investigate the electronic properties of the crosslinked NP film, current–voltage (*I*–*V*) curves were recorded by applying a DC bias across the film with a top contact. As shown in Fig. 4, the NP patterned surfaces showed a linear *I*–*V* behavior with a conduction on the order of 10^{-11} s. No coulomb blockade-like phenomenon was observed, which is possibly due to the relatively large size of the gold NPs we used.[21] In comparison, the surface with only a PEI film showed no obvious current response from −0.5 to 0.5 V, demonstrating that the conductivity is due to the NP layer.

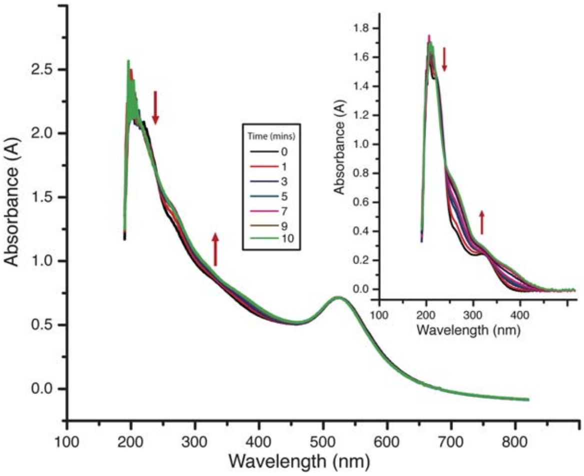

Fig. 1 Overlaid UV-vis spectral changes upon irradiation of NP with UV light (365 nm) and inset shows the spectra for ligand.

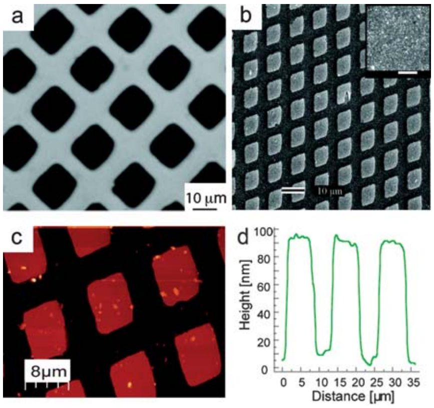

Fig. 2 (a) Bright field image of NP pattern, (b) SEM image of NP pattern, inset shows discrete NP structures in a magnified image (scale bar 100 nm), (c) AFM image of NP pattern and (d) Z-height profile for the NP pattern.

In summary, we have demonstrated the use of photoactivable NPs to provide functionalized nanostructures *via* charge reversal of the ligands on NPs upon UV irradiation. This structural motif can be used to generate platforms for photonics, nonvolatile memories, microfluidics, biosensors, floating gates, and optoelectronics. Moreover, orthogonal functionalization of these NP patterns *via* non-covalent (electrostatic) assembly of QDs shows potential applications to fabricate metal–semiconductor junctions. We are currently applying this strategy to the creation of functional electronic devices.

Experimental

Synthesis of NPs

NPs/QDs and their ligands were prepared as described in previous reports.[16,22]

Film preparation

Solutions consisting of 400 mg PEI, 10 mg of diglycidyl ether of bisphenol-A (DGEBA) and 10 mg of an accelerant 2,4,6-tris(dimethylaminomethyl)phenol in 30 mL of 1 : 3 methanol/chloroform were prepared. The solution was filtered and spin-coated at 3000 rpm for 60 s onto a silicon substrate, yielding a thin film of PEI (~25 nm). This film was crosslinked by heating at 100 °C for 5 hours in air.

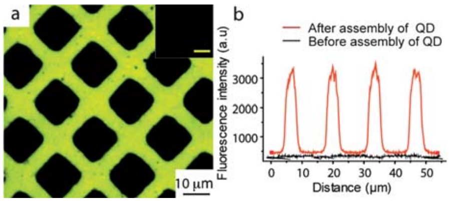

Fig. 3 (a) Fluorescence image of NP pattern after assembling QD *via* electrostatic assembly, inset shows before QD assembly (b) fluorescence profiles of NP pattern before and after assembly of QDs. Scale bar in the inset is 20 μm.

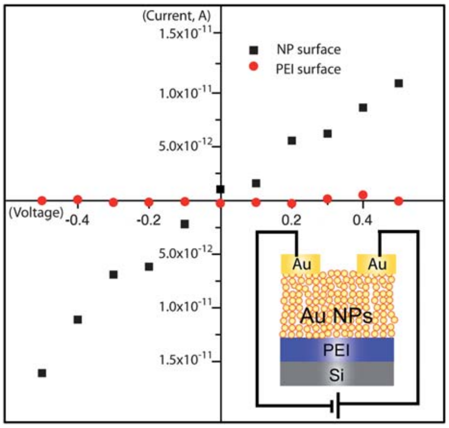

Fig. 4 *I–V* curves of the PEI film before and after patterning of NPs and inset is a scheme for the *I–V* measurement.

A thin layer of NPs was applied to the top of the PEI layer by spin coating a 1% (wt) NPs in methanol solution. Then, photolithography was carried out at 365 nm wavelength for 30 minutes. Finally, the patterns were developed by washing the surface with methanol.

Electrostatic assembly

The substrate was incubated in an aqueous solution containing dihydrolipoic acid functionalized semiconductor QDs (1 mL, 0.02 mg mL^{-1}) at pH 7.5 for 30 minutes. After QDs deposition, the substrates were washed with double distilled water and then dried under a stream of argon gas.

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