Reversible Formation of Molecular Junctions in 2D Nanoparticle Arrays**

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Molecular electronics[1] is attracting increasing research attention, primarily supported by the possibilities offered by synthetic chemistry for the tailoring of single molecules to achieve specific electronic functions.[2–4] Whereas various experimental approaches have been devised to form and electrically study molecular junctions,[5–11] the integration of individual junctions into functional electronic circuits remains a demanding task, requiring innovative approaches in fabrication philosophy and circuit structure.[12,13] We show here that an approach combining the self-assembly[14] and microcontact printing[15] of ligand-protected metallic nanoparticles, followed by an in situ ligand-exchange reaction,[16] allows the preparation of stable 2D networks of molecular junctions.[17] A significant decrease in resistance (up to three orders of magnitude) after the exchange of alkanethiol ligands with conjugated, double-ended organic wires (thiolated oligo(phenylene ethynylene), OPE) confirms a proper interlinking of neighboring nanoparticles. We also demonstrate that the formation of the molecular junctions is reversible, making nanoparticle networks a promising platform for the development of molecular electronic circuits. The flexibility of this approach lets us envisage the realization of more complex networks, for instance, by intermixing ensembles of bimodal nanoparticles[18] of different materials. Both experimental and theoretical evidence shows that the electronic properties of molecular junctions are not only dictated by the molecules contacted but also depend on the anchoring groups and the electrodes forming the junction.[3,11] The use of nanometer-sized metallic colloids as electrodes appears, therefore, as an elegant solution to build molecular junctions with well-defined geometry and electronic properties. Recent results on colloid dimers interlinked by a conjugated molecule demonstrate the validity of this approach.[19] The demonstration here of the fabrication of reversible 2D networks of hybrid metallic colloid organic-molecule junctions opens new possibilities for the realization of molecular circuits.

Alkanethiol-capped 10 nm gold nanoparticles were first self-assembled into 2D close-packed arrays at the air/water interface.[20] A polydimethylsiloxane (PDMS) stamp with the desired imprinted structures was then prepared to print patterned nanoparticle monolayers on a solid substrate.[15] Figure 1a shows a scanning electron microscopy (SEM) image of dodecanethiol-capped nanoparticle monolayers printed with a PDMS stamp on a SiO$_2$–Si substrate. The lines have a typical width of 25 μm and a spacing of 30 μm. In contrast to other approaches for the preparation of interlinked nanoparticle arrays, such as layer-by-layer assembly,[21] the Langmuir–Blodgett technique,[22] and multiple deposition on solid substrates,[23,24] the stamping technique yields spatially well-positioned arrays (Fig. 1a and c) free of multilayer regions (Fig. 1b). High-magnification SEM images (Fig. 1d–f) reveal that the nanoparticles are well separated from each other by...
the alkanethiol chains and order in a hexagonal close-packed structure. The interparticle distance can be increased by using alkanethiols with increasing lengths, as shown by the SEM images of nanoparticle arrays prepared with octanethiol (C8), dodecanethiol (C12), and hexadecanethiol (C16) ligands (Fig. 1d–f, respectively).

The stamped nanoparticle arrays remain stable for several weeks in air at room temperature without showing aggregation and can resist common solvents, such as tetrahydrofuran (THF), ethanol, or toluene. This good mechanical and chemical stability enables us to use the nanoparticle arrays as a “colloidal breadboard” to fabricate networks of molecular junctions.

To investigate the electrical transport through the patterned nanoparticle arrays, contact pads (with a thickness of 5 nm Ti and 45 nm Au) were deposited on top of the printed monolayer lines using a transmission electron microscopy (TEM) grid as a shadow mask. Figure 2a shows an SEM image of a typical device composed of two square-shaped contact pads evaporated on a line of octanethiol-encapsulated nanoparticles. The rectangular particles array between two contact pads is typically 12 μm in length (l) by 25 μm in width (w). According to SEM inspection, the arrays are kept intact, with no noticeable change of the structures observed after evaporation of the contact pads.

The electrical measurements of the devices were performed on a probe station in air at room temperature. For the comparison of various devices, we will consider the sheet resistance \( R_{\text{sheet}} = R_{w} = \frac{l}{w} \), where \( R \) is the measured resistance of an array, with \( L \) and \( w \) the length and width defined as in Figure 2a. Figure 2b shows typical DC current–voltage (I–V) curves of a device measured at four steps in the course of a molecular-exchange experiment. Curve 1 shows the electronic behavior of an as-prepared device (C8 ligands) with sheet resistance \( R_{\text{sheet}} = 4.4 \times 10^{10} \) Ω. The device was then immersed in a 1 mM OPE solution in THF for 24 h, followed by a 10 min rinse in THF. The sheet resistance after OPE exchange (curve 2) was found to be \( R_{\text{sheet}} = 6.3 \times 10^{7} \) Ω, a decrease by more than two orders of magnitude.

A maximum bias voltage of 10 V was applied to the device, yielding a maximum voltage drop over one molecular junction of 10 mV, since the device is formed by about 1000 junctions in series. This value is lower than the thermal energy \( k_B T \), amounting to 26 meV at room temperature, and therefore ensures a linear response of the device. In addition, the single-electron-charging energy of individual nanoparticles is estimated to be smaller than \( k_B T \).

We attribute the significant decrease of resistance observed between curves 1 and 2 to the formation of interlinked molecular junctions by the dithiolated OPE molecules. In the as-prepared device, nanoparticles are separated by octanethiol molecules, as shown by the schematic in Figure 2c (left). The average edge-to-edge distance of neighboring particles was found to be about 2.4 nm, very close to the S–S length of the OPE molecule (~2.1 nm). It has been demonstrated that alkanethiolate monolayer-protected gold clusters can be functionalized by introducing new thiolate ligands through a place-exchange reaction. During the device immersion in the OPE solution, the incoming organic molecules can penetrate the octanethiol monolayer and bind to the nanoparticle. For molecules with two anchoring groups, neighboring nanoparticles have a significant chance to be interlinked, thereby forming a network of molecular junctions. This process is schematically represented in Figure 2c. With OPE being a conjugated compound and, therefore, a better electron carrier than alkanethiols, the resistance of the OPE-interlinked array is expected to be smaller than
that of unlinked arrays. This is true as long as the contacts (the thiol linkers) provide a sufficient electronic coupling of the molecule with the colloids. An SEM inspection of the devices before and after OPE exchange revealed that the morphology and general structure of the nanoparticle array remained unchanged during the exchange process, as shown in Figure 2d. The gold-nanoparticle array forms a robust nanoelectrode skeleton, a “colloidal breadboard”. Control experiments show that devices immersed in pure THF, without OPE molecules, do not substantially change their resistance. We also measured that the resistance between two contact pads without a nanoparticle array is above 10 TΩ, both before and after OPE treatment. We are therefore confident that the significant change of resistance observed can be attributed to the interlinking of neighboring nanoparticles by the OPE molecules.

Remarkably, the formation of molecular junctions has been found to be reversible. After the OPE exchange described above, we immersed the same device for 24 h in a 0.5 M octanethiol solution in THF, followed by a 24 h immersion in a pure octanethiol solution. The DC $I$–$V$ curve (curve 3) of the device after this treatment showed similar behavior to that of the as-prepared device. The sheet resistance was measured to be $R_{\text{sheet}} = 5.4 \times 10^{10}$ Ω, indicating that OPE molecules had been replaced by octanethiols. A second OPE exchange (curve 4), following the above-described procedure, caused the sheet resistance to drop to $R_{\text{sheet}} = 7.2 \times 10^{7}$ Ω, a similar value to that obtained after the first OPE exchange ($6.3 \times 10^{7}$ Ω).

Figure 2c shows the evolution of the sheet resistance of a device immersed in a 1 mM OPE solution in THF at different times during the exchange process (the device was rinsed and dried before each measurement). We observe that the sheet resistance decreases rapidly in the first 40 min and then saturates. This is consistent with the results of Murray and co-workers,[16] who determined the rate of place exchange on monolayer-protected clusters.

The stamping technique permits the simultaneous preparation of hundreds of devices on a single chip, an essential asset for the characterization of molecular devices. Figure 3a presents the sheet resistance of 29 devices selected randomly on one chip during two successive cycles of molecular exchange: all devices exhibit the same behavior. The average sheet resistances measured at various stages, namely i) as-prepared, ii) after a first OPE exchange, iii) after an octanethiol exchange, and iv) after a second OPE exchange, were $3.8 \times 10^{10}$, $6.4 \times 10^{7}$, $5.2 \times 10^{10}$, and $6.5 \times 10^{7}$ Ω, respectively. These data show the high yield and very good reproducibility of the reversible formation of molecular junctions.

In Figure 3b, we summarize the results obtained from 100 devices measured on five different chips. We show here the sheet resistance of each device before (top section) and after (bottom section) OPE exchange. It is clear that, no matter what the resistance is before exchange, the resistance of the interlinked arrays is around a few tens of megaohms for most devices, after exchange. We attribute the chip-to-chip resistance differences of the as-prepared devices (top) to variations in the average interparticle distance. Different surface pressures during the arrays self-assembly at the air/water interface can lead to this effect, as also observed by Heath and co-workers.[25] After exchange (bottom), we observe a remarkable attenuation of these variations, showing that the OPE molecules can (at least partially) overcome a distribution of intercolloid distances by self-adjusting within the gap. This also points towards a real interlinking mechanism rather than an intermolecular charge transport due to the possible overlap of OPEs linked to neighboring nanoparticles, although the latter cannot be excluded. We obtain values of $R_{\Box}$ ranging typically between 10 and 100 MΩ, yielding an average value (over the hundred devices) of $R_{\Box} = 54$ MΩ.

Figure 3. Reproducibility of the exchange process. a) Sheet resistance of 29 nanoparticle arrays on one chip. The sheet resistance of each octanethiol device was measured “as-prepared” (■) and after a first exchange with the OPE molecules (○). A subsequent exchange with octanethiols reversed the devices to their initial state (△) and a second exchange with OPEs proved the full reversibility of the process (▽). The bottom inset is an electron microscopy image of devices fabricated by evaporation of gold contact pads on nanoparticle monolayer lines. Scale bar: 50 μm. b) Sheet resistance of 100 devices on five different chips (■, ○, △, ▽, ◆) measured before (symbols in top section) and after OPE exchange (symbols in bottom section). The horizontal dashes show the average sheet-resistance values. The large sheet-resistance differences between chips in the as-prepared devices are strongly reduced after molecular exchange.
therefore, not only reduce the spread in $R$ after the assembly of dithiolated OPEs, but it is also observed that this mechanism favors the self-formation of single molecular junctions, an asset for producing robust building blocks in molecular electronics.

In conclusion, we have demonstrated the reversible formation of molecular-junction networks using a molecular-exchange technique in 2D metallic nanoparticle arrays. The stability, high yield, and reproducibility of the devices shall establish this method as a promising tool for the development of molecular circuits. Functional molecular devices might be fabricated by assembling hybrid structures composed of nanoparticles (metallic or semiconducting) linked by conducting wires and electro- or photoactive molecules.

**Experimental**

Gold colloidal particles with a diameter of 10 nm were synthesized using the method described by Slot and Gauze [27]. Unless mentioned, all reagents were purchased from Fluka and used as received. A 20 mL solution containing 4 mL 1 % (w/v) trisodium citrate and 1 mL 1 % chloroauric acid (all solutions at 60 °C). The nanoparticles were first transferred from water to ethanol by centrifugation and mixed together with a 0.5 mL solution of alkanethiols in ethanol. After 12 h, the nanoparticles were properly capped with alkanethiols and precipitated at the bottom of the container. The precipitates were washed with ethanol in order to remove excess alkanethiols. Finally, the alkanethiol-capped nanoparticles were dispersed in chloroform by ultrasonic treatment.

2D arrays of nanoparticles were prepared by self-assembly at an air/water interface [15]. In a typical experiment, 400 µL of ca. 2 x 10$^{-3}$ particles/mL alkanethiol-encapsulated gold nanoparticles dissolved in chloroform were cast with a syringe at the air/water interface of a Teflon container filled with pure, deionized water. The shape of the water surface was adjusted to be slightly convex. After evaporation of the solvent (fume hood, air velocity at 100 ft s$^{-1}$ (30.5 m s$^{-1}$)), the nanoparticles self-assembled into a 2D array at the water surface.

The PDMS stamps were prepared by casting a mixture of a prepolymer gel and a curing agent (Sylgard 184, Corning) on a master that had the desired patterns. After degassing at room temperature for 30 min and baking at 60 °C for 1–2 h, the PDMS stamps were peeled off the master and cut into the desired shape.

A 1 mL solution of OPE in THF was used for the molecular exchange of octanethiol with the OPE molecules. Samples were immersed in 2 mL of the OPE solution for more than 20 h. The solution was bubbled with Ar before immersion of the samples and kept under Ar during the exchange process. After exchange, the samples were rinsed in THF to remove the unreacted materials and dried with nitrogen gas.

Received: May 8, 2006