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Selective Growth of Organic 1-D Structures on Au Nanoparticle Arrays

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ABSTRACT

We demonstrate that the growth of F16CuPc 1-D nanostructures can be directed by templates of gold nanoparticles. The growth occurs via vapor-phase transport, whereby the gold nanoparticles act as nucleation sites for $F_{16}CuPc$ molecules and promote their anisotropic growth. The $F_{16}CuPc$ 1-D structures adopt diameters of ∼15–30 nm independent of the nanoparticle size. This approach enables a technologically simple and inexpensive fabrication of very uniform organic 1-D structures (aspect ratio of ∼30) and precise control of their location and packing density.

The search for novel properties and low-cost electronic devices has led to an extraordinary increase in the research and technical development of organic semiconductors in the last decades. Among the different explored semiconducting organic materials, small aromatic molecules have been recognized as promising candidates for future applications because they can be grown in films of high crystalline order, thus fulfilling one of the important prerequisites for high charge carrier mobility.[1−6] Although ordered organic films have been successfully implemented in electronic devices (such as OFETs or OLEDs), the controlled growth of organic semiconducting nanostructures, which is one of the basic requirements for their integration in functional nanoscale devices, remains an experimental challenge. In this area, only few studies in the literature have reported methods with substantial potential to achieve this goal.[7−9]

This situation is in contrast to inorganic semiconductors, where the controlled fabrication of one-dimensional (1-D) semiconducting structures has opened new promising avenues for new nanoscale devices with novel functions. Different synthesis strategies have been successfully developed to grow 1-D structures, such as by using templates of metal aggregates.[10−15]

In this work, we demonstrate that templates of gold nanoparticles can be used to nucleate and direct the assembly of uniform 1-D organic nanostructures. We employed micellar nanolithography to pattern Si (100) substrates with gold (Au) nanoparticles whose size (*D*) and lateral separation

(*L*) can be adjusted.[16−19] We have chosen copper-hexadecafluorophthalocyanine ($F_{16}CuPc$) molecules because they exhibit an intrinsically anisotropic growth, governed by strong intermolecular coupling of π-electrons on adjacent molecules. $F_{16}CuPc$ is one of the few organic semiconducting molecules with air-stable *n*-channel behavior in combination with gold electrodes.[20−22] The aforementioned anisotropy is usually mirrored in a characteristic morphology of terraces or crystallites elongated along the packing direction of the cofacial stack.[22−25]

Si (100) wafers were cleaned and coated with gold nanoparticles as described in ref 16. The size of the Au nanoparticles was then increased by an additional electroless deposition step.[26] The $F_{16}CuPc$ molecules were deposited on Au nanoparticle arrays by vapor deposition in ultrahigh vacuum (1×10^{-9} mbar) at a low rate (∼3 Å/min). Note that, on flat SiO_2 substrates, these experimental conditions lead to the formation of $F_{16}CuPc$ smooth films with ordered out-of-plane structure of standing upright molecules. Larger lateral domains are assured by increasing the substrate temperature (above 100 °C).[27] All samples discussed in this letter have a nominal $F_{16}CuPc$ coverage of 8−10 nm. Before growth, the Au nanopatterned surfaces were heated to 450 °C under ultrahigh vacuum (UHV) conditions for 2 h in order to desorb remnant impurities and contamination.

To have an in situ monitor of the $F_{16}CuPc$ coverage, we prepared substrates which exhibit the Au nanodot array only on one-half of the surface and have a smooth SiO_2 substrate on the other half (see scheme in Figure 1a). The as-grown nanostructures were characterized by field emission scanning electron microscopy (FE-SEM). The scanning electron
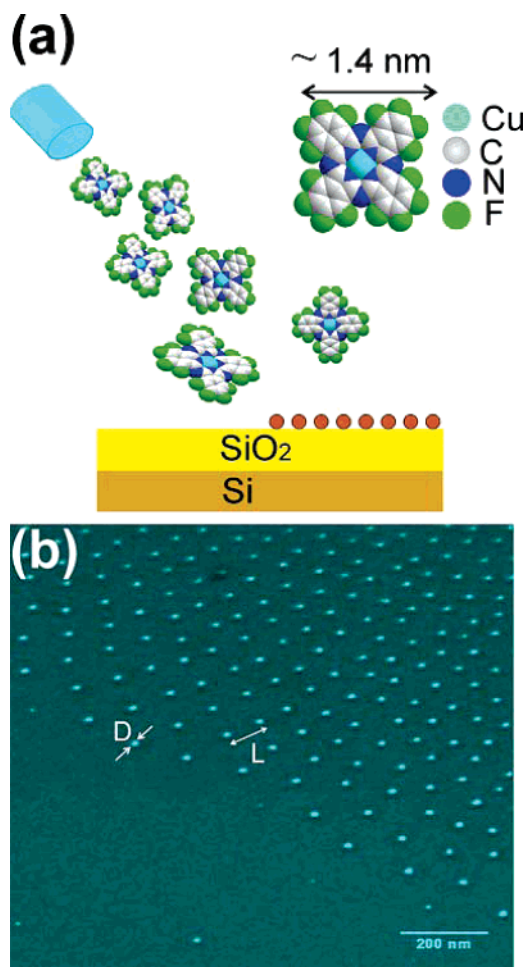
Figure 1. (a) General scheme of the growth of $F_{16}CuPc$ onto the template of gold nanoparticles. Half of the substrate is left uncovered as reference. (b) SEM image (55° tilt) of the substrate at the boundary between the nanoparticle array and the bare SiO_2. The distance L between the gold nanodots and their size D are externally controlled parameters.

Figure 2. SEM image illustrating the vertical growth of $F_{16}CuPc$ wirelike nanostructures on top of the gold nanoparticles with width of 20−25 nm. Inset: typical SEM image on another sample (tilt angle of 55° in both).

Figure 3. (a) SEM image (45° tilt) taken at the boundary between the gold template and the SiO_2, showing the high selectivity of the 1-D $F_{16}CuPc$ growth. The gold particle lateral separation is $L \sim$ 120 nm and their size varies between $\sim$25−40 nm. (b) Typical SEM image (top view) on another sample (mean gold particle size of $D \sim$ 30 nm and average distance of $L \sim$ 150 nm), showing the network of $F_{16}CuPc$ 1-D nanostructures connecting nearby Au nanoparticles.

micrograph in Figure 1b shows the boundary between the patterned and unpatterned region of the sample.

The resulting $F_{16}CuPc$ growth structures are shown in Figure 2: while the expected growth of a smooth film is found on the nonstructured reference area of the SiO_2 substrate, the SEM micrographs disclose $F_{16}CuPc$ 1-D nanostructures, with a typical diameter of $d = 20$ nm, which grow standing on top of the Au nanoparticles. Apparently, the Au nanoparticles act as nucleation sites for the $F_{16}CuPc$ molecules and promote their wirelike growth. These organic nanostructures are found to be stable after several weeks of storage in air. The high degree of selectivity of this Au nanoparticle-assisted 1-D growth is illustrated in Figure 3a, which zooms in onto the boundary between the reference SiO_2 surface and the gold nanoparticle array. As can be seen in a higher resolution SEM image in Figure 3b (taken on another sample), uniform $F_{16}CuPc$ 1-D nanostructures connect the Au nanoparticles, thereby forming a network. We attribute this behavior to electrostatic forces between the Au nanoparticles and the organic structures, which are negatively charged by the electron beam. This would in fact imply that
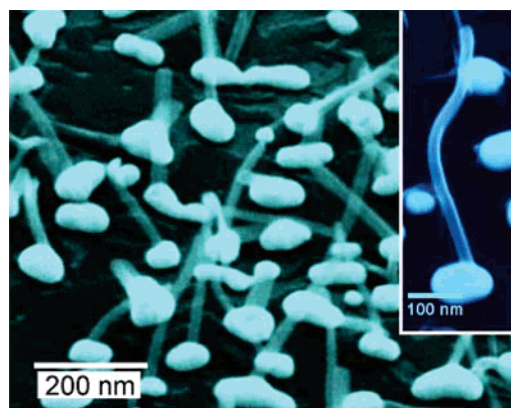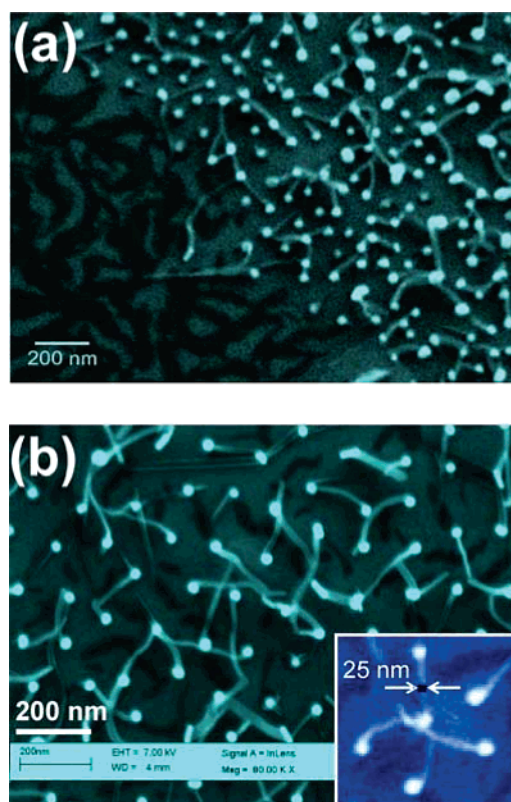
the growth direction of a single 1-D $F_{16}CuPc$ structure could be controlled by applying an electric field between nanostructured gold electrodes. On the other hand, this charging effect renders the SEM observation of the standing $F_{16}CuPc$ 1-D structures rather difficult because these soft nanostructures are bent down to the surface by the action of the electron beam.
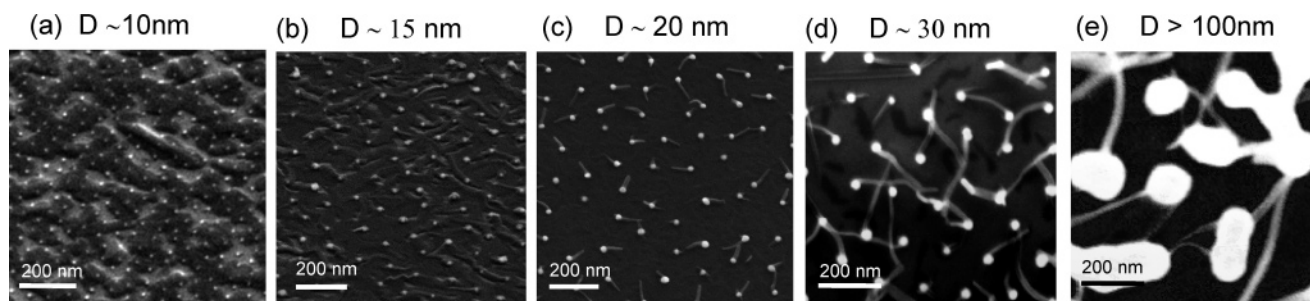
Figure 4. SEM images illustrating the influence of the Au particle size on F_{16}CuPc 1-D growth. Single structures emerge from each Au particle when the size of the nanoparticle exceeds a critical linear dimension of $D^* = 20$ nm. The width of the F_{16}CuPc 1-D structures is independent of the Au nanoparticle size.
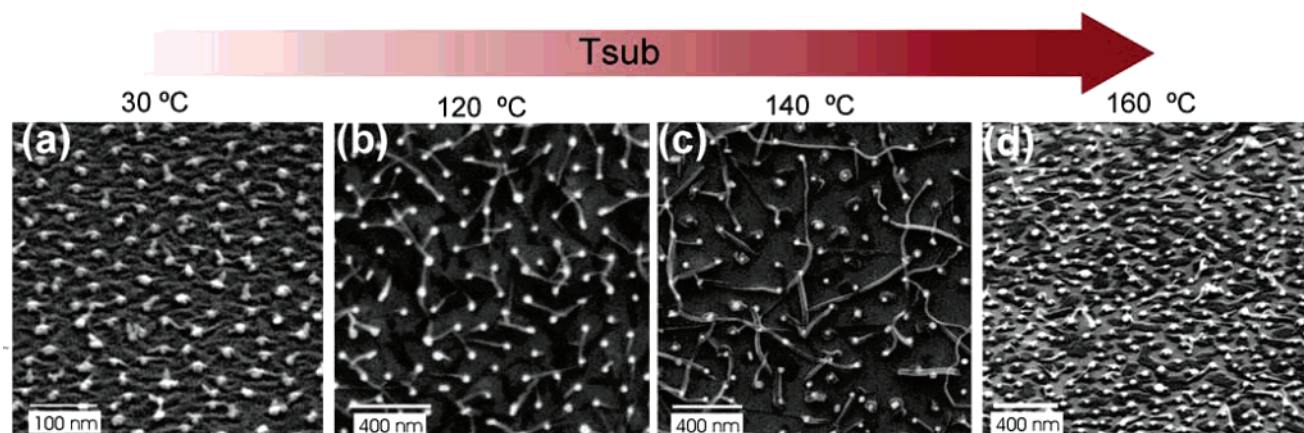

Figure 5. SEM images illustrating the influence of substrate temperature on F_{16}CuPc 1-D growth. The optimal temperature is about 140 °C.

The distance, L, between the Au nanoparticles and their size, D, are externally controlled parameters. The former enables control of the packing density of the F_{16}CuPc 1-D structures. Interestingly, the F_{16}CuPc 1-D structures grow with a fixed diameter ($d \approx 15-30$ nm) regardless of the Au nanoparticle size D (see inset in Figures 2 and 3b). The origin of the selection of this length scale is yet unclear. It is, however, in striking contrast to the formation of inorganic nanowires, which adopt a diameter dictated by the size of the metallic seed.[13] The effect of the Au nanoparticle size D on F_{16}CuPc growth is summarized in Figure 4, which shows the growth structures obtained from $D = 10, 15, 20, 30$, and >100 nm Au nanoparticles. Stunningly, the deposition of F_{16}CuPc onto templates with Au nanoparticles with sizes $D \leq 15$ nm leads to the growth of a smooth thin film like that obtained on bare SiO$_2$ (Figure 4a,b). Apparently, there exists a critical particle size D^* to induce F_{16}CuPc 1-D growth. Single 1-D structures emerge (from each Au particle) when the nanoparticle size exceeds a critical linear dimension of $D^* = 20$ nm (which is in good compliance with the mean diameter of the F_{16}CuPc 1-D structures), implying that the 1-D growth is only possible when the nanoparticle size exceeds the intrinsic diameter of the F_{16}CuPc 1-D structures (Figure 4c,d,e). It is also interesting to note that several of these structures grow on one Au nanoparticle for particles with diameters $D > 100$ nm (Figure 4e).

The substrate temperature also plays a critical role for the growth of the 1-D F_{16}CuPc nanostructures. Figure 5 shows typical SEM micrographs for samples grown at different substrate temperatures. When F_{16}CuPc deposition is performed at room temperature (Figure 5a), none or only very truncated 1-D structures (with maximum lengths of ~40 nm) are observed to grow on the Au nanoparticles. Higher substrate temperature promotes the growth of longer 1-D structures: lengths of about 300 and 800 nm are formed for growth at 120 °C (Figure 5b) and 140 °C (Figure 5c), respectively. At $T \approx 160$ °C, 1-D growth is considerably hindered (Figure 5d) due to molecular desorption, which sets in at this temperature. The observed temperature-dependent morphology gives clear evidence that the 1-D growth of F_{16}-CuPc on Au nanoparticles is a thermally activated process. The assembly of F_{16}CuPc in such uniform 1-D nanostructures is apparently governed by thermodynamic forces, i.e., by the minimization of surface energies (resulting in 20 nm-width 1-D structures) together with kinetic parameters (nucleation at the Au nanoparticles is clearly mediated by surface and bulk diffusion).

We have performed a preliminary cross-sectional transmission electron microscopy (TEM) study on one sample with F_{16}CuPc 1-D structures, previously protected by a Pt capping layer and sectioned by focused ion beam (FIB). The cross-sectional TEM image (Figure 6) confirms the growth of standing or vertically oriented 1-D nanostructures. It can be appreciated that the 1-D structure stands perpendicular to one of the gold nanoparticle facets and hence with a tilt of about 25° with respect to the surface normal. This TEM
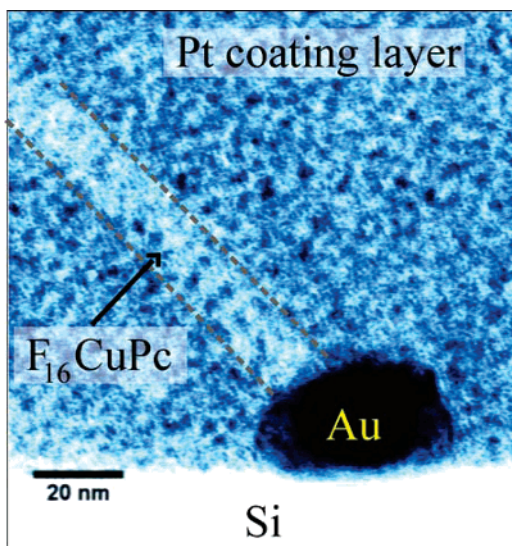
Figure 6. Cross-sectional TEM image from one of the samples. The TEM specimen has been prepared by low-current Ga ion-beam sectioning. A protective Pt capping layer is e-beam deposited in the FIB system prior to sectioning. The TEM image shows one $F_{16}CuPc$ 1-D structure standing perpendicular to one of the facets of the gold nanoparticle.

study strongly suggests that the gold nanoparticle facets may play a decisive role in determining the growth direction and, possibly, the width of the resulting $F_{16}CuPc$ 1-D nanostructure (Figure 6). Unfortunately, the Pt layer, which acted as a protective layer during the FIB process, hindered the observation of the atomic structure of the gold nanoparticle and the identification of the facet. Further investigation is required to elucidate the mechanisms responsible for this novel growth and whether this is a general phenomenon observable for other metallic seeds and organic systems.

In conclusion, we have demonstrated the growth of uniform $F_{16}CuPc$ 1-D structures (diameter $\sim 15-30$ nm) whose precise localization and packing density can be accomplished by templates of Au nanoparticles. We are convinced that this strategy, which is technologically simple and inexpensive, is vastly applicable to other small aromatic molecules with strong intermolecular coupling between π-orbitals.

This provides us with exciting systems to test fundamental questions about localization excitons and quantum transport in organic 1-D structures. The fact that the $F_{16}CuPc$ 1-D structures assemble in a network connecting gold nanoparticles by the action of electrostatic forces suggests promising avenues for the bottom-up fabrication of integrated organic circuits.

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NL062057A