

Anisotropic Assembly of Colloidal Nanoparticles: Exploiting Substrate Crystallinity

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We show that the crystal structure of a substrate can be exploited to drive the anisotropic assembly of colloidal nanoparticles. Pentanethiol-passivated Au particles of ~ 2 nm diameter deposited from toluene onto hydrogen-passivated Si(111) surfaces form linear assemblies (rods) with a narrow width distribution. The rod orientations mirror the substrate symmetry, with a high degree of alignment along principal crystallographic axes of the Si(111) surface. There is a strong preference for anisotropic growth with rod widths substantially more tightly distributed than lengths. Entropic trapping of nanoparticles provides a plausible explanation for the formation of the anisotropic assemblies we observe.

I. INTRODUCTION

Directional assembly of nanoparticles to form linear or one-dimensional structures is a fascinating, but challenging, area of state-of-the-art nanoscience. While DeVries *et al.*[1] have pioneered a clever “target molecule” strategy to generate nanoparticle chains, a number of approaches based on the exploitation of patterned substrates and/or anisotropic dewetting to drive linear assembly have also been described. These include the formation of lines of Au nanoparticles on organic templates fabricated via photolithography[2], friction transfer[3], or Langmuir-Blodgett methods[4]; the use of contact line instabilities[5]; and the controlled decoration of carbon nanotubes[6] and DNA-functionalized nanotubes[7]. As pointed out by Tang and Kotov[8] in a recent review article, however, reports on the synthesis of 1D nanoparticle assemblies are relatively rare due to the difficulty of producing directional forces between what are effectively spherical objects.

A complementary approach to one-dimensional assembly formation common in ultrahigh vacuum-based nanostructure fabrication is the exploitation of the crystal structure of the substrate to direct the self-assembly process[9]. This approach has particular advantages because control of size, shape, and orientation can be imposed, generally in a relatively facile fashion, via the choice of substrate symmetry and surface reconstruction. Here we extend this templating technique to nanoparticles *deposited from a colloidal solution* onto a hydrogen-passivated Si(111) surface[10, 11], yielding linear assemblies (rods) aligned with the principal crystallographic axes of the substrate. In addition to the orientational ordering imposed by the substrate, the distribution of the widths of the nanoparticle rod assemblies is significantly narrower than that for their lengths. We propose that entropic barriers[12] play an important role in the anisotropic assembly process.

II. EXPERIMENTAL

Pentanethiol-passivated Au nanoparticles were prepared in toluene using the method pioneered by Brust

et al.[13]. Small angle X-ray scattering at the XMaS beamline of the European Synchrotron Radiation Facility (ESRF) was used to characterise the average nanoparticle diameter (1.92 nm) and size distribution (standard deviation: 0.16 nm). A 25 μ l droplet of an appropriately diluted solution was then placed on a native oxide-terminated, or hydrogen-passivated (see below) Si(111) substrate and the sample subsequently spun at 4 krpm. An Asylum Research MFP-3D atomic force microscope (AFM) system operating in intermittent contact mode with closed loop control was used to image the resulting nanoparticle assemblies. Olympus AC240 silicon probes (spring constant: 2 Nm⁻¹, resonant frequency: 70 kHz, and radius of curvature: ~ 10 nm) were used throughout.

Preparation of H:Si(111) samples

Native oxide-covered Si(111) samples were first ultrasonicated for ten minutes in ethyl lactate, acetone, methanol, and isopropanol to remove soluble organic contaminants. The samples were then cleaned in an oxygen plasma at 150°C for five minutes before being placed in “piranha” solution (H₂SO₄:H₂O₂) at 140° for ten minutes. This produces a homogeneous oxide layer. Following this cleaning/oxide regrowth process, the samples were placed in a 7:1 H₂O:HF solution for 30 seconds, briefly rinsed in deionised water, then plunged into a H₂O:NH₄F solution for 30 seconds before a final deionised water rinse.

III. RESULTS AND DISCUSSION

Thiol-passivated Au nanoparticles, when deposited onto native oxide-terminated silicon substrates, form a panoply of non-equilibrium patterns[14–19] arising, as for many other colloidal nanoparticle-substrate systems, from the coupling of the particle and solvent dynamics[20–22]. As expected for deposition onto an amorphous substrate, nanoparticle assemblies on native oxide-terminated silicon are structurally isotropic. In particular, two-dimensional Fourier transforms show

no evidence of orientational order[16, 18].

Fig. 1 shows tapping mode AFM images of the assemblies formed by pentanethiol-passivated Au nanoparticles on SiO₂. We have chosen the nanoparticle concentration such that a small number of second layer assemblies also form. These are highly reminiscent of those which arise from diffusion limited aggregation (DLA) in many other colloidal systems. As expected for deposition on the amorphous SiO₂-covered substrate, the DLA features are structurally isotropic. The network structure visible in the first layer arises from evaporative solvent dewetting[14, 22].

The morphology of the nanoparticle assemblies

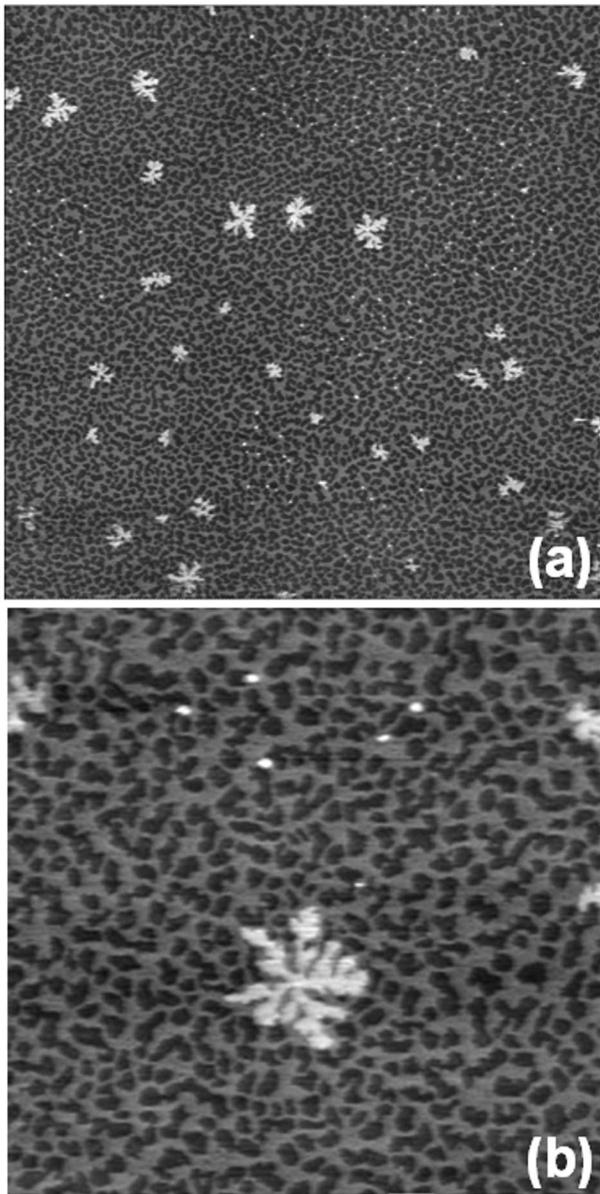


FIG. 1: (a) A $20 \times 20 \mu\text{m}^2$ AFM image of pentanethiol-passivated 2nm diameter Au nanoparticles deposited from toluene onto a native oxide-terminated Si(111) surface. (b) A higher resolution ($5 \times 5 \mu\text{m}^2$) image where the branched assemblies formed by the second layer nanoparticles are more clearly resolved.

changes dramatically when a H:Si(111) surface is used as a substrate. As shown in Figs. 2(a) and 2(b), the adsorbed nanoparticles form highly anisotropic structures which are best described as rods. Perhaps the most striking feature of the AFM images shown in Fig. 2 is the degree of alignment of the rods along particular directions. A histogram of the orientations of the rods is shown in Fig. 2(c) from which it is clear that the rods are oriented predominantly along vectors with angular separations of $\pm 60^\circ$. These angles are entirely consistent with the structural symmetry resulting from treatment of Si(111) surfaces using HF solutions, where etching proceeds in the $\langle \bar{1}\bar{1}2 \rangle$, $\langle \bar{2}11 \rangle$, and $\langle \bar{1}2\bar{1} \rangle$ directions. A two-dimensional Fourier transform of the AFM image of Fig. 2(a) (inset to Fig. 2(a)) also highlights the transfer of the substrate symmetry to the orientations of the nanoparticle rods.

Although the rods appear as quasi-1D objects in the AFM images, with a mean width[23] of ~ 70 nm (Fig. 3), their heights span a broad distribution ranging from 2 nm to ~ 9 nm (see inset to Fig. 3). The distribution of rod heights also appears to be trimodal with sharp peaks at ~ 2 nm, ~ 3.5 nm, and a much broader peak centred at ~ 5 nm. In addition, the distribution of rod lengths is significantly broader than that for the rod widths by a factor of approximately six (Fig. 3). The mean aspect ratio is 4.3:1. It should also be noted that the rod width and length histograms are heavily skewed and not well-described by Gaussian distributions. (The rod width distribution is log-normal).

We propose that our results can be rationalised, at least in part, within the entropic control framework first proposed by Dinsmore *et al.* over a decade ago for binary colloidal mixtures. A key result of Dinsmore *et al.*'s experiments on the motion of sub-micron colloidal particles was the observation of effectively free diffusion along a step edge while in the direction perpendicular to the edge there was a strong free energy barrier. The step edge acted to generate an entropic force field due to excluded volume effects. Entropic fields have previously been invoked to explain the templated assembly of nanoparticles on PTFE lines created by friction transfer[3]. We argue that the presence of entropically-derived free energy barriers provides a natural explanation for the otherwise perplexing results of Fig. 2. In particular, the relatively monodisperse rod width distribution is indicative of an appreciable barrier for attachment of nanoparticles in the direction parallel to the minor axis of a rod. Moreover, the standard two-phase reduction method used for nanoparticle synthesis in our case produces a relatively polydisperse particle distribution - an essential element of the entropic force-field model[3, 12].

We show in Fig. 4 an AFM image where the organisation of nanoparticles in the first layer is resolved. Anisotropic assembly, driven by the substrate crystal structure, is clearly present. As is clear from the histogram of rod heights (inset to Fig. 3), the rod structure seen in the first layer regions of Fig. 4 is preserved in nanoparticle assemblies which can be up to ~ 9 nm high. This is an intriguing result and begs the question:

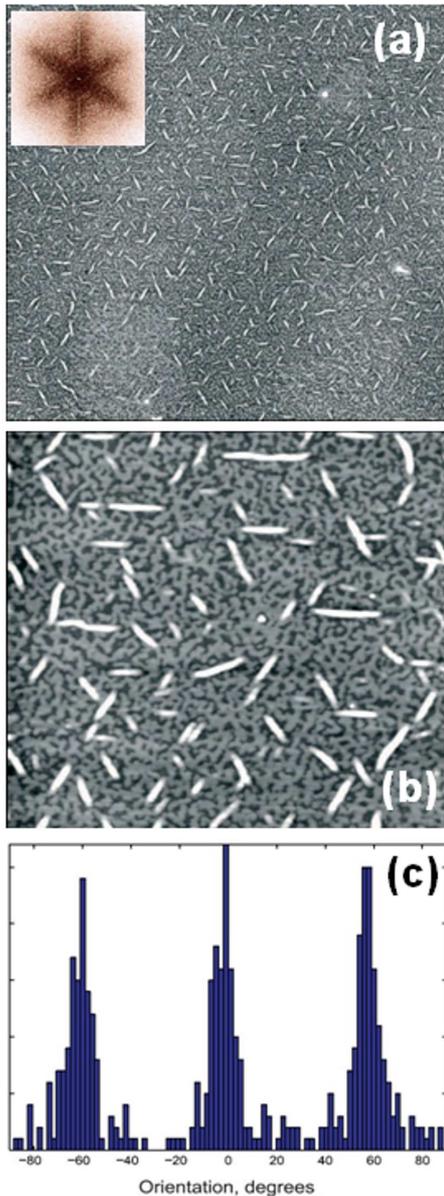


FIG. 2: (a) A $20 \times 20 \mu\text{m}^2$ AFM image of pentanethiol-passivated 2nm diameter Au nanoparticles deposited from toluene onto a H:Si(111) surface formed via HF etching. The colloidal nanoparticle solution used to form this sample was identical to that used for Fig. 1. **Inset:** A 2D Fourier transform of the image highlighting the orientations of the nanoparticle assemblies. (b) A higher resolution ($5 \times 5 \mu\text{m}^2$) image showing both the rod assemblies and the first nanoparticle layer in more detail. (c) Histogram of rod orientations relative to the scan direction (0°).

to what height is it possible to stack nanoparticles in this fashion? To this end, we are currently exploring the effects of nanoparticle concentration, and the addition of excess surfactant molecules to the colloidal solution, on the nanoparticle assembly process on H:Si(111).

Our ability to drive anisotropic nanoparticle diffusion via crystal templates represents an exciting new method of self-assembly with potential applications in a broad variety of areas including nanoelectronics and

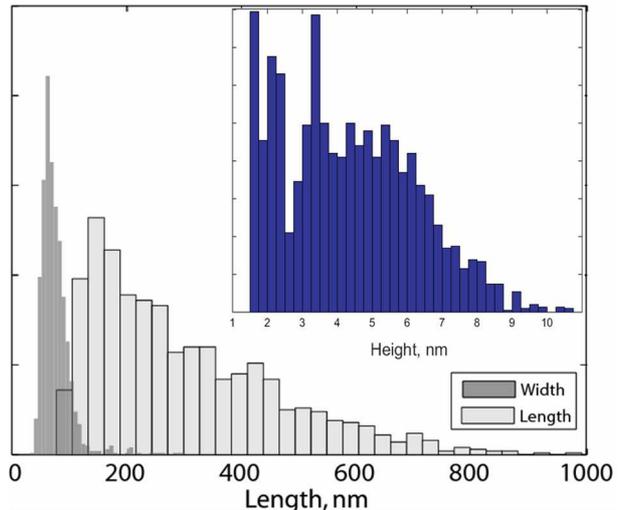


FIG. 3: Histogram of the widths (dark grey columns) and lengths (light grey columns) of the rod assemblies. Note the much narrower distribution for the rod widths and the skewed (log-normal) distributions in each case. (Different bin sizes have been used for the histograms). **Inset:** Histogram of rod heights.

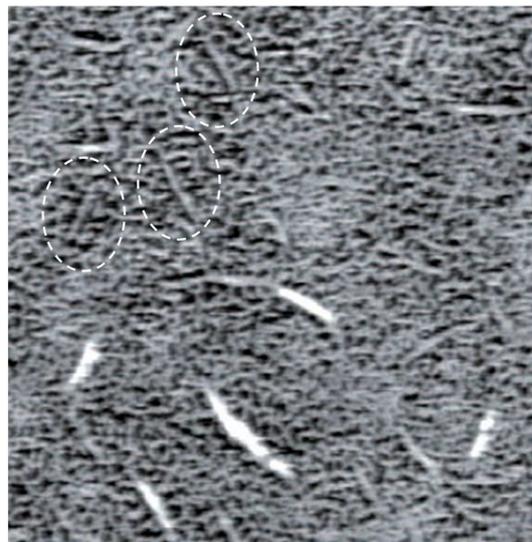


FIG. 4: An AFM image showing the formation of anisotropic nanoparticle assemblies (highlighted) in the *first* layer.

plasmonics. In future work we will be particularly keen to determine whether different Si planes (e.g. (100), (211), (311)) can be used to control the relative orientations and symmetries of nanoparticle assemblies.

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