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Quasi one-dimensional gold cluster arrangements

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Patterns consisting of 10 nm stripes of $Au_{55}(PPh_3)_{12}Cl_6$ clusters have been generated by degradation of two-dimensional, ordered cluster monolayers on a water surface. Applying a modified Langmuir–Blodgett technique stripe formation is induced by fast withdrawing (10 cm min^{-1}) of a substrate, deposited underneath the monolayer, under an angle of 20°. The stripes, each consisting of 3–4 cluster rows, show a separation of 8 nm from each other. Slow transportation of the substrate (2–3 cm min^{-1}) led to hexagonal patterns of crossing stripes. This effect is attributed to the existence of partially overlapping islands of monolayers.

Introduction

The knowledge that ligand stabilized metal clusters in the size range of 1–2 nm exhibit pronounced quantum size behaviour already at room temperature[1–10] (quantum dots) makes them promising candidates for future nanoelectronic applications. A condition for their use, for instance in data storage, is their specific arrangement in a two- or one-dimensional manner. Two-dimensional, highly ordered structures of $Au_{55}(PPh_3)_{12}Cl_6$ have recently been described by us[11,12] and are meanwhile routinely available. First investigations of the electronic properties of such monolayers have been performed.[13,14] Much more difficult is the one-dimensional arrangement of these or similar clusters. First successes have been achieved by means of appropriate polymer molecules and DNA as substrates for the one-dimensional positioning of the Au_{55} clusters,[15,16] however, these methods will probably not be well suited as an easily reproducible technique. For that reason we chose another procedure, using the existence of the above mentioned monolayers as a primary step and which is based on the well-known phenomenon of the oscillation of a water meniscus at a substrate.[17–21] In the following we report on the relatively easy access to ordered 10 nm stripes of rows of $Au_{55}(PPh_3)_{12}Cl_6$ clusters.

Experimental

The synthesis of $Au_{55}(PPh_3)_{12}Cl_6$ is described elsewhere.[22,23] The experiments were carried out with a self-developed modified Langmuir–Blodgett device. It consisted of a sample motor (Newport Actuator 850 F for speeds <3 cm min^{-1} and Actuator 850 G-HS for speeds >3 cm min^{-1}, respectively) and a control unit (Newport Motion Control MM 4000) which was operated by a commercial PC. The sample motor was constructed in a way that at the end of the motor arm samples could be fixed *via* a holder. It enabled dipping angles of the substrate of 15–90°. A barrier motor (Actuator 850 F) moved a Teflon barrier in order to compress the surface if necessary. The trough also was Teflon coated. A constant size of 4.7 cm × 4.0 cm was adjusted by means of the barrier. The temperature of the desalinated water was kept at 20 °C by means of a thermostat. A carbon coated copper grid was fixed at the end of the sample arm and was dipped under the water surface. Then, 100 µL of a $Au_{55}(PPh_3)_{12}Cl_6$ solution in CH_2Cl_2 (Fluka, p.a.) (3.8×10^{-6} M) were carefully distributed on the surface using a syringe. After evaporation of the solvent in air the cluster monolayer was transferred onto the grid. For this purpose the sample was withdrawn from the water under an angle of 20°. The transfer speed was varied between 2 and 10 cm min^{-1}. After the transfer the sample was dried in air. The characterization of the generated patterns was achieved by transmission electron microscopy (Philips CM 2000 FEG) at 200 kV.

Results and discussion

As recently described, hexagonal and square-planar cluster monolayers can easily be made at the phase boundary water/dichloromethane, while a film of polymers such as poly(vinylpyrrolidone) (PVP) or poly(phenylenethynylene) (PPE), which has been generated at the phase boundary previously, supports the formation of transportable monolayers.[12] If this self organization process is varied in such a way that it is carried out without a polymer layer and with evaporation of the dichloromethane before transferring the cluster film, cluster layers can be observed as well. Fig. 1 shows a cutout of such a monolayer.

However, due to the lack of a stabilizing polymer layer these monolayers are obviously easily destroyed when transferred to solid substrates. On the other hand, this behaviour can be utilized to selectively generate patterns of stripes of Au_{55} clusters. For this purpose we used a self-made miniaturized Langmuir–Blodgett device. The substrate onto which the cluster should be transferred was linked with a motor *via* an arm. In the present case a carbon coated copper grid for electron microscopy was used. It was dipped underneath the

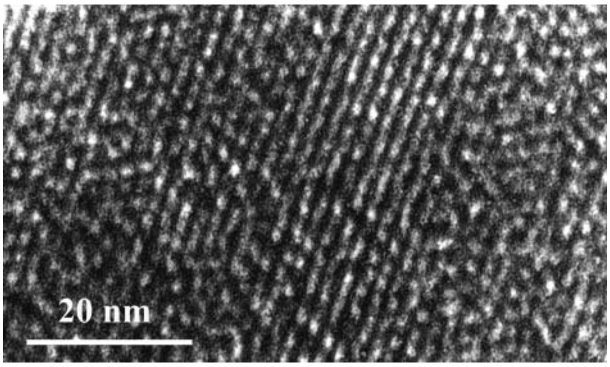

Fig. 1 TEM image of an ordered monolayer of $Au_{55}(PPh_3)_{12}Cl_6$ clusters which has been generated on a water surface in the absence of any additives.

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water surface with an angle of 20°. Then, a thin film of a very dilute solution of the clusters in dichloromethane was produced using a syringe. Thereafter, CH_2Cl_2 was evaporated in air, followed by withdrawing the substrate by means of the motor with a speed which was varied between 2 and 10 cm min^{-1}. Transmission electron microscope (TEM) investigations of the grid surface were performed after drying in air.

Fig. 2a and b show typical images of stripe patterns generated by this procedure. On average each stripe consists of 3–4 individual rows of clusters. From Fig. 2b it can be seen that the lines are composed of single equidistant clusters.

The cluster–cluster distance is 2.2–2.3 nm in agreement with the calculated diameter of $Au_{55}(PPh_3)_{12}Cl_6$ clusters. Within the stripes the clusters are on the whole of square and not of hexagonal order. The question, as to if this arrangement relates with the structure of the monolayer the cluster rows originate from, is presently uncertain. The formation of these bands, consisting of single cluster rows, is attributed to a phenomenon which is known from the transfer of Langmuir–Blodgett films, *e.g.* of fatty acids, onto solid substrates. Extensive stripe patterns of L-α-dipalmitoylphosphatidylcholine on mica surfaces have recently been generated by Chi and coworkers[21] However, the resulting stripe width was found to be 200 nm.

The complex mechanism of the formation of such structures is described in the literature and can be understood in a simplified manner as an oscillation of the water meniscus at the substrate, inducing the generation of stripe patterns running parallel to the meniscus.

Fig. 3a shows a simplified sketch of the possible formation process. As the probability that the transfer direction is exactly perpendicular to the orientation of the cluster rows in the monolayer is very low, a breakoff of individual cluster rows occurs, as can be seen from Fig. 2a.

In some cases crossing stripes of clusters can be observed. A typical pattern is shown in Fig. 4.

The pattern formation by the described transport process is mainly dependent on the speed at which the substrate is moved. At speeds of *ca.* 10 cm min^{-1} the formation of parallel stripes was always observed, as is shown in Fig. 2. Markedly slower speeds of 2–3 cm min^{-1}, however, usually resulted in crossing stripes, as can be seen in Fig. 4.

The formation of crossing stripes is obviously attributed to the existence of partially overlapping islands of monolayers at the beginning of the process. Overlapping islands of monolayers are well known from many TEM investigations. Fast motion of the substrate separates them, forming exclusively parallel stripes. However, slow drawing speeds keep the overlapping islands intact. Double layers of bands of like orientation are formed in the overlapping regions. These reorganize during evaporation of residual water to give the more stable hexagonal structure, as can be seen from Fig. 4.

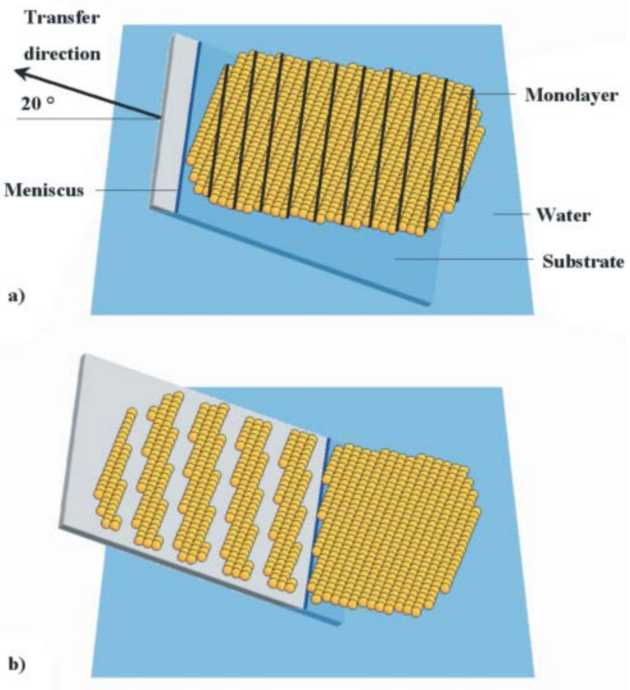

Fig. 3 Sketch of the formation of cluster stripes from an ordered monolayer. The monolayer is oriented toward the substrate edge and the meniscus, respectively, by a non-predetermined angle. Owing to the movement of the substrate from the water and the herewith linked transfer of the monolayer onto the substrate surface, the monolayer is fractured along the black lines due to the oscillation of the meniscus. Stripes of 3–4 rows of clusters lying side by side are formed. The stripes run parallel to the water meniscus.

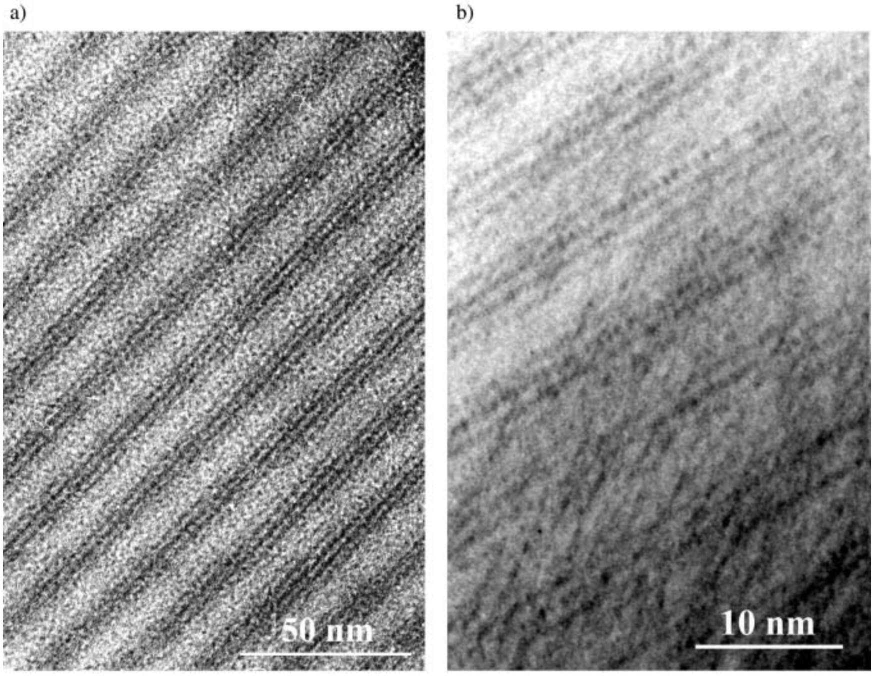

Fig. 2 a) TEM image of cluster stripes consisting of 3–4 cluster rows. b) Magnified cutout. The cluster rows consist of equidistantly ordered clusters.

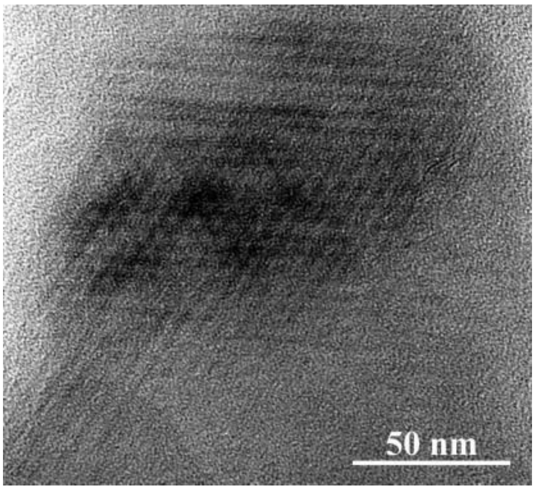

Fig. 4 TEM image of partially crossing stripes.

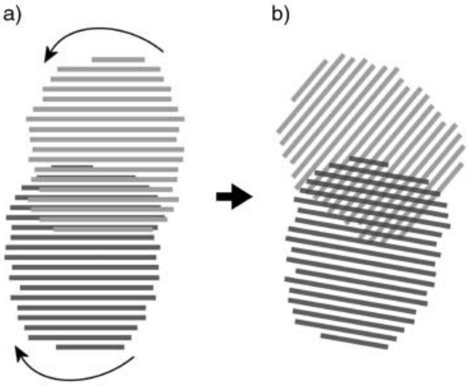

Fig. 5 Possible explanation of the formation of crossing stripes. Due to the transfer the originally overlapping islands get separated into stripes of like orientation. During drying the stripes are reorganized into a more stabile hexagonal lattice.

Fig. 5 elucidates this process, at the end of which a hexagonal and thermodynamically stable arrangement of two layers of bands exists. The quality of the TEM images so far has not allowed a clear distinction to be made as to if the clusters in the crossing stripes are of square or, corresponding to the super structure, are also of hexagonal order.

Conclusion

With the planned and reproducible preparation of parallel rows of $Au_{55}(PPh_3)_{12}Cl_6$ clusters we succeeded for the first time in generating quasi one-dimensional structures of quantum dots of about 10 nm width. This work completes the techniques, recently discovered by us, to construct ordered two-dimensional structures of these nanoparticles and represents another important step to use the quantum properties of clusters of this size-range.

Acknowledgements

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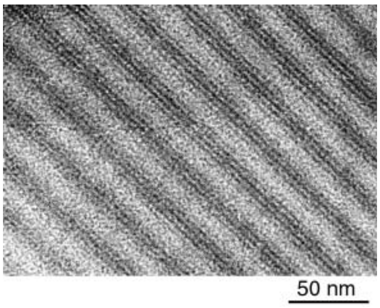

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