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Observations of non-close-packed arrangements in multilayers of passivated gold clusters

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ABSTRACT: The stacking of second and third layers of supercrystals of self-assembled passivated gold nanoparticles has been investigated using transmission electron microscopy. We report for the first time nanoparticles occupying the twofold saddle site in the third layer.

1. INTRODUCTION

The unusual properties of nanometre-scale metal and semiconductor particles have triggered intensive studies of size selected clusters (Goldby *et al.* 1996, Carroll *et al.* 1998). One of the most fascinating and widely studied phenomena is self-assembly of nanoparticles into superlattices (for a review see Collier *et al.* 1998). Superlattices of surfactant-stabilised nanosized colloidal particles have been reported by several authors, for example Brust *et al.* (1995), Ohara *et al.* (1995), Fink *et al.* (1997), Durston *et al.* (1998), Kiely *et al.* (1998) and Wang (1998). Particles with a narrow size distribution exhibit a hexagonal close-packed arrangement in the first layer (Harfenist *et al.* 1996, Fink *et al.* 1998, Durston *et al.* 1997).

The three dimensional packing of multilayers of passivated particles has been found to be more complicated. Harfenist *et al.* (1996) have shown that passivated nanocrystals with a truncated octahedral shape exhibited face-centred cubic (fcc) packing, corresponding to the occupation of the threefold hollow sites with ..ABCABC.. stacking. For multiply twinned particles, however, hexagonal close-packing (hcp) was observed corresponding to ..ABAB.. stacking (Harfenist *et al.* 1997).

Other studies have shown that particles in the second layer can also occupy the twofold saddle site leading to line or ring structures in projection (Fink *et al.* 1997, Korgel *et al.* 1998, Zanchet *et al.* 1999). Crystallographic descriptions for multilayers in such sites have been described by Aindow *et al.* (1999). In this paper we report for the first time experimental evidence for the existence of such structures.

2. EXPERIMENTAL

The passivated gold clusters used here were produced using the inverse micelle method which has been described elsewhere (Wilcoxon *et al.* 1993). The particles consist of a charge-neutral gold core (4 - 4.5 nm in diameter) surrounded by $C_{12}H_{25}S$ ligands (1.8 nm in length). The clusters were dissolved in a toluene solution. Amorphous carbon substrates

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were produced by evaporating a thin film of carbon onto a glass slide. The film was then floated off in water and transferred onto a Cu support grid. The clusters were deposited by dropping the solution onto the substrate and allowing the solvent to evaporate. The samples were examined in a top-entry JEOL 200CX TEM operating at 200kV.

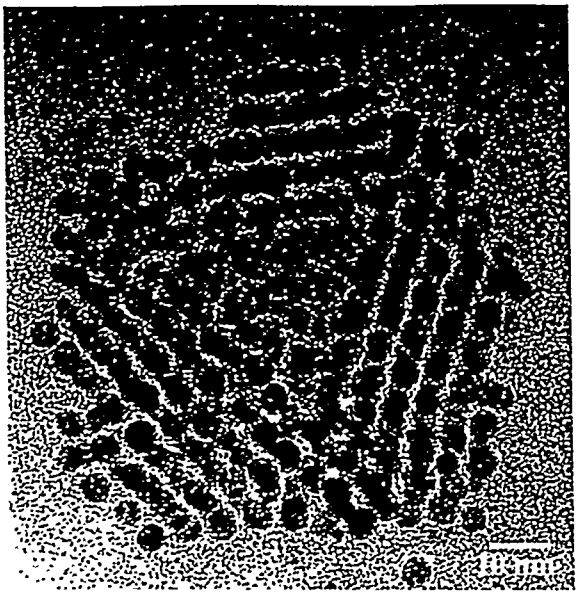

Fig. 1 Bilayer island of gold clusters with a second layer visible as lines.

3. RESULTS AND DISCUSSION

Figure 1 is a bright field (BF) TEM image of a bilayer island which exhibits distinctive lines in three domains which lie at 120° to one another. As explained by Fink *et al.* (1997), lines (or sometimes even rings) arise when nanoparticles in the second layer occupy the two-fold saddle sites in the first layer instead of the three-fold hollow sites as defined in fig. 2a. Although one would expect intuitively the occupation of three-fold hollow sites (fig. 2b) for near-spherical particles, the occupation of the two-fold saddle sites (fig. 2c) is also observed experimentally. It has been suggested that the latter configuration is caused by electrostatic repulsion forces (Fink *et al.* 1998) or shape dependent van-der-Waals forces between the particles (Korgel *et al.* 1998). However, the latter explanation holds only for particles with a truncated octahedral shape. We have observed the occupation of two-fold saddle sites even in samples which contained many multiply-twinned particles which have been shown to behave like spheres (Harfenist *et al.* 1997). Zanchet *et al.* (1999) have shown recently that ring structures arise if the lattice in the second layer is rotated and contracted leading to an energy minimisation. Unfortunately this promising approach fails to explain the development of lines.

We now consider the stacking of the third and subsequent layers. The stacking of nanocrystals into threefold hollow sites leads to the well-known fcc or hcp structures, both of which have been observed experimentally (Harfenist *et al.* 1996, Harfenist *et al.* 1997). The arrangements produced by stacking the third layers and subsequent layers into two-fold

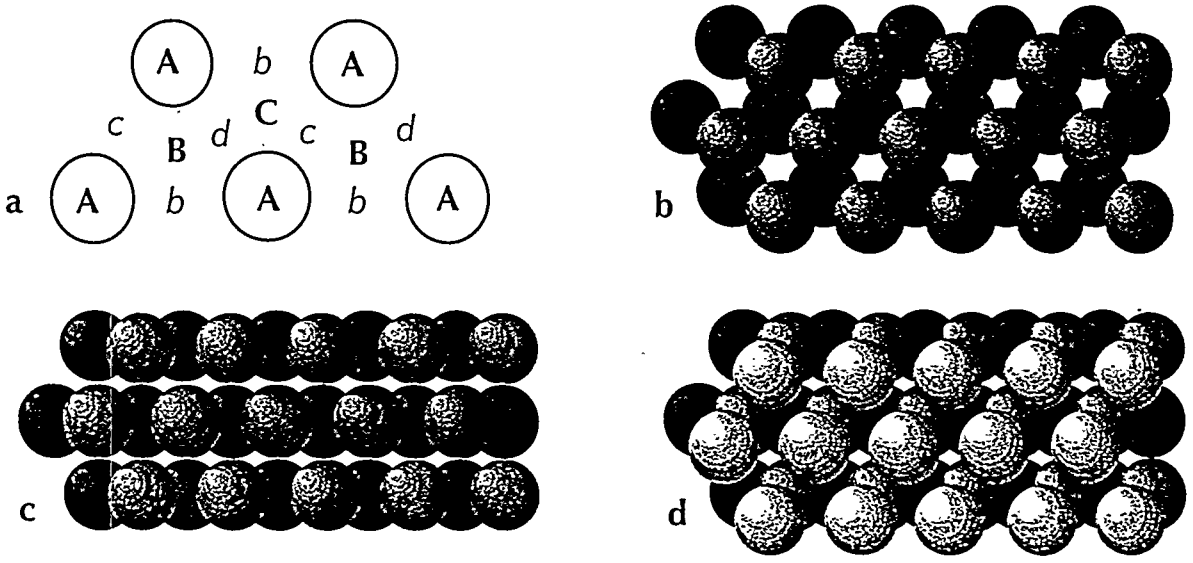

Fig. 2 Schematic representation of multilayers of nanoparticles a) possible occupation sites; projection of particles occupying b) the threefold hollow sites in the second layer (AB stacking), c) the twofold saddle sites in the second layer (Ab stacking), d) the twofold saddle sites in the second and the third layers (Abc stacking).

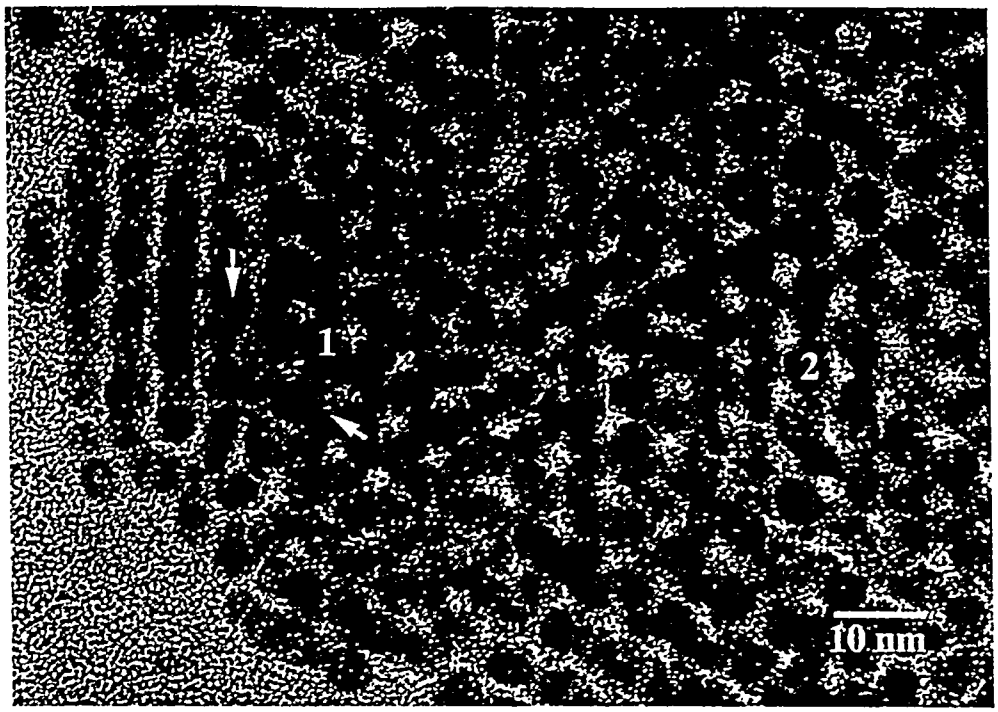

Fig. 3 BF TEM image of an island of gold clusters, with characteristic bilayer lines on the periphery (c.f. fig. 1) and distinct structures in the interior at regions 1 and 2.

saddle sites has been considered by Aindow *et al.* (1999) who noted that the superstructures produced would correspond to disordered forms of the atomic structures adopted by transition metal disilicides. Occupation of the twofold site above the first layer would lead to AbA stacking corresponding to the $C11_b$ $MoSi_2$ structure (space group I/mmm). This structure would be seen as lines and could not be distinguished from a stacking which contains only two layers in projection (compare with fig. 2c). Occupation of one of the other twofold sites (e.g. c sites) would lead to Abc stacking corresponding to the C40 $CrSi_2$ structure (space group $P6_222$). As noted by Aindow *et al.* (1999), in projection this arrangement would resemble hcp stacking (compare Figs. 2b and 2c) but could be distinguished from it by differences in the detail of the arrangements.

This is revealed most clearly in experimental images such as fig. 3 which shows a nanoparticle array in which several different structures can be distinguished. The periphery exhibits the distinctive lines indicating that the second layer of nanoparticles reside in the twofold saddle sites. Within the island, however, two different superstructures are evident. In region 1, the structure appears denser and consists of two sets of lines (arrowed) which are parallel to those on the edges of the island. Towards the centre of the island, however, in region 2, a less dense pattern with three-fold symmetry can be seen. This suggests that the

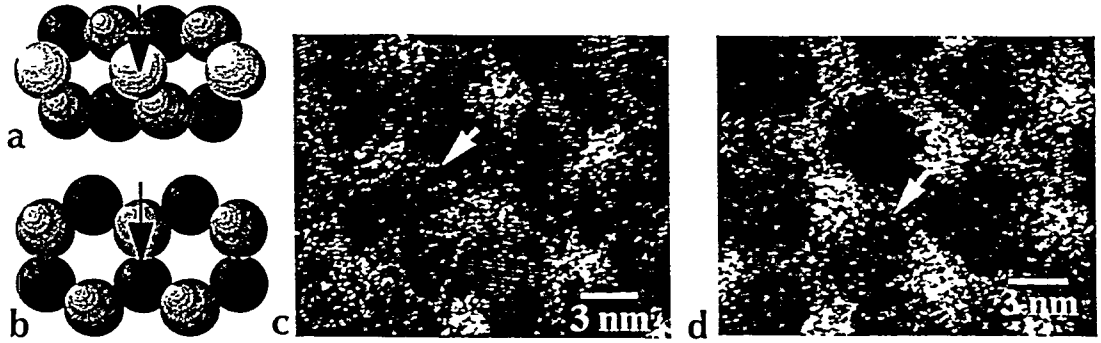

Fig. 4 Detail of cluster arrangements around projected holes with the midpoint between adjacent holes arrowed; a) Abc stacking, b) AB stacking, c) and d) magnified images of regions 1 and 2 in fig 3, respectively.

pattern in region 1 corresponds to the Abc stacking of the C40 $CrSi_2$ structure as shown in fig. 2d, whereas region 2 corresponds to the AB stacking of the hcp structure (fig 2b). A reliable distinction between the two structures can be made by a closer examination of the projected holes in the arrangement (fig. 4). Figures 4a and 4b are schematic diagrams of the cluster arrangements around the holes for Abc- and AB-stacking, respectively. Both consist of a network of closed hexagons but the difference becomes clear if we consider the point midway between two adjacent holes in the projected arrays (arrowed in figs. 4a-d). For Abc-stacking (fig. 4a) this corresponds to the centre of a particle, whereas for AB-stacking (fig. 4b) it is the midpoint between two neighbouring particles. This test can be applied to regions 1 and 2 in fig. 3 which are shown at higher magnification in figs. 4c and d, respectively. In fig. 4c a particle can be seen clearly at the midpoint between the two neighbouring holes. This confirms that region 1 exhibits the Abc-stacking of the C40 $CrSi_2$ structure. In contrast, fig. 4d shows clearly that the midpoint between adjacent holes lies between adjacent particles and thus region 2 exhibits the AB- stacking of the hcp structure.

Further stacking of the fourth and subsequent layers of nanoparticles into twofold saddle sites could give rise to AbAb.. stacking ($C11_b$ $MoSi_2$ structure), AbcAbc.. stacking (C40 $CrSi_2$ structure), AbcdAbcd.... stacking (C54 $TiSi_2$ structure) or mixtures of these. The former two would resemble the arrangements shown in figs. 2c and d, respectively, whereas abcd... stacking would appear as a dense raft of nanoparticles which could not be distinguished from fcc or random threefold hollow site packing in this projection.

5. CONCLUSION

We have shown for the first time experimental evidence of nanoparticles occupying the twofold saddle site in the third layer (Abc stacking) corresponding to the C40 $CrSi_2$ structure. In projection, this pattern resembles closed packed AB stacking in the second layer but it has been shown that the patterns can be distinguished by a careful examination of the cluster arrangement around the projected holes. The analysis of the experimental data shows that Abc- and AB stacking can coexist in the same self-assembled island.

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