Self-assembly of tetraalkylammonium salt-stabilized giant palladium clusters on surfaces

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Nanostructured palladium clusters, stabilized by a monomolecular coat of sufactants $N(C_8H_{17})_4Br$ or $N(C_{18}H_{37})_4Br$, self-assemble on carbon surfaces in an ordered manner with the formation of hexagonal close packed structures.

Self-assembly of preformed nanostructured transition-metal clusters on solid surfaces in ordered structures constitutes a formidable preparative challenge.[1] Investigations in this field of material science is driven by the prospect of fabricating structurally uniform materials having unique electronic and/or magnetic properties. For example, placing finite-sized clusters onto surfaces in geometrically well defined arrays may open the way to single-electron tunnel devices. Recently we have shown that a variety of nanostructured metal clusters and bimetallic clusters stabilized by tetraalkylammonium salts can be prepared electrochemically in a size-selective manner by correct adjustment of the current density and proper choice of solvent.[2] A combined STM–TEM study revealed that each individual cluster is surrounded by a monomolecular layer of the NR_4X salt.[3] Whereas many TEM studies of NR_4X- stabilized metal clusters have been carried out previously in order to determine the average size of the metal core,[2–4] unusual phenomena relating to self-assembly on the surface have not been observed to date. In this paper we describe ordering phenomena involving high purity monodisperse NR_4X-stabilized palladium clusters on carbon supports, as observed by transmission electron microscopy.

In all experiments the surfaces upon which the clusters were deposited consisted of carbon support films, produced by means of an impact evaporator, and placed on copper grids (400 mesh in^{-1}).[5] Simple dip-coating using solutions of $N(C_4H_9)_4Br$-, $N(C_8H_{17})_4Br$- or $N(C_{18}H_{37})_4Br$-stabilized palladium clusters[2] having average inner core sizes of 2.5, 5.9 and 5.9 nm, respectively, was performed,† followed by TEM analysis. In the case of the $N(C_4H_9)_4Br$-stabilized palladium clusters, the TEM micrographs failed to show any signs of order, irrespective of the conditions used in the dip-coating process. Completely random distributions of clusters on the surface were observed. Similar observations were made upon employing larger sized palladium clusters stabilized by $N(C_4H_9)_4Br$. In complete contrast, the samples stabilized by $N(C_8H_{17})_4Br$ led to high degrees of ordering. The respective clusters self-organize in a hexagonal close packing structure. Interestingly, the system self-assembles in ordered stacks of such layers, these being arranged in almost perfect steps and terraces. High-resolution TEM clearly reveals the first few individual layers (Fig. 1).

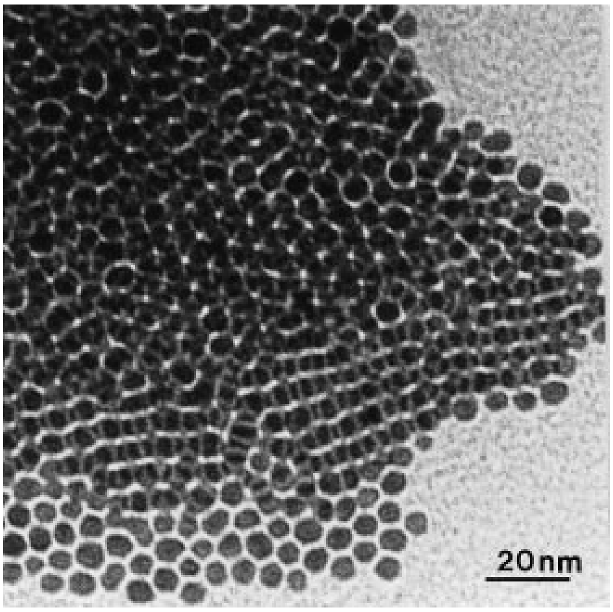

Fig. 1 Electron micrograph of palladium colloid of the first, second and third monolayer, which are stepwise ordered in a three- dimensional structure after deposition on carbon support films

Besides the stacks of layers, clear domains of monolayers were obtained, as shown by typical TEM images (Fig. 2). Again hexagonal close packing occurs. The corresponding two-dimensional Fourier-transformed image is shown in Fig. 3. Close inspection of individual clusters at atomic resolution reveals lattice fringes characteristic of face centred cubic (fcc) crystallinity.

Careful analysis of the geometric features of the surface structure reveals some interesting features. We have previously shown by STM measurements that the thickness of the $N(C_8H_{17})_4Br$ protective coat surrounding palladium clusters having different core sizes amounts to 1.2 nm, which is in line with simple force-field calculations (1.1 nm).[3] In the present case assumption of a bilayer between the ordered clusters leads to the prediction that the distance between the centres of the metal cores should amount to 8.3 nm. The observed value of 8.2 nm is in excellent agreement with this expectation, which means

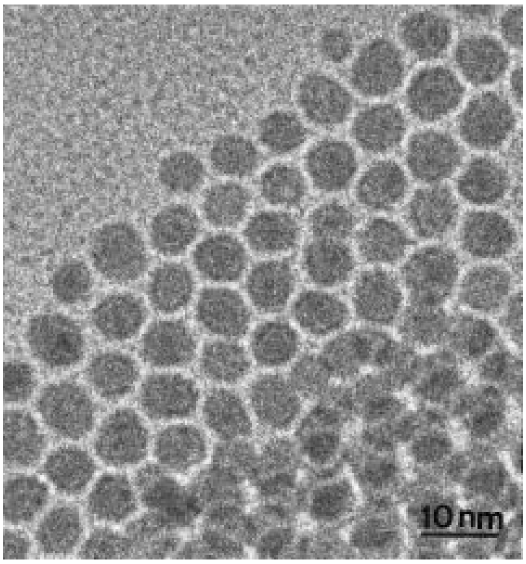

Fig. 2 Electron micrograph of palladium colloid hexagonal close packed arranged in the first monolayer

that the protective mantles on the surface touch each other without damage or interpenetration. This means that nanoengineering on surfaces should be possible simply by varying the length of the alkyl groups of the ammonium stabilizer. For example, upon using $N(C_{18}H_{37})_4Br$-stabilized palladium clusters having an inner metal core size of 5.9 nm, it is predicted that the average distance between the centres of the clusters should be 10.3 nm. Indeed, upon employing the 5.9 nm sized $N(C_{18}H_{37})_4Br$-stabilized palladium clusters, hexagonal close packing was again observed, the distance between the centres of the clusters this time amounting to 10.2 nm.

An unusual effect was observed in the case of the $N(C_8H_{17})_4Br$-stabilized palladium clusters. A few highly ordered domains were discerned in which hexagonal close packing clearly does not occur (Fig. 4). Although cursory inspection suggests cubic close packing (coordination number four in the two-dimensional layer; twelve in the three-dimensional arrangement), careful analysis reveals that the material is in fact non-close packed. The distance between the centres of the clusters amounts to 6.3 nm. The reason for the formation of such unusual ordered domains is presently unclear. It appears that this molecular structure begins to have the characteristics of a three-dimensional crystalline superlattice (Fig. 4), in which the particles are ordered.

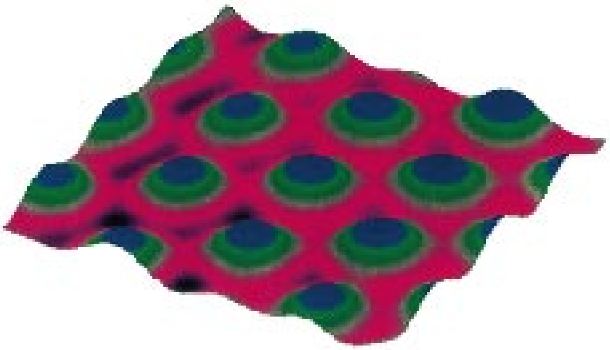

Fig. 3 Individual hexagonal close packed palladium colloid after digital image processing

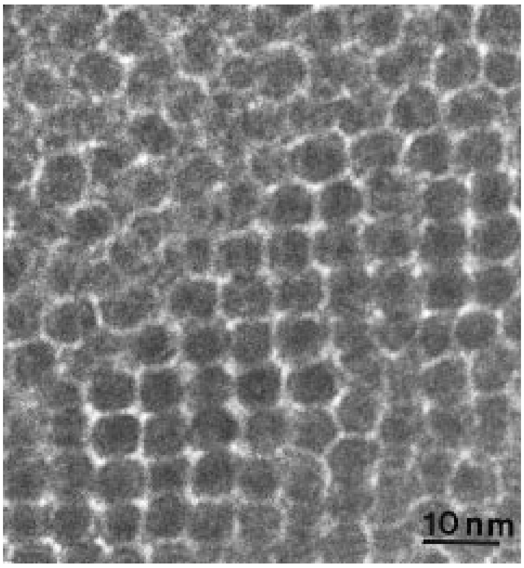

Fig. 4 Electron micrograph of palladium colloid ordered in a non-closed packed cubic-like arrangement

In summary, we have demonstrated for the first time that certain NR_4X-stabilized metal clusters self-organize on supports, forming two-dimensional films and three-dimensional superlattices. By varying the length of the alkyl chains of the ammonium ions, predictable structural ordering is possible. Preliminary experiments show that variation of the palladium cluster core size is another useful parameter which also allows for nanoscale engineering. Extension to other metal clusters and bimetallic analogues as well as the corresponding nanostructured NR_4X-stabilized metal oxide clusters[6] should be straightforward.

Footnote

† A TEM grid (400 mesh in^{-1})[5] was dipped into a 10^{-3} m solution of a NR_4Br-stabilized palladium cluster[2] in thf for 2–3 s. Following removal from the solution, the grid was dried in air at room temp. for 2–3 h.

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