The Microstructure of Colloidal Silver: Evidence for a Polytetrahedral Growth Sequence

Daniel G. Duff,[a] Andrew C. Curtis,[a] Peter P. Edwards,[a] David A. Jefferson,[a] Brian F. G. Johnson,[a] and David E. Logan[b]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, U.K.*

High resolution electron microscopy of very small (*ca.* 40 Å diameter) colloidal silver particles establishes their decahedral morphology.

Between the conventional domains of atomic and molecular chemistry and of macroscopic condensed-matter physics, there exists an intermediary class of small aggregates or clusters which has become increasingly important during the past decade or so. The study of these ultra-small particles (typically containing 10^5 atoms or less) is important not only for understanding their intrinsic physical and chemical properties, but also for their potential applications in a range of commercial processes. A fundamental problem in this area concerns the changes in electronic and structural properties as the particles become so small that the behaviour of the bulk is lost: the so-called quantum size-effect.[1,2] This is especially true of metals.

There are two conflicting views of the structure of small metal particles. They can be regarded as having the same structures as bulk metals (hexagonal or cubic close packed, h.c.p. or c.c.p.) with changes in properties arising solely from the gradual loss of a long-range translational lattice as the particle size is reduced. An alternative and perhaps more controversial view, however, is to regard these small aggregates as being produced by growth from nuclei with a structure fundamentally *different* from that of bulk face-centred cubic (f.c.c.) metal. In particular, the scheme illustrated in Figure 1, where construction of a lattice takes place by the successive addition of individual metal atoms to the simplest stable unit, *viz.* the tetrahedron, leads to the inevitable conclusion that for small numbers of atoms a polytetrahedral growth sequence is preferred over an f.c.c. sequence. This leads ultimately to pentagonal symmetry, *viz.* the decahedron (Figure 1d) or the icosahedron (Figure 1g) and cannot therefore progress to an infinite stable lattice without a major change in structural development, namely the addition of atoms in normal metallic packing, as shown for the decahedron in Figures 1e and 1f. A growth process of this type could well explain the formation of multiply-twinned particles (m.t.p.s) found in microcrystalline metals prepared by evaporation, super-cooling, or colloidal

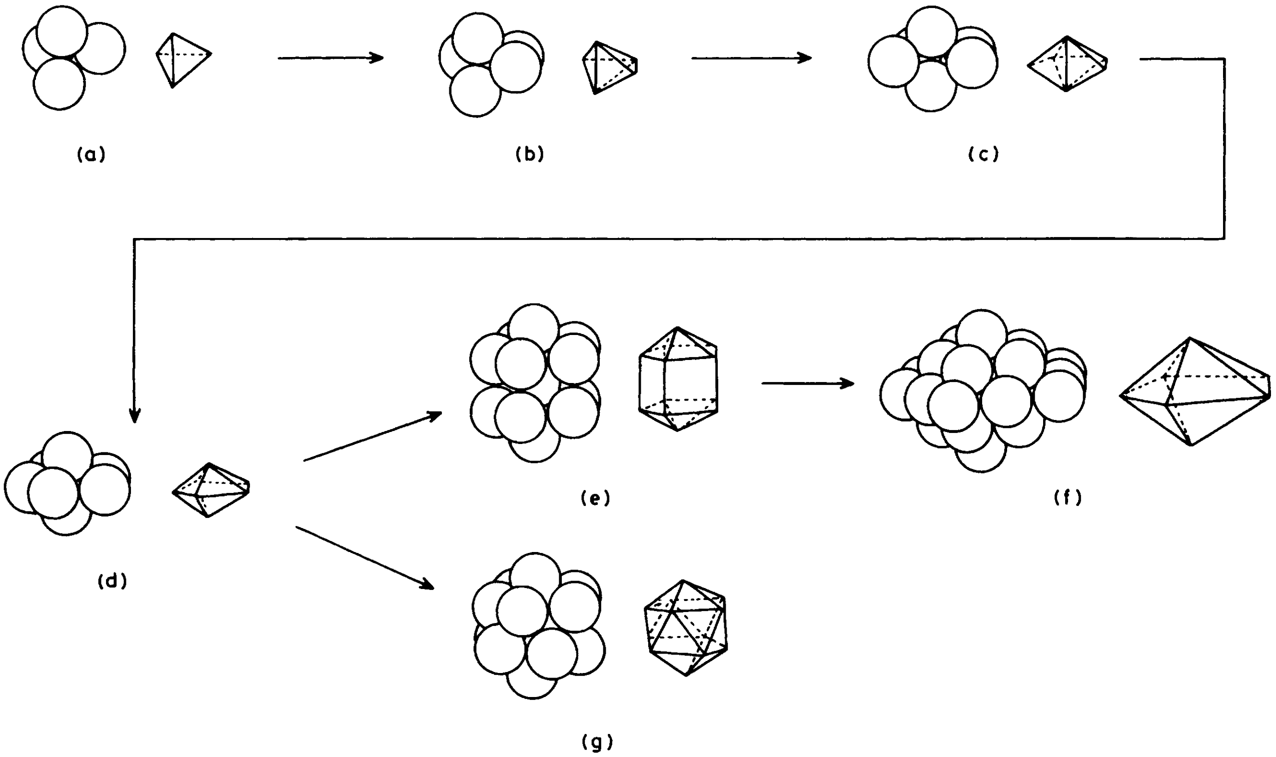

Figure 1. Successive additions of single atoms to a tetrahedral cluster (a) leads to a trigonal bipyramid (b), a capped trigonal bipyramid (c), and a simple decahedron or pentagonal bipyramid (d). Further addition of atoms in normal metallic packing leads to a development of the decahedron (e) and (f), or if tetrahedral packing is maintained, to the icosahedron (g).

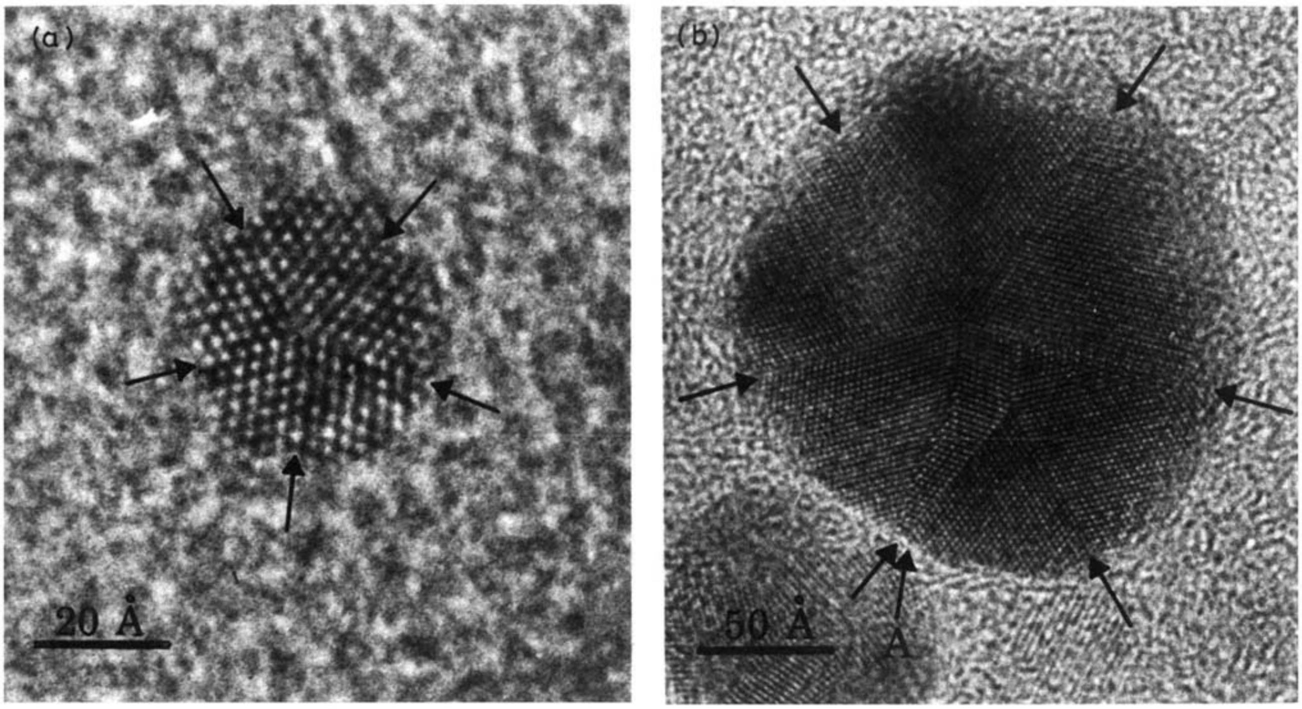

Figure 2. (a) Perfect decahedral crystal of colloidal silver viewed down the five-fold axis. The objective lens settings are such that the defocus is beyond the optimum value and the atoms are imaged as white dots. The boundaries between individual regions in the particle are arrowed. (b) A larger particle, with a residual five-fold axis, but with seven individual components. A boundary with discontinuities (designated A) is clearly visible.

methods.[3—6] This suggests that the structure and electronic properties of very small crystallites might differ fundamentally from those of the bulk. In this communication we report the preparation and characterisation of small colloidal particles of silver which fall in this size range.

Samples of colloidal silver were prepared by the reduction of silver nitrate using polyethyleneimine (PEI) in acetonitrile using a method similar to that of Thiele and von Levern for gold.[7] Using a modification of this method, we have observed that, under appropriate conditions,[8] small particles of a controllable size regime suitable for high resolution electron microscopic (h.r.e.m.) studies could be prepared by evaporating the solvent from a mixture of silver nitrate and PEI on a microscope grid covered with a thin carbon film. In each preparation the particles were found to exhibit a narrow size distribution. Structure and morphology of the particles were determined by direct imaging at an interpretable point resolution of 1.95 Å using a modified JEOL JEM-200CX electron microscope.[9] Because of their small size, no attempt was made to orient the small particles relative to the electron beam, suitably aligned particles being located by systematic screening.

In the samples studied, the decahedral morphology appeared to be more common than the icosahedral m.t.p.s, in contrast to earlier work on evaporated gold. In the very small size regime (*ca.* 40 Å diameter) the particles appeared to be perfectly decahedral with no evidence of either strain contrast or discontinuities between the individual regions, an example being shown in Figure 2a. In these images although the atomic structure is revealed directly the resolution is such that small atomic displacements are not apparent: however, discontinuities such as dislocations would be clearly visible. Consequently the core of such a particle cannot have an f.c.c. structure. Computer image-simulation studies using the multislice method[10] confirm that particles of this type contain no more than 1500 silver atoms. As the particle size increases, however, a fundamental change in microstructure takes place, as shown in Figure 2b. In this case, although the particle is reminiscent of the decahedral type, it now contains seven units, one of the original five units having apparently divided into three sub-units, and at least one of the boundaries is no longer coincident with a crystallographic direction. One must therefore conclude that, by the time this size regime has been reached, the structural mismatch imposed by the non-f.c.c. nucleus of the particle is therefore incompatible with the normal f.c.c. packing by which further growth proceeds, and dislocations must be introduced.

These observations are in accord with the principle of nucleation in a polytetrahedral nucleus. Whether they apply in a more general way is not certain but studies of other colloidal systems lend supporting evidence. For example, the greater numbers of icosahedral m.t.p.s in gold[8] suggest that the nucleation process goes as far as Figure 1g or even further before normal metallic growth commences, whereas studies of platinum,[9] where only simple twins are observed, imply that metallic growth takes place once the structure of Figure 1b is reached. A systematic programme of synthesis of a wide range of colloidal particles is continuing.

We thank Johnson Matthey, I.C.I., and the S.E.R.C. for support. P. P. E. also thanks the Nuffield Foundation for the award of a Research Fellowship.

Received, 2nd December 1986; Com. 1710

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