A Study of Chemically Prepared Small Metal Clusters in the Nonmetallic Regime

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Small gold clusters [mean diameter (d) $\lesssim$1.4 nm], unlike larger clusters, show a higher Au(4f) binding energy relative to the bulk value and the presence of a conductance gap in tunnelling measurements, just as the molecular cluster compound, $Au_{55}(PPh_3)_{12}Cl_6$; small platinum clusters show similar nonmetallic features.

The synthesis and properties of ultrafine metal particles have been topics of considerable interest in recent years, and such particles have been examined extensively by electron microscopy.[1–6] Most reports in the literature employing chemical methods of synthesis deal with relatively large particles with mean diameters (d) > 5 nm. Of particular interest to us is the study of small metal clusters with $d < 2$ nm, since it is of value in understanding the transition in electronic and other properties on going from the bulk metal to that of molecular clusters containing small numbers of atoms.[1–3,7,8] In this context, the recent report of Duff *et al*[9] on the preparation of small gold particles with a mean $d \sim 1.5$ nm by the reduction of chloroauric acid with tetrakis(hydroxymethyl)phosphonium chloride (THPC) in basic medium is significant. We considered it important to examine the electronic properties of such small clusters in comparison with those of similar

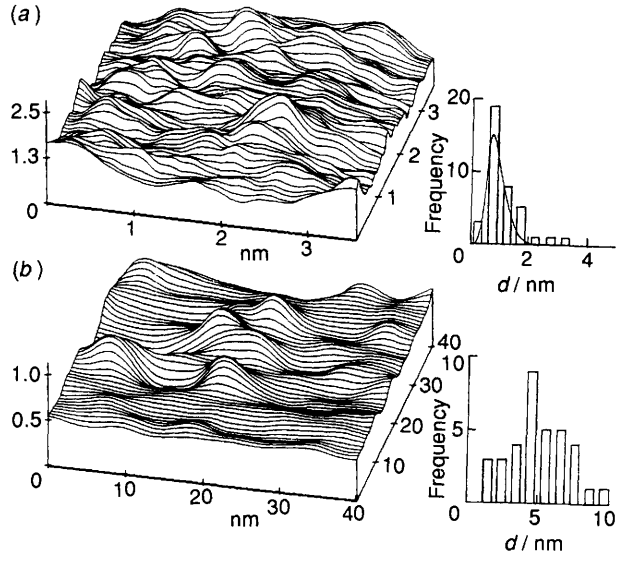

Fig. 1 STM contour plots of gold clusters deposited on highly oriented pyrolytic graphite (HOPQ) alongside histograms showing the size distributions: (*a*) Au hydrosol prepared by THPC reduction; (the curve in the histogram represents the size distribution obtained from HREM) and (*b*) Au sol prepared by alkalide reduction

dimensions prepared by the resistive evaporation of the metal as well as with the high nuclearity Au cluster compound, $Au_{55}(PPh_3)_{12}Cl_6$. First we have characterized the different Au cluster systems by scanning tunnelling microscopy (STM) using a Nanoscope II (Digital Instruments Inc.) and high resolution electron microscopy (HREM) (with a JEOL 200 CX) and then measured the Au(4f) binding energy of the clusters (using a VG ESCA3 Mk II spectrometer). Since the metal core level binding energies depend markedly on the cluster size, increasing with decreasing cluster size in the small cluster area,[8,10] the Au(4f) binding energy provides an important means of characterizing the clusters. We have carried out scanning tunnelling spectroscopic (STS) measurements to obtain direct information on the conductance gap, if any, in the metal clusters. It is noteworthy that STM measurements[11] provide an atomic probe ideally suited for the study of individual metal clusters.

Fig. 1, compares the STM contour plot of the small gold clusters prepared by THPC reduction[9] with that of the larger clusters prepared using the alkalide, $K^+(18\text{-crown-6})K^-$, as the reducing agent.[12] The small clusters obtained by THPC reduction exhibit a narrow size distribution [see the histogram next to the contour plot in Fig. 1(*a*)] with a mean *d* of 1.4 nm, while the large clusters obtained by alkalide reduction show a broader distribution with a mean *d* of 4 nm [Fig. 1(*b*)]. The size distribution obtained for the small clusters by STM is similar to that obtained by HREM. The Au($4f_{7/2}$) binding energy of these small clusters is higher than the bulk value (84.0 eV) by 0.25 eV, while the larger clusters obtained by alkalide reduction show the bulk value. Small clusters with a mean diameter of $\lesssim$1 nm, obtained by the resistive evaporation of the metal in a ultra-high vacuum chamber of the electron spectrometer, show an increase of 0.8 eV relative to the bulk value. The increase in the Au($4f_{7/2}$) binding energy in the Au clusters can be understood with reference to the calibration curve established by us based on the measurement of the Au($4f_{7/2}$) binding energy with clusters of known sizes. This curve shows the binding energy to increase sharply when the mean cluster diameter goes below ~2.5 nm, with an increase of ~1 eV over the bulk metal value when the cluster size is less than 1 nm. It is noteworthy that $Au_{55}(PPh_3)_{12}Cl_6$, with a metal nucleus of 1.4 nm, shows an increase in Au(4f) energy of 0.3 eV over the bulk metal value, similar to the clusters prepared by THPC reduction.

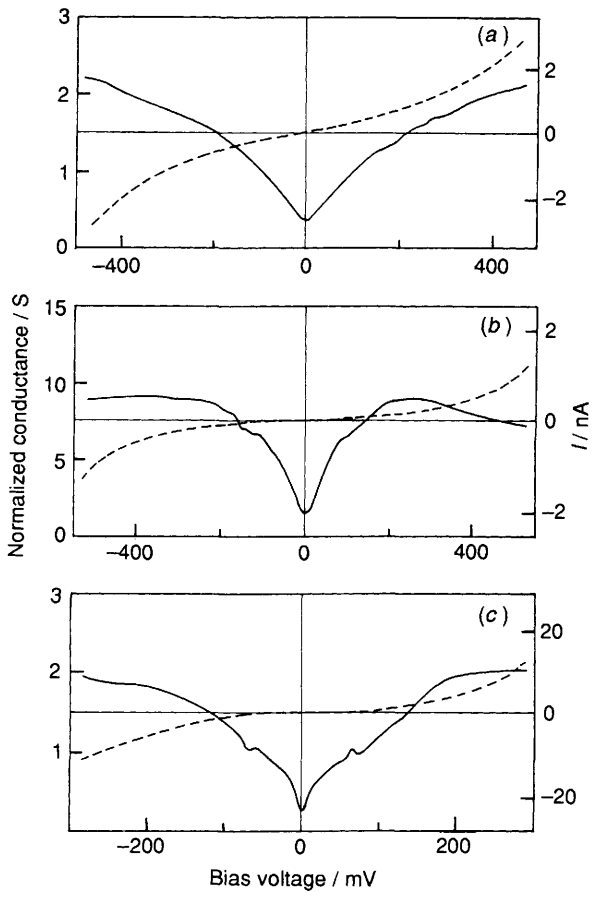

Fig. 2 Variation of the normalized conductance with bias voltage of gold clusters of known dimensions: (*a*) gold cluster (*d* ~4 nm) present in the sol prepared by alkalide reduction; (*b*) gold cluster (*d* = 0.8 nm) from the sol prepared using THPC; (*c*) gold cluster (*d* = 0.8 nm) obtained from resistive evaporation of the metal. Dashed curves show I–V characteristics of the same. Notice the absence of the conductance gap in the large clusters (*a*).

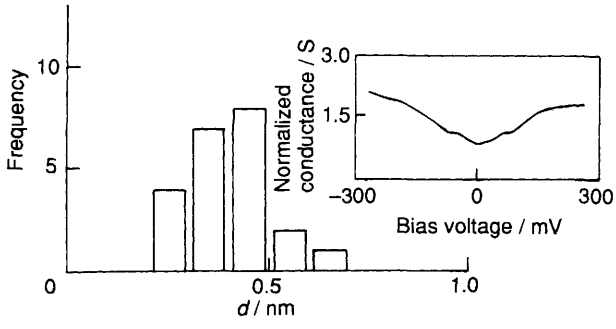

Fig. 3 Size distribution of clusters in a fresh platinum sol prepared using $NaBH_4$. Inset shows variation of normalized conductance with bias voltage of a cluster (*d* ~ 0.8 nm).

Direct information on the metallicity of Au clusters is provided by the conductance data from STS (Fig. 2). The small Au clusters (*d* = 1.4 nm) prepared by THPC reduction as well as those obtained from the resistive evaporation of the metal ($\lesssim$1 nm) show rectifying behaviour over a bias voltage range of $-80 \rightarrow +80$ mV, while the large clusters (*d* ~ 4 nm) prepared by alkalide reduction show finite current for near-zero voltages indicating metallicity. We estimate the gap in the small clusters from the normalized conductance curves to be in the 120–180 meV region. What is interesting is that $Au_{55}(PPh_3)_{12}Cl_6$ shows a gap of 145 meV indicating the close similarity in the electronic properties of the small, bare metal clusters and the cluster compound.

We have carried out preliminary measurements on fine platinum particles ($\lesssim$1 nm) prepared by the reduction of chloroplatinic acid using sodium borohydride.[13] By taking fresh sol soon after addition of $NaBH_4$, we have achieved a narrow size distribution (Fig. 3) as revealed by STM. These small clusters show a conductance gap of 150 meV unlike the larger particles prepared by the same method, which show metallic behaviour. Further studies are in progress on gold and other metal clusters of a wide range of sizes prepared by vacuum evaporation and soft landing as well as by chemical methods.

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