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Gold nanoparticles from self-assembled gold(I) amine precursors†

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The reaction of AuCl(THT) (1) with long chain primary amines ($C_nH_{2n+1}NH_2$; n = 8, 12, 16) leads to the formation of the complexes $AuCl(NH_2R)$ (R = C_8H_{17}, 2; $C_{12}H_{25}$, 3; $C_{16}H_{33}$, 4) which are characterized by classical methods and shown to self-organize in the solid state into a fibrous material; decomposition of the complexes inside the supramolecular framework yields a monolayer of ordered gold nanoparticles.

There is presently a considerable interest for the physical properties of nanomaterials (electronics, magnetism, catalysis, mechanical properties, …). If one excepts near field experiments, the study of these properties implies an ordering of the materials in 1, 2 or 3 dimensions.[1–4] It has been proposed recently that the formation of self-assembled gold nanowires could be an alternative to photolithography.[4] In many cases, gold appears as a metal of choice for applications regarding, *e.g.* microelectronics but, while the synthesis of gold nanoparticles has been known for 150 years,[5] a study of the recent literature reveals the need for new preparative methods leading to monodisperse particles of adjustable size and shape.[6–12]

Gold particles are commonly prepared by chemical reduction of a chloride precursor. For example, the well-known Turkevich method involves reduction of $HAuCl_4$ by sodium citrate in water[13] while Schmid has demonstrated that the reduction of $AuCl(PR_3)$ by B_2H_6 leads to Au_{55} nanoclusters.[14] Several new methods have been developed in the last few years which involve the reduction of gold chlorides by sodium borohydride or super-hydride.[11,12] The stabilization of the particles is generally performed by thiolate ligands or by a polymer (PVA, PVP) but, recently, amines have also been used as stabilizers.[15] It has for example been possible, using a two phase method in the presence of a long chain quaternary ammonium salt as phase transfer agent, to produce particles of regular size which could be assembled into a mono- or a bi-layer.[16–20] Alternative syntheses involve vacuum deposition onto graphite[6] or silica[7] or UV irradiation of aqueous $HAuCl_4$ solution in the presence of a polymer.[8]

In our group, we have been interested for some time in the synthesis of metal nanoparticles from organometallic precursors.[21–23] The reasons for this interest were (i) the possibility to control the kinetic of the decomposition of the precursor and therefore the size of the particles, (ii) the possibility to prepare novel structures because of the mild conditions involved and (iii) the control of the surface contamination.[22,23] Concerning gold, no readily available and purely organometallic precursor was known but some gold(I) complexes have been reported to be unstable.[24,25] We have previously shown that the chloride gold(I) complex AuCl(THT)[26] (**1**; THT = tetrahydrothiophene) could be decomposed by CO or H_2 in the presence of a polymer (PVP or nitrocellulose).[24] This prompted us to investigate the decomposition of AuCl(THT) in the presence of amine which could act as HCl acceptor. We use in this study primary amines containing long alkyl chains since these compounds are known to self-assemble and have been used as templating agents for the synthesis of mesoporous materials.[27]

We describe here the synthesis of three new gold(I) amine complexes, their supramolecular arrangement and their decomposition into gold nanoparticles.

The reaction of AuCl(THT) (**1**) in toluene at room temperature leads within a few minutes to the precipitation of gold as a polycrystalline powder. GLC-MS analysis of the solution demonstrates the formation of chlorotoluene as a mixture of its three isomers and the decoordination of THT. This indicates that, unexpectedly and probably through a mechanism analogous to that of the Friedel–Crafts reaction, toluene is a good reductant of Au(I). However, the same reaction, when carried out in the presence of one equivalent of a primary long chain amine ($C_nH_{2n+1}NH_2$; n = 8, 12, 16), leads to the formation of a white powder, insoluble in toluene, soluble in THF and acetone for n = 8, and only slightly soluble in THF and DMSO for n = 12 and 16. The solutions are however not very stable and change colour to purple after a few minutes in DMSO and a few hours in THF and acetone. These powders correspond to the complexes $AuCl(NH_2R)$ (R = C_8H_{17}, **2**; $C_{12}H_{25}$, **3**; $C_{16}H_{33}$, **4**); they were characterized by microanalysis, infrared and ^1H and ^{13}C NMR spectroscopy, and TGA.† Mass spectra obtained using the DCI or the FAB techniques only evidenced the presence of the free amine ligand because of the decomposition of the compounds. It was however possible to follow the decomposition of **2**–**4** in the solid state by TGA experiments which demonstrate the successive elimination of the chloride and amine ligands. GLC-MS analysis of the solution shows the presence of free THT but chlorotoluene is not detected. All these data are in agreement with a simple substitution of THT by amine.

A powder of complex **2** was investigated by TEM (Transmission Electron Microscopy; see Fig. S1, ESI†). At the microscopic level, the powder is formed from nanocrystals the size of which is found near 2 nm see Fig. S1(*b*), ESI.† It is possible to determine by WAXS analysis (WAXS: Wide Angle X-ray Scattering) that these nanocrystals are ordered and that the first Au–Au distance is *ca.* 3.25 Å. This result rules out the presence of metal–metal bonds (Au–Au distance in bulk gold: 2.88427 Å) but is in agreement with the presence of aurophilic contacts such as the ones recently found in the crystal structure of AuCl(piperidine) (Au···Au: 3.301(5) Å).[25]

In the solid state, complexes **2**–**4** are stable under argon but, when slightly heated or left in air, their decomposition into metallic gold is visible through the colour change of the materials from white to purple and eventually to gold. The reaction can be monitored by infrared spectroscopy. For example, in the case of **2**, a change in the N–H stretching bands, from sharp peaks at 3251 and 3211 cm^{-1} to a broad signal in the same region, indicates the decoordination of the amine ligand. The powder XRD spectra (XRD: X-ray Diffraction) of complex **2** illustrates this transformation: at room temperature several features are visible which were not attributed but, when heated at 70 °C, new peaks are visible which correspond to metallic

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† Electronic supplementary information (ESI) available: experimental details and full characterization of complexes **2**–**4**, powder XRD spectra of **2** and TEM micrographs of **2** and gold nanoparticles. See http://www.rsc.org/suppdata/cc/b0/b005327i/

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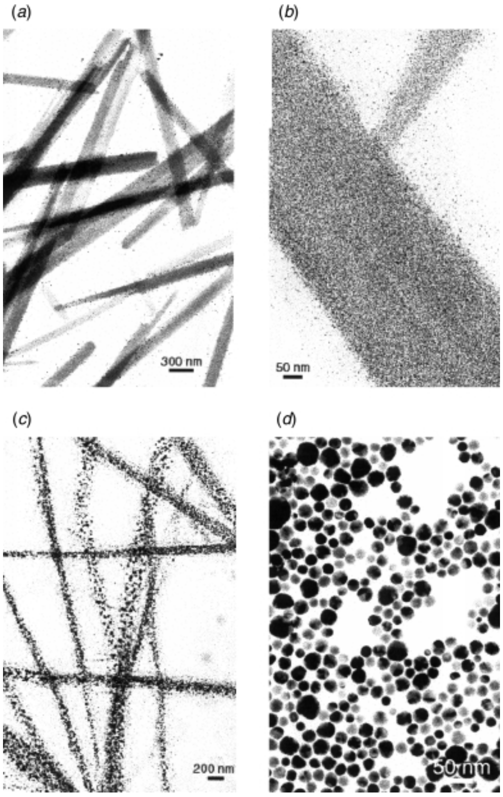

Fig. 1 TEM micrographs of AuCl($NH_2C_8H_{17}$) (**2**) after deposition using a microinjector for ordering (*a*, *b*) and decomposition in the solid state into gold nanoparticles (*c*, *d*).

gold. At 80 °C, the transformation is complete and sharp peaks corresponding to well-crystallised fcc gold are observed (see Fig. S2, ESI).†

At the mesoscopic level, the nanoparticles of these complexes display a supramolecular organization into a fibrous material as shown in Figs. S1(*a*), 1(*a*) and 1(*b*).† These fibers are composed of interconnected self-assembled cylinders which organize spontaneously at the surface of the microscopy grid and are presumably present in solution. This probably accounts for the unexpected low solubility of these materials. Attempts at orienting the fibers were made by depositing a drop of a solution of **2** onto a microscopy grid using a microinjector; it is visible on Figs. 1(*a*), 1(*b*) that fibers can adopt privileged directions but further developments are necessary in order to achieve regular arrays.† In agreement with the XRD experiments, the transformation of the gold(I) complexes into gold nanoparticles can also be observed on a microscopy grid prepared by deposition and evaporation of a droplet of a solution (suspension) of **2–4** in THF. When a grid supporting complex **2** is left in air for a few days, the initial complex nanocrystals transform into regular gold nanocrystals within the frame of the supramolecular arrangements described here-above (see Figs. 1(*c*), 1(*d*)). The size distribution of the nanoparticles is at the end of the growth process relatively broad and centred at 23 nm [±6 nm; Fig. 1(*d*)]. This order of magnitude of size is frequently obtained for gold nanoparticles and suggests a poor, if any, control of the particle growth by the amine ligands. This is not unexpected since the poor stabilization of the soft gold centres by the hard amine ligands has already been discussed in the literature.

The decomposition of **2** can also be carried out in a THF solution under 3 bars H_2 at room temperature, in the presence or not of an excess of amine. After 15 hours, the resulting purple solution does not contain any precursor any more but well-crystallised gold nanoparticles of *ca.* 10 nm (±3 nm) which self-assemble on the microscopy grid used for TEM characterizations as shown in Fig. S3.† After several days, no gold is present in solution any more and a gold mirror is observed on the walls of the Fisher-Porter bottle.

In conclusion, we have described a new method for the preparation of gold nanoparticles using a gold(I) amine precursor. If this method does not appear to allow a good control of the particles size, it leads surprisingly to a good control of the size dispersity and, which is unexpected and more important, it allows a self-organization of the particles. There is presently a growing need for the controlled deposition of nanoparticles on physical or microelectronic devices. Several routes are possible and employed: sputtering, OMCVD, sol–gel, deposition of organized solutions of nanoparticles, … The growth of nanoparticles, in the solid state, as monolayers within the frame of a supramolecular arrangement is an alternative process of interest, for example for gold deposition onto microstructures. These studies are presently in progress.

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