

The self-assembly of gold and SCd nanoparticle multilayer structures studied by quartz crystal microgravimetry

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The self-assembly of nanometre-sized Au and CdS particles to well defined multilayer structures on dithiol derivatised gold surfaces is quantitatively studied by quartz crystal microgravimetry.

The investigation and preparation of nanostructured materials has become a very dynamic and exciting area of research, which is driven both by fundamental interest and by the prospect of a wide range of innovative applications for example in catalysis, sensor science, nonlinear optics and molecular electronics. Recent developments seem to indicate that future research will be directed towards the controlled and rational design of both nanometre-scale architectures, and bulk materials built up from nanometre-sized constituents.^{1,2} One of the most striking examples is the achievement of three-dimensional CdSe quantum dot superlattices, reported by Bawendi and coworkers.³ These novel materials exhibit collective bulk properties, which emerge from the ordered array of their constituents. Alivisatos and coworkers constructed the first opto-electronic device based on the self-assembly of nanometre-sized particles, a light emitting diode, which is tuned by a layer of CdSe particles.⁴ Recent examples of nanostructured materials from the Schiffrin group include cross linked nano-networks of Au particles with controllable electronic properties, both as bulk materials⁵ and as thin film multilayer structures,⁶ and stable functionalised Au nanoparticles, which could serve as versatile building blocks.⁷ Giersig and Mulvaney⁸ prepared highly ordered monolayers of Au particles by electrophoretic deposition, and some recent reports on the chemical attachment of Au particles to suitably functionalised surfaces have appeared.^{9–11} These materials exhibit very interesting spectroscopic and electrochemical properties, as well as biocompatibility, and are currently intensively studied by several groups. Here, we demonstrate that the quartz crystal microbalance is a convenient analytical tool to study the growth of such systems, and give further evidence that subsequent deposits of saturating monolayers are indeed formed. It is also shown that layers of CdS particles can be incorporated into these assemblies. The quartz crystal microbalance (QCM) used in these experiments allows determination of whether the measured changes in resonance frequency originate from the resistance (R) or the inductance (L) elements of the QCM equivalent electrical circuit.¹² Thus the uptake of rigid mass attached to the crystal could be distinguished from viscoelastic loss in real time. Measurements were taken at intervals of 1 s. The preparation of stable toluene solutions of gold particles of *ca.* 8 nm diameter, and the self assembly of mono- and multi-particulate layers on a dithiol functionalised gold surface was carried out as described by Schiffrin and coworkers.^{5,6} Aqueous solutions of CdS particles of *ca.* 4 nm diameter were prepared following the method of Spanhel *et al.*¹³ The thin-film structures were deposited on one side of a gold covered AT cut quartz crystal (diameter 14 mm, thickness 0.168 mm, active area 0.196 cm², International Crystal Manufacturing Co. Inc., Oklahoma City, cat. 31210) after derivatisation of the gold surface with nonane-1,9-dithiol (Aldrich) by contact for 1 h with a 50 mmol dm⁻³ solution of the dithiol in toluene. Prior to derivatisation the quartz crystal

was glued with silicon rubber (3145 RTV adhesive, Dow Corning Co.) to a hole in the bottom of a glass cell, so that only one of the gold coated quartz crystal surfaces was exposed to the derivatising solution. The gold surfaces were used as received, without further cleaning procedures. The derivatised surfaces were rinsed five times with toluene, and once with a 1.3 mmol dm⁻³ solution of tetraoctylammonium bromide (Fluka) in toluene, before the colloidal gold solution was added to the cell. The last rinsing step was carried out as a precaution, to minimize possible errors due to ion adsorption after the addition of the colloidal gold solution, which also contained tetraoctylammonium bromide as a stabilizing agent. The gold contents of the solutions were 250 and 125 mg dm⁻³, respectively, and the mass increase was monitored until saturation was reached (Fig. 1). This procedure was repeated several times, *i.e.* the gold surface was alternately derivatised with further layers of nonane-1,9-dithiol and gold particles, leading to a multilayer structure as schematically shown in the graphical abstract. CdS particles were deposited from aqueous solution. For this purpose the dithiol-terminated surface was rinsed five times with ethanol and three times with water, before addition of the solution containing the CdS particles. The increase of mass as a function of time, due to the attachment of the Au particles to the surface, is shown for four consecutive steps in Fig. 1. Independent of the concentration of Au particles in solution a total mass of *ca.* 6 $\mu\text{g cm}^{-2}$ was obtained for the first layer, and *ca.* 8 $\mu\text{g cm}^{-2}$ for the consecutive layers. The measurements show clearly that saturating monolayers are obtained, *i.e.* the process of self-assembly comes to a halt, when

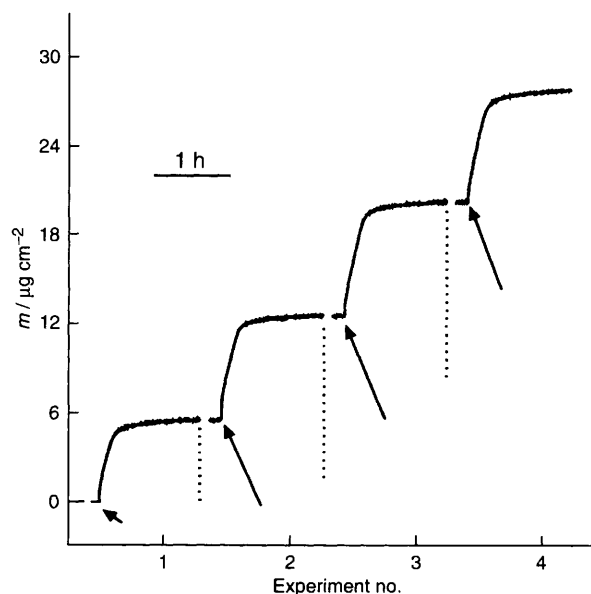


Fig. 1 Deposition of gold colloidal layers. Each experiment is separated by dotted lines. Additions of gold colloidal solutions of 250 mg dm⁻³ are shown with arrows. Initial masses for each experiment are absolute. The mass for an adsorbed monolayer is *ca.* 0.1 $\mu\text{g cm}^{-2}$.

all accessible surface sites are consumed. The obtained values for the mass of the individual layers are in agreement with expected values. Assuming a particle radius of 4 nm and a complete coverage of the surface, a mass of $9 \mu\text{g cm}^{-2}$ can be expected. However, it has been demonstrated that for a random attachment of particles to a surface, only 50–60% of the total available surface area is accessible,¹⁴ so that $6 \mu\text{g cm}^{-2}$ for the first monolayer appears to be a reasonable value. The larger values obtained for further layers could be due to an increase in surface roughness caused by the attachment of the first monolayer. Fig. 2 shows the attachment of a monolayer of CdS particles, which expectedly has a much smaller mass than the Au layer, due to the smaller particle size and lower density of the material. This experiment was carried out to demonstrate that the construction of nanoparticle multilayer structures is not limited to particles of only one material, and it can be envisaged that similar techniques will be used to assemble more complex systems in the near future. We report here only the measurement of mass changes which are due to the attachment of colloidal particles. Mass changes have also been observed during the immobilization of the dithiol molecules, but the results obtained were close to the employed resolution. More interestingly, an increase in the rigidity of the system can be observed during the

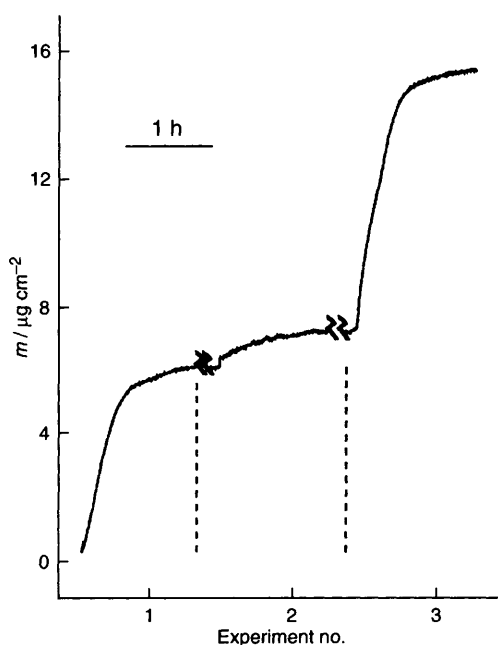


Fig. 2 Successive deposition of gold, CdS and gold colloid layers. As in Fig. 1 dithiol is adsorbed between each layer deposition.

derivatisation of the colloid terminated surface with dithiols, which is probably due to the bridging of neighbouring particles by dithiol molecules. A more detailed investigation of these effects is in hand. It should be noted, however, that the observed value of R , the equivalent viscous resistance, and its change are small enough as compared to changes in the electrical equivalent parameter, L , to allow accurate rigid mass measurement in each successive layer. Finally, it should be mentioned that Au particles also attach to a surface which has been derivatised with monothiols instead of dithiols, but the maximum coverage is ten times less than on dithiol derivatised surfaces, and saturation is reached already a few minutes after the addition of the gold particle solution.

It is concluded that Au nanoparticles do indeed self-assemble to well defined multilayer structures as first reported by Schiffrin and coworkers on the basis of UV–VIS, electrochemical, ellipsometrical, STM and conductivity measurements,^{6,15} and that QCM can provide important information on the growth characteristics of nanometre scale systems. It is believed that a large variety of similar structures will be developed in the near future and that QCM will play a key role as an analytical tool in this area of research.

The authors gratefully acknowledge the support of the University of Buenos Aires.

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Received, 16th May 1996; Com. 6/03410A