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'Sticky' gold colloids through protection–deprotection and their use in complex metal–organic–inorganic architectures†

Marcus Bartz, Nicole Weber, Jörg Küther, Ram Seshadri‡ and Wolfgang Tremel*

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany. E-mail: tremel.wolfgang@t-online.de

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Exposing bare gold colloids to long-chain dithiols results in their precipitation owing to cross-linking of the thiol groups with gold surfaces; here, we demonstrate that through the use of a dithiol that has one of the thiol groups protected, we can, through attachment followed by deprotection, prepare gold colloids with exposed thiol; the uses of such 'sticky' colloids in creating complex architectures is demonstrated by using them to template the growth of PbS particles.

The notion that gold colloids in the nanometre range provide surfaces on which thiol self-assembly can be achieved has been employed by us for a variety of new functionalizations. Using suitable thiols, we have, for example, attached polymerization catalysts on colloid surfaces.[1] The use of thiol monolayer surfaces on gold in templating the crystallization of inorganic minerals such as calcium carbonate[2,3] has been extended by us to the use of thiol-coated colloids as crystallization nuclei.[4,5] This has opened a new dimension of surface-templated crystallizations since a dispersed, spherical colloid offers a very different geometry from a large, planar surface.

In coating gold colloids with thiols in solution, there are a few points that need to be examined. The first is that the thiol should protect the colloid and keep it in solution. The second is that the surface functionality of the thiol (the ω group on the long chain) should be compatible with the use to which the colloids are put. For example, in a previous work, we used long chain glycol-based thiols to take colloids into aqueous solution but the surfaces so formed on the colloids inhibit the crystallization of calcium carbonate.[5] We have been interested in coating dithiols on gold colloids since particles so coated would offer an SH functionality on the surface (the ω group) that would be compatible with inorganic sulfides. However, if dithiols are added to a gold colloid sol, immediate precipitation results owing to the cross-linking of the thiols with the colloid surfaces.[6]

The strategy that we present here borrows from peptide chemistry and uses a protection group for the thiol functionality.[7] We have prepared half-protected dithiols **1** with $n = 6$, 10 and 12.§ The self-assembly of these thiols on flat gold surfaces and the possibility to deprotect the ω thiol functionality with aq. NH$_3$ has been established using surface plasmon resonance spectroscopy (SPS), as has the propensity of the deprotected surface to stick gold colloids. The thiols have been assembled on gold colloids¶ in a toluene solution. The colloids are precipitated by and washed with methanol followed by redissolving them in CH$_2$Cl$_2$ where the protecting group is removed with aq. NH$_3$. These 'sticky' colloids are then dissolved in THF and PbS‖ is deposited around them. The templated growth of PbS particles on SAM surfaces has been studied extensively by Meldrum *et al.*[8]

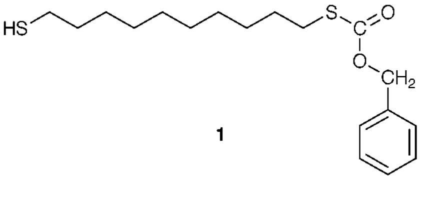

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Fig. 1 displays the SP spectra** of a clean gold surface and the surface after various steps of thiol self-assembly, deprotection, exposure to colloids, *etc.* as explained in the figure caption and associated scheme. These establish the possibility to deprotect the surface as well as to subsequently stick gold colloids on it. Fig. 2 displays SE micrographs of PbS particles grown from THF solutions in the absence (a) and in the presence of dithiol-coated gold colloids (b,c). The thiol group in Fig. 2(b) is still protected so the significant modification in the morphology of the particles and their spherical shape, suggests that the particles are grown around the colloids with unprotected thiol groups in (c). At the present time, we are unable to establish whether it is a single colloidal particle that nucleates the growth of a PbS shell or a cluster of particles. We have determined that it is not the thiol alone that results in the morphologies displayed in (c) (through the inhibition of certain surfaces for example) so the colloid does play a critical role. Attempts to understand the nature of the architecture through the preparation of smaller shells and the use of TE microscopy are under way.

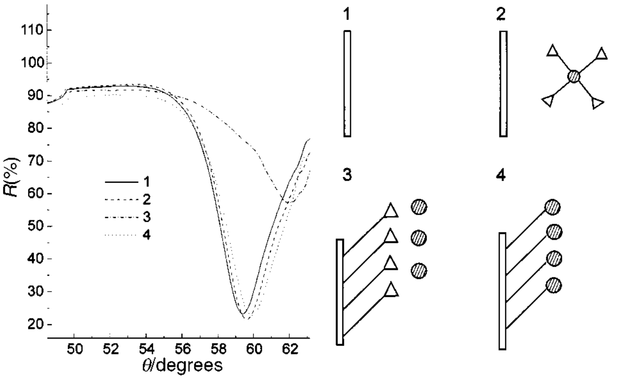

Fig. 1 Surface plasmon spectra of a clean gold surface (1), a clean gold surface exposed to protected gold colloids (2), a gold surface modified with the half protected decanedithiol and exposed to bare gold colloids (3) and a gold surface after deprotection of the dithiol and exposure to bare gold colloids (4). The schemes on the right correspond to the different SP spectra with rods indicating the thiol, spheres the gold colloids, and triangles the protecting groups.

PbS is a semiconductor and the thiol layer is insulating. We recognize links between the structures of MOSFETs (Metal oxide semiconductor based field effect transistors) and of the metal colloid, thiol, PbS architectures presented here. The materials that are the subject of the present work could perhaps be referred to as 'MOSFETs in a test tube'.

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† Dedicated to Professor Felsche on the occasion of his 60th birthday.

‡ Present address: Solid State & Chemistry Unit, Institute of Science, Bangalore 560 012, India.

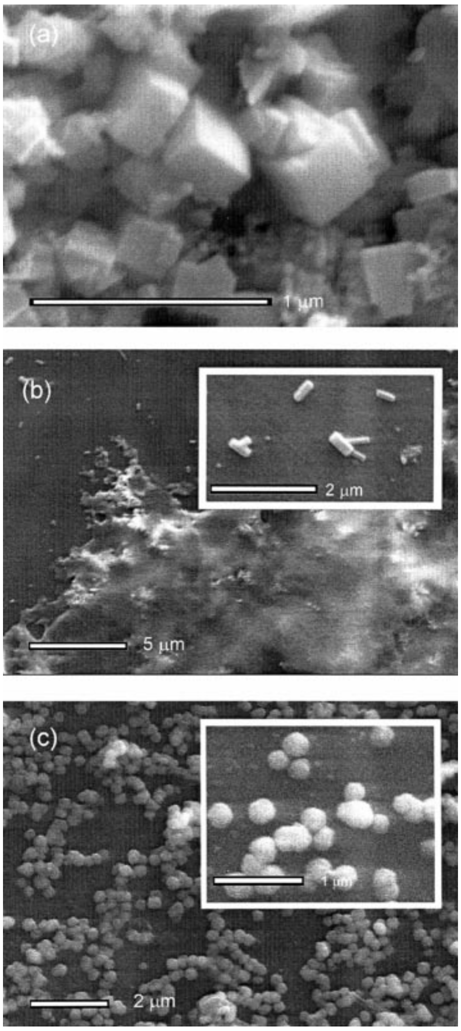

Fig. 2 Scanning electron micrographs of the products obtained after crystallization of PbS. (a) Crystallization in the absence of gold colloids. The crystals so formed correspond to the cubic system of lead sulfide; (b) image of products crystallizing in the presence of protected gold colloids; (c) round particles found after crystallization of PbS in the presence of unprotected gold colloids.

Notes and references

§ The dithols were prepared from 1,*n*-dibromo alkanes using the Bunte Salt method.[1,9] The protection of one of the thiol groups using the benzoyloxocarbonyl group was achieved using a procedure of Scott and Harrison after modification.[10] Briefly, to the dithiol (5 g) in acetone (50 ml) with 2 M NaOH in water (60 ml), benzoyloxycarbonyl chloride (2.8 g) in acetone (20 ml) and 2 M NaOH (40 ml) in water were added simultaneously dropwise, over 30 min while cooling with ice. After stirring overnight at room temp. the acetone was removed and the residue was worked up with diethyl ether. The organic layer was separated and chromatographed on silica to separate **1** from the unprotected and diprotected compounds.

¶ Gold colloids were prepared in toluene following the method of Brust *et al.*[11] Deprotection could be carried out with aq. NH_3 (40 ml) in CH_2Cl_2 (40 ml), stirring overnight. The deprotected colloids in the organic layer were collected after removing the solvent and dissolved in THF for the crystallization experiments.

‖ Crystallization of PbS was carried out using an aqueous solution (3 mmol) of $PbNO_3$ (3 ml) in THF (100 ml) and deprotected gold colloids (0.1 g) were added. After glass slides were placed at the bottom of the vessel it was exposed to an H_2S-atmosphere in a desiccator for 24 h. The solvent was removed and the glass slides were dried at room temperature. The material collected on the slides were studied by X-ray diffraction (Siemens D5000, transmission, Cu-Kα_1 radiation) to confirm the NaCl structure of PbS and by SE microscopy (Zeiss DSM 962).

** SPS measurements were performed in the Kretschmann configuration.[12] Optical coupling was achieved with a LASFN9 prism (n = 1.85 at λ = 632.8 nm) and index matching fluid (n = 1.70) between the prism and the BK270 glass slides. The plasmon was excited with p-polarized radiation using a He–Ne laser (632.8 nm, 5 mW). The glass slides were cleaned with aq. NH_3–H_2O_2–water (1:1:7) for 10 min at 80 °C and coated with gold using a Balzers BAE250 vacuum coating unit under a pressure of $< 5 \times 10^{-6}$ hPa, typically depositing 48 nm of gold after first depositing 2 nm of Cr. The slides were exposed to the organic thiol solution (10 mmol) for 24 h.

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