Photo-deposition and film formation of benzenethiol monolayer protected clusters in halogenated media

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2.1 nm benzenethiol monolayer protected gold clusters undergo solvent dependant photoinduced deposition with potential applications in the field of nanoparticle film formation.

Investigations into arenethiol monolayer protected clusters (MPCs) deviate from the well studied field of the analogous alkanethiol systems. Synthetic methods and routine characterization of a variety of nanoparticle sizes have been reported using both one[1,2] and two phase methods,[3] with the resulting nanoparticles exhibiting surface plasmon resonances depending on their dimensions. The ease of functionalisation of the *para* position of the aromatic ring has great potential in the development of molecular hybrid devices based on these novel MPCs.[4]

We have recently shown using femtosecond transient absorption spectroscopy that the 2.1 nm benzenethiol MPCs studied herein possess molecular-like behavior.[2] As yet, no photochemical process or novel applications have been realised for these systems, which possess a full conjugated monolayer. Herein, the photochemical stability of benzenthiol nanoparticles is investigated, and solvent selective photoinduced aggregation is observed which results in the formation of aggregate nanoparticle films. Previously, nanoparticle films have been synthesised using a variety of methods, such as salting out[5] and electrochemical deposition.[6] Due to the presence of the surface plasmon confined to the dimensions of the nanoparticle, these gold films have different optical properties compared to that seen for bulk metal, synthesised *via* evaporation.[7] "Rough" nanoparticle based gold films have applications in continuum generation[8] and in producing SERS (surface enhanced Raman spectroscopy) active substrates.[9]

Photoinduced aggregation of unprotected gold nanoparticles dispersed in organic media was first reported by Kimura.[10–12] Citrate stabilized systems were studied and photoinduced coagulation was observed.[13] In both cases aggregation is thought to result from a change in van der Waals forces, that allow particles to aggregate upon collision. Examples also exist where gold hydrosols undergo oxidation from solvent molecules reforming the Au^+ ions, hence losing the characteristic red surface plasmon resonance absorption.[14] In contrast to the previous investigations on nanoparticle photochemistry, the systems in this study are protected by a monolayer of benzenethiol making them much more robust toward aggregation, reaction and changes in solvent behaviour, resulting from the physical separation between the potentially reactive gold and the surrounding media.

Thiobenzene protected gold clusters were prepared based on the general one phase method devised by Brust[1] and purified by repeated precipitation and washing with acetonitrile.[2] NMR confirmed the sample was clear of any starting materials or by-products which may interfere in the photochemical investigations. TEM analysis of the nanoparticles show them to exist as relatively monodisperse single entities, having an average diameter of 2.1 ± 0.7 nm, see Fig. 1a.

The UV/Vis absorption spectra of the nanoparticles displays a band that increases continuously in intensity towards the blue over the visible spectrum (Fig. 2). The absorption spectra of these 2.1 nm particles originates from the interband transition of the gold core. No distinct surface plasmon band is seen. The UV/Vis spectra and femtosecond transient absorption measurements confirm that these systems exhibit molecular-like behaviour due to their small size.[2] Irradiation was carried out at 355 nm with a 3–4 ns pulsed Nd:YAG laser† in dichloromethane. After irradiation for 20 seconds a burn mark is seen at the interface between the cell surface and solution, while the spectrum of the solution remains practically unchanged. The solution was subsequently left for 24 hours and a distinct colour change from brown to purple was observed (see Fig. 1b). This colour change was found to be a result of the formation of a homogenous purple film on the surface of the cell. Indeed, the liquid phase is shown by UV/Vis spectroscopy to no longer contain any absorbing solutes, and its evaporation leaves no solid residue. Similar behaviour was observed when irradiation was perfomed in other halogenated solvents, such as chloroform and tetrachloromethane. By contrast, when irradiation was performed in the complete range of non-halogenated solvents in which the nanoparticles were soluble (dimethylsulfoxide, benzene, toluene and tetrahydrofuran), no

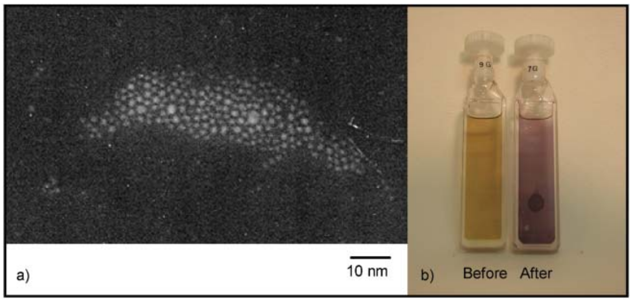

Fig. 1 a) TEM image of benzenethiol nanoparticles, showing the average size distribution of 2.1 nm. b) Photograph of quartz cuvette, containing benzenethiol in DCM, before and after irradiation. The violet colour is a result of the formation of a gold nanoparticle based film on the surface of the cuvette.

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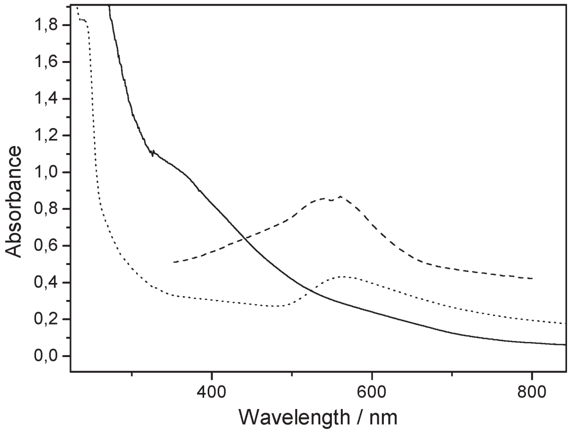

Fig. 2 UV/Vis spectra of benzenethiol nanoparticles, —: nanoparticles dissolved in DCM before irradiation, ---: nanoparticle film on surface of cuvette, 24 hours after 20 seconds of 355 nm irradiation, ···: nanoparticle film on mica substrate, used in AFM analysis.

appreciable photoreaction took place. In all cases the UV/Vis spectra after 24 and 48 hours were virtually identical to those measured prior to irradiation, although the surface of the cell showed evidence of burning. A control experiment performed where the nanoparticles were dissolved in dichloromethane and left in the dark for 24 hours showed no detectable change in the UV/Vis spectra. Hexanethiol gold nanoparticles of similar size and UV/Vis spectum dissolved in dichloromethane were also irradiated under the same conditions. No photochemical reaction (change in UV/vis spectra or film formation on the cuvette after 24 hours) was observed.

The UV/Vis spectrum of film formed on the surface of the cuvette shows a broad band maximum at 560 nm. The band position and broadness is typical of clusters of aggregated nanoparticles[11,15] or of larger ~100 nm nanoparticles in the extrinsic size regime.[16] AFM measurements‡ of a gold film deposited on a mica substrate with a similar transmission UV/Vis spectra, was performed in order to understand the structure of the film, see Fig. 3. It is clear from inspection of the images that the surface consists of spherical domains with a broad fractal-like size distribution, with diameters ranging from <30 nm up to 150 nm. These domains consist of aggregates of the initial 2.1 nm nanoparticles. The maximum surface height is *ca.* 700 nm. The structure of the film is seen to be nanoporous with a high surface area.§ The optical properties of the film are thought to arise from these domains of aggregated nanoparticles exhibiting coupled surface plasmons.[11,15]

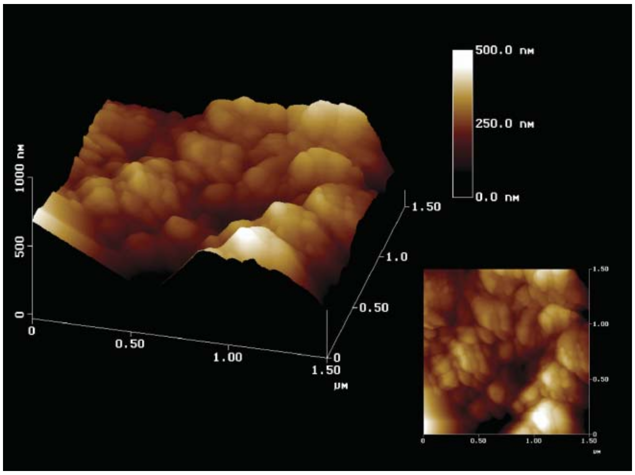

Fig. 3 3D AFM image, (1.5 × 1.5 µm) of the nanoparticle aggregate film on mica. Maximum height of film is *ca.* 700 nm.

Based on the stability of the nanoparticles in the dark it can be concluded that aggregation is a photoinduced process. After a short photolysis time (20 seconds), MPC aggregation and film formation is observed to be fully complete in 24 hours. Such behaviour is indicative of autocatalysis, where excitation of a small fraction of the whole solution produces sufficient amounts of reactive species to subsequently induce aggregation of all the nanoparticles. The colour change of the nanoparticle from brown to red results from the appearance of the surface plasmon resonance, as larger particles are created[17] and/or aggregate.[11,15] Aggregation studies on unprotected gold nanoparticles suspended in organic solvents show that mercury lamp UV radiation plays a key role in the aggregation, indicating that either very high energy excitation of the nanoparticle or direct solvent excitation may cause radical formation/photoionisation, that may subsequently produce the reactive species. For the benzenethiol MPCs, the excitation wavelength is well below the absorption tail of all solvents studied, indicating that the reaction is not initiated by a unimolecular solvent ionisation or radical formation. The power is also thought to be too low for any multiphoton events to occur. Interband excitation of the nanoparticle is thought to be the sole absorption process occurring upon 355 nm excitation.[2] Interestingly, *photoinduced deposition was only observed in halogenated solvents.*¶ All the non-halogenated solvents in which the experiments were performed (dimethylsulfoxide, benzene, toluene, and tetrahydrofuran) were shown to be perfectly stable after 48 hours. This disparity in reactivity is evidence of a mechanistic step succeeding excitation, involving both solvent and nanoparticle.

Unprotected gold nanoparticles,[18] are thought to accept electrons from the solvent and have been said to oxidize propan-1-ol, both in the dark and under irradiation.[11] In the case of the nanoparticles studied herein, it is proposed that photon absorption excites an interband transition based on the nanoparticle. The excited nanoparticle subsequently undergoes dissociative charge transfer with the halocarbon solvent, producing chloride ions and a solvent radical ($CH_2Cl^{\bullet}$ in the case of dichloromethane). Photochemical dissociative charge transfer to halocarbon solvents has been extensively documented at the molecular level.[19] The fact that the *photoreactivity is specific to the benzenethiol nanoparticles* (hexanethiol nanoparticles show no sign of photoreactivity under the same solvent/irradiation conditions) could be related to two types of reasoning: (i) their very small size, that brings molecular-like behavior and long excited-state lifetimes,[17,20] (ii) the electronic transparency of the arenethiol layer.[21] Both of these effects should facilitate charge transfer to the halocarbon solvent. Aggregation is due to interactions between electronically/structurally modified nanoparticles, which are produced either directly from charge transfer with the solvent, or through an ensuing reaction of solvent radicals with the nanoparticles. Once the aggregating nanoparticles reach a critical size they adhere to the surface of the cell. The formation of the homogeneous film as opposed to a complete precipitation of the nanoparticle aggregate, is probably related to the slow kinetics of aggregation. This process should be further investigated by controlling the concentration of the solution and its exposure to irradiation. Further characterisation of the gold structure should be performed using optical ellipsometry and XPS as well as surface enhanced Raman in order to characterize the nature of the benzenethiol bonded to the gold, and to assess the enhancement effects pertinent to the material. The deposition process has potential applications in the surface coating of high surface area porous/fractal like nano/micro structures[22] which cannot be functionalised *via* evaporation or salting out methods. Furthermore, since the process is simply photoinitiated there are no prerequisites for substrate properties, such as conductivity, a crucial factor in the electrodepositing coating process.

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Notes and references

† Continuum, Surelite II, USA operating at 10 Hz with an output of *ca.* 30 mJ pulse^{-1} and 5 mm spot diameter.

‡ AFM images were obtained in tapping mode using a Nanoscope III, scanning probe microscope produced by Digital Instruments, Santa Barbara, CA, USA. In order to prepare samples for AFM analysis, 20 second irradiation of the solution in dichloromethane was performed, the reaction mixture was poured into a dish containing a freshly cleaved mica slide, and film formation was allowed to occur on the mica surface. After 24 hours the DCM solution was seen to be clear and the transparent mica took on a red tinge.

§ It is not known whether the spherical particles that make up the gold film consist simply of the aggregated original 2.1 nm particles or include larger (poly)crystalline domains.

¶ Dependence of the solvent on the photoinduced precipitation rate of unprotected nanoparticles has been mentioned previously.[12]

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