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ChemComm
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Electrical property and water repellency of a networked monolayer film prepared from Au nanoparticles

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Received (in Cambridge, UK) 11th December 2002, Accepted 20th March 2003

Gold nanoparticles, modified with alkyl thiol, formed a film on polystyrene substrate, and it was found that the deposited film drastically changes its conductivity and hydrophobicity, depending on the alkyl chain length of the thiol used.

The 'nanotechnology' has remarkably grown up as a branch of science, and a number of attempts have been made to create ordered nanostructures, such as self-assembled monolayer,[1] Langmuir–Blodgett,[2] honeycomb,[3] and conducting polymer modified-films.[4] Current interest of many researchers is focused on developing novel nanomaterials and their applications to construct nanodevices, because the regular array and spatial arrangement of nanoparticle structures lead to the quasi-sized and surface plasmon resonance effects. For similar applications, significant interest has aroused in using Au-colloid films, which can provide active surfaces for association of biomaterials, such as antibodies, cells, and oligonucleotides.[5–7] An immunosorbent assay system integrated into a microchip with a Au-colloid conjugated anti-s-immunoglobrin A antibody and a DNA array detection system in the binding of oligonucleotides have been proposed.[6–8]

Many researchers have reported that Au-colloid superstructures consisting of three-dimensional arrays can be prepared on ITO glass plate by using 3-aminopropyltriethoxysilane as a binder molecule between Au colloid and the glass.[7–13] These techniques, now well known as a conventional way for the preparation of a layered Au-colloid film, can form Au-colloid layers by the following two-step protocols: a washed ITO glass plate is derivatized with the organosilane (step 1) and then immersed in an aqueous Au colloid dispersion for time periods ranging from a few minutes to several days (step 2).[7–13] The Au colloid layers thus scattered on a glass, however, have low conductivity, so that the Au colloid film must be formed on a conductive ITO glass plate when the electrical property of the film is examined. In contrast, our preparation technique presented here can simply produce a conducting Au-colloid film by the following single modification procedure: a polystyrene (PS) plate (15 × 2.5 × 1.0 mm) rinsed with ethanol and water is stirred at room temperature in an aqueous solution consisting of $1.5 \times 10^{-5} - 3.0 \times 10^{-4}$ M thiol as a binder (butanethiol, pentanethiol, hexanethiol or heptanethiol) and a colloidal Au solution (0.14 g L^{-1}).[14]

A beautiful lustrous Au gilt-PS plate was obtained after 4 h immersion. The surface of the resulting Au gilt-PS plate was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB210 spectrometer, FISONS), field emission scanning electron microscopy/electron probe microanalysis (FE-SEM/ EPMA, EMAX-7000, HORIBA), and atomic force microscopy (AFM, SPM-9500 JIII, Shimadzu). The electrical resistance of the plate was measured with a digital multimeter (Model 2000, Keithley) under a standard four-probe configuration at room temperature.

XPS spectra of PS substrates treated with the Au-colloid solution for 0–12 h indicated that the PS surface was saturated with the Au particles in 4 h. The FE-SEM microphotographs of the Au-gilt PS plate revealed that an ordered nanoparticle structure (diameter *ca.* 50 nm) arrayed as a monolayer was created (Fig. 1). It appears that some part of oligomeric PS was dissolved in butanethiol and redeposited on and in the Au particle monolayer.

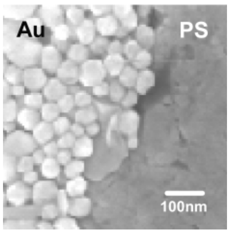

Fig. 1 A SEM image of the Au nanoparticle monolayer using butanethiol as a binder.

In order to confirm the modification of the Au particles with thiol, the static contact angle of a water droplet on the Au colloid monolayer was measured as a function of alkyl chain length (*n*) of thiol (Fig. 2). The static contact angle of bare PS plate was 86.3°, and the angle of the Au particle film was decreased from 144.7° ($n = 9$) to 119.5° ($n = 4$) with a decrease in the number of carbon atoms involved in the alkyl chain.[15] It has been found that the hydrophobicity of Au colloid monolayer film depends on the hydrophobicity of thiol on a Au particle.[15,16]

Fig. 3 shows the contact mode AFM images recorded under three different surface conditions. From these results, deposition seems to proceed as follows: at first, the -SH group of the binder molecule adsorbs to the Au particle surface (Reaction 1),[17] and

$$\mathrm{Au + R{-}SH\ (thiol\ as\ binder) \rightarrow R{-}S{-}Au + 1/2H_2} \qquad (1)$$

$$\mathrm{PS + R{-}S{-}Au \rightarrow PS\cdot\cdot R{-}S{-}Au} \qquad (2)$$

then the hydrophobic alkyl chain of the thiol molecule interacts with the surface of PS (Reaction 2).

The image (b) represents a crater due to the dissolution and removal of oligomeric PS with butanethiol. The self-assembled Au nanoparticles are then adsorbed on the PS surface through the interaction with the hydrophobic alkyl chain of butanethiol (c). Finally, Au particles cover the total surface of the PS substrate as shown in Fig. 1. An experiment carried out without using the binder revealed that no robust Au film was formed on the PS surface.

Fig. 4 demonstrates that the electrical resistance of the Au gilt-PS plate prepared in this fashion is dependent on the

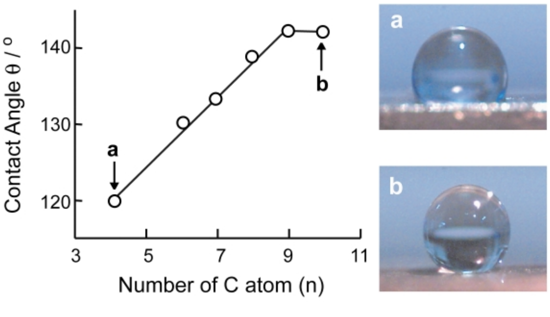

Fig. 2 The contact angle of a water droplet on the Au-gilt plates. The alkyl chain length of binder thiol molecules is shown as the number of C atoms (*n*). Butanethiol, $n = 4$ (a); decanethiol, $n = 10$ (b).

DOI: 10.1039/b212226j

concentration of the thiol molecule. Depending on the thiol used, minimum electrical resistance occurs at a different thiol concentration. An insufficient amount of the -SH sites on the PS surface, which occurs at binder concentrations less than those for the minimums, makes the average Au particle distance longer than that required for the formation of an electrically conducting compact assembly, hence leading to higher resistance of the Au layer. Contrary, the excess thiol would again lead to a greater Au particle distance due to loose multilayered packing of thiols formed on the surface. Additionally, optical microscope observation confirmed our results.

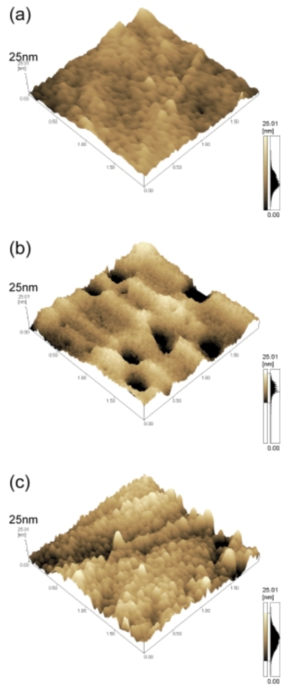

Fig. 3 AFM images (2 μm × 2 μm) of PS washed (a), after etching with butanethiol (b), and after Au nanoparticle monolayer deposition (c).

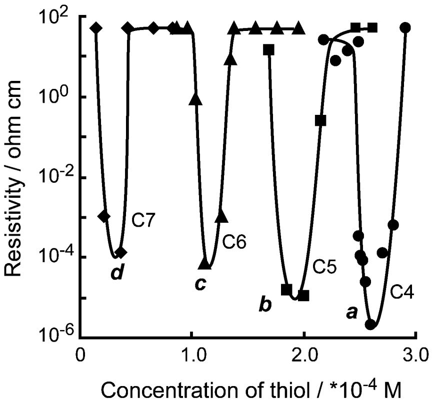

Fig. 4 Dependence of the electrical resistivity of Au gilt-PS plates on the concentration of binder in the aqueous solution, which consisted of a given amount of thiol and colloidal Au (0.14 g L^{-1}). The thiols used were butanethiol (a), pentanethiol (b), hexanethiol (c), and heptanethiol (d). The resistance of 50 Ω cm indicates the upper detection limit of the instrument.

It is interesting to note here that the value of the resistance minimum depends on the alkyl chain length of thiol, and the minimums for longer thiols appear at smaller thiol concentration. The dependence of the resistance minimum indicates that the particle distance for the closest packing increases as the chain length increases. The shift of the minimums with the thiol concentration also indicate that such optimal configurations require sparser implantation for longer thiols.[18]

The resistivity of Au-gilt PS prepared with butanethiol was less than 2.1×10^{-6} Ω cm, which corresponds approximately to the resistance of metallic gold (1.3×10^{-6} Ω cm). On the other hand, thiols with longer alkyl chains led to an increase in electrical resistance (pentanethiol 1.1×10^{-5} Ω cm, hexanethiol 7.1×10^{-5} Ω cm, and heptanethiol 1.4×10^{-4} Ω cm), implying longer thiol molecules act as tunnelling barriers. The increase in the number of the C–C bonds increases each Au nanoparticle distance by up to ~0.3 nm, resulting in more than a six-fold increase in the electrical resistance.[19]

This simple technique using alkyl thiol as a binder molecule allows one to prepare a robust Au particle surface-nanostructure on an insulating plastic substrate with controlled properties of electrical conductivity and hydrophobicity and is expected to have a variety of applications, such as electronic nano-devices and sensors.

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