

Suppressed electron hopping in a Au nanoparticle/H₂S system: development towards a H₂S nanosensor†

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Received (in Cambridge, UK) 10th December 2004, Accepted 26th January 2005

First published as an Advance Article on the web 16th February 2005

DOI: 10.1039/b418559e

We herein report and discuss electron transport within a Au/H₂S nanoscale device and thereby highlight a phenomenon that may be used in the development of a novel on-chip H₂S sensor.

The toxic and corrosive nature of hydrogen sulfide (H₂S) presents serious problems to both industry and environment. As a consequence, the development of appropriate H₂S sensors has been the subject of scientific investigation and technological significance. Existing methods for detection of H₂S gas are based on materials and apparatus at macroscopic scale. These include the use of gas chromatography,¹ laser spectroscopy,² surface acoustic wave,³ tin oxide^{4,5} and gold thin films.⁶ In contrast to these traditional sensing methods, increasing interest has been directed to miniaturisation and the development of a nanoscale H₂S sensor as a small sensing device offers clear advantages in many ways. For example, an array of sensing units may be constructed on a small chip by integration, and the sensor may be particularly suitable in an environment where the working space is very limited such as 'downhole' detection of H₂S gas in oil wells. In the course of our studies of the interaction between H₂S and gold (Au) nanoparticles, we find that the adsorption of H₂S molecules onto the nanoparticles may significantly change the hopping behaviour of electrons through the particles. Here we report for the first time a suppressed hopping phenomenon, and demonstrate that this phenomenon may be used as a new approach in the development of a H₂S nanosensor.

To demonstrate the ability of an electron to hop through a matrix of gold nanoparticles in experiment, we have constructed a set of four nanoscale sensing cells, each with different shape and size, on a Si wafer. A schematic representation of the device is shown in Fig. 1, while the real nanostructure can be seen from the scanning electron microscopic (SEM) images shown in Fig. 2. In each sensing cell, two electrodes, source and drain, are made to have a nanoscale gap between them. A typical gap-width of *ca.* 40–60 nm has been achieved. Au nanoparticles are placed randomly over the gap area. The device was patterned using electron beam lithography on the substrate. The electrodes were made by first depositing 5 nm thick chromium followed by a 20 nm gold layer. Deposition of the Au nanoparticles over the gap area was carried out by a wet chemistry method, similar to that described in our previous report.⁷ Briefly, an electronically fabricated Si wafer was first functionalised with a self-assembled monolayer using a 0.5% aqueous solution of aminopropyl-trimethoxysilane. Consolidation

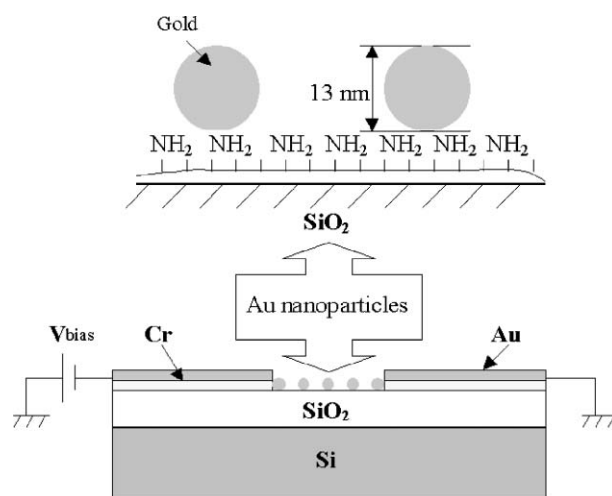


Fig. 1 A schematic diagram shows the basic structure of the microelectronic device for observation of the depressed hopping of electrons in the matrix of Au nanoparticles upon exposure to H₂S gas.

of the covalent bonding between Si atoms of the organic molecules and O atoms on the substrate was realised by heating the sample at 100 °C for 1 hour. Gold nanoparticles (12–14 nm) were synthesized by reducing H₂AuCl₄ using trisodium citrate at 110 °C, then deposited onto the substrate and bonded *via* the amino groups of the derivatised surface.

The hopping of electrons was measured by recording the current–voltage (*I*–*V*) profile after application of an external electrical field. Fig. 3 shows one of the measured results. It is seen that without H₂S, the *I*–*V* curve appears like a platform when the applied voltage is small. However, when $V \geq 2$ V, the increase of *I* becomes significant with the increase of *V*. The exponential increase of *I* indicates that the conduction was contributed by the tunnelling of electrons through the matrix formed by the separated Au nanoparticles. However, on exposure of the device to H₂S, loss of the current was observed, and the observation was totally reproducible. For example, at $V = 2.5$ V, *I* was 1.79×10^{-11} A prior to H₂S exposure. But this *I* value reduced to 1.46×10^{-11} A after the introduction of H₂S (18% drop in magnitude). This current loss became even more significant at higher voltages. For example, at $V = 3.0$ V, *I* dropped from 3.0×10^{-11} to 1.72×10^{-11} A, a loss of about 43%.

The apparent current loss observed here is consistent with the measured increase of resistance using thin gold film.⁶ It may arise from a change in the surface properties of the Au nanoparticles following the adsorption of H₂S molecules as a result of the strong

† Electronic supplementary information (ESI) available: HRTEM images of the H₂S-treated Au nanoparticles. See <http://www.rsc.org/suppdata/cc/b4/b418559e/>
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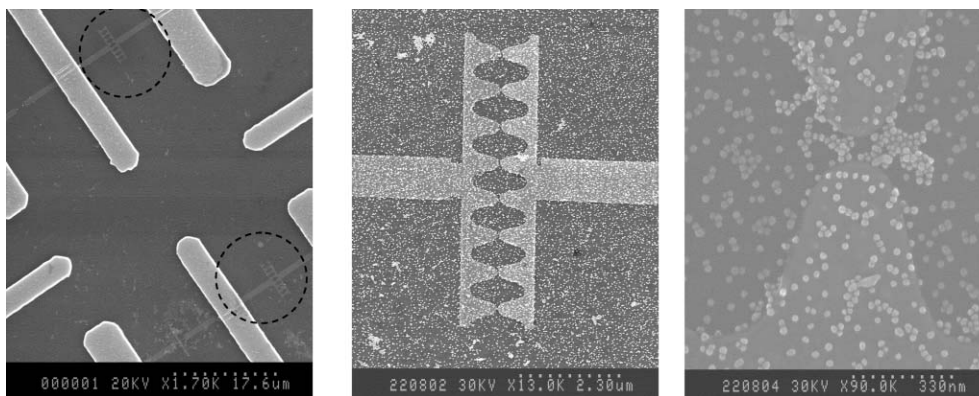


Fig. 2 A series of scanning electron microscopy (SEM) images shows the structure of the microelectronic device employed in the experiment. From left to right: (a) image of the whole device shows the four electronic terminals each having a sensing cell connected to the electrodes; the experimental results presented in this work were obtained from the two cells marked with circles; (b) higher magnification image shows the structure of the cells marked with circles in image (a); (c) a higher magnification image shows the detailed structure of a typical gap area between the teeth-shaped electrodes after adsorption of H_2S ; this picture demonstrates the normally observed bridging in the gaps by the loosely-aggregated Au nanoparticles. Scale bars: see the above images.

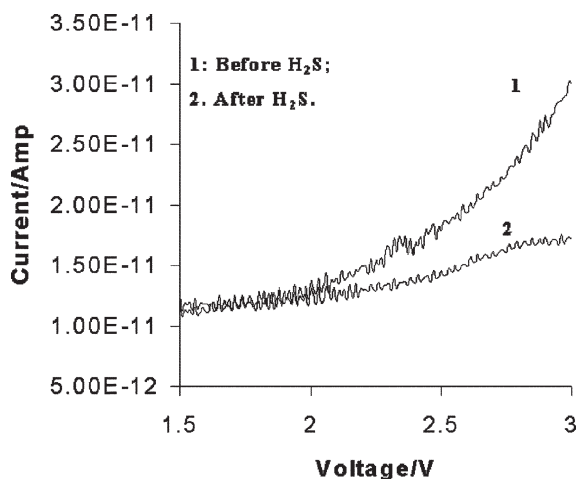


Fig. 3 Measurement of the I - V curves before and after the H_2S exposure (3 minutes exposure, pure H_2S gas, at room temperature).

chemical affinity between Au and S ($D_{208}^0 = 418 \pm 25 \text{ kJ mol}^{-1}$).⁸ This assertion is supported by the gold-sulfur interactions already widely studied in the past decade. It has been established that the gold-sulfur bonding in alkythiol self-assembled monolayers (SAMs) on the particle surface takes the form of Au-SR (R: alkyl chain), with the loss of the thiol hydrogen in the bond formation process.⁹⁻¹² The excellent correspondence observed thus far, between the properties of thiols adsorbed on planar and colloidal surfaces, indicates that the gold-sulfur interactions in the nanoparticle system are transferable to the planar Au-SR monolayers.^{9,10} Direct adsorption of H_2S onto planar gold surface has been studied by Leavitt and Beebe using the clean Au(111) surface with the temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS).¹³ Their results show that H_2S molecules easily undergo adsorption and desorption molecularly at low temperatures ($\leq 165 \text{ K}$). However, with the increase of temperature to above 165 K but below 520 K, the adsorbed H_2S molecules decompose to form SH species which are chemically

adsorbed on the Au(111) surface. At the same time, the produced H_2 molecules are released into the gas phase. These results support many of the conclusions asserted by theoretical calculations by Sellers and co-workers,^{14,15} including the prediction that H_2S will bind to the ontop position on the Au(111) surface and form a weak physisorption bond, while the SH fragment will bind in the three-fold hollow sites of the (111) surface, where it forms a strong chemisorption. The adsorption of H_2S has also been studied by Jaffey and Madix on the clean Au(110) surface using the TPD and low energy electron diffraction (LEED).¹⁶ Like the case on the Au(111) surface, the result shows the evidence of the formed SH groups on the surface. Moreover, their result also suggests that SH may undergo further disproportionation reaction to form H_2S gas and adsorbed S when the Au(110) surface is heated above 270 K. In addition, gold nanoparticles synthesised by reduction of Au(III) derivatives using trisodium citrate have a rather loose shell of ligands, and thus could be substituted by alkythiolate ligands and the nanoparticles are often used as a precursor for synthesis of valuable Au-nanoparticle based materials.^{9,17,18}

Considering these existing results and also comparing our experimental conditions with those reported in the literature, we propose the following mechanism for the observed phenomenon with respect to the suppressed hopping of electrons in the Au nanoparticle- H_2S system. Chemical adsorption of the H_2S molecules onto the nanoparticles brings about partial substitution of the citrate layer, producing possible Au-SH or Au-S type species on the particle surface. This in turn produces a sulfide shell, which inhibits the transfer of charge from one particle to the next. This mechanism, on the basis of the sulfide-generated barrier of charge transport, is also consistent with the conductance measurements in our previous work¹⁹ and the report by Andres *et al.* using organic alkane dithiol-linked gold nanoparticles.²⁰ Moreover, we found that some reversibility of the I - V characteristics could be observed by simply heating the sample in air to around 200 °C for a few minutes. The 'regenerated' sample showed a reduced electron hopping current (*ca.* 20% less) and displayed depressed hopping characteristics when resulfided (within experimental error). Up to five cycles were measured.

Evidence that electron hopping suppression is surface-driven is also provided by observations using high-resolution electron transmission microscopy (HRTEM) (see ESI),[†] wherein the H₂S treated Au nanoparticles showed no change in their bulk crystal structure.

In summary, we have demonstrated a nanoscale Au nanoparticle–H₂S sensing method that is in contrast to the traditional technique based on continuous gold thin film at macroscopic scale. The ‘wet’ chemistry method employed in this work has the advantages of simplicity, large area and low cost. The Au nanoparticles can be synthesized from a variety of methods with controllable sizes and morphologies. They offer surface and catalytic properties that differ from the bulk gold because of their high surface-area, high surface-energy per unit volume and unusual electronic properties. The electronic properties of the nanoparticles may be tuned by the control of the size and ligation. In addition, our ultra-small sensing device, with each sensing cell occupying an area of $\approx 12 \mu\text{m}^2$ in the total of eight tunneling gaps, holds the prospect of achieving higher integration levels if the device is used in circuitry. Patterning the cells on a single silicon chip for multi-channel measurements is significant for data treatments in the post-sensation process through signal averaging techniques and for the increase of the detection accuracy. Given all these, we believe that this nanotechnology-based strategy paves the way for the design and production of a potentially nanoscale H₂S sensor for wide-ranging applications.

We acknowledge the HRTEM work assisted by Dr David Jefferson (Chemistry Department, Cambridge University). We also thank support given by Professor H. Ahmed (Microelectronics Research Centre, University of Cambridge), Dr Tim Jones and Dr Li Jiang (Schlumberger Cambridge Research) and Dr Wuzong Zhou (Chemistry Department, Cambridge University). J.G. wishes to thank Schlumberger Cambridge Research and Cambridge Newton Trust for financial assistance during the tenure of which this work was carried out. D.S. would like to thank Peterhouse and The Royal Society for financial assistance during the tenure of which this work was carried out.

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Notes and references

- 1 J. Radford-Knoery and G. A. Cutter, *Anal. Chem.*, 1993, **65**, 976.
- 2 V. Weldon, J. O’Gorman, P. Phelan, J. Hegarty and T. Tanbun-Ek, *Sens. Actuators, B*, 1995, **29**, 101.
- 3 J. D. Galipeau, R. S. Falconer, J. F. Vetelino, J. J. Caron, E. L. Wittman, M. G. Schweyer and J.C. Andle, *Sens. Actuators, B*, 1995, **24–25**, 49.
- 4 J. Tamaki, T. Maekawa, N. Miura and N. Yamazoe, *Sens. Actuators, B*, 1992, **9**, 197.
- 5 G. Sberveglieri, S. Groppelli, P. Nelli, C. Perego, G. Valdre and A. Amanzi, *Sens. Actuators, B*, 1993, **15–16**, 86.
- 6 (a) J. J. McNerney, P. R. Buseck and R. C. Hanson, *Science*, 1972, **178**, 611; (b) K. S. Yoo, I. W. Sorensen and W. S. Glaunsinger, *J. Vac. Sci. Technol., A*, 1994, **12**, 192.
- 7 (a) J. Geng, B. F. G. Johnson, M. D. R. Thomas, D. S. Shephard and L. Jiang, *Inorg. Chim. Acta*, 2002, **330**, 33; (b) T. Sato, D. Brown and B. F. G. Johnson, *Chem. Commun.*, 1997, 1007.
- 8 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 1997, **78**, 9–52, 9–74.
- 9 M. C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293.
- 10 A. Badia, L. Demers, L. Dickinson, F. G. Morin, R. B. Lennox and L. Reven, *J. Am. Chem. Soc.*, 1997, **119**, 11104.
- 11 M. Brust, J. Fink, D. Bethell, D. J. Schiffrin and C. Kiely, *J. Chem. Soc., Chem. Commun.*, 1995, 1655.
- 12 M. J. Hostetler, A. C. Templeton and R. W. Murray, *Langmuir*, 1999, **15**, 3782.
- 13 A. J. Leavitt and T. P. Beebe, Jr., *Surf. Sci.*, 1994, **314**, 23.
- 14 H. Sellers, *Surf. Sci.*, 1993, **294**, 99.
- 15 H. Sellers, A. Ulman, Y. Shnidman and J. E. Eilers, *J. Am. Chem. Soc.*, 1993, **115**, 9389.
- 16 D. M. Jaffey and R. J. Madix, *Surf. Sci.*, 1991, **258**, 359.
- 17 J. Turkevitch, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55.
- 18 T. Yonezawa and T. Kunitake, *Colloids Surf., A*, 1999, **149**, 193.
- 19 T. Sato, H. Ahmed, D. Brown and B. F. G. Johnson, *J. Appl. Phys.*, 1997, **82**, 696.
- 20 R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney and R. G. Osifchin, *Science*, 1996, **273**, 1690.