ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 11318–11320

www.rsc.org/chemcomm

COMMUNICATION

Metallisation of gel surfaces under ambient conditions†

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Received 22nd July 2011, Accepted 4th September 2011
DOI: 10.1039/c1cc14472c

A room temperature method to coat a non-conducting gel phase with a metal is described, which uses galvanic displacement. Electrolytes are dissolved in the gel phase to allow metal deposition from an immiscible liquid electrolyte solution. Conformal deposition was achieved by imprinting the gel, followed by galvanic displacement of gold.

The metallisation of the surface of insulators is a process of considerable technological interest. Metallisation can be achieved by methods such as chemical vapour deposition, sputtering and evaporation, however one significant drawback with such "line of sight" based methods is their inability to achieve conformal deposition, *i.e.* to form uniform deposits within recesses. Accordingly, there has been much interest in the use of methods based on solution phase redox processes to achieve metallisation, with control over the deposit structure on the (sub-)micron scale a particular goal.[1] Electrodeposition has attracted much attention in recent years as a route to the precise deposition of thin layers, a significant body of work now exists on the control over this process to yield uniform, conformal deposits.[2,3] One intrinsic disadvantage of electrodeposition, however, is the requirement that the deposition substrate is a conductor.

An alternative approach is based on electroless deposition, which in some circumstances allows the catalytic deposition of metals on insulating surfaces (*e.g.* polymers, oxides).[4] For example, Abbott *et al.* have reported the electroless deposition of Au onto the surface of micron-sized SiO_2 particles, with further functionalisation with alkanethiols to permit their use as substrates for the reversible adsorption of enzymes.[5] A disadvantage with the application of the electroless approach to insulating surfaces is that a prior "surface activation" step is needed to form nanoparticulate centres, from which metal film formation occurs. Notably, Smoukov *et al.* have reported the electroless deposition of copper on gel surfaces moulded by soft lithographic methods.[6] Although able to yield complex metallised shapes, which can be removed in some cases as free-standing films, this approach still relies on the prior activation of the surface, specifically with Sn^{2+} sensitisation followed by reduction of Pd^{2+} to form nanoparticulate Pd nucleation sites. Because of the miscible nature of the (aqueous-based) gel and the aqueous deposition solution, diffusion of the activating colloids through both phases is possible, hence deposition is not necessarily restricted to a purely conformal zone. An alternative approach to achieve the conformal deposition of metal on an insulating substrate is reported herein, where a gel phase containing a metal precursor is placed in contact with an immiscible electrolyte solution. Metal deposition can then be performed at this electronically insulating surface. This novel method is based on the liquid–liquid electrochemical approach, which can give interfacial metal deposition either by electrolytic deposition[7] or by spontaneous metallisation.[8] Here this concept is extended to the gel/immiscible electrolyte interface, the advantage being that this "soft" interface can be stamped or moulded with patterns whose image is retained in the conformal deposition process. Agar is employed as the insulating mouldable substrate in the present study. Conductivity is imparted to the gelled phase *via* the salts dissolved to form a polymer electrolyte.[9]

The surface of the gel was covered with a Au deposit by a spontaneous reduction of Au^{3+} by decamethylferrocene (DmFc, dissolved in 1,2-dichloroethane, 1,2-DCE, see supporting information for details†). Once deposited, the Au film was used as a working electrode: a Pt wire (Advent, diameter 0.5 mm, 99.99%) was brought into contact with the film, glued to the side of the glass cell with epoxy resin (Araldite™) and left to dry. Once dried, the contact between the Pt wire and the Au film was improved by a small amount of conductive Ag paint (SPI Supplies).

The solution for electrochemical experiments consisted of p-chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone, 5×10^{-3} M, Lancaster, 98+%) and tetrabutylammonium perchlorate (TBAP) (0.1 M) as the organic electrolyte in 1,2-DCE. The pseudo-reference electrode was made in-house by oxidation of a Ag wire (diameter of 0.75 mm, Advent, 99.99%) immersed in a saturated solution of LiCl. Platinum gauze (Alfa Aesar, 99.9%) was used as the counter electrode. A commercial Au working electrode (IJ Cambria Scientific, working diameter of 2 mm) was also used to compare against the deposited Au film.

For conformal growth on the gel, a solution of 3×10^{-3} M $NaAuCl_4$ with 0.1 M LiCl and 0.1 M $LiClO_4$ was heated in a water bath with the agar as described above. On cooling, the gel mixture was poured into a dish. Before the gel had fully set, a stamp with a recognisable feature was pressed against the gel and left until the gel was solid. This stamp was then removed

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† Electronic supplementary information (ESI) available: Gel and solution preparation, and details of reagents. See DOI: 10.1039/c1cc14472c

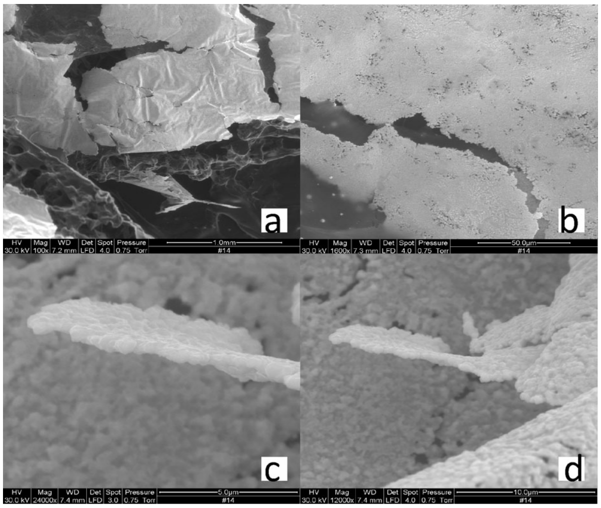

Fig. 1 Electron micrographs at successively higher magnification of the Au film galvanically formed on an aqueous gel; (a) scale bar of 1.0 mm, (b) scale bar = 50 µm, some cracks can be observed, (c) scale bar = 5 µm, and (d) scale bar = 10 µm where a section of the Au film has come away from the gel.

to leave a distinct impression on the gel. A 1,2-DCE solution of DmFc and TBAP (concentrations as above) was poured on top of the gel in an approximate 1 : 1 ratio. The Au deposition process is rapid, occurring on a time-scale of minutes. The gel/organic solution system was therefore left for one hour to allow complete formation of the Au film. Following deposition, the gel structure was probed using scanning electron microscopy (SEM). For this, the gel samples were thinly sliced and placed onto a carbon tab attached to an Al SEM stub. The metal covered gels were prepared so that the minimum amount of gel needed to preserve the structural integrity of the metal film was analysed.

The deposited Au was analysed *via* SEM, the micrographs can be seen in Fig. 1. In particular, Fig. 1c and d show a section of the Au film coming away from the gel and folding back on itself. This allowed an approximate measurement of the Au film thickness, which was in the region of 600 nm. It was found that leaving the gels exposed to the air caused collapse of the gel, due to evaporation of water, and consequent shrinkage and fracture of the deposited Au film. The resultant optical image of the film can be seen in Fig. 2. The deposited Au film was used as a working electrode to test its integrity, by adding the solution of p-chloranil in DCE above the Au film.

The voltammetric response was compared to the response of the same system at a standard Au working electrode. p-chloranil is known to undergo two successive electron transfer processes, to the radical anion and then to the di-anion, respectively,[10] however, only the former reduction was probed here as the di-anion can undergo unwanted side reactions. The apparent diffusion coefficient of p-chloranil was calculated for the standard system, using voltammograms recorded at different scan rates and the Randles-Sevčik equation (eqn (1)):[11]

$$I_p = 0.4463(nF/RT)^{1/2}A^{1/2}D^{1/2}\nu^{1/2}c \qquad (1)$$

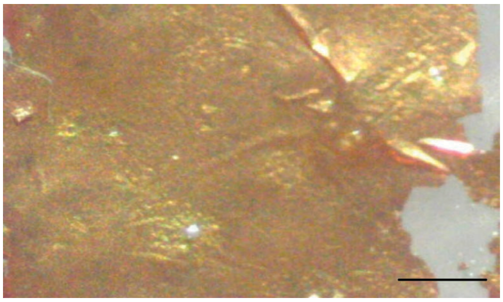

Fig. 2 Optical image of the Au film deposited on the surface of the gelled aqueous phase, scale bar = 0.5 mm.

where I_p is the peak current, n is the number of electrons transferred per molecule, F is Faraday's constant, A is the active area, D is the diffusion coefficient of the probe molecule, c is the concentration of the probe and ν is the scan rate. All other symbols have their usual meanings. This gave an apparent diffusion coefficient for p-chloranil in 1,2-DCE solution, which was then used to determine the active area of the deposited Au film. Cyclic voltammograms for p-chloranil using the Au film as a WE are shown in Fig. 3. In contrast to the commercial electrode, where an ideal 0.06 V peak separation was seen, the voltammograms obtained for the deposited film show a slight increase in peak separation with increasing scan rate. The apparent diffusion coefficient was found to be 7.4 (±0.4) × 10^{-6} cm^2 s^{-1} for the standard Au working electrode. Compton *et al.* found the diffusion coefficient for p-chloranil in acetonitrile to be 1.7 × 10^{-5} cm^2 s^{-1},[12] which yields a D in 1,2-DCE of 7.2 × 10^{-6} cm^2 s^{-1} if solvent viscosity is corrected using the Stokes–Einstein equation (eqn (2)):

$$D = kT/(6\pi\eta r) \qquad (2)$$

where η is the viscosity of the medium, r is the hydrodynamic radius of the solute and all other symbols have their usual meanings.[13]

Voltammograms were recorded for the system with the deposited Au at different scan rates and the peak current dependence plotted to find A *via* eqn (1). For the solution of p-chloranil, A was found to be 1.24 cm^2, compared to the geometric area of the deposited Au determined by the diameter of the glass cell, of 2.01 cm^2. It should be noted, however, that the uncompensated resistance visible in Fig. 3 will depress the peak currents and therefore means that the A value is an underestimate. On closer inspection of the SEM images at higher magnifications (Fig. 1), it can be seen that the Au film is not continuous. The thickness of the Au film deposited was calculated to be 0.67 µm, assuming a 100% reduction

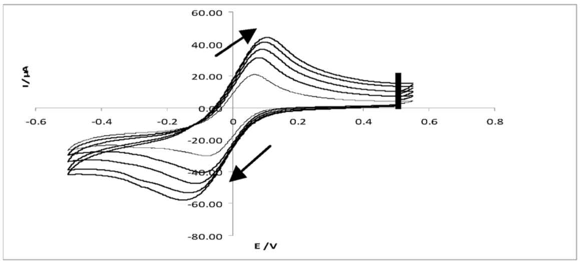

Fig. 3 Cyclic voltammograms, obtained for a solution of 5 mM p-chloranil and 0.1 M TBAP on the deposited the Au film, recorded at different scan rates. Arrows indicate the direction of the scan and vertical line indicates the starting potential.

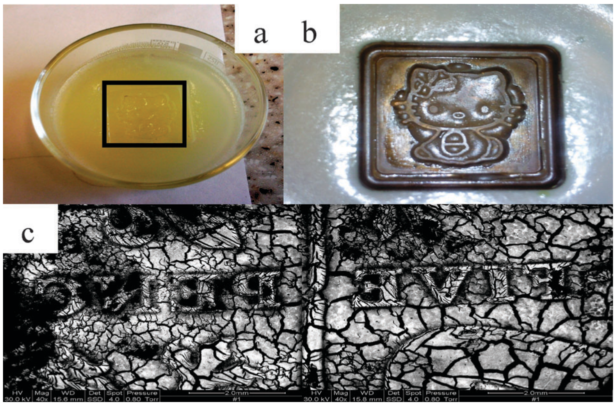

Fig. 4 Optical images of (a) the gelled aqueous phase containing 3 mM $AuCl_4^-$ with 0.1 M of $LiClO_4$ and 0.1 M LiCl that has an image stamped into it. The black square outlines the imprinted image before the deposition reaction and the (b) image recorded after metallisation by reaction between the gel and 9 mM DmFc and 0.1 M TBAP in DCE. The cell diameter is 0.564 cm. (c) SEM images of the Au deposited into the features imprinted from a 5 pence coin.

efficiency, based on the amount of Au ion added to the gel, while the final deposit thickness was measured to be 0.6 μm (Fig. 1c).

While the maximum area is determined by the cell in use, it should be noted that the preparation of the film involved exposing the gel, whilst the epoxy resin and conductive paint dried, meaning the gel would have shrunk in size due to water loss. This would decrease the size of the active area, as the Au film will also break up as the gel shrinks. Analysis of the film using SEM, even under a low vacuum, would however have caused greater shrinkage of the gel and breakage of the Au film. It is, therefore, unclear from the SEM analysis whether the gaps and cracks seen in the film result from gel shrinking, either naturally or under vacuum for microscopic analysis, a combination of both, or whether the Au film forms in this state on a gelled medium.

Conformal growth of Au was achieved on a gelled electrolytic phase; Fig. 4a shows an image recorded for the gelled aqueous phase with an imprint of the stamp's features prior to the deposition reaction. The highlighted black square illustrates where the rubber stamp was positioned before the gel had fully set. Fig. 4b shows the galvanically displaced Au coated image of the stamp. The organic phase containing the reducing agent was specifically placed inside the indentation left by the stamp, thus in Fig. 4b, the gold covered image can be seen surrounded by the bare gel surface. The deposited Au is formed in the channels left by the stamp and so the image can be seen clearly. A coin (British decimal five pence coin) was used as a stamp with features smaller than the patterned stamp, shown in Fig. 4c. The coin, following cleaning, was held in place on top of a cooling gelled aqueous phase containing the gold salt and electrolyte. Once the gel had set, the coin was removed and resultant observation showed that metallic gold was deposited where the gel and coin had come into contact with each other. The coin is minted from an alloy consisting of 75% Cu and 25% Ni.[14] Spontaneous deposition of Au therefore has occurred when the Cu–Ni coin has come into contact with the gel containing the gold precursor cation, with oxidation of the coin and reduction of the metal salt occurring at the surface of the gel network to form the gold film seen in Fig. 4b. Fig. 4c show the gold galvanically deposited in the features of the coin, the letters forming the words "five" and "pence" can clearly be distinguished from the gold deposit. Concurrently, it is noted that the surface of the coin has been oxidised and is discoloured.

A novel method of metallising a soft insulating phase *via* galvanic displacement is reported. The incorporation of electrolytes into a polysaccharide gel imparts ionic conductance. This allowed metallic deposition to be performed at the surface of the gel. Au^{3+} species dissolved in the gel are deposited as metallic gold on the gel surface upon contact with an immiscible electrolyte solution containing a reducing agent.

The deposited film could be used as an electrode; although electrically conducting, the voltammetric analysis indicated that the active area was smaller than the geometric area of the gel surface. Traditional techniques of metal coating such as sputtering, deposition and film formation from molten metals require a vacuum chamber and/or high temperatures, and are not readily applicable to conformal deposition. It has been demonstrated that coating a gel with a pattern imprinted on its surface is possible with galvanic displacement at room temperature without the need for a vacuum chamber. Imprinting ionically conductive gels with features in the size range of hundreds of microns to centimetres, and successfully depositing gold within these features has been achieved without the need for additives or catalysts. Applications of the deposited film, for example as electrodes in gel electrophoresis, are currently being explored.

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