Synthesis, processing and forming gold structures from a 0.1 wt. % concentration solution

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Abstract

A very low concentration (~0.1 wt. %) of spherical 15nm diameter gold nanoparticles were produced by the sodium citrate reduction method and later transferred to ethanol using poly vinyl pyrrolidone (PVP) as a stabilizing agent. The alcosol was then subjected to electrohydrodynamic atomisation to generate fine droplets with an average droplet diameter of < 30µm and deposited on substrates accordingly. With the assistance of various deposition methods, three different microstructures were produced. Firstly, the droplets produced by atomisation with the help of an electric field were deposited at various times on a substrate to fabricate gold films with a thickness range of ~500nm to 2000nm. Secondly, the droplets were deposited on a moving table which is computer controlled to form an array of inter-connected droplets, thus enabling us to pattern microstructures containing gold nanoparticles of different geometries (electrohydrodynamic atomisation printing). Thirdly, to reduce the track size as well as to form a dense assembly of particles in the microstructures templates were used in conjunction with electrohydrodynamic atomisation (template-assisted patterning). In order to encapsulate gold nanoparticles in a fibre a co-axial needle set-up was used with a polyethylene oxide (PEO) and polyethylene glycol (PEG) mixture as the encapsulating media. Lastly, a gold hydrosol was used to produce near-monodisperse gold microbubbles with the help of a T-junction device having an average diameter of ~150µm. The ability to generate such a range of structures starting from a very low concentration of gold is a significant achievement.

Keywords: atomisation, electrohydrodynamic, jet, gold, patterning, forming, encapsulate, bubbling, film, tracks

Introduction

Throughout history, gold has been the most widely used noble metal due to its beauty and permanence. Gold has been used for many decorative, ceremonial and religious artefacts for many years. However, due to its unique chemical and physical properties, the usage of gold has increased in a wide range of industrial applications. Some important properties of gold are its high thermal and electrical conductivity, its excellent biocompatibility and its outstanding resistance to corrosion. Current diverse use of gold and its alloys range from medical implants through to emerging nano-technological applications. However, the major current uses of gold in industrial applications are within electronic components and in dental alloys [1]. Even though the electronic industry relies on gold's electrical conducting properties, it is also an excellent optical reflector of light and its compounds exhibit photoluminescent properties and this puts the metal in good shape for future applications in optical and electronics sectors [2].

In addition to their enhanced absorption and the ability to scatter light gold nanoparticles offer good biocompatibility [3] and other targeting moieties [4], making them suitable for biochemical sensing and detection [5] and therapeutic applications [6]. Another notable use of gold nanoparticles has been as contrast agents in cellular and biological imaging [7-10]. Contrast agents in medical and biological imaging [11] improve the sensitivity and diagnostic ability of the imaging modality by site-specifically labelling tissues or cells of interest.

In this paper, we describe methods of forming gold microstructures using a very low concentration solution by electrohydrodynamic atomisation routes and bubbling carried out via a specially-designed and constructed novel T-junction device. Electrohydrodynamic atomisation has been extensively studied over the last two decades by many scientists since its importance was discovered in mass spectrometry [12]. The jet break-up of a droplet under the influence of an electric field was first explored by Zeleny over 90 years ago [13] but since then, especially in the last decade, tremendous interest has been generated in the use of this phenomenon for advanced materials processing.

In this process, a liquid is forced through a conducting capillary, which is raised to a kilo-voltage with respect to a ground electrode aligned with the exit of the capillary. The liquid which is flowing through the capillary acquires a charge and a jet evolves at the exit of the capillary and breaks into individually charged droplets (atomises). Many modes of atomisation such as micro-dripping, spindle, cone-jet together with their numerous manifestations have been reported [14]. In this processing methodology, the main

parameters are the applied voltage to the capillary with respect to the ground electrode, the flow rate and the liquid properties, electrical conductivity, viscosity, surface tension, density and relative permittivity. A balance in these three controlling parameters forms what is widely referred to as the cone-jet mode of jetting, which can produce a monodisperse distribution of droplets.

The main advantage of this processing route is the controlled generation of individual droplets. Thus, these droplets generated by an electric field have been used to form films and coatings [15,16]. The droplets produced by atomisation have also been used to fabricate micro- and nano-particles from solutions or colloidal suspensions [17] and moreover this technique has been extended to produce microbubble suspensions by co-axial atomisation [18]. Electrospraying has also been employed in forming self-assembled nanostructures [19] and deposition of biomaterials [20] and biopolymers [21]. Furthermore this technique has also been used in fabricating two- and three-dimensional microstructures [22,23]. Recently, electrohydrodynamic atomisation has been utilised to atomise highly concentrated cellular suspensions into cell bearing threads and scaffolds [24] and fabrication of cell micro-integrated blood vessels [25].

Experimental details

a) Materials

Preparation of gold hydrosol

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and trisodium citrate were purchased from Aldrich. All chemicals were used as received. Milli-Q water was used to make up all solutions ($R > 18.2\Omega \text{ mm}$). Small gold colloids with an average diameter of 15nm and 10% polydispersity were synthesized according to the sodium citrate reduction method. This method consists of boiling 95 mL of $5 \times 10^{-4} \text{ M}$ HAuCl_4 and adding 5mL of a warm sodium citrate solution (1 wt.%) to the stirred solution [26].

Preparation of gold alcocol

Tetrachloroauric acid and trisodium citrate were purchased from Aldrich. Poly(vinylpyrrolidone) (PVP, molecular weight 10,000) was supplied by Fluka. All chemicals were used as received. Milli-Q water was used to make up all solutions ($R > 18.2\text{M}\Omega \text{ cm}$).

Gold nanoparticles with an average diameter of 15nm and 10% polydispersity were synthesized according to the standard sodium citrate reduction method [26] by boiling $5 \times 10^{-4} \text{ M}$ HAuCl_4 in the presence of $1.6 \times 10^{-3} \text{ M}$ sodium citrate for 15 min. After cooling down, the particles were transferred into ethanol upon functionalization with PVP [27]. Briefly, an amount of PVP sufficient to coat the particles with 60 PVP monomers per nm^2 was dissolved by ultrasonication for 15 min in water and added to the gold colloid. The

polymer was allowed to adsorb to the gold particles overnight while stirring. The particles were subsequently centrifuged (3500 r.p.m.) to remove the unbound PVP and redispersed in ethanol.

Preparation of polymer mixture

Polyethylene oxide (PEO) (98.5% purity) and polyethylene glycol (PEG) (99% purity), both supplied by Sigma-Aldrich, Poole, UK and having an average molecular weight of 2,000,000 and 8000, respectively, were used for the preparation of a polymer solution. PEO and PEG, both solids were mixed at a weight ratio of 1:2. Tetrahydrofuran (THF, 99.5% purity) solution supplied by Sigma-Aldrich, Poole, UK was mixed at 4:3 weight ratio with respect to the PEO and PEG mixture. De-ionized water was added to the polymer mixture at a weight ratio of 10:1 and the resulting solution was stirred for 24 hours before spraying.

b) Processing equipment

Single needle electrohydrodynamic atomisation

A stainless steel needle was held in epoxy resin. The needle was connected to a high voltage power supply unit (Glassman Europe Ltd., Tadley, UK) which can supply a voltage up to 30kV. The inlet of the needle was connected to a Harvard PHD 4400 programmable syringe pump (HARVARD Apparatus Ltd., Edenbridge, UK) using a silicone rubber tube, and the flow rate of suspension to the needle exit was varied between $10^{-12} - 10^{-9} \text{ m}^3\text{s}^{-1}$. A fibre optic light source was used for illumination. A microscope lens in conjunction with a high speed camera (Weinberger AG, Dietikon, Switzerland), which was connected to a portable computer, allowed observation of the colloid while undergoing atomisation (Figure 1).

Figure 1

Schematic diagram of the single needle electrohydrodynamic experimental rig

Co-axial electrohydrodynamic atomisation

The equipment set-up used is shown in Figure 2. The flow to the outer (internal diameter 850 μ m and external diameter 1240 μ m) and inner (internal diameter 250 μ m and external diameter 460 μ m) needles at a pre-set flow rate was maintained using two syringe pumps. The jet break-up was viewed using a Leica stereozoom camera. The jetting action captured by the camera was fed to a data video (DV) unit. The output from the DV was fed to a data recorder and also to a disc recorder whose output could be simultaneously viewed on a monitor. In order to prevent the jet from getting attracted and travelling towards the camera a pyrex shield was set up between the co-axial needle and the camera.

Figure 2

Schematic diagram illustrating the co-axial needle electrohydrodynamic experimental rig

Printing device configuration

A purpose built printing device was used to pattern microstructures on substrates. This device has been used in conjunction with gold patterning [28] and brief details are given here. The device used consists of a stepper motor driven 2D system. The X and Y tables are mounted on one another keeping the 2-axis profile very low and the system is computer-controlled using a programmable motion controller. A datum and an end of travel limit sensor are fitted on each of the tables to trigger the controller when a respective carriage reaches a limit. A perspex table is mounted firmly on the 2-axis system. The top of the table accommodates a frame for holding firmly upto an A4 sheet of substrate. Using motion planner software X and Y coordinates can be created and downloaded to the 2-axis controller, allowing the 2-axis system to write the path described by the co-ordinates provided (Figure 3).

Figure 3

Electrohydrodynamic printing device configuration

T-junction setup

The ends of two capillaries having 150 μ m internal diameter were axially aligned and encased within a rigid polymer block (10mm thick) separated by a distance of 70 μ m. A third tube was inserted into the polymer block so that it was perpendicular to the axis of the other two tubes to facilitate a complete T-junction. Each tube was secured mechanically to the block in a fashion that it could take maximum pressure without slipping away from the junction. This design was found to be both robust and rigid, withstanding the very high pressures generated at the T-junction (up to 600kPa). The top tube of the T-junction was connected to a pressurised tank supplying gas at constant pressure (measured by a digital manometer connected to the top tube) whereas the tube perpendicular to the top tube was connected securely using leak proof mechanical coupler to a 20ml stainless steel syringe (KD Scientific, Holliston, MA, USA). The suspension was supplied to the T-junction via the syringe using a Harvard pump to maintain a constant flow rate (Figure 4).

Figure 4

T-junction set-up used for bubbling

C) Characterization

Droplet sizing

Droplet size distribution resulting from atomisation of the gold alcosol was measured using a Sympatec Helos Model KF (helium laser optical spectrometer) sizing system (Sympatec Ltd., System Partikel-Technik, Bury, UK), which recorded and subsequently plotted the data. The laser system was incorporated in the electrohydrodynamic atomisation equipment by placing it so that the 2.2mm diameter laser beam was approximately at the same distance where collection of the droplets took place to form different structures. The laser beam travels perpendicular to the needle and measurements were synchronised with the appearance of the droplets in the measurement zone by monitoring the decrease in laser light transmission caused by droplet scattering. The experiment was repeated several times to verify reproducibility.

Scanning electron microscopy

Samples were coated with carbon before scanning electron microscopy and energy dispersive X-ray analysis. A JEOL JSM-6301F scanning electron microscope (SEM) was used. Elemental analysis was performed with an Oxford INCA Energy 200 X-ray Energy Dispersive Spectrometer (EDS) system. The SEM was operated in the secondary electron mode with an accelerating voltage up to 10kV and with the working distance varied up to 15mm.

Transmission electron microscopy

Transmission electron microscopy was carried out using JEOL JEM 100CX and JEOL JEM 2010 transmission electron microscopes, the latter was equipped with an Inca ISIS system (Oxford Instruments, Oxford, UK), which was used to carry

out energy dispersive X-ray analysis on the samples. All transmission electron microscope (TEM) images were recorded on film and scanned using a high resolution scanner.

Results and discussion

Film fabrication

Due to the high surface tension and the high electrical conductivity of the gold hydrosol it was not possible to obtain a stable jet by electrohydrodynamic atomisation. Therefore a gold alcosol was prepared and subjected to electrohydrodynamic atomisation and the droplets produced from atomisation were deposited on silicon wafer for fabricating gold films [29]. The gold alcosol was stable and no sedimentation occurred on standing indefinitely. To find out the optimum parameters such as flow rate, voltage, distance and deposition time, the gold alcosol was subjected to electrohydrodynamic atomisation at various flow rates, voltages and needle exit to substrate distances. The voltage and the flow rate were varied from 0 - 5kV and 10^{-11} - 10^{-9} m^3s^{-1} , respectively. From the initial experiments it was evident that with increasing spraying time the droplet-relics agglomerate after deposition. This is due to slow evaporation of the solvent (ethanol) and the high frequency of the droplets generated by stable cone-jet atomisation. Since the frequency of the droplets produced by jet disintegration is not easy to control, it was decided to increase the evaporation rate of the solvent after deposition. A hot plate was kept underneath the substrate in order to increase the temperature of the substrate. The initial experiments were repeated again with different substrate temperatures.

Figure 5

Mode selection map for the gold alcosol. Needle exit to silicon substrate distance is 2.8mm

Figure 6

Thickness variation at different spray times. a) 60s b) 210s and c) 300s. Scale bar indicated is 1μm

Various modes of atomisation were observed when the alcosol was subjected to atomisation. Figure 5 shows the mode selection map for the gold alcosol at different flow rates and applied voltages. From the mode selection map, the flow rate and applied voltage of $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and 2.3kV respectively, were selected as the optimum conditions. This value was selected as the droplet size is directly proportional to flow rate [30]. However, if the flow rate is too low, stable cone-jet mode jetting was regularly disturbed or the jet was not stable for a sufficient time span to enable film fabrication. In all these experiments the distance between the needle and substrate was 2.8mm and the substrate temperature was set at 50°C.

Using the above mentioned parameters droplets were deposited onto silicon wafer used as the substrate at different deposition times. The deposition time was varied from 60 –

300s. Prior to deposition, silicon substrates were cleaned with ethanol and dried at the ambient temperature. The sprayed samples were allowed to dry at the ambient temperature (22°C) for 24 hours before sintering in air. The films then underwent heat treatment by ramping the temperature from the ambient temperature to 400°C at 2°C min^{-1} . The films were cooled from 400°C down to the ambient temperature at 2°C min^{-1} .

Figure 6 shows the cross section of the centre of the sintered films at different spray times and Figure 7 shows the thickness variation with increase in spray time. Although the films appear uniform at low magnification, high resolution scanning electron micrographs (Figure 8) reveal that the films have a morphology containing several “hillocks”. The formation of hillocks is due to preferential landing of charged droplets on the substrate [31] and is a characteristic of electrohydrodynamic deposition.

Figure 7

Film thickness variation with increasing deposition time

Figure 8

Side view of the surface of a gold film prepared in this work

Printing

Electrohydrodynamic printing is an emerging direct write technology which uses charged droplets to pattern microstructures onto a substrate. The gold alcosol was subjected to electrohydrodynamic atomisation and the droplets were collected on a silicon wafer in order to fabricate micro-patterns. After setting up the equipment, the needle and the ground electrode were aligned. The flow rate of the alcosol was selected as $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and the applied voltage was increased until stable cone-jet mode was observed. Different distances between the needle exit and substrate; substrate and the ground electrode, were used in printing to find out the optimum printing distance.

High applied voltages and a lower flow rates were both found to be beneficial to print finer tracks. However, in general, increase of applied voltage ultimately resulted in discharge and at lower flow rates a stable cone-jet could not be maintained for continuous patterning. Also the distance between the needle and the substrate was selected as 0.4mm and the distance between the substrate and the ground electrode was selected as 4mm because they gave the finest line width without any scattering of the droplets. When the distance between the substrate and needle, substrate and ground electrode was increased it produced a significant amount of scattering and when the distance was

Figure 9

Tracks produced at different needle exit to substrate distances, a) 1mm and b) 0.4mm

decreased, a stable cone-jet was not achieved. Figure 9 shows optical images of the track printed at different distances from the substrate.

The droplets generated by the cone-jet were measured using the sympatec device and was in the range of 0.25 – 60 μm (Figure 10) but ~65 % of the droplets were in the range 20 - 60 μm . The average droplet size was ~26 μm . The finest gold track deposited was ~110 μm wide [28]. However, immediately after deposition, most of the particles can be seen clustering together at the edges of the line and a random distribution of the particles can be seen at the centre of the track (Figure 11). This is due to rapid evaporation of the solvent and particle movement as discussed below.

When the contact angle of the droplet on the substrate is $< 90^\circ$, evaporation initially proceeds with an accompanying decrease in the contact angle, but with almost no change in the contact radius. This contact line pinning during evaporation plays a critical role in drying-mediated self-assembly from a dilute colloidal droplet on the wetted surface, as demonstrated by Deegan et al. [32]. Since the evaporation rate is higher at the edge of the track when compared with the centre of the

Figure 10

Typical droplet size distribution obtained by electrohydrodynamic atomisation of the gold alcosol. Duplicate plots refer to repeated experiments

Figure 11

SEM image of the printed tracks showing the particle size-distribution along the length

track, there must be a continuous outward radial flow of the solvent from the centre of the contact area to the contact line of the printed track to compensate for the liquid removed by evaporation. This convective flow and the suspended particles it carries are responsible for forming particles at the contact line [33]. The random patterning at the centre of the tracks can be attributed to three reasons, (i) low concentration of the particles in the solution (ii) weak van der Waals and capillary forces – not strong enough to attract all the particles to the contact line, (iii) non uniform solvent evaporation across the contact line.

Figure 12

SEM images of the tracks prepared by template-assisted spraying with spray time set as (a) 90s and (b) 240s. Figure (a) insert shows a high resolution image of the marked area indicating the pores (dark). Scale bar indicates 1 μm

Figure 13

SEM images of sintered tracks prepared using templating method: (a) whole track, (b) centre of track and (c) edge of track and (d) elemental analysis of the track

Template-assisted spray patterning

As demonstrated in the previous section, with electrohydrodynamic print patterning, the limiting continuous track width was $\sim 110\mu\text{m}$. In a previous paper [28] we have shown that this is much larger than the limiting track width obtained using other techniques such as micro contact printing and lithography, although it must be noted well that this technique is economical and easy to operate, also we have used a very low concentration of gold particulates and this is very helpful for gold conservation. In order to reduce the track size, we have attempted this template-assisted track preparation.

Cu templates were used in conjunction with droplets produced by electrohydrodynamic atomisation. A silicon wafer (substrate) was placed and a template (G400P Parallel Bar, Gilder Grids, Grantham, UK) was kept on top of the wafer and spraying was carried out for different times in order to find out the optimum spray time. With increasing spray time it was evident that the droplet-relics aggregate into a larger droplet-relics thus deforming the template pattern. This is due to slow evaporation of the carrier liquid, namely ethanol, and the high frequency of the droplets produced after jet

break-up. Since it is difficult to reduce the frequency of the droplet generation, again a heating device was used to increase the substrate temperature to increase the evaporation rate of the solvent in a droplet produced by atomisation. When the distance between the substrate and the needle exit increased; it was evident that spray time also increases to form dense micro-patterns.

The distance between the substrate and the needle exit was selected as 2.8mm and the substrate temperature was set at 50°C in all template-assisted patterning work. The flow rate and the applied voltage were varied from 0 – 3 kV and 10^{-11} – $10^{-9} \text{ m}^3\text{s}^{-1}$ respectively, in order to determine the optimum spraying conditions for template-assisted patterning. Thus, the flow rate was selected as $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and applied voltage was fixed at 2.3kV for this part of the work. Different spray times were used and it was evident that with increasing spray time the line width increased and the porosity of the track decreased (Figure 12). To overcome the size segregation effect [34] and to get an even distribution throughout the template the printing device mentioned in the previous section was used with the above parameters to facilitate movement while deposition. The needle was moved

Figure 14

(a) Co-axial jetting of gold and polymer solution (b) Fibre mesh collected on microscopic glass slide and (c) TEM image of gold encapsulated fibre. Dotted line in (a) indicates the inner jet and white dots in (c) indicates gold nanoparticles

1mm s⁻¹ throughout the template and tracks prepared using this method with time set at 240s were sintered at 400°C using the conditions mentioned in film preparation methodology. Figure 13 shows the structural features of the sintered tracks with accompanying elemental analysis.

Co-axial electrohydrodynamic processing

In order to encapsulate gold particles in a fibre, co-axial electrohydrodynamic processing technology was employed. Initially, the polymer solution and the gold hydrosol were atomised using a single needle. The ability of these media to undergo a stable jetting process was thereby assessed. The polymer mixture flowed in the outer needle, and in the inner needle the gold hydrosol was delivered. Thus, the polymer and the gold hydrosol were subjected simultaneously to the process of co-axial jetting. The flow rate of the polymer and gold hydrosol was varied from 10⁻¹¹ – 10⁻⁸ m³s⁻¹. First the gold hydrosol was forced into the inner needle and the applied voltage was increased gradually. Subsequently, polymer solution was forced through the outer needle and simultaneously the applied voltage was increased in order to maintain the stability of the co-axial jet.

In these experiments, as the electric field is gradually increased, the electric force over comes the surface tension of the droplet at the exit of the needle and a charged co-axial jet was ejected from the tip of the outer cone. At an applied voltage of 7.8kV and inner and outer flow rates of 5 x 10⁻¹¹ m³s⁻¹ this co-axial jet streams down to undergo whipping by which solvent evaporates leaving behind a mesh of charged polymer fibres, having gold nanoparticles encapsulated within them (Figure 14).

Figure 14c shows TEM images of the fibres which were collected 200 mm below the needle exit. From the TEM images it's apparent that the gold nanoparticles disperse in a random order, this is due to turbulent flow encountered in the jetting operation which causes intense mixing in the cone [35,36]. The mixing of the gold alcosol and the polymeric medium has helped the turbulent flow and the dispersion of the gold nanoparticles in the product. By careful tailoring of the gold concentration and the processing parameters it should be possible to reach the percolation threshold in the composite and this will pave the way for preparing polymeric sheaths with pre-designed electrical conductivity / insulation.

Microbubbling by T-Junction

Microbubbles are very important vehicles in medical diagnostics, and they are also significant therapeutic agents [37], and this market is only just being explored. One important method of stabilising microbubbles and enhancing their non-linear behaviour is to reinforce them with particulates [38,39] and Au nanoparticles is an ideal source for this.

The gold hydrosol can also be subjected to bubbling using a T-junction device at various flow rates and air pressures.

In order to bubble successfully the surface tension of the gold hydrosol need to be reduced. In order to achieve this, a small amount of surfactant, polyethyleneglycol-40-stearate (PEG40S), was added to the gold suspension and dispersed using a sonicator (Misonix XL200, Labcaire, Dorset, UK) operating at an average power of 8W (level 1 – 6 varied continuously) for 240s, to yield an aqueous suspension

containing 0.06 wt.% gold nanoparticles and 0.01 wt.% PEG40S.

In the next set of experiments liquid flow rate was maintained at $6.67 \times 10^{-9} \text{ m}^3 \text{ s}^{-1}$ and air pressure was maintained at 320kPa. In order to prevent the liquid flowing upstream, the air pressure was increased to suite. As air pressure was increased, the air stream starts breaking up at constant rate and this event is repeatable. When the air pressure was increased further atomisation of the gold hydrosol was observed, whereas below this threshold stable bubbling was observed. It is important to increase air pressure very gradually to ensure that the air jet was surrounded by liquid at the T-junction, sudden increase in air pressure can shut down the liquid supply to the junction.

Figure 15a-d shows the typical bubble formation process captured using a Phantom V5 high-speed camera. As shown in Figure 15(a), first, the air jet enters liquid column downstream to establish two-phase flow. The introduction of air in the liquid column reduces effective area for liquid to flow, thus increasing liquid pressure at the interface to maintain the constant flow rate imposed by the pump, thus there will be a sharp increase in liquid pressure. A sharp increase in liquid pressure normal to interface starts decreasing air column radius as shown in Figure 15(b). The air quanta keeps on growing until it finally detaches from main air column Figure 15(c).

The microbubbles prepared by this method were collected on glass slides held at the end of the outlet capillary tube of the T-junction and subsequently investigated by optical microscopy. The average diameter of the bubbles was $\sim 150\mu\text{m}$ (Figure 15e) and the polydispersity of obtained bubbles were in the range $\pm 0.1\%$. For further analysis the microbubbles were collected on standard transmission microscopy copper grids of $10\mu\text{m}$ aperture. The grids were immediately frozen at -30°C and transferred to a mini-lyotrap (LTE Scientific Ltd., Oldham, UK) held at -10°C and held in vacuum overnight to facilitate freeze drying. The freeze-dried structures were investigated using transmission electron microscopy. Due to capillary forces between the particles, the gold nanoparticles assembled at the interface of the microbubble (Figure 16). By using finer capillaries even finer bubbles can be prepared this way. This work is in progress as it is important to achieve bubble diameters of $< 10\mu\text{m}$ in order to facilitate diagnostic and therapeutic applications.

Figure 15

T-junction bubble generation process. (a) Air meets liquid at the T-junction and two-phase flow is established. "Pinching-off" of a bubble shown by sequence (b) and (c). Bubble generation is continuous as illustrated in (d) and (e) optical micrograph of the bubbles generated using T-junction device

Conclusions

In this paper, we elucidate several novel processing routes for a very low concentration of gold solutions ($\sim 0.1 \text{ wt. } \%$) containing 15nm diameter particulates, to prepare a wide range of structures. Gold films with a thickness ranging from $\sim 500\text{nm}$ have been produced by electrohydrodynamic atomisation. By using a computer-controlled printing device gold tracks with a minimum width of $\sim 110\mu\text{m}$ have been

Figure 16

Transmission electron micrographs of freeze dried bubbles prepared using the T-junction device. (a) Cross-section through a bubble showing the gold nanoparticles concentrated at the surface. (b) Magnified image of region 'X' in (a) showing gold nanoparticles at the interface, (c) High resolution image of region 'Y' in (b) showing 15nm gold nanoparticles and (d) Energy dispersive X-ray analysis confirming the presence of gold at the bubble surface

deposited on silicon wafer. In order to reduce the track width, templates in conjunction with electrohydrodynamic atomisation have been used to fabricate tracks of $\sim 20\mu\text{m}$. By co-axial electrospinning gold nanoparticles were encapsulated within a polymeric fibre and lastly, a T-junction device was used to produce near-monodisperse gold microbubbles with an average diameter of $150\mu\text{m}$.

Acknowledgements

The authors would like to thank the EPSRC (UK) for supporting this work under platform grants GR/S52636 and EP/E045839; Prof. Luis Liz-Marzan of the University of Vigo, Spain is thanked for the provision of the gold nanoparticle solutions; SRS acknowledges the PhD scholarship awarded by UCL, which enabled this work. The help of the Chemistry and Archaeology Departments of the University College London is acknowledged for technical assistance with the microscopy.

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