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Direct plasma printing of nano-gold from an inorganic precursor

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Plasma printing and plasma-assisted printing of functional nanomaterials are being developed as important alternative fabrication techniques. Nano-gold is used in many applications including organic photovoltaics, flexible electronics, nanomedicine, catalysis and sensing, taking advantage of its unique optical, electrical and physical properties, which depend on particle shape, size and distribution. A direct one-step nano-gold printing process using an HAuCl₄ solution precursor injected into an atmospheric-pressure plasma jet is demonstrated. Atomized droplets of the solution are reduced to gold nanoparticles in the plasma and deposited on the substrate. The gold film has minimal Cl content, and its structure can be controlled by the deposition time, from nanometer-size particles to a dense film that fully covers the substrate. Printing is demonstrated on substrates including silicon, alumina filter membrane, vertical graphene, and paper. The applicability of the nano-gold film as a SERS (surface-enhanced Raman scattering) platform is demonstrated by sensing of a 0.25 and 0.7 amol µm⁻² of Rhodamine B on an Si and paper substrate respectively, a level undetectable in the absence of nano-gold.

Introduction

The unique optical, electrical and physical properties of nanogold have inspired investigation and development of many different processing methodologies in recent decades, leading to an expanded range of applications. In the chemical reduction of metal precursors, solvated electrons are known to play an important role as an efficient and fast reducing agent. Plasmas are an effective source of excess electrons and their effectiveness in enabling the direct reduction of metal ions at a liquid surface has been demonstrated in plasma–liquid electrochemistry and synthesis research. However, the synthesis of metallic nanoparticles by plasma has been done in aqueous electrochemical cells, which cannot be compatible with in-situ deposition or printing. There has been no successful demonstration of a direct nanometal printing process with in-situ reduction of a soluble precursor, probably due to the difficulty of controlling the complex plasma–metal-precursor interaction.

Plasma-enhanced chemical vapor deposition (PECVD) is an attractive approach for plasma printing, since it offers the advantage of accelerated chemical reactions, allowing modification of gas and liquid phase precursors within the plasma. Traditionally PECVD uses low pressures, but atmospheric-pressure plasma sources have been intensively studied in the last two decades and commercialized for deposition of organosilicon barrier coatings from liquid precursors, as well as being actively studied for many plasma polymerization applications. An air plasma jet was used to deposit an antibacterial film of SiOₓ containing silver nanoparticles using HMDSO (hexamethyldisiloxane) and AgNO₃ precursors; the reduction in this case was likely driven by thermal energy. Recently, in-situ reduction of graphene oxide on a paper substrate for flexible electronics applications was reported, demonstrating the ability of plasma chemical reactions to control the reactive gas environment. However, PECVD, in particular at atmospheric pressure, has not been considered to be an ideal choice for metallic layer deposition because of the complexities of plasma–metal-precursor interactions. Hence, post-reduction processes or physical deposition from a colloidal form of nano-metal ink has been viewed as more practical approaches to obtain a conducting film or pattern, thereby dispensing with the potential benefits of direct interaction between plasma and precursor molecules. Recently, Maguire et al. demonstrated in-flight synthesis of gold nanoparticles using fine microfluidic control of the soluble gold precursor HAuCl₄ in the high electron density of an RF (13.56 MHz) plasma. Airborne microdroplets of median diameter 15 µm were generated with an average period of 20 µs using a parallel path atomization nebulizer and introduced
the Au (III) present to Au(0). This delay time increased delays caused by the intermediate metastable species Au (II) and Au(I).15, 16 The high-density solvated electron is known to be highly effective in increasing the analyte sensitivity, detection limit and plasma stability in combination with an infrared-heated spray chamber.11

While Maguire et al. demonstrated that plasma reduction of soluble gold precursors is possible, the precursor injection rate was limited to 10 nmol min⁻¹, and the reduction level to Au was estimated to be as low as 50%. Although the throughput may be suitable for biomedical applications such as drug delivery, it is not sufficient for printing applications, and further a reduction level approaching 100% is preferred.

We have made several fundamental changes to the methods of Maguire et al. to greatly improve throughput and reduction level. Our discharge volume is 100 times larger, and we use a low-frequency AC power source with higher applied voltage, obtaining around 95% reduction with a 25-times greater injection rate. We demonstrate one-step plasma printing of a ligand-free thin gold film using an HAuCl₄ solution as the precursor. A wide range of substrates has been tested, both conducting and non-conducting, and including temperature-sensitive substrates such as paper. Further, the applicability of a nano-gold film as an effective SERS substrate to observe that no Au crystals were formed in an HAuCl₄ solution until the liquid was irradiated with infrared-heated spray chamber.11

Results of XPS analysis of deposited Au film: Au 4f signal (a) at 6 kV and (b) at 5 kV

The direct plasma printing system for nano-gold deposition consists of an atmospheric-pressure plasma jet installed on table top CNC (computer numerical control) machine (High Z – cnstep.de), gas and liquid flow rate control units and high voltage AC power supply as shown in Fig. 1 (a). Fine control of atomized liquid source is critical for this nano-gold deposition process, as in every PECVD application. The combination of a syringe pump (Harvard PHD 2000) and parallel-path pneumatic nebulizer (Burgener Research Inc., X175) provide a stabilized liquid supply. The plasma jet is produced using two parallel ring-shape electrodes surrounding a Pasteur pipet glass tube (soda-lime glass, inner diameter 6 mm, thickness 0.5 mm), as shown in Fig. 1 (b). For the liquid precursor atomization, Ar is supplied through the central gas port and to guide the atomized precursor stream, a supporting He flow is introduced. A Trek 20/20C high-voltage amplifier, fed by a 10 kHz sine wave, was used as the power source. The estimated spatially and temporally averaged electron number density was measured to be in the range of 10¹⁰ cm⁻³ using a charge–voltage Lissajous plot,12,13 as we have previously described.14 The optimized peak voltage was 6 kV when the flow rate of HAuCl₄ precursor was set at 20 µl min⁻¹, and the flow rates of Ar and He were respectively 0.6 – 0.8 lpm and 4 – 5 lpm. Results were also obtained for 5 kV. For the gold precursor, 1% w/v HAuCl₄ ·3H₂O aqueous solution was prepared and further mixed with ethanol (with 2% methanol - Wilmar) in 1:1 volume ratio to enhance atomization. The deposited film for the cases presented here was 2-3 mm depending on the exact diameter of the glass tube used for each different sample. However, by modifying the gas supporting flow and adaptor design, the diameter of the plasma tube, i.e. the size of the plasma printing nozzle can be reduced to less than 1 mm.

Results and discussion

Influence of applied voltage on reduction

In a conventional chemical batch process without reducing agent, reduction of the ionic gold Au(III) in HAuCl₄ solution to metallic gold Au(0), requires process times of hours due to the delays caused by the intermediate metastable species Au(II) and Au(I).15, 16 The high-density solvated electron is known to be one of the most effective reductants to avoid this multistep slow reduction process.17 Park et al. used transmission electron microscopy (TEM) to observe that no Au crystals were formed in an HAuCl₄ solution until the liquid was irradiated with almost half the electron dose required for the reduction of all the Au(III) present to Au(0). This delay time increased

Experimental
quadratically with the liquid volume. This suggests that a fine control of liquid droplets and the availability of a high density electron supply are crucial for maximizing the effectiveness of the metal reduction process.

Our process for direct plasma reduction of the metal precursor has been designed to reflect these two important features, a high density electron supply and well-controlled atomization of the precursor, as illustrated in Fig. 1(c), so that the formation of intermediate ionic gold species is minimized. It is also possible that the high energy metastable species He* (> 20 eV) and Ar* (> 11.5 eV) in the plasma can play an important role in dissociation of the precursor molecule and other reactions, as they do in processes involving organosilicon or metal organic precursors.18,19

In order to investigate the influence of input power and electron number density, a conductive silicon substrate was prepared with a BSA (bovine serum albumin) coating to promote adhesion of the nanogold layer. XPS measurements were performed using a Specs 150 SAGE instrument with an Mg Kα X-ray source with energy 1253.6 eV. As shown in Fig. 2, the deposited Au film has a high degree of reduction into metallic gold with predominant Au⁰ 4f core level peak at 84.1 eV and 87.8 eV and minimal Cl content. In order to optimize the fit, ionic Au³⁺ 4f⁴/₂ and 4f⁷/₂ component were introduced for deconvoluting Au 4f peak. The Au film deposited for 1 min at 6 kV showed a higher contribution from the metallic Au⁰, Au⁰/Au(III) were 94.7\%/5.3\% and 81.4\%/18.6\% for 6 kV and 5 kV, respectively, corresponding to a factor 1.2 increase in total average power density. The estimated average electron number density increased by only 10\%, from 2.0 x 10¹⁰ cm⁻³ to 2.2 x 10¹⁰ cm⁻³ at 5 and 6 kV, respectively. However, the local electric field near the substrate surface will increase by a larger factor, and the net discharge power increased from 2.9 W to 4.6 W. Increased electron density will increase the precursor reduction rate, and increased discharge power will also assist by enhancing droplet evaporation.

Measurements of film thickness on an SiO₂-coated silicon wafer and on glass using a surface profiler (Veeco Dektac 150) showed that the deposition rate for optimum film quality was 27 ± 14 nm min⁻¹. As the flow rate increases, the deposition rate can be increased up to 100 nm min⁻¹, but the uniformity and the level of reduction are degraded.

**Deposited nanogold film on different substrates**

Fig. 3 shows that coatings on different substrates have different surface morphologies and optical properties. The XPS survey scan results shown in Fig. 4 for the given samples in Fig. 3 suggests minimized Cl content in the deposited gold film. In Table 1, the estimated chemical compositions and the reduction rates in the form of Au⁰/Au(III) ratios are provided for the different substrates, (the detailed deconvolution results and Cl 2p spectra are given in the Supplementary Information.) The level of reduction to metallic gold was high in all cases, in the range (88–95\%), as determined by the proportion of the area of the Au⁰ feature as a proportion of in the Au⁴f peak. Further evidence of high reduction level is given by the performance of the gold deposited on paper and on Si in the SERS application; such a strong plasmonic response is only possible from a highly reduced metallic nanoparticle distribution.

Time-resolved imaging of the plasma20 showed that the target substrate strongly influences plasma jet evolution and hence plasma chemistry in the jet. The presence of the surface elongates the plasma plume by local enhancement of the electric field and the surface charge. Conductive substrates lead to higher current density and hence electron density; this can also generate a much higher density of neutral radicals such as O and OH in open-air operation.21 We observed changes in the current density and discharge uniformity depending on the
electric conductivity and also the roughness and porosity of the substrate. Further investigation may be required to understand the influence of the surface and plasma interaction in the presence of a liquid precursor. However, by scanning the plasma jet at different speeds it was possible to control and improve the uniformity and size distribution of nanogold on different substrates. This is important as the size distribution of nanogold has implications in a number of applications, including SERS and catalysis.

The substrate temperature is measured using a thermistor (OPEGG WTS-3A-16) attached to the rear side of the glass substrate to be only 29°C after 5 min. of continual deposition at a fixed position which shows the reduction process is not significantly influenced by thermal energy.

**Performance of nanogold film as a SERS platform**

**Silicon substrate**

To confirm the applicability of the deposited nanogold film for surface molecule sensing, samples were deposited for times of 5 s, 10 s, 20 s, 30 s, 1 min and 2 min on BSA-coated Si substrates. SERS (surface-enhanced Raman spectroscopy) is a highly sensitive technique for molecular detection with an enhancement factor as high as $10^{12}$.$^{23}$ Gold is the most frequent choice of material, particularly in applications related to living organisms, because it offers easy controllability of size and distribution, outstanding stability, and biocompatibility.$^{22}$

The SEM images in Fig. 5 shows that the morphology of the deposited gold film can be controlled by the deposition time. The film thickness and its microstructure vary within the 2 mm diameter of the deposited spot. The SEM images and the Raman measurements shown in Fig. 6 were taken at the region between ½ radius to ¾ radius in order to provide a consistent characterization of each sample. The estimated average diameter of the deposited gold particles was 32 ± 13 nm for 5 s deposition time, corresponding to Fig. 5 (a). As the position of the plasma jet was fixed and the deposition was performed on
a smooth Si substrate, the particles quickly merged to give a non-circular shape that resulted in an overestimate of the diameter. The size distribution of the gold particles can be controlled and improved by scanning of the plasma jet or by using different substrates. SERS measurements were performed using a 10^{-5} M Rhodamine B (RhB) solution in ethanol as a Raman indicator. 5 μl of the diluted RhB was drop cast to cover the whole area of the deposited Au sample and the ethanol was allowed to evaporate, giving an RhB concentration of 0.25 amol μm^{-2}.

The Raman spectroscopy was performed using a Renishaw In Via confocal Raman microscope system with He–Ne laser (633 nm) as the excitation source at an incident power of 1.7 mW. As shown in Fig. 6, the RhB was not detected on the reference silicon substrate or on the thick Au films (deposition time 1 and 2 min) covering the entire Si substrate. However, an enhanced SERS signal was found for the non-continuous Au films with shorter deposition times, with a deposition time of 10 s giving the most-strongly enhanced SERS signal.

**Conclusion**

In summary, direct one-step plasma printing of gold on several substrates was demonstrated using an atmospheric-pressure plasma jet with HAuCl₄ precursor. This PECVD-based technique has the potential to be a more flexible and cost-effective approach than existing plasma processes such as post reduction or printing with nano-Au ink. The deposited gold film has a high proportion of metallic gold, demonstrating strong reduction of the Au(III) precursor. Moreover, the film morphology can be controlled by the deposition time. The applicability as a SERS sensing platform was confirmed by showing that nano-gold deposition on an Si substrate as well as on paper enabled the detection of low levels of RhB molecules. The one-step plasma-printing process is expected to be a versatile tool for applications including those requiring metallic or non-metallic films in complex patterns; printing of composite multifunctional materials will also be readily achievable by simply mixing different soluble precursors.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

1. C. Richards and R. M. Sankaran, Appl Phys Lett, 2008, 93, 131501.
2. R. Hawtof, S. Ghosh, E. Guart, C. Xu, S. Mohan and J. N. Renner, Science Advances, 2019, 5, eaat5778.
3. H. B. Zhang, L. J. Sang, Z. D. Wang, Z. W. Liu, L. Z. Yang and Q. Chen, Plasma Sci Technol, 2018, 20, 063001.
4. S. Simovic, D. Loic and K. Vasilev, Chem Commun, 2010, 46, 1317-1319.
5. O. Beier, A. Pfuch, K. Horn, J. Weisser, M. Schnabelrauch and A. Schimanski, Plasma Process Polym, 2013, 10, 77-87.
6. A. Dey, S. Krishnamurthy, J. Bowen, D. Nordlund, M. Meyyappan and R. P. Gandhiraman, Acs Nano, 2018, 12, 5473.
7. S. W. Lee, D. Liang, X. A. F. Gao and R. M. Sankaran, Adv Funct Mater, 2011, 21, 2155.
8. T. J. Wu, C. Y. Chou, C. M. Hsu, C. C. Hsu, I. Z. Chen and I. C. Cheng, Rsc Adv, 2015, 5, 99654.
9. N. D. Connor, R. P. Gandhiraman, C. Doyle, B. James, D. E. Williams and S. Daniels, J Mater Chem, 2012, 22, 9485.
10. P. Maguire, D. Rutherford, M. Macias-Montero, C. Mahony, C. Kelsey, M. Tweedie, F. Perez-Martin, H. McGauid, D. Diver and D. Mariottit, Nano Lett, 2017, 17, 1336.
11. Y. Makonnen, J. Burgener and D. Beauchemin, J Anal Atom Spectrom, 2015, 30, 214.
12. H. E. Wagner, R. Brandenburg, K. V. Kozlov, A. Sonnenfeld, P. Michel and J. F. Behnkis, Vacuum, 2003, 71, 417.
13. J. H. Kim, Y. H. Choi and Y. S. Hwang, Phys Plasmas, 2006, 13, 093501.
14. J. M. Hong, M. Aramesh, O. Shimoni, D. H. Seo, S. Yick, A. Greig, C. Charles, S. Prawer and A. B. Murphy, Plasma Chem Plasma P, 2016, 36, 917-940.
15. E. Gachard, H. Remita, J. Khatouri, B. Keita, L. Nadjo and J. Belloni, Phys Plasmas, 2006, 13, 093501.
16. Y. Fong, B. R. Visser, J. R. Gascooke, B. C. C. Cowie, L. Thomsen, G. F. Metha, M. A. Buntine and H. H. Harris, Langmuir, 2015, 31, 2247.
17. J. H. Park, N. M. Schneider, J. M. Grogan, M. C. Reuter, H. H. Bau, S. Kodambaka and F. M. Ross, Nano Lett, 2015, 15, 5314.
18. W. Kulisch, Surf Coat Tech, 1993, 59, 193-201.
19. H. Rauscher, Massimo Perucua, and Guy Buyle, Plasma Technology for Hyperfunctional Surfaces, WILEY-VCH Verlag GmbH & Co, Weinheim, Germany, 2010.
20. O. Guaitella and A. Sobota, J Phys D Appl Phys, 2015, 48.
21. Y. F. Yue, X. K. Pei, D. Gidon, F. Wu, S. Q. Wu and X. P. Lu, Plasma Sources Sci 7, 2018, 27, 064001.
22. Y. Q. Wang, B. Yan and L. X. Chen, Chem Rev, 2013, 113, 1391.
23. L. Perez-Mayen, J. Oliva, A. Torres-Castro and E. De la Rosa, Nanoscale, 2015, 7, 10249.