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In situ synthesis of Au-shelled Ag nanoparticles on PDMS for flexible, long-life, and broad spectrum-sensitive SERS substrates

B. Fortuni,* T. Inose,* S. Uezono, S. Toyouchi, K. Umemoto, S. Sekine, Y. Fujita, M. Ricci, G. Lu, A. Masuhara, J. A. Hutchison, L. Latterini and H. Uji-i

A simple and fast one-step fabrication method of silver nanoparticles (AgNPs) on a polydimethylsiloxane (PDMS) film and their improvement as highly sensitive surface enhanced Raman scattering (SERS) substrates via thin Au atomic coatings are demonstrated.

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First (given) name(s)	Last (family) name(s)	ResearcherID	ORCID
B.	Fortuni		

T.	Inose		0000-0003-2757-8817
S.	Uezono		
S.	Toyouchi		
K.	Umemoto		
S.	Sekine		
Y.	Fujita		0000-0003-1302-1436
M.	Ricci		
G.	Lu		0000-0003-1722-0176
A.	Masuhara		
J. A.	Hutchison		0000-0002-0595-9961
L.	Latterini	H-1925-2012	0000-0002-1021-9423
H.	Uji-i		0000-0002-0463-9659

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B. Fortuni,^{‡,*a} T. Inose,^{§*b} S. Uezono,^b S. Toyouchi,^a K. Umemoto,^c S. Sekine,^c
Y. Fujita,^{¶ad} M. Ricci,^a G. Lu,^{ae} A. Masuhara,^c J. A. Hutchison,^f L. Latterini^{ibg} and
H. Uji-i^{idab}

A simple and fast one-step fabrication method of silver nanoparticles (AgNPs) on a polydimethylsiloxane (PDMS) film and their improvement as highly sensitive surface enhanced Raman scattering (SERS) substrates via thin Au atomic coatings are demonstrated. The thin Au layer provides oxidation resistivity while maintaining the broad spectral range SERS sensitivity of Ag nanoparticles.

Surface-enhanced Raman scattering (SERS) is an attractive spectroscopic tool used for many applications such as (bio-)chemical sensing and environmental monitoring, offering highly sensitive, non-destructive, and reliable molecular fingerprinting.^{1–6} The enormous (as much as 10¹²) amplification of Raman signals of analyte molecules in SERS relies on the enhancement of local excitation and scattering electromagnetic (EM) fields near noble metal nanostructures, resulting from excitation of their localized surface plasmon resonances (LSPRs).⁷ The properties of the LSPRs, in particular their resonance frequency, linewidth, and mode volume strongly depend on the metal employed and the size and shape of the nanostructures as well as on their aggregation. Large EM enhancements can be realized at nano-gap regions between adjacent metal nanostructures^{2,8} and/or at sharp facets of a nanostructure.^{6,9} In order to increase the performance of SERS

substrates, various methods including photo/e-beam lithography,^{8,10,11} shape-controlled syntheses,¹² and assembly of NPs¹³ have been reported.¹⁴ For such fabrication, solid supports, such as silicon wafers and glass slides, are commonly used for the deposition of metal nanostructures although their rigid and brittle properties can limit their application potential.

The polydimethylsiloxane (PDMS) elastomer has recently attracted much attention as a support material for SERS substrates,^{15–19} not least due to its high optical transparency, stability, uniformity, and cost-effective and easy preparation. An outstanding quality of PDMS substrates in terms of high-performance SERS detection however is its ability to conformally contact curved and rough surfaces. This brings the nanoparticle surface, where the highest SERS enhancement occurs, as close as possible to the analyte of interest as was demonstrated recently for pesticide detection on fruits.¹⁸ Despite these unique properties, the preparation of PDMS-based SERS substrates, or more generally of solid-supported substrates, normally requires multiple steps, namely, wet-chemical synthesis of metal NPs, surface preparation *via* silane coupling, and deposition of NPs, each of which can drastically affect fabrication reproducibility. In order to overcome this issue, we have recently developed one-step *in situ* synthetic methods to grow Au nanostars (AuNSs) directly on PDMS films and performed high-reproducibility and high-sensitivity SERS spectroscopy.¹⁹

Even with optimal materials, compromises must be made in the choice of metal nanoparticles to employ. While gold nanoparticles are highly resistant to oxidation, broad absorption by inter-band transitions begins to damp LSPRs below 600 nm. Near-IR LSPRs and near-IR excitation sources are preferred with practical consequences for nanomaterials, optical components and safe use. Silver on the other hand can support LSPRs right across the visible spectrum;²⁰ however their low resistance to oxidation is a drawback to long-life substrates.²¹ These practical compromises are clear for instance during SERS-based local pH-sensing studies monitoring the carboxylic and carboxylate stretches of 4-mercaptobenzoic acid (4-MBA).^{22–25} Studies using gold nanoparticles employed nanoshells with LSPRs resonant with 785 nm

^a Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200G-F, 3001 Heverlee, Belgium.
E-mail: Betrice.Fortuni@kuleuven.be

^b RIES, Hokkaido University, N20W10, Kita-Waird Sapporo, 001-0020, Japan.
E-mail: Inose@es.hokudai.ac.jp

^c Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, 992-8510, Japan

^d Toray Research Center, Inc., 3-3-7, Sonoyama, Otsu, Shiga 520-8567, Japan

^e Institute of Advanced Materials & Key Laboratory of Flexible Electronics, National Jiangsu Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, P. R. China

^f School of Chemistry and Bio21 Institute, University of Melbourne, Victoria 3010, Australia

^g Department of Chemistry, Biology and Biotechnology, University of Perugia, via Elce di sotto 8, Perugia, Italy

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‡ These authors contributed equally to this work.

excitation,²³ while studies with silver nanoparticles (including here) prefer LSPRs resonant with visible excitation.^{22,24,25} Of course, the ideal SERS nanoparticle substrate would combine the low loss (low imaginary component of dielectric function) of silver across the visible wavelength range with the stability to oxidation of gold nanoparticles, and be able to conformally contact surfaces of interest.

In this contribution, we propose a simple chemical route to obtain a film of mono-disperse AgNPs covered with Au shells on a flexible PDMS substrate, providing oxidation-resistance and SERS sensitivity under visible excitation. To this end, we first develop an *in situ* synthesis of morphologically controlled AgNPs on a PDMS surface, followed by coating with a thin shell of Au by the gentle replacement of surface Ag atoms with Au atoms from the solution. The resulting thinly Au-coated AgNP PDMS substrates show remarkable oxidation resistance with SERS activity being retained for weeks. First and foremost, we find that the Au-coated AgNP PDMS substrates remain functional for SERS studies with 532 nm excitation, performing pH sensing using 4-MBA. This combination of desirable properties is attributed to the ultra-thin nature of the Au shell such that the dielectric properties of the hybrid particles are still dominated by silver, with the oxygen resistance of Au right at the surface.

The *in situ* growth of AgNP on a PDMS film and Au coating are schematically depicted in Fig. 1a. Thin films of PDMS elastomers were prepared by pouring a mixture of Sylgard[®] 184 silicone elastomers and a curing agent (w/w = 10:1) on a polystyrene container and leaving it overnight at room temperature. After the polymerization, a piece of PDMS was peeled off from the container

and the side facing polystyrene was used for further reactions. AgNPs were synthesized *in situ* on PDMS by applying 40 μ L of ascorbic acid (AA) (25 mM), 40 μ L of sodium citrate (Cit) (25 mM), and then 40 μ L of silver nitrate (AgNO_3) (25 mM) on the PDMS surface, sequentially. Immediately after that, the solution was mixed by gentle pipetting. During the pipetting, the colour of the solution gradually changed from transparent to pale blue, and finally turned to dark blue after a few minutes. After 5 minutes of incubation, the film was rinsed with Milli-Q water and dried with N_2 gas. Fig. 1b displays a typical SEM image of the obtained monodisperse AgNPs on PDMS, where nanoparticle sizes of several hundreds of nm are found. The obtained AgNPs show a flower-like morphology with small protrusions on their surfaces.

The presence of Cit seems to be important to obtain small NPs with less aggregation. Using a combination of AgNO_3 and AA without Cit, only large AgNPs ($> 1 \mu\text{m}$) are produced (see ESI[†], Fig. S1). This indicates that NP growth and aggregation are regulated by Cit. Cit can form $\text{Ag}_x\text{-Cit}$ complexes due to its strong chelating ability through the carboxyl group. As reported previously, this strong chelating action leads to isotropic growth of the crystal nucleus, contributing to the many protrusions visible on the particle surface. Similar morphologies of AgNPs have been fabricated *via* liquid phase reduction.²⁶ The phase of the AgNPs was characterized to be the (111) and (200) planes of the face-centered-cubic phase by electron diffraction (ED) (Fig. S2, ESI[†]).

As a next step, the AgNP PDMS film was subjected to Au coating. First, as-synthesized AgNP PDMS films were immersed in 0.25 attomolar (aM) HAuCl_4 aqueous solution for 1 h. It is worth mentioning that the AgNP film was not dried before the coating, otherwise Au deposition was insufficient and heterogeneous due to fast oxidation of AgNPs in air. However, the contact of the AgNP-substrate with an aqueous solution containing only HAuCl_4 resulted in a remarkable morphology loss of the flower-like AgNPs, as can be seen in Fig. 1c, where highly aggregated NPs were observed. As reported by other groups, a simultaneous replacement of Ag atoms by Au atoms occurs rapidly and forms Ag-Au alloys in galvanic replacement reactions,²⁷ resulting in an evident morphological change.

To suppress this instantaneous galvanic replacement, the AgNP PDMS film was instead immersed in 2 mL of 0.25 aM HAuCl_4 aqueous solution containing 50 mM ascorbic acid (AA) and 125 mM NaOH for 1 h. It has been reported that the rate of the galvanic reaction can be controlled by a fast parallel reduction of HAuCl_4 and Ag^+ by AA, thus suppressing the galvanic replacement.²⁸ After this reaction we found that the NPs still maintained their flower-like morphology (Fig. 1d). Note that pH is also crucial for this reaction; pH > 10 is required in order to maintain a high parallel reducing power of AA.²⁹ Otherwise, the galvanic replacement becomes dominant and the resulting NPs show a similar morphology to those in Fig. 1c. Furthermore, to ensure the presence of the Au coating, the Au-treated AgNP PDMS film was treated with 2% H_2O_2 aq. If the AgNPs are not coated with Au, they are rapidly oxidized and delaminate from the PDMS surface, as demonstrated for AgNP PDMS films in the ESI[†] (Fig. S3). For the Au-treated AgNP PDMS film however, as shown in the inset of Fig. 1e, most NPs remained on the surface. SEM images

Fig. 1 Schematic illustration of *in situ* growth of AgNPs@Au-shell on PDMS (a). SEM images of AgNPs (b), prepared without ascorbic acid (c), AgNP@Au-shell (d), and AgNP@Au-shell treated with H_2O_2 (e). The inset images show photographs of PDMS films after the synthesis for each process.

1 reveal that the density of NPs does not drastically change and the
 2 flower-like morphology remains even after 3 hours of H_2O_2 treat-
 3 ment (Fig. 1e). The Au shell formation was further confirmed by
 4 energy-disperse X-ray spectroscopy (EDS) (Fig. S4a and b, ESI†). We
 5 successfully detected Au signals on the Au-coated AgNPs (referred
 6 to as AgNP@Au-shell_ H_2O_2) (Fig. S4b, ESI†). Elemental mapping
 7 on AgNP@Au-shell_ H_2O_2 reveals the Au shells together with Ag
 8 remaining inside the nanoparticles (Fig. S4c and d, ESI†). Typical
 9 TEM images of flower-like AgNPs and AgNP@Au-shell_ H_2O_2 are
 10 shown in Fig. S5 (ESI†). The edges of AgNP@Au-shell_ H_2O_2 appear
 11 to be more rounded in shape compared to those of AgNPs. From
 12 these results we conclude that AgNPs are successfully coated with
 13 thin Au layers.

14 The optical properties of these NPs were investigated using
 15 dark-field (DF) spectroscopy. The DF spectra are very broad
 16 because of the large size and aggregation of NPs. Nevertheless,
 17 the highest scattering was observed around 680 nm on AgNPs
 18 (Fig. S6 and S9a, ESI†). After coating with the Au shell, two
 19 major peaks were observed at around 640 and 760 nm (Fig. S7
 20 and S9b, ESI†). The peak around 640 nm disappeared after the
 21 treatment with H_2O_2 (Fig. S8 and S9c, ESI†), indicating the
 22 AgNPs without Au-shells are removed by H_2O_2 . These spectral
 23 changes confirm Au shell deposition on most of the AgNPs, but
 24 overall the optical response is not strongly affected.

25 The SERS activity and lifetime of our flower-like AgNPs on
 26 PDMS before and after Au coating were investigated using 4-
 27 mercaptobenzoic acid (4-MBA) as a Raman reporter at 532 nm
 28 excitation (see the experimental details and SERS spectra excited at
 29 785 nm in the ESI†). Fig. 2a and c show the SERS spectra of freshly
 30 prepared AgNPs and AgNPs@Au-shell_ H_2O_2 , both functionalised

with 4-MBA. A 532 nm laser was used as the excitation source. The
 two SERS substrates showed two specific peaks at 1100 and 1590
 cm^{-1} , which are both attributed to the $\nu(\text{C}-\text{C})$ benzene ring
 breathing mode.^{25,30} A SERS map of the AgNPs, shown in
 Fig. 2b, revealed a relatively homogeneous signal intensity over a
 large scanned area ($10 \times 10 \mu\text{m}^2$), resulting from the high density
 of NPs on the surface. On the other hand, a map of the AgNP-
 s@Au-shell_ H_2O_2 film also reveals a homogeneous enhancement
 of signal intensity in most of the film region (Fig. 2d). The SERS
 enhancement factor (EF) was estimated to be 1.19×10^5 and 1.07
 $\times 10^5$ for AgNPs and Au-shell AgNPs, respectively, by following
 other studies (see the detail in the ESI† Fig. S12).^{31–33}

In order to investigate the lifetime of the SERS substrate, in
 particular the oxidation resistance, both samples were left in air for
 one week and then subjected to the SERS measurement. A huge
 background was observed on AgNPs (Fig. 2e), while no significant
 change in SERS spectra was observed on AgNP@Au-shell_ H_2O_2
 (Fig. 2g). The low quality spectrum obtained from the aged AgNPs
 PDMS film is most likely due to oxidation of the AgNPs. The aging
 is clearly seen also in the SERS mapping of AgNP substrates, where
 SERS enhancements become heterogeneous (Fig. 2f), indicating
 that some of the AgNPs have lost SERS activity. In contrast, the
 thin Au shell seems to prevent the oxidation of AgNPs giving a
 long-lived stable SERS substrate as expected (Fig. 2h). The Au shell
 thickness plays an important role in the increased resistance, for
 instance an Au shell formed with an Au^{3+} concentration below 0.25
 aM is not consistent enough to protect AgNPs from oxidations.
 Note that the oxidation resistance observed here by forming an Au
 shell coating on AgNPs has been reported by others.²⁸

Most importantly, the fingerprint region stretches of the
 carboxylic group of 4-MBA are clearly detected in the SERS
 spectra both on AgNPs and AgNP@Au-shell_ H_2O_2 . The broad
 band around 1360 cm^{-1} is attributed to the carboxylate stretch-
 ing mode ($\nu_s(\text{COO}^-)$), which has been used for SERS-based local
 pH sensing.^{22–25} This peak could hardly be detected on AuNPs
 treated with the same concentration of 4-MBA in our previous
 study with 633 nm excitation,¹⁹ but is possible to measure
 using 785 nm excitation,²³ a wavelength region where gold
 becomes much less lossy.²⁰ This suggests that the Au-shell
 thickness on our sample is thin enough that AgNP@Au mostly
 retains the dielectric properties of bare AgNPs, allowing SERS
 sensitivity for visible excitation wavelengths.

Finally, we demonstrate the potential of our AgNP@Au-
 shell_ H_2O_2 substrate for pH-sensing applications for visible exci-
 tation wavelengths (Fig. 3). In this study, SERS of 4-MBA on
 Ag@AuNPs_ H_2O_2 was measured in buffers at various pH values
 ranging from 3.9 to 12. As seen in Fig. 3, at higher pH conditions
 (pH 7.4–12), the intensity of the $\nu_s(\text{COO}^-)$ band clearly increased
 at 1420 cm^{-1} and a weak band corresponding to $\delta(\text{COO}^-)$ also
 appeared at 844 cm^{-1} . The broad band of $\nu_s(\text{COO}^-)$ is thought to
 include contributions from both surface-bound COO^- groups
 around $1370\text{--}1380 \text{ cm}^{-1}$ and non-bonded COO^- groups of the
 more vertically oriented 4-MBA molecules at higher wavenumbers
 around 1420 cm^{-1} .³⁴ At lower pH conditions (pH 3.9–6.3), a new
 band around 1710 cm^{-1} corresponding to the $\text{C}=\text{O}$ stretching
 mode and a band corresponding to the $\text{C}-\text{O}$ stretching mode at

Fig. 2 4-MBA SERS spectra and mapping images measured on fresh and one week-old samples; freshly-prepared AgNPs (a and b) and AgNP@Au-shell_ H_2O_2 (c and d), and one week-old AgNPs (e and f) and AgNP@Au-shell_ H_2O_2 (g and h). The peak at 1590 cm^{-1} was used for the mapping. Mapping size: $10 \times 10 \mu\text{m}^2$, λ_{ex} : 532 nm, exposure time: 1 s.

Fig. 3 SERS spectra measured on 4-MBA-functionalized AgNP@Au-shell_H₂O₂ at various pH values ranging from pH 3.9 to pH 12. All spectra were normalized at the maximum intensity (at 1590 cm⁻¹) for easier comparison.

1318 cm⁻¹ were enhanced, suggesting the existence of neutral carboxylic acid groups. These results clearly indicate that our long-lived Ag@AuNPs_H₂O₂ on PDMS substrates function as pH sensors over a large pH range. The Au shell thickness also seems crucial for the chemical sensitivity in this experimental configuration. Increasing the concentration of Au ions in the coating solutions from 0.25 aM to 0.25 fM, and thus increasing the shell thickness, causes the peak intensity at 1590 cm⁻¹ to decrease (Fig. S14, ESI†).

In conclusion, a new fabrication method for AgNPs on flexible PDMS elastomers and their coating with a thin Au shell have been developed. SERS activity was confirmed both on AgNPs and AgNPs coated with an Au-shell, using 4-MBA as a Raman reporter. The Au-shell coating increases the oxidation resistance of AgNPs, leading to long-lived SERS substrates, which are sensitive for visible excitation. The substrates were successfully applied for pH sensing based on Raman peak shifts of 4-MBA under acidic and basic conditions. Nanoparticles which simultaneously show optical responses close to silver and oxidation resistivity could be of wide utility in bio-applications. More specifically, they might prevent the deleterious effects of the many reactive oxygen species (ROS) existing in cells that would otherwise oxidize the AgNPs, releasing Ag ions into the cell, and resulting in serious cytotoxicity.

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Conflicts of interest

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