Results in Materials 8 (2020) 100139

Contents lists available at ScienceDirect

Results in Materials

journal homepage: www.journals.elsevier.com/results-in-materials

Highly reproducible, large scale inkjet-printed Ag nanoparticles-ink SERS substrate

Samir Kumar [a,*], Kyoko Namura [a], Daisuke Kumaki [b], Shizuo Tokito [b], Motofumi Suzuki [a]

[a] Department of Micro Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto, 615-8540, Japan
[b] Research Center for Organic Electronics, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata, 992–8510, Japan

ARTICLE INFO

Keywords:
Surface-enhanced Raman scattering
Ag nanoparticle
Inkjet printing

ABSTRACT

We report the fabrication of a low-cost, and highly reproducible large scale surface-enhanced Raman spectroscopy (SERS) substrate using an inkjet-printed Ag nanoparticle-ink (AgNI). The AgNI SERS substrates were evaluated for SERS using *trans*-1,2-bis(4-pyridyl)ethylene (BPY) as a molecular probe. AgNI substrates significantly enhanced the SERS signals with the limit of detection of 1.8×10^{-7} g/mL for BPY. The printed AgNI dot arrays exhibit an excellent SERS performance and reproducibility. The batch-to-batch and spot-to-spot standard deviation value of less than 10% was obtained. The results reveal the reproducibility of the AgNI SERS dot arrays and its potential application for SERS substrates.

1. Introduction

Surface-enhanced Raman scattering (SERS) is the enormous enhancement of the Raman signal of the scattering molecules adsorbed onto metal surfaces under certain conditions [1,2]. The localized surface plasmon resonances (LSPR) of the metal nanoparticles of the substrate is predominantly responsible for the amplification of the local electromagnetic fields that allow for the detection of analytes at exceptionally low concentrations, even at a single molecular level [3–5]. An ideal SERS substrate should be able to generate an intense, reproducible, and uniform SERS signal [6–8]. It should also be inexpensive and easy to fabricate on a large scale [9].

There are various studies on the large-scale fabrication of SERS substrates fabricated by different methods [10]. These methods include electrochemical [11], lithography [12], dyeing [13], electrospinning [14], inkjet printing [15], and screen printing [16]. Presently, all the methods described above for SERS substrates are often complicated and laborious. Wu et al. fabricated SERS substrates utilizing screen printing Ag nanoparticles on a plastic PET (Polyethylene terephthalate) substrates [16]. Miccichè et al. fabricated inkjet printed customizable platform on glass substrate to control the surface concentration of analyte molecules and the number and position of hot spots [17]. Yang et al. fabricated a highly reproducible SERS-active spot array by inkjet printing-assisted self-assembly of the monodispersed AuNPs [18]. Yu et al. fabricated a SERS substrate on paper by inkjet printing [15]. With most of the fabrication method, the standard deviation (SD) value of the SERS signal is between 10 and 20%. The poor reproducibility of the SERS substrate is one of the major challenges for the development of SERS sensing technology.

Inkjet printing is suitable for the large-area fabrication of SERS substrates where patterns can be formed in a single step. It is a simple fabrication process in which the ink is used for the printing of plasmonic patterns.

Therefore, many efforts have been devoted to developing highly reproducible SERS substrates [19]. Herein, we report a large-scale fabrication method of flexible, and highly reproducible Ag nanoparticle-ink (AgNI) SERS dot arrays substrates by employing an inkjet-printing method. The printed AgNI dot arrays exhibit an excellent SERS performance and reproducibility. A batch-to-batch and spot-to-spot SD value of less than 10% has been obtained. The results demonstrate the reproducibility of the AgNI SERS dot arrays and its potential application in the field of trace detection.

2. Experimental details

2.1. Fabrication of Ag nano ink printed SERS substrates

Ag nanoparticles (AgNPs) were synthesized using oxalate-bridged silver amine complexes [20,21]. In this synthetic mechanism, the oxalate ligand ($C_2O_4^{2-}$) acts as a two-electron reducing agent. Without using

* Corresponding author.
E-mail address: drsamirkumar2017@gmail.com (S. Kumar).

https://doi.org/10.1016/j.rinma.2020.100139
Received in revised form 23 July 2020; Accepted 15 August 2020
Available online 3 September 2020

any additional synthetic organic solvents and reducing agents, the precursor complex can be directly transformed into oleylamine-stabilized Ag nanoparticles. The typical Ag particle sizes were 10–15 nm (d50). The AgNPs were dissolved in the mixture solvent of dodecane and 1-nonanol with 35 wt%. The prepared AgNI was patterned by an inkjet printer (Fujifilm:DMP-2831) on polyethylene naphthalate (PEN) film with a 125 μm thickness. The jetting condition of AgNI was optimized by controlling a waveform of the applied voltage in the cartridge. The AgNI droplets were deposited with a dot-to-dot spacing of 60 mm. The Ag dot patterns of 5 mm diameter were formed on the PEN film. After inkjet pattering, the PEN film was baked on the hotplate for 30 min at 150 °C. The AgNPs are fused with each other by the sintering process, and then, conductive passes are formed in Ag layer. The thickness of the Ag layer was about 100 nm.

2.2. Optical and SERS measurements

The optical property of the AgNI dot arrays substrates was investigated using UV–Vis reflectance measurements. The reflectance spectra were collected using an Ocean Optics (USB4000) spectrometer. LambdaVision (RAM200) Raman spectrometer was used for the collection of SERS spectra. trans-1,2-bis(4-pyridyl) ethylene (BPY, 99.9+%, Sigma) was used as the molecular probe for the SERS study. A 785 nm laser with a 50 × objective and 15 mW power on the sample was used for the excitation with a spectral acquisition time of 1 s. The SERS measurements were performed at seven random spots on the substrate. All the measurements were performed at room temperature. A 10 μL droplet of BPY solution was released onto the AgNI substrates and allowed to dry prior to data acquisition.

2.3. Surface morphology

A scanning electron microscope (SEM; Hitachi High Tech. SU3800) with a LaB_6 detector in the secondary electron mode operating at an acceleration voltage of 10 kV was used to conduct surface morphology analysis of the baked and unbaked samples.

3. Results and discussion

3.1. Morphology of AgNI dot arrays

Fig. 1(d) shows the photograph of the printed unbaked and baked AgNI dot arrays on the PEN substrate. The AgNPs stick firmly to the PEN substrate and form a uniform Ag layer. The SEM micrographs of the baked and unbaked AgNI dot arrays are shown in Fig. 1. Fig. 1(a) and (b) indicate that for unbaked AgNI, most of the AgNPs were quasi-spherical with a mean diameter of 20 ± 5 nm. The unbaked AgNI samples were uniformly distributed. Whereas after baking the AgNPs coalesce with the formation of percolation holes. The uniform surface coverage is a crucial factor that determines the spot-spot SERS uniformity.

3.2. Optical and SERS characterization

The UV–Vis reflectance spectroscopy showed a reflectance minima at around 420 nm, which is due to LSPR of AgNPs. The unbaked AgNI sample showed higher absorption around the LSPR wavelength and lower reflectance at long wavelengths suggesting a better LSPR performance. The overall reflectance of the AgNI increases after the baking process, and that may be because of the more uniform distribution of the Ag. The SERS spectrum of the AgNI substrates was taken by dropping 10 μL of 10^{-4} aqueous solution of BPY on the substrate. The SERS spectra of the bare PEN substrate, BPY on baked and unbaked AgNI samples are shown in Fig. 2(b). The PEN substrate shows sharp peaks at around 780, 1222, 1390, 1480, 1635, and 1719 cm^{-1}. Upon printing of the AgNI dot arrays, the background peaks of the PEN substrate are suppressed, and the characteristic BPY peaks can be observed. The SERS spectra of BPY has four main bands at around 1013, 1228, 1294, and 1610 cm^{-1} that are associated to the pyridine ring breathing, ring deformation, the C = C in-plane ring mode, and the C = C stretching mode, respectively [22,23]. The unbaked AgNI sample showed a better SERS response as compared to

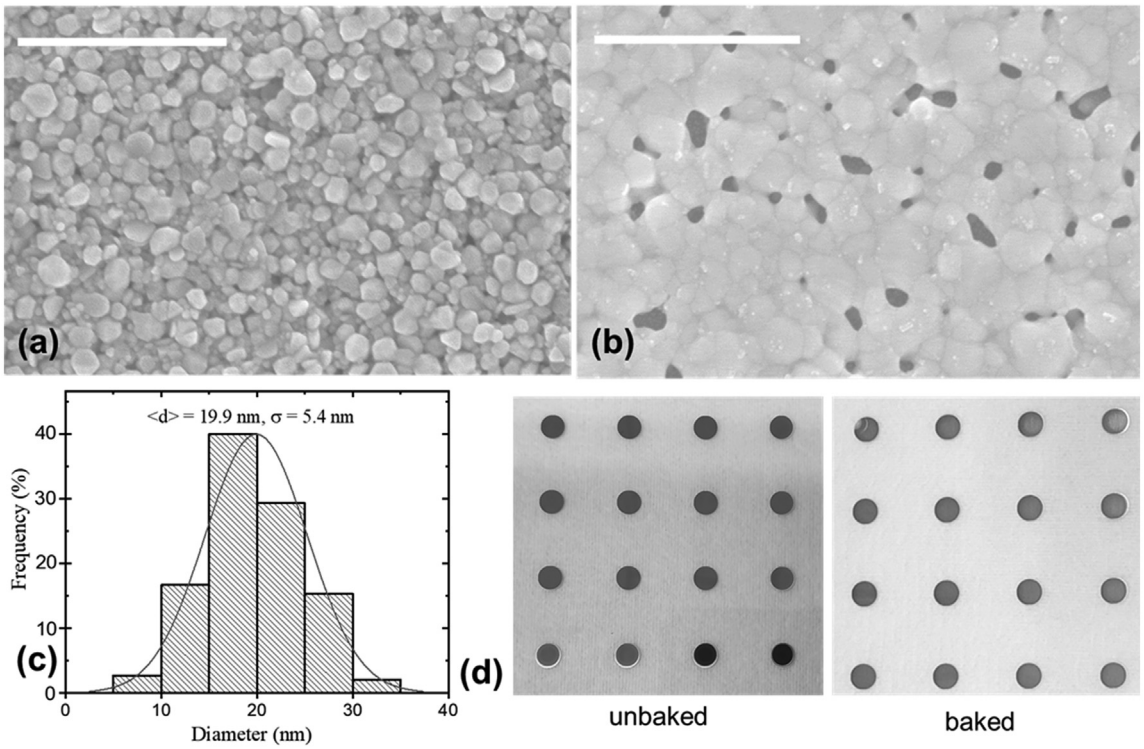

Fig. 1. SEM micrographs of (a) unbaked, and; (b) baked AgNI dot arrays samples. Scale bar equals to 500 nm; (c) particle size distribution on unbaked AgNI sample. <d> denotes the mean diameter, and σ is the standard deviation.; (d) A photograph of unbaked and baked AgNI samples.

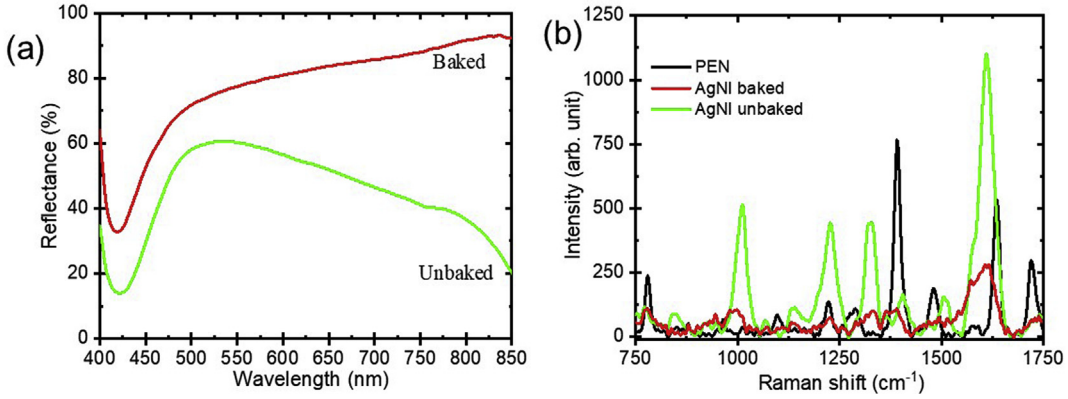

Fig. 2. (a) UV–Vis reflectance spectra for baked and unbaked AgNI samples. Aa reflectance minimum at around 420 nm, which is due to LSPR of the Ag nanoparticles; (b) Raman spectrum of the bare PEN substrate and SERS spectra of BPY on unbaked and baked AgNI dot arrays.

that of the baked AgNI. We were able to detect BPY down to a concentration of 1.8×10^{-7} g/mL on the unbaked AgNI dot arrays showing a good sensing capability of the unbaked AgNI sample.

The better SERS response of the unbaked AgNI is because AgNPs had a quasi-spherical shape with a high degree of uniformity. The SERS intensity of the Raman probe depends on the size and shape of the nanoparticles on which they are adsorbed [24]. The uniform quasi-spherical AgNPs may enhance the SERS signal not only due to the LSPR. They may also produce unusually large electromagnetic enhancement around the sharp edges, referred to as a lightning rod effect [25]. The electric field that is generated at the sharp edges would be much higher than other parts of the nanoparticles. The plasmonic coupling of the LSPR between two AgNPs with a separation of less than 50 nm may also further enhance the SERS intensity [26].

3.3. Reproducibility of AgNI SERS substrates

Batch-batch and spot-spot uniformity on the same sample are critical concerns for large scale SERS substrates fabrication. A common barrier to quantitative detection for the SERS substrates is spot-to-spot reproducibility of the signal [27]. The intensity peak at 1610 cm^{-1} for 10^{-4} M BPY solution was used to measure the batch-batch and spot-spot SERS signal reproducibility, Fig. 3. Batch-batch variation of the SERS signal was very low, with a standard deviation of less than 10%. The standard deviation of the SERS measurements at different positions on the sample was also around 6%. This shows a good reproducibility of our printed AgNI SERS samples.

The factors that influence the Raman signal intensity are 1) the electric field at the substrate; 2) the number density of molecules and the differential Raman cross-section per molecule; 3) the optical system conditions. In our experiment, the same system was utilized for the collection of Raman spectra, and also the concentration and type of analyte on the SERS substrate was the same for all the measurements. So the only factor that will influence the SERS intensity is the uniformity of the electric field on the substrate and the adequate number of molecules in the hot-spot regions.

The size, aggregation, and distribution of nanoparticles may lead to a significant difference in SERS intensity, therefore making it challenging to obtain a good reproducibility. Our synthesis method of silver nanoparticles can precisely control the introduction of surfactants that coat the silver nanoparticles. By using our synthesis method, it is possible to realize the wettability, viscosity, and drying characteristics of AgNI suitable for the inkjet printer. Therefore, it is possible to form AgNP patterns that have exceptionally smooth and high shape uniformity without bleeding. Although the geometry of nanoparticles is much better from the SEM images, the size and shape may still have some variations to some degree. These small variations can bring a notable difference in the SERS intensity and consequently lead to poor reproducibility. The eccentricityε uniquely characterizes the deviation from a circular shape. Theε of the AgNPs was calculated to analyze the uniformity of the nanoparticles as

$$\varepsilon = \frac{r_{max} - r_{min}}{r_{max} + r_{min}} \tag{1}$$

where r_{max} and r_{min} are the maximum and minimum radii of the AgNPs. The ε was found to be approximately 0.05 ± 0.03, indicating that for

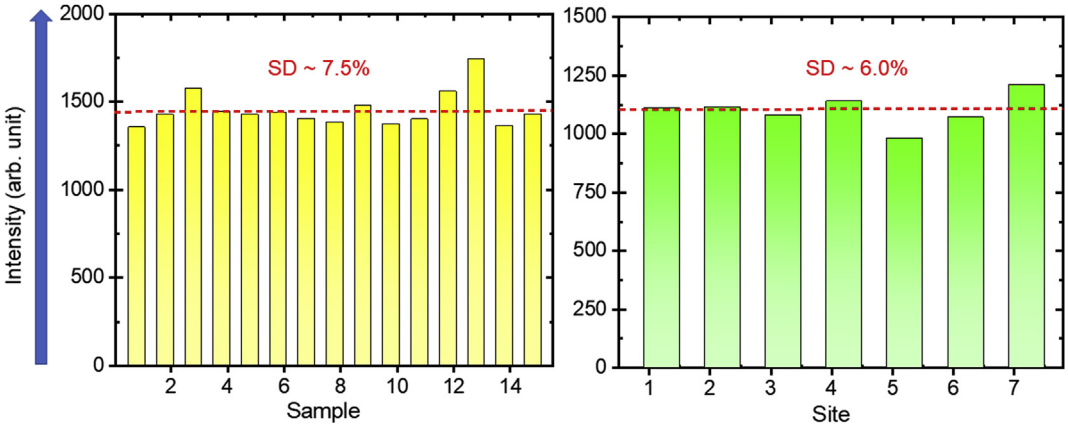

Fig. 3. (a) Batch-to-batch variation of the peak around 1610 cm^{-1} peak; (b) spot-to-spot variation and the standard deviation of the SERS measurements at different positions on the AgNI sample.

unbaked AgNI, most of the AgNPs were uniform quasi-spherical in shape. The aggregation and distribution of nanoparticles determine the resonance condition and the variation in the electric field. Since AgNPs of about 20 nm is dispersed uniformly without aggregation, a dense silver thin film can be formed by inkjet printing. Furthermore, the laser spot used for Raman spectroscopy in this study was 8 μm^2 as obtained from the wavelength and numerical aperture of the objective lens for an ideal focusing. A large number of AgNPs and, thus, hot spots may contribute greatly to the high reproducibility of SERS arrays because the laser spot covered several hundred nanoparticles, and the resulting signal was an average of the signals from these nanoparticles. Hence, the reproducibility can be attributed to the uniform size and uniform distribution of AgNI hot spots in a large area.

Another factor attributed to reducing the measurement variability is that ideally, the adequate number of molecules should be present in enough number of hot-spot regions within the laser spot. To obtain a uniform distribution of analyte molecules, a droplet of BPY solution equal to the Ag dot diameter was released on the Ag dot patterns of 5 mm diameter. The drop was allowed to evaporate, resulting in a uniform distribution of the analyte along the radius of the Ag dot, as a strong capillary flow due to evaporation, moved the analytes from the edge to the center [28]. This procedure increases the concentration of the analyte due to contact line pinning, solvent evaporation, and capillary flow over a small area of the Ag dot, thereby increasing reproducibility through uniform distribution of the analyte molecules.

4. Conclusions

In conclusion, we fabricated a large scale highly reproducible inkjet-printed Ag nano ink SERS substrate. An oxalate ion was used as an inexpensive reducing agent for the synthesis of oleylamine stabilized Ag nanoparticles. The minimum detection limit was 1.8×10^{-7} g/mL for BPY molecules. The inkjet-printed AgNI sample displayed excellent reproducibility with batch-to-batch and spot-to-spot standard deviation of less than 10%. This study can result in large-scale production of flexible SERS substrates.

Funding

This work was supported by JST COI Grant Number JPMJCE.1307 and JPMJCE.1312.D:\MYFILES\ELSEVIER\RINMA\00100139\SCE\gs1

Declaration of competing interest

The authors declare that they have no competing interests.

Acknowledgments

The authors thank Dr. Kosuke Ishikawa of Kyoto University for assisting us with the SEM observations.

References

[1] K.A. Arunkumar, E.B. Bradley, J. Chem. Phys. 78 (1983) 2882.
[2] V. Bochenkov, J. Baumberg, M. Noginov, F. Benz, H. Aldewachi, S. Schmid, V. Podolskiy, J. Aizpurua, K. Lin, T. Ebbesen, A.A. Kornyshev, J. Hutchison, K. Matczyszyn, S. Kumar, B. de Nijs, F.R. Fortuño, J.T. Hugall, P. de Roque, N. van Hulst, S. Kotni, O. Martin, F.J.G. de Abajo, M. Flatté, A. Mount, M. Moskovits, P. Ginzburg, D. Zueco, A. Zayats, S.-H. Oh, Y. Chen, D. Richards, A. Belardini, P. Narang, Faraday Discuss 178 (2015) 435.
[3] J.P. Camden, J.A. Dieringer, Y. Wang, D.J. Masiello, L.D. Marks, G.C. Schatz, R.P. Van Duyne, J. Am. Chem. Soc. 130 (2008) 12616.
[4] B. Sharma, M. Fernanda Cardinal, S.L. Kleinman, N.G. Greeneltch, R.R. Frontiera, M.G. Blaber, G.C. Schatz, R.P. Van Duyne, MRS Bull. 38 (2013) 615.
[5] S. Kumar, P. Goel, J.P. Singh, Sensor. Actuator. B Chem. 241 (2017) 577.
[6] S. Kumar, D.K. Lodhi, J.P. Singh, RSC Adv. 6 (2016) 45120.
[7] M. Suzuki, W. Maekita, Y. Wada, K. Nagai, K. Nakajima, K. Kimura, Takao Fukuoka, Y. Mori, Nanotechnology 19 (2008) 265304.
[8] S. Kumar, D.K. Lodhi, P. Goel, Neeti, P. Mishra, J.P. Singh, Chem. Commun. 51 (2015) 12411.
[9] S. Kumar, Y. Doi, K. Namura, M. Suzuki, ACS Appl. Bio Mater. 3 (2020) 3226.
[10] J.F. Betz, W.W. Yu, Y. Cheng, I.M. White, G.W. Rubloff, Phys. Chem. Chem. Phys. 16 (2014) 2224.
[11] M. Zarei, Biosens. Bioelectron. 98 (2017) 494.
[12] Q. Qi, C. Liu, L. Liu, Q. Meng, S. Wei, A. Ming, J. Zhang, Y. Wang, L. Wu, X. Zhu, F. Wei, J. Yan, *Micromachines* 10 (2019) 282.
[13] Y. Chen, F. Ge, S. Guang, Z. Cai, Appl. Surf. Sci. 436 (2018) 111.
[14] D. He, B. Hu, Q.-F. Yao, K. Wang, S.-H. Yu, ACS Nano 3 (2009) 3993.
[15] W.W. Yu, I.M. White, Anal. Chem. 82 (2010) 9626.
[16] W. Wu, L. Liu, Z. Dai, J. Liu, S. Yang, L. Zhou, X. Xiao, C. Jiang, V.A.L. Roy, Sci. Rep. 5 (2015) 1.
[17] C. Miccichè, G. Arrabito, F. Amato, G. Buscarino, S. Agnello, B. Pignataro, Anal. Methods 10 (2018) 3215.
[18] Q. Yang, M. Deng, H. Li, M. Li, C. Zhang, W. Shen, Y. Li, D. Guo, Y. Song, Nanoscale 7 (2015) 421.
[19] M. Suzuki, K. Nakajima, K. Kimura, T. Fukuoka, Y. Mori, Anal. Sci. 23 (2007) 829.
[20] Y. Yoshida, H. Wada, K. Izumi, S. Tokito, Jpn. J. Appl. Phys. 56 (2017), 05EA01.
[21] M. Itoh, T. Kakuta, M. Nagaoka, Y. Koyama, M. Sakamoto, S. Kawasaki, N. Umeda, M. Kurihara, J. Nanosci. Nanotechnol. 9 (2009) 6655.
[22] T. Lu, T.M. Cotton, R.L. Birke, J.R. Lombardi, Langmuir 5 (1989) 406.
[23] M. Muniz-Miranda, J. Raman Spectrosc. 27 (1996) 435.
[24] K.G. Stamplecoskie, J.C. Scaiano, V.S. Tiwari, H. Anis, J. Phys. Chem. C 115 (2011) 1403.
[25] K. Jiang, M. Bosnick, L. Brus Maillard, J. Phys. Chem. B 107 (2003) 9964.
[26] L. Du, X. Zhang, T. Mei, X. Yuan, Optic Express 18 (2010) 1959.
[27] P.L. Stiles, J.A. Dieringer, N.C. Shah, R.P. Van Duyne, Annu. Rev. Anal. Chem. 1 (2008) 601.
[28] A. Hussain, D.-W. Sun, H. Pu, Food Addit. Contam. 36 (2019) 851.