# Silver Nano-Colloid Characterization for Printing Application

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Sithara Pavithran Sreenilayam<sup>1,a\*</sup>, Éanna McCarthy<sup>1,b</sup>, Lorcan McKeon<sup>2,c</sup>, Oscar Ronan<sup>2,d</sup>, Karsten Fleischer<sup>1,e</sup>, Valeria Nicolosi<sup>2,f</sup> and Dermot Brabazon<sup>1,g</sup>

<sup>1</sup>I-Form, Advanced Manufacturing Research Centre, & Advanced Processing Technology Research Centre, School of Mechanical and Manufacturing Engineering, Dublin City University, Glasnevin, Dublin-9, Ireland

<sup>2</sup>I-Form and AMBER research centers, School of Chemistry, Trinity College, Dublin 2, Ireland <sup>a\*</sup>sithara.sreenilayam@dcu.ie, <sup>b</sup>eanna.mccarthy@dcu.ie, <sup>c</sup>lmckeon@tcd.ie, <sup>d</sup>oronan@tcd.ie <sup>e</sup>karsten.fleischer@dcu.ie, <sup>f</sup>NICOLOV@tcd.ie, <sup>g</sup>dermot.brabazon@dcu.ie

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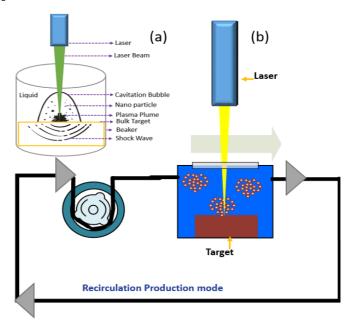
**Abstract.** Silver nano-colloids have been generated *via* Laser Ablation Synthesis in Solution (LASiS) system. Nanoparticle formation with particle size below 50 nm in DI water was confirmed using UV-VIS spectroscopy, Dynamic Light Scattering (DLS) technique, and transmission electron microscopy (TEM). Supercapacitor structure, having dimension 11 mm x 10 mm, was successfully Aerosol Jet printed on an untreated polymer substrate using as produced LASiS silver nano-colloid.

#### Introduction

Flexible electronics [1, 2], a class of lightweight electronic components and devices on flexible and stretchable substrates (e.g., paper [3], polymer [4], textiles [5] etc.), offer opportunities in many novel applications in different sectors such as smart packaging and logistics, consumer electronics, textiles, energy and photovoltaics, healthcare and wellbeing, building and construction, and automotive industry [6]. The most attractive characteristic is the ability to bend or stretch, in contrast to electronic devices or components developed on rigid materials. The global market of flexible electronic and device technology is estimated to rise from \$31.7 bn in 2018 to over \$77.3 bn by 2029 [7]. Printed electronic technologies, a novel way to manufacture electronic components, are an important tool in producing flexible electronics. This technique is used to manufacture electronic components and devices by printing them on various flexible or stretchable substrates. The method is one of the fast growing technologies, allowing high throughput, large volume, cost effective fabrication for numerous every-day products. The most common printing methods used for making electronics with solution based inks on the flexible substrates are screen printing, flexographic printing, inkjet printing, Aerosol Jet printing, and roll-to-roll gravure printing [8, 9]. In comparison to traditional electronics, flexible printed electronics are key to manufacture portable, bendable, low cost, and light weight electronics, with parts which can be recycled easily avoiding waste accumulation and reducing the environmental footprint.

Organic materials, for example, 2D materials, polymers, cellulose, *etc.*, are used as substrates (to print on) and functional materials (to print with) [8, 9]. Flexible printed electronic technologies rely on the fact that even in a deformed state polymeric materials maintain their structural and electrical properties. Inorganic and metallic materials are also used in this technology [10]. In recent years, functional conductive inks have received much attention due to their popularity and application in flexible printed electronics [11]. To meet the growing demand for large volume, low cost fabrication methods and the challenges faced in producing printed electronics, advancements in innovative materials and methods for conductive ink production are required. Numerous functional inks, for example aluminum [12, 13], nickel [14, 15], copper [16, 17], gold [18, 19], graphene [20], carbon nanotube [21, 22], silver [23, 24] *etc.* for printed electronic application have been synthesized. Among the functional inks, silver nanoparticle based inks exhibit excellent conductivity and stability. The conductive structures based on the silver nanoparticle inks can be sintered relatively at low

temperature. These characteristics makes silver ink suitable for producing flexible printed electronic circuits and components including sensors [25], light-emitting devices [26], radio frequency identification device tags (RFID) [27], touch screen panel [28], antenna [29], thin-film transistors [30], and solar cells [31].



**Figure 1**. Schematic of (a) nanoparticle generation in aqueous media, and (b) LASiS system in recirculation production mode.

Laser Ablation Synthesis in Solution (LASIS) is a physical approach of producing nanomaterials in a liquid environment (Fig. 1a). In this method, a pulsed laser irradiates a metal target immersed in solvent, where its absorption by the target material produces plasma plumes, which generate nanomaterials in the aqueous medium. The production rate and nanomaterial properties strongly depends on the laser parameters (*i.e.* repetition rate, pulse duration, wavelength, and laser fluence) and the target material. The LASiS technique is capable of producing additive free non-toxic stable colloidal dispersions of nanostructures (*e.g.*, aluminium [32], carbon [33], gold 34], nickel [35], copper [36], carbon nanotube [37], and silver [38]) in both organic and aqueous media. Therefore, the eco-friendly, cost effective LASiS technique has received much attention for the industrial production of conductive functional nanomaterials. This work reports the generation of silver nanocolloids in DI water using dynamic LASiS technique and their Aerosol Jet printing on a polymer sheet.

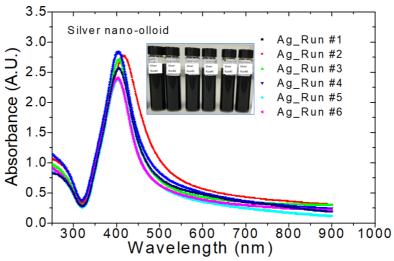
#### **Materials**

Silver targets sourced from Goodfellow Cambridge Ltd. were used in this study. The DI water for LASiS nano-colloid formation was purchased from Merck (LC-MS Grade LiChrosolv).

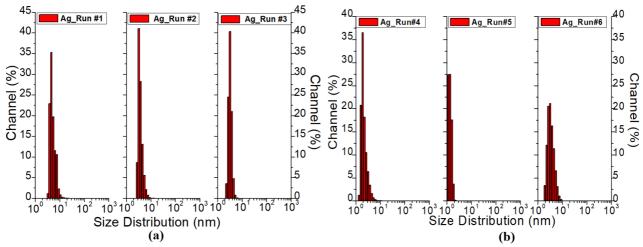
## **Results and Discussions**

Silver nano-colloids have been generated in 10 mL DI water using a dynamic LASiS set-up (Fig. 1b) in a recirculation production mode. The produced colloids were characterized using UV-VIS Spectrophotometer (Biochrom Inc., USA, scan range 200–1200 nm with scan rate 600 nm min<sup>-1</sup>) (Fig. 2) to confirm nanoparticle formation. The absorption peaks in the 400 nm wavelength region confirm silver nanoparticle formation under the experimental conditions: pulse repletion rate,  $f_{PRF} = 20 \text{ kHz}$ , process duration, t=30 min, and laser bean scan speed, v =2.2 mm s<sup>-1</sup> in DI water [39]. The inset of Fig. 2 shows a picture of LASiS silver nanocolloids produced for the corresponding UV-VIS spectra. In order to check the reproducibility, the experiments were repeated six times with the same parameters under study. The particle size distribution and shape of the particles in the as-produced

silver nanocolloids were then analyzed using dynamic light scattering (DLS, Microtrac Ltd.), and transmission electron microscope, TEM, FEI Titan (S)TEM (FEI, USA) with beam energy of 300 keV. In DLS, the scattering intensity of laser beam in a colloidal solution fluctuates with time due to the Brownian motion of particles leading to the constructive or destructive interference by the surrounding particles in the colloid. Figure 3 shows the average particle size distribution of the six colloidal samples produced corresponding to the UV-VIS spectra, and they were all found to be below 50 nm.



**Figure 2.** UV-VIS absorption spectra with the corresponding picture of (inset) LASiS silver colloids.

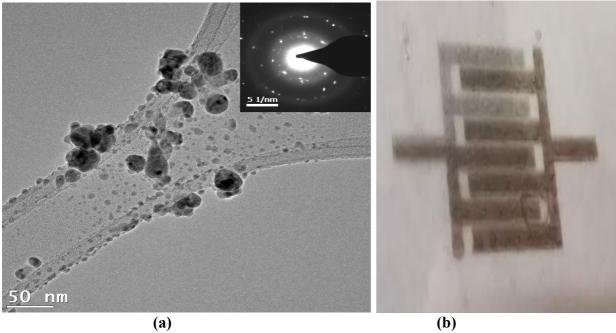


**Figure 3** (a) and (b) DLS size distribution plots of silver nano-colloid in 10 mL DI water for repeated six different experiments, all carried out under the same parameters ( $f_{PRF} = 20 \text{ kHz}$ , t=30 min, and  $v=2.2 \text{ mm s}^{-1}$ ) and experimental conditions.

The silver colloidal sample was characterized using TEM. Figure 4(a) shows the Bright Field TEM picture of an as-produced silver nano-colloid, with the inset Selected Area Electron Diffraction picture showing polycrystallinity of the sample studied. The TEM imaging observation was in agreement with the DLS studies. The manual calculation, by taking silver target weight measurements before and after the ablation process in DI water, shows ~0.9 mg mL<sup>-1</sup> productivity for the parameters  $f_{PRF} = 20 \text{ kHz}$ , t=30 min, and  $v=2.2 \text{ mm s}^{-1}$ . The as-produced LASiS silver colloid was successfully Aerosol Jet printed on a polymer substrate. Figure 4(b) shows the single layer super capacitor structure on an acetate sheet printed using an AJP 300 Aerosol Jet Printer. A print nozzle of 300  $\mu$ m was used for printing alongside nitrogen carrier gas. Gas pressures was adjusted to maintain consistent mass flow. The dimension of the supercapacitor structure shown in Fig. 4(b) is 11 mm x 10 mm (not including the two lines out from either side).

## **Summary**

In this work, colloidal silver nanoparticles were prepared by dynamic flow based LASiS system in a recirculation production mode and successfully Aerosol Jet printed single layer supercapacitor structure on an acetate sheet for the first time using the as-produced LASiS silver colloid with  $\sim$ 0.9 mg mL<sup>-1</sup> productivity, which was achieved with the parameters,  $f_{PRF} = 20$  kHz, t=30 min, and v=2.2 mm s<sup>-1</sup>. The UV-VIS, TEM, and DLS studies confirm silver nanoparticle formation, with the average particle size below 50 nm. The reproducibility of the LASiS nano-colloids was studied and confirmed with six repeated experiments for the same parameters under study. This work reports the high yield LASiS silver nano-colloid production and its Aerosol Jet printing application on the flexible polymer substrate.



**Figure 4**. (a) TEM picture of as produced silver nano-colloid. Inset Selected area electron diffraction showing polycrystallinity. (b) Aerosol Jet printed supercapacitor structure on a polymer sheet (dimension: 11 mm x 10 mm (not including the two lines out from either side)).

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#### References

- [1] D.-H. Kim, R. Ghaffari, N. Lu, J. A Rogers, Flexible and stretchable electronics for biointegrated devices, Annu Rev Biomed Eng. 14 (2012) 113.
- [2] J. Perelaer et al., Printed electronics: the challenges involved in printing devices, interconnects, and contacts based on inorganic materials, J. Mater. Chem. 20 (2010) 8446.
- [3] T. Leng et al., Printed graphene/WS2 battery-free wireless photosensor on papers, 2D Mater. 7 (2020) 024004.

- [4] S. Cui, Z. Dai, Q. Tian, J. Liu, X. Xiao, C. Jiang, W. Wu, V. A. L. Roy, J. Wetting properties and SERS applications of ZnO/Ag nanowire arrays patterned by a screen printing method, Mater. Chem. C 4 (2016) 6371.
- [5] J. Ferri, C. P. Fuster, R. L. Llopis, J. Moreno, E. Garcia-Breijo, Integration of a 2D Touch Sensor with an Electroluminescent Display by Using a Screen-Printing Technology on Textile Substrate, Sensors (Basel). 18 (2018) 3313.
- [6] D. Corzo, G. T.-Blázquez, D. Baran, Flexible Electronics: Status, Challenges and Opportunities, Front. Electron. 1, (2020) 594003.
- [7] https://www.flexenable.com/blog/five-benefits-of-flexible-electronics-for-displays-and-sensors/
- [8] S. P. Sreenilayam, et al. Advanced Materials of Printed Wearables for Physiological Parameter Monitoring. Materials Today 32 (2020) 147.
- [9]S. P. Sreenilayam, et al. MXene materials based Printed Flexible Devices for Healthcare, Bio-Medical and Energy Storage Applications. Materials Today 43, (2021) 99.
- [10] V. Correia, et al. Development of inkjet printed strain sensors, Smart Mater. Struct. 22 (2013) 105028.
- [11 S. Sreenilayam, Y. Afkham, C. Hughes, I. Ul Ahad, L. Hopper, A. Boran, D. Brabazon, Wearable Devices for Monitoring Work related Musculoskeletal and Gait Disorders, 2020 International Conference on Assistive and Rehabilitation Technologies (iCareTech), IEEE, (2020) 103.
- [12] L. H. Moon, C. Si-Young, K. K. Tae, Y. Jung-Yeul, J. D. Soo, P. S. Bin, P. Jongwook, A novel solution-stamping process for preparation of a highly conductive aluminum thin film, Adv. Mater. 23 (2011) 5524.
- [13] S.-h. Jung, D.Y. Choi, H.M. Lee, Roll-to-roll processed, highly conductive, and flexible aluminum (Al) electrodes based on Al precursor inks, RSC Adv. 8 (2018) 19950.
- [14] S.-G. Kim, Y. Terashi, A. Purwanto, K. Okuyama, Synthesis and film deposition of Ni nanoparticles for base metal electrode applications, Colloids Surf. A Physicochem. Eng. Asp. 337 (2009) 96.
- [15] L. Jong-Gun et al., Supersonically sprayed copper-nickel microparticles as flexible and printable thin-film high-temperature heaters, Adv. Mater. Interfaces 4 (2017), 1700075.
- [16] W. Li, H. Zhang, Y. Gao, J. Jiu, C.-F. Li, C. Chen, D. Hu, Y. Goya, Y. Wang, H. Koga, S. Nagao, K. Suganuma, Highly reliable and highly conductive submicron Cu particle patterns fabricated by low temperature heat-welding and subsequent flash light sinter-reinforcement, J. Mater. Chem. C 5 (2017) 1155.
- [17] S. Jeong, H. C. Song, W. W. Lee, S. S. Lee, Y. Choi, W. Son, E. D. Kim, C. H. Paik, S. H. Oh, B.-H. Ryu, Stable aqueous based Cu nanoparticle ink for printing well-defined highly conductive features on a plastic substrate, Langmuir 27 (2011) 3144.
- [18] X. Liu, M. Kanehara, C. Liu, K. Sakamoto, T. Yasuda, J. Takeya, T. Minari, Spontaneous patterning of high-resolution electronics via parallel vacuum ultraviolet, Adv. Mater. 28 (2016) 6568.
- [19] T. Minari, Y. Kanehara, C. Liu, K. Sakamoto, T. Yasuda, A. Yaguchi, S. Tsukada, K. Kashizaki, M. Kanehara, Room-temperature printing of organic thin-film transistors with junction gold nanoparticles, Adv. Funct. Mater. 24 (2014) 4886
- [20] W. Yang, C. Wang, Graphene and the related conductive inks for flexible electronics, J. Mater. Chem. C 4 (2016) 7193.
- [21] M. Ha, Y. Xia, A. A. Green, W. Zhang, M. J. Renn, C. H. Kim, M. C. Hersam, C. D. Frisbie, Printed, sub-3V digital circuits on plastic from aqueous carbon nanotube inks, ACS Nano 4 (2010) 4388.
- [22] S. K. Eshkalak, A. Chinnappan, W. A. D. M. Jayathilaka, M. Khatibzadeh, E. Kowsari, S. Ramakrishna, A review on inkjet printing of CNT composites for smart applications, Appl. Mater. Today 9 (2017) 372.
- [23] M. Grouchko, A. Kamyshny, C. F. Mihailescu, D. F. Anghel, S. Magdassi, Conductive inks with a "Built-In" mechanism that enables sintering at room temperature, ACS Nano 5 (2011) 3354.

- [24] J. R. Greer, R. A. Street, Thermal cure effects on electrical performance of nanoparticle silver inks, Acta Mater. 55 (2007) 6345.
- [25] Y. Zhang, N. Anderson, S. Bland, S. Nutt, G. Jursich, S. Joshi, All-printed strain sensors: building blocks of the aircraft structural health monitoring system, Sens. Actuators A Phys. 253 (2017) 165.
- [26] Z. Yu, Q. Zhang, L. Li, Q. Chen, X. Niu, J. Liu, Q. Pei, Highly flexible silver nanowire electrodes for shape-memory polymer light-emitting diodes, Adv. Mater. 23 (2011) 664.
- [27] R. Singh, E. Singh, H. S. Nalwa, Inkjet printed nanomaterial based flexible radio frequency identification (RFID) tag sensors for the internet of nano things, RSC Adv. 7 (2017) 48597.
- [28] Y. Lee, S. Y. Min, T. S. Kim, S. H. Jeong, J. Y. Won, H. Kim, W. T. Xu, J. K. Jeong, T. W. Lee, Versatile metal nanowiring platform for large-scale nano- and opto-electronic devices, Adv. Mater. 28 (2016) 9109.
- [29] A. Russo, B. Y. Ahn, J. J. Adams, E. B. Duoss, J. T. Bernhard, J. A. Lewis, Pen-on-paper flexible electronics, Adv. Mater. 23 (2011) 3426.
- [30] K. Fukuda, T. Sekine, D. Kumaki, S. Tokito, Profile control of inkjet printed silver electrodes and their application to organic transistors, ACS Appl. Mater. Interfaces 5 (2013) 3916.
- [31] H. Markus et al., Comparison of fast roll-to-roll flexographic, inkjet, flatbed, and rotary screen printing of metal back electrodes for polymer solar cells, Adv. Eng. Mater. 15 (2013) 995.
- [32] R. M. Altuwirqi, B. Baatiyah, E. Nugali, Z. Hashim, H. Al-Jawhari, Synthesis and Characterization of Aluminum Nanoparticles Prepared in Vinegar Using a Pulsed Laser Ablation Technique, Journal of Nanomaterials, 2020 (2020) 1-5.
- [33] K. Bagga, R. McCann, M. Wang, A. Stalcup, M. Vázquez, D. Brabazon, Laser assisted synthesis of carbon nanoparticles with controlled viscosities for printing applications, Journal of colloid and interface science 447 (2015) 263-268.
- [34] W. Norsyuhad, W. M. Shukri, H. Bakhtiar, S. Islam, N. Bidin, Synthesis and Characterization of Gold-Silver Nanoparticles in Deionized Water by Pulsed Laser Ablation (PLAL) Technique at Different Laser Parameter, International Journal of Nanoscience, 17 (2018) 1850015.
- [35] R. G. Nikov, N. N. Nedyalkov, D. B. Karashanova, Laser ablation of Ni in the presence of external magnetic field: Selection of microsized particles, Appl. Surf. Sci. 518 (2020) 146211.
- [36] S. Sato, T. Arai, Y. Akimoto, K. Kitazumi, S. Kosaka, N. Takahashi, Y. F. Nishimura, Y. Matsuoka, T. Morikawa, Low-Overpotential Electrochemical Water Oxidation Catalyzed by CuO Derived from 2 nm-Sized Cu2(NO3)(OH)3 Nanoparticles Generated by Laser Ablation at the Air-Liquid Interface, ACS Appl. Energy Mater. 3 (2020) 8383–8392.
- [37] T. F. Kuo, C. C. Chi, I. N. Lin, Synthesis of Carbon Nanotubes by Laser Ablation of Graphites at Room Temperature, Jpn. J. Appl. Phys. 40 (2001) 7147–7150.
- [38] S. S. Pavithran, R. McCann, É. McCarthy, B. Freeland, K. Fleischer, S. Goodnick, S. Bowden, C. Honsberg, D. Brabazon, Silver and Copper nano-colloid generation via Pulsed Laser Ablation in Liquid: Recirculation nanoparticle production mode, ESAFORM 2021 24th International Conference on Material Forming (2021).
- [39] B. Freeland, R. McCann, P. O'Neill, S. Sreenilayam, M. Tiefenthaler, M. Dabros, M. Juillerat, G. Foley, D. Brabazon, Real-time monitoring and control for high-efficiency autonomous laser fabrication of silicon nanoparticle colloid, The International Journal of Advanced Manufacturing Technology 114 (2021) 291-304.