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SYNTHESIZING AND PRINTING OF TIN OXIDE NANOPARTICLES USING A SINGLE ULTRAFAST LASER SYSTEM: A FEASIBILITY STUDY

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ABSTRACT

In laser-based manufacturing, processing setup customization is one of the popular approaches used to enhance diversity in material processing using a single laser. In this study, we propose setup design modification of an ultrafast laser system to demonstrate both Tin Oxide (SnO2) nanoparticle synthesis from bulk metal, and post printing of said nanoparticles using Laser Induced Forward Transfer (LIFT) method. Using the Pulse Laser Ablation in Liquid (PLA-L) method, nanoparticles were synthesized from a bulk tin metal cube submerged in distilled water. Such nanoparticles dispersed in water can form colloidal ink that can be used for different printed electronics applications. Pulse energy was varied to investigate the influence on morphological properties of the nanoparticles. It was observed that a decrease in average particle size, and an increase in the number of particles synthesized occurred as the pulse energy was increased. In our study, we adapted the same laser system to enable LIFT operation for printing of the SnO2 nanoparticles. The colloidal ink prepared was then used in LIFT method to study feasibility of printing the synthesized nanoparticles. By varying not only the laser parameters but process parameters such as coating thickness and drying time, printed results can be improved. Experimental results show great potential for both synthesizing and printing of the nanoparticles using a single laser system. This study serves as a proof of concept that a single laser system can turn bulk metal into nanoparticles-based applications without the need for extra processing from other machines/systems, opening the door to highly customizable prints with reduced lead times.

Keywords: Nanoparticle Synthesis, Laser Induced Forward Transfer, Pulse Laser Ablation, Ultrafast Laser System

1. INTRODUCTION

Ultrafast lasers are versatile devices widely used in various material processing applications. Setup modification allows for completely different forms of manufacturing techniques and opens new opportunities in material processing. The synthesis of nanoparticles in conjunction with Laser Induced Forward Transfer (LIFT) can be done using a single laser through a modification in the laser system.

Nanoparticles have attracted attention over recent years due to their unique properties that cannot be observed in bulk materials. Synthesis of nanoparticles using Pulsed Laser Ablation (PLA) is a simple green method with great potential and its variation, PLA- In Liquid has even more advantages over other methods in that it does not require expensive equipment such as vacuum chambers while still achieving highly pure NP colloidal solutions. Through the use of a concentrated laser on a target surface, ablation causes the surface material to evaporate thus creating nanoparticles. Pioneered in 1987 by Patil et al., iron in water was irradiated by pulsed laser ablation to create iron oxide [1]. In recent years numerous metals have been used for nanoparticle synthesis using PLA [2–5].

Laser Induced Forward Transfer an additive process that can deposit material in micrometer resolution consists of a pulsed laser source, a donor substrate, and a receiving substrate, can print a wide range of materials without having to worry about clogging. Historically, LIFT is believed to have begun in 1988 when Bohandy et al., used a very similar set up to the current one, to transfer copper and silver films onto a substrate [6]. The use of LIFT method to print metal and metal-oxide nanoparticles has been researched extensively [7–9]. Femtosecond laser ablation typically requires lower pulse energies and has better spatial and depth resolutions compared to nanosecond laser ablation [10].

The material in use is Tin Oxide (SnO2), an inexpensive material with a wide band gap of 3.6 eV, which has been widely researched in the printed electronics field due to its high chemical stability and its various applications in gas sensing [5,11–14]. Aligning the process requirements is critical for this study to work since both PLA and LIFT share one laser source, in other words, laser parameters should be within the capabilities of the system. A single laser that can manufacture both the ink

and the printed application would not only give the user more control over the material and print characteristics, but it could greatly reduce costs and simplify the manufacturing process.

2. MATERIALS AND METHODS

To prove the feasibility of synthesis and printing using a single laser system, PLA and LIFT experiments were carried out using a Spectra Physics Spirit One femtosecond laser with a center wavelength of 1040 nm, pulse duration of 500 fs, and a maximum pulse energy of 40 µJ at 200 kHz. Using three Aerotech stages the X, Y, and Z axis were controlled through a motion controller. The set up for which both PLA and LIFT system are based off is shown below in Figure 1. The morphology and material composition of the resulting synthesized nanoparticles were analyzed using a Scanning Electron Microscope (SEM and energy dispersive X-ray spectroscopy (EDS).

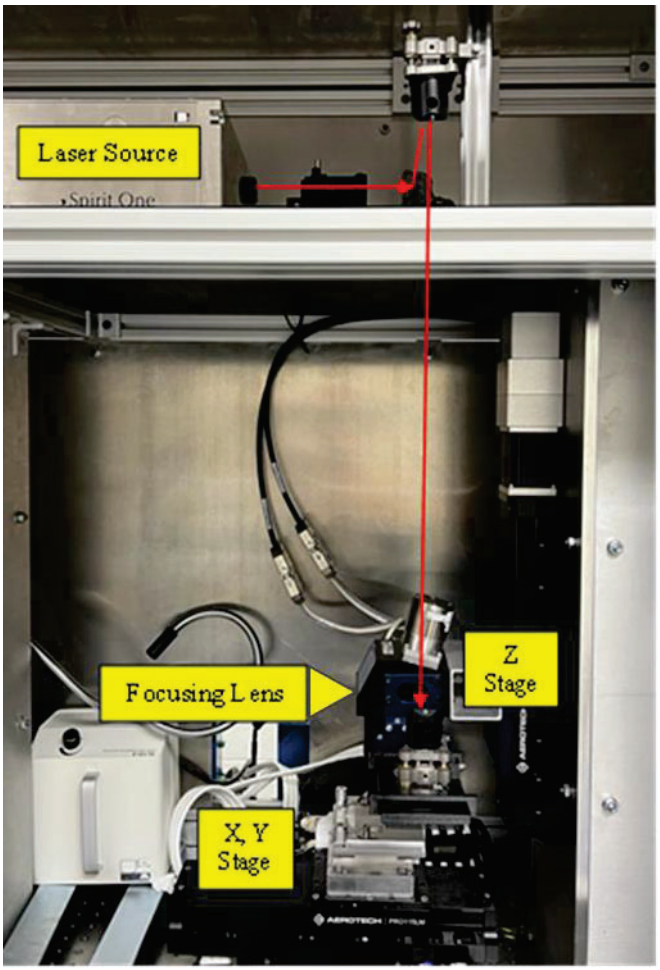


FIGURE 1: LASER SYSTEM USED FOR PLA AND LIFT

2.1 Pulsed Laser Ablation

In order to synthesize SnO2 nanoparticles, a highly pure 99.99% Tin metal cube of 10 mm is fixed to the bottom of a glass beaker and submerged in distilled water (1.5-2 mm above the target surface) as shown in Figure 2. Using the X and Y stages we maintain constant movement to have uniformity in the ablation process. Focusing the laser on the surface of the target we ablate in a stair like pattern using pulser energy of 16 microjoules and scanning speed of 10 mm/second. The colloidal solution is then transferred to a test tube.

In PLA in Liquid as described per Figure 2, when the laser is concentrated in the Tin target that is submerged in distilled water, the ablating process causes a plasma plume that disperses nanoparticles into the water. The water reacts with the laser generated nanoparticles to oxidize the Tin particles at the time of synthesis. The use of a femtosecond laser enhances the photon efficiency of the target causing the break in chemical bonding allowing for better reaction with the ambient media in this case water.

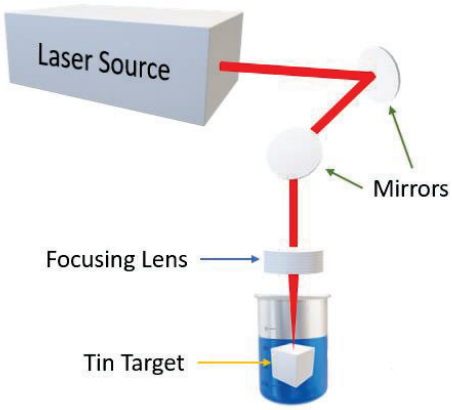
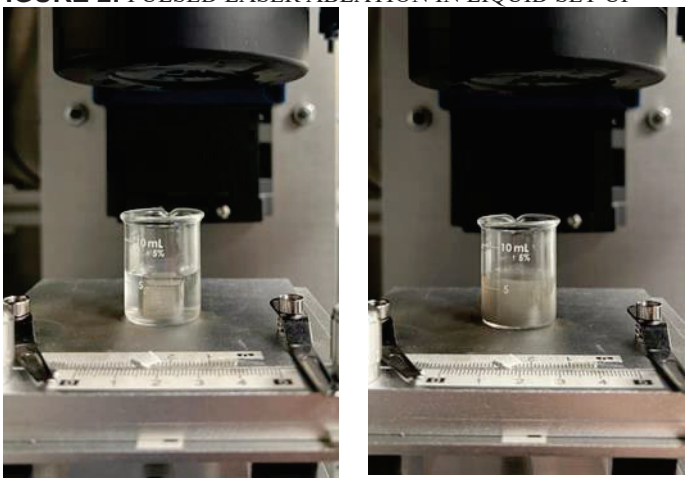


FIGURE 2: PULSED LASER ABLATION IN LIQUID SET UP



(a) (b)

FIGURE 3: PLA OF A TIN TARGET IN DISTILLED WATER (BEFORE AND AFTER PLA)

2.2 Laser Induced Forward Transfer

The colloidal solution Figure 3(b) containing the SnO2 particles were coated onto a glass slide with a thickness of 400 micrometers and placed with the coated surface facing down on top of the donor slide with spacers. The gap between donor and receiving substrate measured 500 micrometers. Figure 4 describes the set up used for printing via LIFT. Laser energies of

4-16 microjoules with a fixed pulse picker divider of 10 were tested, for which printing was unsuccessful. Using laser energy of 12 microjoules, pulse picker divider of 100, and printing 10 lines over the same area of 8mm in length achieved printable results.

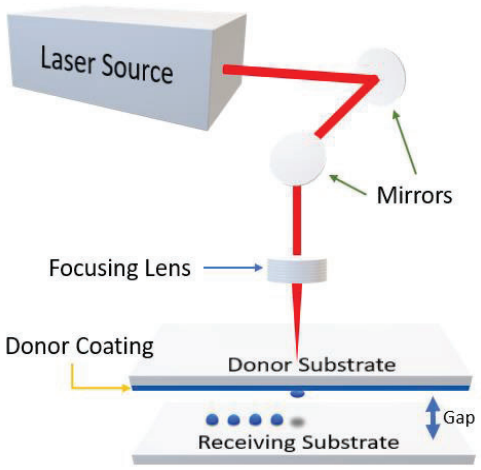


FIGURE 4: LASER INDUCED FORWARD TRANSFER SET UP

To acquire nanoscale transfer spots, ultrashort (femtosecond) laser pulses are preferred over other lasers. A femtosecond laser allows incident energy to be confined to the electrons without much of the electron-lattice energy being transferred during the pulse duration [15].

3. RESULTS AND DISCUSSION

3.1 Pulsed Laser Ablation

Figure 5 shows the samples that were collected, and air dried in preparation for the SEM, the image of SnO2 nanoparticles were synthesized at laser energy of 4 μJ, Pulse Picker Divider (PPD) of 1, and scanning speed of 10 mm/s. The visible nanoparticles mostly appear to be spherical in shape. The results of the SEM showed the presence of a wide range of nanoparticles with most particles being well below 131.5 nm in size. However, the SEM image shows the presence of smaller nanoparticles which cannot be measured at this magnification. The authors believe the presence of larger nanoparticles depends on the collection method. The SEM micrograph also shows an apparent crack in the sample which is believed to appear during the drying process of the nanoparticle paste.

Figure 6 shows the general area that was used to perform the EDS analysis, making sure to include all morphologies that could be appreciated. As shown in Figure 7, the EDS showed that there was in fact a presence of the elements Sn, O, Au and C. All three of the elements were expected as the bulk Sn interacts with the water as the nanoparticles are formed, therefore creating SnO2. The presence of Au is due to 15 seconds of gold sputtering required to analyze the sample in SEM, while carbon is present due to having the samples expose to the environment in the drying phase. The elemental analysis of the sample shows a significant oxidization of the sample as shown by the steep peak of Oxygen in Figure 7.

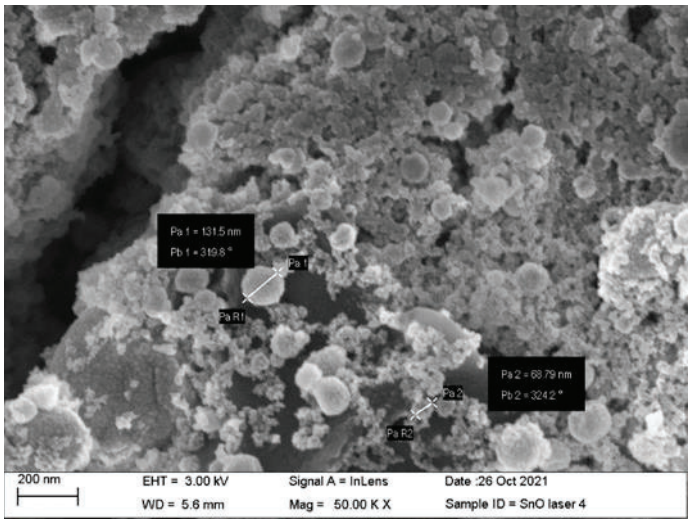


FIGURE 5: SEM IMAGES OF SYNTHESIZED SNO2 NANOPARTICLES

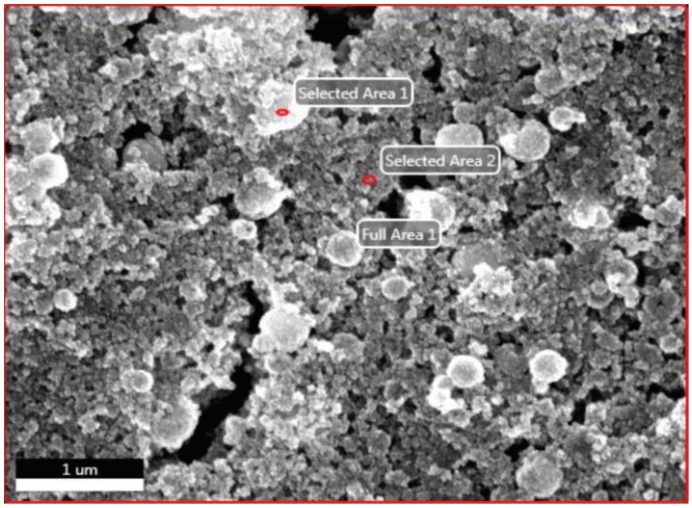


FIGURE 6: SEM IMAGE USED FOR EDS ANALYSIS

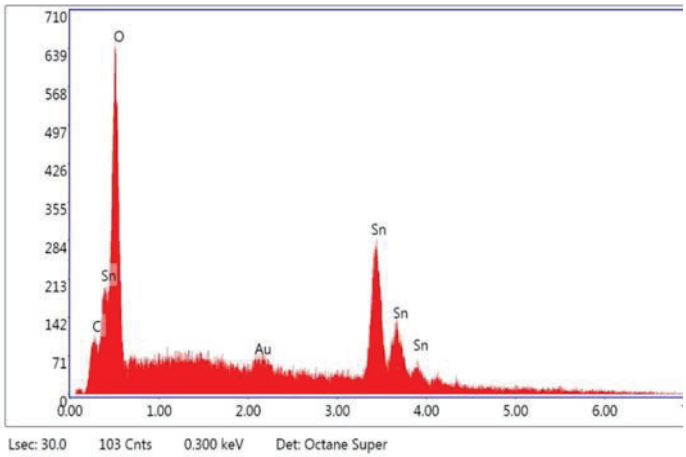


FIGURE 7: EDS GRAPH OF SYNTHESIZED SNO2 NANOPARTICLES

3.2 Laser Induced Forward Transfer

Nanoparticle observed in Figure 5 was used to prepare the colloidal ink which was then printed using the LIFT method (Figure 8). The parameters for printed pattern (a) showed a thinner and more defined line than those of printed pattern (b). As seen in Figure 9, the magnified images show that the morphology of the printed line (a) contains smaller droplets with better patterning. In contrast line (b) contains larger droplets with extensive splattering. The splattering shown in both lines although more apparent in line (b) could mean that the laser parameters have not been optimized, or the colloidal ink requires performance-enhancing additives to improve the printability. It is known that factors such as particle size, sintering methods and the number of printed layers influence the final conductivity and quality of printed patterns. For example, a change in laser energy improved the printed result as seen from 8(b) to 8(a). Stabilizing the jet requires optimization of the laser parameters, that depend on the rheology of the ink and thickness of the donor layer [16]. An extensive experimental analysis involving coating thickness, additives, and number of layers needs to be conducted to stabilize the jet and consequently optimize the printing pattern using LIFT process.

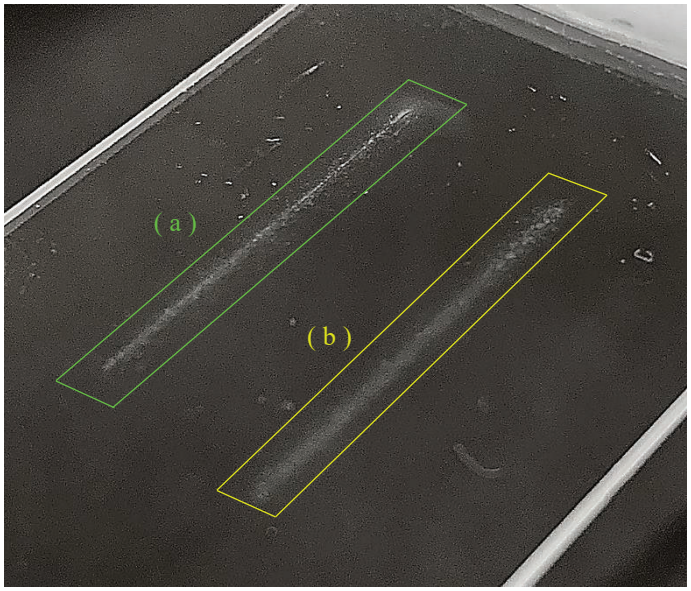
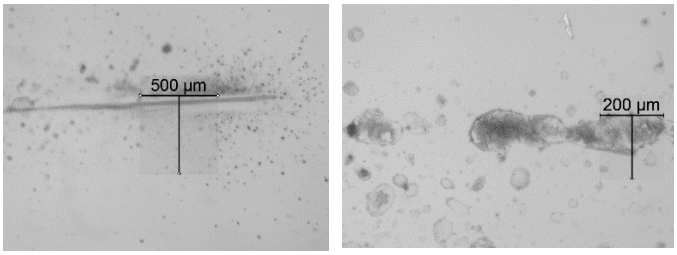


FIGURE 8: PRINTED SNO2 NP USING LIFT METHOD



(a) (b)

FIGURE 9: PRINTED SNO2 NP USING LIFT METHOD

4. CONCLUSION

The feasibility of synthetizing nanoparticles and printing them using a single laser system was proven through the successful transformation of bulk Sn into SnO2 nanoparticle ink that was printed. Producing nanoparticles well below 150 nanometers and printing a line with such nanoparticles using LIFT shows great potential for this single laser system approach. Future work will focus on optimizing parameters for synthesis and printing to improve average nanoparticle size and quality of print. To have full implementation of this technology altering the ink formula with additives may be considered in future studies.

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REFERENCES

[1] Patil, P. P., Phase, D. M., Kulkarni, S. A., Ghaisas, S. V., Kulkarni, S. K., Kanetkar, S. M., Ogale, S. B., and Bhide, V. G., 1987, "Pulsed-Laser-Induced Reactive Quenching at Liquid-Solid Interface: Aqueous Oxidation of Iron," Phys. Rev. Lett., **58**(3), pp. 238–241.

[2] Singh, S. C., and Gopal, R., 2008, "Synthesis of Colloidal Zinc Oxide Nanoparticles by Pulsed Laser Ablation in Aqueous Media," Phys. E Low-dimensional Syst. Nanostructures, **40**(4), pp. 724–730.

[3] Nath, A., Laha, S. S., and Khare, A., 2011, "Effect of Focusing Conditions on Synthesis of Titanium Oxide Nanoparticles via Laser Ablation in Titanium–Water Interface," Appl. Surf. Sci., **257**(7), pp. 3118–3122.

[4] Gondal, M. A., Drmosh, Q. A., and Saleh, T. A., 2010, "Preparation and Characterization of SnO2 Nanoparticles Using High Power Pulsed Laser," Appl. Surf. Sci., **256**(23), pp. 7067–7070.

[5] Ismail, R. A., Erten-Ela, S., Ali, A. K., Yavuz, C., and Hassoon, K. I., 2020, "Pulsed Laser Ablation of Tin Oxide Nanoparticles in Liquid for Optoelectronic Devices," Silicon 2020 139, **13**(9), pp. 3229–3237.

[6] Bohandy, J., Kim, B. F., Adrian, F. J., and Jette, A. N., 1988, "Metal Deposition at 532 Nm Using a Laser Transfer Technique," J. Appl. Phys., **63**(4), pp. 1158–1162.

[7] Sahner, K., and Tuller, H. L., 2010, "Novel Deposition Techniques for Metal Oxide: Prospects for Gas Sensing," J. Electroceramics, **24**(3), pp. 177–199.

[8] Mattle, T., Hintennach, A., Lippert, T., and Wokaun, A., 2013, "Laser Induced Forward Transfer of SnO2 for Sensing Applications Using Different Precursors Systems," Appl. Phys. A Mater. Sci. Process., **110**(2), pp. 309–316.

[9] Nastulyavichus, A., Tolordava, E., Rudenko, A., Zazymkina, D., Shakhov, P., Busleev, N., Romanova, Y., Ionin, A., and Kudryashov, S., 2020, "In Vitro

Destruction of Pathogenic Bacterial Biofilms by Bactericidal Metallic Nanoparticles via Laser-Induced Forward Transfer," Nanomater. (Basel, Switzerland), **10**(11), pp. 1–11.
[10] Sametoglu, V., Sauer, V. T. K., and Tsui, Y. Y., 2013, "Production of 70-Nm Cr Dots by Laser-Induced Forward Transfer," Opt. Express, **21**(15), p. 18525.
[11] Choi, Y.-J., Hwang, I.-S., Park, J.-G., Jin Choi, K., Park, J.-H., and Lee, J.-H., 2008, "Novel Fabrication of an SnO 2 Nanowire Gas Sensor with High Sensitivity," Nanotechnology, **19**, p. 4.
[12] Kassem, O., Saadaoui, M., Rieu, M., Sao-Joao, S., and Viricelle, J. P., 2018, "Synthesis and Inkjet Printing of Sol–Gel Derived Tin Oxide Ink for Flexible Gas Sensing Application," J. Mater. Sci., **53**(18), pp. 12750–12761.
[13] Desarkar, H. S., Kumbhakar, P., and Mitra, A. K., 2012, "Optical Properties of Tin Oxide Nanoparticles Prepared by Laser Ablation in Water: Influence of Laser Ablation Time Duration and Laser Fluence," Mater. Charact., **73**, pp. 158–165.
[14] Tazikeh, S., Akbari, A., Talebi, A., and Talebi, E., 2014, "Synthesis and Characterization of Tin Oxide Nanoparticles via the Co-Precipitation Method," Mater. Sci. Pol., **32**(1), pp. 98–101.
[15] Grant-Jacob, J. A., Mills, B., Feinaeugle, M., Sones, C. L., Oosterhuis, G., Hoppenbrouwers, M. B., and Eason, R. W., 2013, "Micron-Scale Copper Wires Printed Using Femtosecond Laser-Induced Forward Transfer with Automated Donor Replenishment," Opt. Mater. Express, **3**(6), p. 747.
[16] Marcos Fernández-Pradas, J., and Serra, P., 2020, "Laser-Induced Forward Transfer: A Method for Printing Functional Inks," Crystals, **10**(8), pp. 1–17.