

In Situ Synthesis of Self-Assembled Gold Nanoparticles on Glass or Silicon Substrates through Reactive Inkjet Printing**

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Abstract: A facile and low cost method for the synthesis of self-assembled nanoparticles (NPs) with minimal size variation and chemical waste by using reactive inkjet printing was developed. Gold NPs with diameters as small as (8 ± 2) nm can be made at low temperature (120°C). The size of the resulting NPs can be readily controlled through the concentration of the gold precursor and oleylamine ink. The pure gold composition of the synthesized NPs was confirmed by energy-dispersive X-ray spectroscopy (EDXS) analysis. High-resolution SEM (HRSEM) and TEM (HRTEM), and X-ray diffraction revealed their size and face-centered cubic (fcc) crystal structure, respectively. Owing to the high density of the NP film, UV/Vis spectroscopy showed a red shift in the intrinsic plasmonic resonance peak. We envision the extension of this approach to the synthesis of other nanomaterials and the production of tailored functional nanomaterials and devices.

There is a growing interest in colloidal nanoparticles (NPs) as a result of their size- and shape-dependent optical and electronic properties, which lead to potential applications in electronic and energy-harvesting devices,^[1] light-emitting diodes,^[2] and flexible electronics.^[3] Of particular interest is the gold nanoparticle (Au NP) colloidal system.

Au NPs find various applications as a result of their resistance to oxidation, for example, in electrochemical

detection,^[4] electrodes,^[5] and fingerprint detection.^[6] Various methods have been used to deposit Au NPs on a given substrate. Among these, inkjet printing is particularly attractive because it offers significantly reduced and more efficient materials usage as well as real-time patterning of printed NPs.^[7] To date, the Au NP colloidal solution (ink) is prepared prior to its use in inkjet deposition. The preparation procedure involves the synthesis of Au NPs by using various wet chemical methods, their purification, and finally the preparation of stable Au NP ink by dispersing them in an appropriate organic solvent to be used for printing. This process clearly involves two steps; a complicated and long synthetic process, and finally the printing process. We report the synthesis of self-assembled Au NPs by using inkjet printing and a unique solvent/precursor system. This reactive inkjet printing (RIP)^[8–12] technique allows the synthesis of Au NPs with acceptable size uniformity, with diameters as small as (8 ± 2) nm, directly on the substrate. This approach has the advantages of being fast, cost-effective, and suitable for large-scale fabrication, and provides an on-demand facile integration of Au NPs into various active and passive devices. Moreover, this method may open the way for the in situ assembly of Au NPs linked to organic and inorganic materials to fabricate heterostructured nanomaterials with tailored functionality and assembly. In addition, the in situ synthesis of these particles will facilitate their growth inside nanoporous host materials without pore size limitation. To our knowledge, this is the first report of an in situ preparation of relatively uniform self-assembled Au NPs on the substrate using RIP. We also demonstrate the effect of precursors, printing sequence, and solvents on the formation of these particles. We believe that this approach could also be applied to the preparation of other metal and/or semiconductor NPs.

A schematic representation of the in situ formation of the self-assembled Au NPs through RIP is shown in Figure 1. Briefly, Au NPs were synthesized on a silicon wafer by first injecting cartridge A with a mixture of solvents containing a capping/reducing agent and a dispersion solvent (1 mL oleylamine in 10 mL 1,2-dichlorobenzene). The surface tension of the solvent system in this cartridge was measured as 29.68 mN m^{-1} and the contact angle with the silicon-wafer surface as 28.60° . Cartridge B contained a mixture of 0.12 mmol gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) in 10 mL dimethyl sulfoxide (DMSO). The surface tension of the liquid mixture was measured as 43.88 mN m^{-1} and the contact angle with the silicon wafer as 35.75° . To start the synthesis, cartridge A prints the solvent in pL-volume droplets on a precleaned silicon substrate, after which cartridge B prints on top of the previous droplets under the same printing

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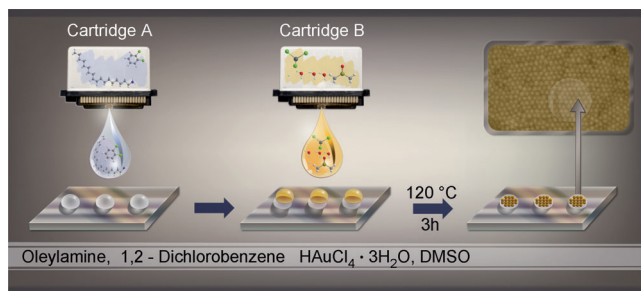


Figure 1. A schematic description of the in situ synthesis of self-assembled Au NPs through reactive inkjet printing.

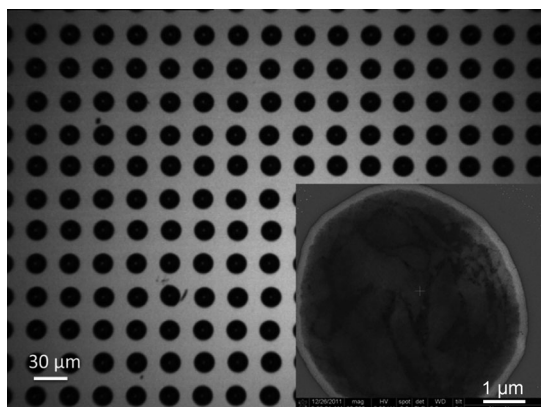


Figure 2. Optical image of a typical printed square array of dots each containing inks A and B, deposited on top of each other on a silicon substrate, prior to heat treatment. The center-to-center distance between adjacent prints was approximately 30 μm . The inset is an SEM image of one of the heat-treated droplets of the printed array. Heat treatment was carried at 120 $^{\circ}\text{C}$ for 3 h.

parameters and at room temperature (Figure 1). A square array of dots with approximately 30 μm spacing (center to center) was printed (Figure 2). The printed substrate is then placed in an oven at 120 $^{\circ}\text{C}$ for 3 h, resulting in the formation of Au NPs on the substrate surface. Scanning electron microscopy (SEM; inset of Figure 2) showed the formation of densely packed self-assembled NPs inside the printed droplets upon reaction completion and drying. The diameter of the Au NPs is approximately (8 ± 2) nm as shown in the high-resolution SEM (HRSEM) image in Figure 3, and transmission electron microscopy (TEM) image in Figure 4. High-resolution TEM (HRTEM) analysis of the Au NPs shows their spherical geometry with clear lattice fringes, thus indicating the highly crystalline nature of these particles (Figure 4). The lattice spacings 2.35 $\text{\AA}$ and 2.03 $\text{\AA}$ obtained from the HRTEM study correspond to (111) and (00-2) planes of the face-centered cubic (fcc) phase of gold.^[13] Additional evidence of the crystallinity of the RIP Au NPs is given by XRD data presented in Figure S1 in the Supporting Information. To determine the chemical composition of the NPs, energy-dispersive X-ray spectroscopy (EDXS) analysis was performed. The results (Figure S2) confirmed the presence of Au without any impurities on the substrate surface. The UV/Vis absorption spectrum showed a red

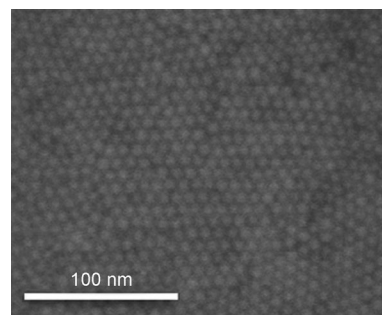


Figure 3. HRSEM image of the Au NPs on silicon substrate after postprinting heat treatment is complete showing self-assembled NPs of an average size of approximately (8 ± 2) nm.

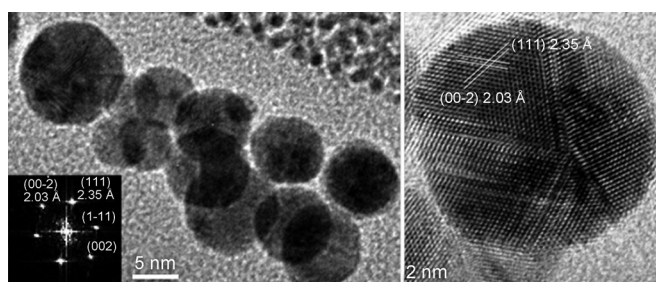


Figure 4. HRTEM of the Au NPs on silicon substrate after heat treatment of the printed drops. Inset: TEM diffraction pattern of gold NPs typical of an FCC crystal structure.

shifted plasmonic peak at approximately 602 nm corresponding to the closely packed Au NPs (Figure 5). The band around 536 nm corresponds roughly to the intrinsic plasmon resonance of isolated Au NPs.^[14] It is worth mentioning that the average particle size can be controlled by adjusting the concentration of the gold precursor and oleylamine. For example, by increasing the concentration of gold precursor and oleylamine, Au NPs with an average diameter of

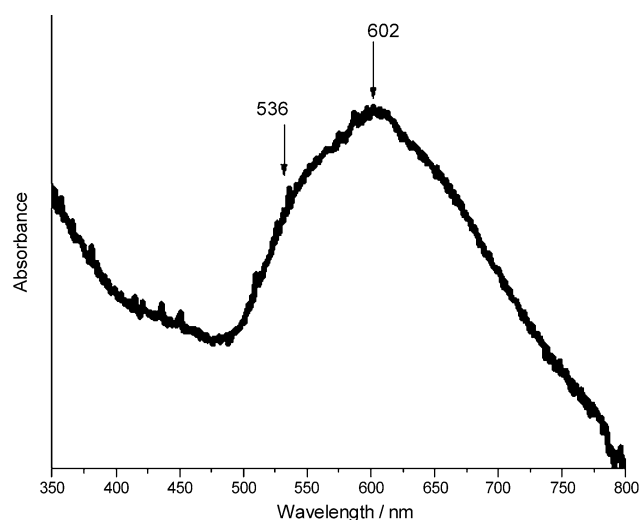


Figure 5. UV/Vis spectrum of the Au NPs synthesized through RIP on glass substrate.

approximately 25 nm can be obtained on silicon substrate following a similar heat-treatment step to that previously mentioned (Figure S3).

Oleylamine acts as a capping agent and a reducing agent.^[15] The reduction process involves two steps: first a partial reduction from Au^{3+} to Au^+ through the formation of oleylamine– AuCl , then a slow reduction from Au^+ to Au . It has been shown that the continuous supply of Au from an oleylamine– AuCl complex causes the nucleation and growth of gold nanowires (NWs).^[15] However, in the present case, Au NPs were formed instead. Although the exact details of nanoparticle growth and assembly are still under study, we suspect that the effects of solvent polarity, temperature, relatively fast reduction at higher temperature, and limited available printed ink volume play a major role in this process under the given experimental conditions. DMSO and 1,2-dichlorobenzene were selected as solvents owing to their comparatively high viscosity and boiling points with acceptable surface tension. Furthermore, owing to its high solubility, the gold precursor forms a stable solution in DMSO. High-concentration solutions can thus be formed. Another advantage of this solvent system is that DMSO and 1,2-dichlorobenzene are miscible, which is very important since oleylamine is not miscible with DMSO. DMSO also acts as an antisolvent soon after the formation of nanoparticles capped by oleylamine, an effect that could also be a factor in the formation of relatively ordered Au NPs over the substrate surface, as shown in Figure 3. Experiments carried out with a different growth time (Figure S4) or temperature (Figure S5) showed no significant change in the formation or size of the Au NPs, but a considerable change in the shape of the Au NPs was observed (Figure S6) when the concentration of gold precursor was increased from 0.12 mmol to 0.4 mmol in DMSO. Similar observations have been made by others.^[16] The printing process was also carried out in the reverse sequence (printing the precursor ink first and the solvent ink second, Figure S7). In this case, the resultant nanoparticles were neither uniform in size nor as highly crystalline as those obtained from the original printing sequence. This may be due to the lower contact angle of the precursor on silicon and glass substrates.

To demonstrate the impact of the choice of solvent system, three other solvent systems were used: 1) gold precursor in water and oleylamine in ethanol, 2) gold in dimethylformamide (DMF) and oleylamine in toluene, and 3) gold in a mixture of ethanol/toluene (1:10) and oleylamine in toluene. The results indicate that gold precursor in DMSO and oleylamine in dichlorobenzene is by far the most suitable solvent system for the RIP synthesis of Au NPs with acceptable size uniformity on a given substrate surface. We suspect that the main reasons behind this are the higher surface tension of water and the lower boiling points of ethanol and toluene. The Au NPs obtained from the ethanol/1,2-dichlorobenzene solvent system showed a noticeably broad size distribution as compared to those obtained from the DMSO/1,2-dichlorobenzene system (Figures S8, S9). Moreover, the use of AuCl_3 instead of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ as the gold precursor also resulted in a broad size distribution

(Figures S10, S11). At this time, we are unable to ascertain the reasons for this variation in size distribution.

We compared the nanoparticles synthesized by RIP with the nanoparticles synthesized by the traditional colloidal method in a flask. The flask method resulted in the formation of Au NPs with a diameter of (15 ± 2) nm, whereas the RIP synthesis resulted in self-assembled nanoparticles with a diameter of (8 ± 2) nm (Figure S12). This could be due to the highly controlled pL volume of the inkjet-printed droplets as opposed to the relatively larger volume in the flask.

In summary, a facile and versatile in situ synthesis of self-assembled Au NPs with a narrow size distribution on glass and silicon substrates through inkjet printing has been demonstrated. We believe that this approach could be developed further and adopted as a low-cost and reliable high-throughput method for the preparation of various types of nanoparticles on a variety of substrates.

Experimental Section

Substrate cleaning: All substrates were cleaned thoroughly by first rinsing them with deionized water and then sonicating in acetone, ethanol, and isopropanol, respectively. The sonication time of each step was 10 min and the substrates were dried with nitrogen at each step.

Inkjet printing parameters: The printer used in this experiment is a piezoelectric drop-on-demand inkjet printer purchased from Fujifilm Dimatix with the model number Dimatix Materials Printer DMP-2800. The Dimatix Materials Printer cartridge used gives 10 pL droplets. The cartridge is placed 0.25 mm above the substrate at room temperature. The print head consists of 16 nozzles, with 254 μm spacing on single line. The nozzle voltage was calibrated between 6–9 volts because the ink viscosity was relatively low. The inks were printed using a square matrix shape with 30 μm spacing between drops.

Surface tension: This was measured at 22.6 °C using a Kruss Tensiometer, k100MK2/SF/C, and contact angle was measured at room temperature using the Kruss EasyDrop Contact Angle System.

Printing process: The sequential printing process involves printing on a silicon (100) surface from cartridge A, which contains the dispersion solvent and capping agent (1,2-dichlorobenzene and oleylamine in 10:1 ratio), followed by printing of the gold precursor (0.12 mmol $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in DMSO (10 mL)) from cartridge B at the same locations as the drops deposited by cartridge A. The substrate was then placed in an oven at 120 °C for 3 h. The printing was also carried out in reverse order.

SEM characterization: An SEM Nova NANO 600 was used to characterize the as-synthesized Au NPs on silicon substrate without any conductive film coating.

TEM characterization: The sample for cross-sectional TEM analysis was prepared by focused ion beam (FIB; Helios 400s, FEI) with the lift-out method. The lamellar was thinned with a Ga ion beam (30 kV, 0.28 nA) and cleaned at 2 kV and 47 pA. We used a Titan ST 300 kV (FEI) for HRTEM imaging.

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