Accurate generation of attolitre droplets for directly printing gold nanoparticles from solution through confined reaction

Yayu Huang¹, Fei Fang¹, Feifei Chen¹, Xian Cui¹, Xian Sun¹, Daming Zhuang¹ and Jinquan Wei¹

¹ State Key Lab of New Ceramics and Fine Processing; Education Ministry Key Laboratory for Advanced Materials Processing Technology; School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China
² Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China

E-mail: jqwei@tsinghua.edu.cn

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1. Introduction

Small droplets exist widely in nature, such as clouds, fogs, mist, haze, and so on, which have diameters ranging from ~10 to 100 μm, corresponding to volumes of 1 ~ 1000 picolitre (pL). The small droplets can carry and transfer various materials, including inks, ions, salts, molecules, and nanoparticles, which make them have attractive applications in electronic printing [1–3], chemical reaction [4, 5], and high-throughput fabrication [6]. It is also possible to confine chemical reactions within a small droplet [7–9], which is believed to be a cost-effective way towards nanomaterial fabrication since it can directly put nanomaterials to the right positions and significantly reduce row materials consumption.

To date, several techniques have been developed to generate small droplets, including drop-on-demand printing [10–12], electrohydrodynamic jet (e-jet) printing [13–16], micro- and nano-fluidics [17, 18], and so on. One can generate small droplets in nano- to picolitre (nL to pL) scale by using these methods. The e-jet printing is a technique that uses electric fields to create fluid flows necessary for delivering inks to a substrate, which enables direct, additive patterning of materials with high resolution within the sub-micrometre range [19–21]. The size of droplets and frequency of jetting are both coupled to the electric field [22]. By superimposing a pulse over the static electric field, both of the size of the droplets and the frequency of jetting are both controlled [23, 24]. Schneider et al prepared single nanoparticle from attolitre (aL) droplets from capillary nozzles with outer diameters of 1 ~ 1.3 μm by the e-jet method [25]. The volumes of the droplets were roughly determined by their footprints. Zhang et al also reported dispensing and manipulation of droplets with volume ranging from aL to μL [26]. However, it is still a great challenge to generate accurately and directly measure the ultrafine droplets with volume down to aL. On one hand, it is difficult to divide the droplet into smaller parts due to its large surface tension and high mobility. It usually needs to reduce the dimension of the nozzles significantly to get ultrafine droplets down to femtolitre (fL) scale [25, 27]. On the other hand, it is difficult to keep the ultrafine droplet in air for a long time for measurement because of their ease of evaporation. The size of droplets were usually measured the trace of the droplets or lines on the substrates [25, 27–30].
Here, we accurately generate attolitre droplets by using the e-jet method from a large nozzle with an outer diameter of ~10 μm. By superimposing a low frequency pulse over the static electric field, the ejection and volume of the droplets are both well controlled. The best accuracy of the ultrafine droplets reaches to 0.3 aL. We also directly deposit gold nanoparticle array on substrate from HAuCl₄/H₂O solution through confined reaction and show a potential application in surface enhanced Raman scattering (SERS).

2. Experiments

The ultrafine droplets were printed on SiO₂/Si substrates (100 nm SiO₂ layer on Si (100), 20 × 20 × 0.5 mm) through quartz capillaries with inner and outer diameters of 5 ~ 12 μm and 10 ~ 20 μm (see figure S1 is available online at stacks.iop.org/NANOX/1/030008/mmedia), respectively. The quartz capillaries were fabricated by drawing through a micropipette puller and then were consequently coated with 10 nm Ti and 50 nm Au films through e-beam evaporation. The Ti/Au coated quartz capillary was then installed on a holder. A SiO₂/Si substrate was mounted on a 3D stage with a linear accuracy of 10 μm/100 mm. The distance between the tip of capillary and substrate was adjusted through the z-axis stage to ~50 μm. By applying an electric field, the liquid was drawn from the capillary and jetted onto the substrate. We used ethylene glycol to measure the volume of the ultrafine droplets.

To prepare Au nanoparticle arrays, we printed 0.4 mM HAuCl₄/H₂O ultrafine droplets onto the SiO₂/Si substrates, and then put them into a chamber with a bottle of diluted hydrazine hydrate solution prepared by adding 0.5 ml hydrazine hydrate (degree of hydration of ~1.5, 50%) in 2 ml water. After pumping the chamber to a low vacuum of ~10 Torr, it formed a reducing environment with hydrazine vapour in the chamber. The HAuCl₄ were reduced to Au nanoparticles by keeping in the reducing environment for 30 min.

The droplets and Au nanoparticles were characterised by an atomic force microscope (AFM) in open air at room temperature. Raman spectra were performed using a confocal Raman microscopy system (WITec Alpha 300R) with an excitation laser wavelength of 532 nm. The laser with a power of 0.1 mW was focused to a spot size of ~500 nm using a 100 × Zeiss objective lens. The integration time of spectral acquisition was set to 10 s. For SERS investigations, 10 μL of the probe molecule of rhodamine 6G (R6G) solutions with concentrations ranging from 10⁻³ to 10⁻⁷ M were dropped onto the SiO₂/Si substrate with Au nanoparticle array. For comparison, we also performed Raman spectra to the R6G powder placed on the Si (100) substrate.

3. Results and discussion

Ultrafine droplets of ethylene glycol are printed on the SiO₂/Si substrate under a dc electric field (>1.5 V μm⁻¹). Figure 1(a) exhibits an AFM image of the ultrafine droplet array of ethylene glycol on the SiO₂/Si substrate, which was measured immediately after e-jet printing. The ultrafine droplet array has a space of about 5 μm. According to the scanning rate of 350 μm s⁻¹, the ejection interval is ~14 ms, which is in consistence with that jetting from a large needle (200 μm) [31]. It implies that the ejection of the ultrafine droplets from a small nozzle is similar to that from a large needle. It is noted that the ultrafine droplets do not align very well, which might be because of the influence of residual charges on the droplets [1].

Figure 1(b) exhibits the volume distribution of the ultrafine droplets, which are calculated from AFM. The corresponding data are provided in table S1. The volume of the ultrafine droplets distributes widely from 0.12 to 4.31 aL with a mean value of 1.38 aL, corresponding to round droplets with diameters ranging from 60 to 200 nm. According to our previous observation, the liquid drawn from the nozzle has a diameter larger than that of the nozzle tip because of inherent hydrophilic properties of the metallic coating [13, 31]. Therefore, the diameter of the droplets depends on the outer diameter, rather than inner diameter of the nozzle which differs from those jetted from nano-capillary [25, 27]. It shows that the diameter of the droplets generated through e-jet method is about 1/50 to 1/160 that of the outer diameter of the capillary.

To confirm the volume of ultrafine droplets, we perform the AFM measurement again 30 min after the first measurement (see figure 1(c)). It is clear that all the droplets stay at the same place, but become smaller. The volume of the ethylene glycol droplets varies from 0.06 aL to 2.84 aL (see figure 1(d) and table S1). The mean volume decreases to 0.94 aL, showing a retention rate of 65%. Therefore, it is reliable to measure the volume of the ultrafine ethylene glycol droplets by AFM.

Figure 1(e) shows a 3D morphology of an ethylene glycol droplet. Although there is transverse broadening error in the AFM, the droplet exhibits a perfect spherical crown shape, with a circularity of ~93%. This droplet has a basal diameter of 460 nm, a height of 50 nm, and a volume of ~2.05 aL. Figure 1(f) shows a cross-sectional image of the droplet, showing a contact angle of 25°, which is very close to that (28°) of a large droplet (5 μL) on the same substrate (figure S2).
To control the volume of ultrafine droplets accurately, we reduce the electric field to \( \sim 0.8 \text{ V} \mu\text{m}^{-1} \), and superimpose a low frequency pulse of square wave over the baseline voltage (see figure S3). At a low electric field, the liquid is drawn slightly out of the nozzle. By superimposing a pulse, ultrafine droplets jet to the substrate. Figure 2(a) shows an AFM image of the ultrafine droplet array generated by superimposing an 8 Hz pulse with a duty ratio of 20%. The droplet array align in a row quite well. The space between two adjacent droplets is about 5 \( \mu\text{m} \), very close to that calculated from the moving rate of the substrate (40 \( \mu\text{m s}^{-1} \)) and the frequency of the pulse. It indicates that the ejection of the droplets is triggered by the pulse. The volume of droplets distributes narrowly from 0.68 to 1.8 aL, with a mean value of 1.05 aL and a coefficient of variation (Cv) of 25% (see figure 2(b)). Therefore, it is a reliable method to generate ultrafine droplets with volumes in aL scale precisely.

We further investigate the influence of pulse parameters on the volume of ultrafine droplets. By keeping the duty ratio at 20%, the mean volume of the ultrafine droplets is well controlled from 1.12 to 3.86 aL with an accuracy of 0.3–0.8 aL by adjusting the frequency of pulse from 5 Hz to 8 Hz (see figure 2(c)). The volume of these droplets distributes very narrow, with a low Cv of about 24% (see figure S4). By keeping the frequency at 8 Hz and adjusting the duty ratio, the average volume of the droplets decreases from 1.05 to 5.33 aL (figure 2(d)), with an accuracy of 0.3–1.5 aL and a CV value lower than 27% (see figure S5). Thus, the volume of the ultrafine droplets is controlled from 1 to 5 aL with the best accuracy of 0.3 aL by tuning frequency and duty ratio of the pulse.

The ejection of droplets is related to the charge accumulation and release under the electric field [1, 13]. The electric charges accumulated on the droplet plays a key role in the ejection. For the dc electric field, charges

**Figure 1.** (a) and (b) are AFM image and volume distribution of the ultrafine droplets measured immediately after printing. (c) and (d) are AFM image and volume distribution of the ultrafine droplets 30 min after the first AFM measurement. (e) 3D AFM image of an individual droplet. (f) Cross-sectional AFM image of the droplet.
accumulate on entire surface of the droplets. A build-up of charges on the printed droplets can alter the dynamics of printing. Therefore, it is difficult to control the ejection and printed direction of the ultrafine droplets. By imposing a pulse voltage, charges mainly accumulate at the tip of the extrusion liquids. The ejection of ultrafine droplets are triggered by the pulse, which is affected by the pulse parameters significantly. At high frequency, the liquid gets low energy in a full period. Therefore, it tends to get smaller droplets than under the dc electric field. At large duty ratio, it inclines to get large droplets since more charges accumulate on the droplets. Since it contains only a tiny amount of solute, we try to fabricate nanomaterials directly by confined chemical reaction within the ultrafine droplets. We print ultrafine droplets of HAuCl₄/H₂O solution on the SiO₂/Si substrate and then place them in a reducing environment with hydrazine hydrate vapour. Figure 3(a) is an AFM image of the gold nanoparticles depositing on the substrate. It is difficult to measure the volume of ultrafine droplets due to its ease of evaporation. The HAuCl₄/H₂O droplets have volumes of about tens of aL according to the trace and contact angle. The HAuCl₄/H₂O droplets are slightly larger than those of the ethylene glycol, which derive from their difference in the solution properties. It shows from figure 3(a) that the gold nanoparticles are confined in a round droplet with a diameter of ~1 μm. Most of the gold nanoparticles have size less than 10 nm according to the AFM profile (figure 3(b)). The number of gold atoms is larger than that calculated from the volume and concentration, which might derive from enrichment of the ions of AuCl₄⁻ at the tip of the nozzle under strong electric field. It takes only ~50 μL to prepare Au nanoparticle array with a dimension of 2 × 2 cm. Thus, it can minimise the consumption of raw materials for preparation of gold nanoparticle array.

We further demonstrate potential application of the Au nanoparticles array using as SERS substrate. As R6G has been well-characterised by SERS [32–36], we use R6G as the probe molecule to examine the SERS performance. As shown in figure 4(a), there are very weak peaks in the Raman spectrum of the R6G powder on the Si substrate without gold nanoparticles (dark). It exhibits prominent characteristic peaks of the R6G at 1130 cm⁻¹, 1181 cm⁻¹, 1309 cm⁻¹, 1369 cm⁻¹, 1507 cm⁻¹, 1571 cm⁻¹ and 1648 cm⁻¹ in the Raman spectrum (red). The Raman peaks are enhanced on the SERS substrate, showing the SERS effect of the Au nanoparticles. The Raman intensity changes slightly as the concentration of R6G decreases from 10 mM to 1 μM (figure 4(b)), showing that the SERS substrate R6G with concentration at least 10⁻⁶ M (see figure 4(b)). Our preliminary results shows a detection limit of the R6G is 10⁻⁷ M, which is comparable to that of the Ag nanoparticles.

Figure 2. Characterisation of the ethylene glycol ultrafine droplets prepared by superimposing a pulse of square wave (frequency: 8 Hz, duty ratio: 20%) over a constant voltage. (a) Typical AFM image of the ultrafine droplet array. (b) Volume distribution of 74 ultrafine droplets. The effect of pulse parameters on the volume of the ultrafine droplets, (c) frequency, (d) duty ratio.
synthesised by traditional chemical reduction [37, 38]. We believe that the detection limit of the SERS substrate will be improved by tuning the size, shape, morphology and distance between two adjacent Au nanoparticles of the SERS substrate. To verify the reliability and reproducibility of the SERS substrate, the SERS spectra of R6G on several positions of the substrates prepared under the same conditions were measured, as shown in figures 4(c) and S6. It shows that it is high reliability and good reproducibility of the SERS substrates preparing from the ultrafine droplets through confined reaction.

4. Conclusion

Ultrafine droplets in attolitre scale are accurately generated through an e-jet method. By superimposing a square wave signal over a static electric field, the volume of the ultrafine droplets is accurately controlled from 1 to 5 aL with a coefficient of variation of about 25% and the best accuracy of 0.3 aL. Gold nanoparticles are directly deposited onto the substrate from the ultrafine droplets through confined reduction. It is a cost-effective method to prepare nanoparticle array. The Au nanoparticle array prepared by the confined reaction within ultrafine droplets shows high sensitivity and reliability in SERS detection.

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ORCID iDs

Jinquan Wei  https://orcid.org/0000-0002-5827-2231
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