Electronic Supplementary Material (ESI) for Analytical Methods.

ELECTRONIC SUPPLEMENTARY INFORMATION

Inkjet Printing Ag nanoparticles for SERS hot spots

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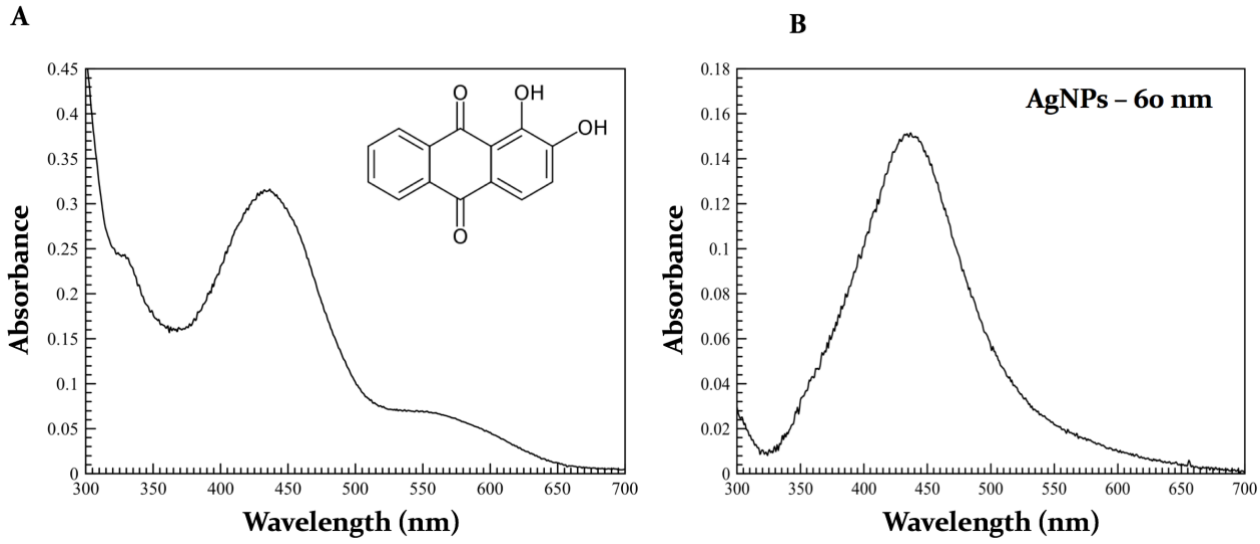

Figure S1. (A). UV-vis spectra of Alizarin 10^{-4} M in ethanol and (B) Ag NPs 60 nm diluted 1:10 in water.

In Figure S2, we report the Derby plot that illustrates the different regimens of inkjet printing. The conventional double pulse waveforms - used for commonly employed printable fluids - can easily cause satellite droplets on aqueous inks[1] as the ones employed in this work (see the red dot). On the other hand, double pulse waveform can be used to print aqueous protein inks spiked with high viscous additives like glycerol[2] in order to tune viscosity and surface tension at values compatible with printable fluids regime.

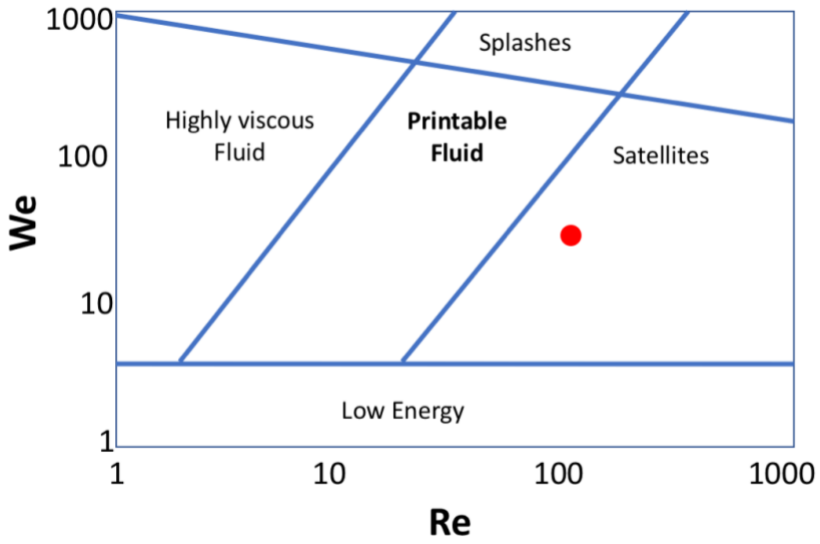

Figure S2. Collocation of the employed aqueous inks (red dot) within the Derby plot which illustrates the different regimens of inkjet printing. It is clear to observe that our ink represents a classical example of a fluid which would easily form satellites.

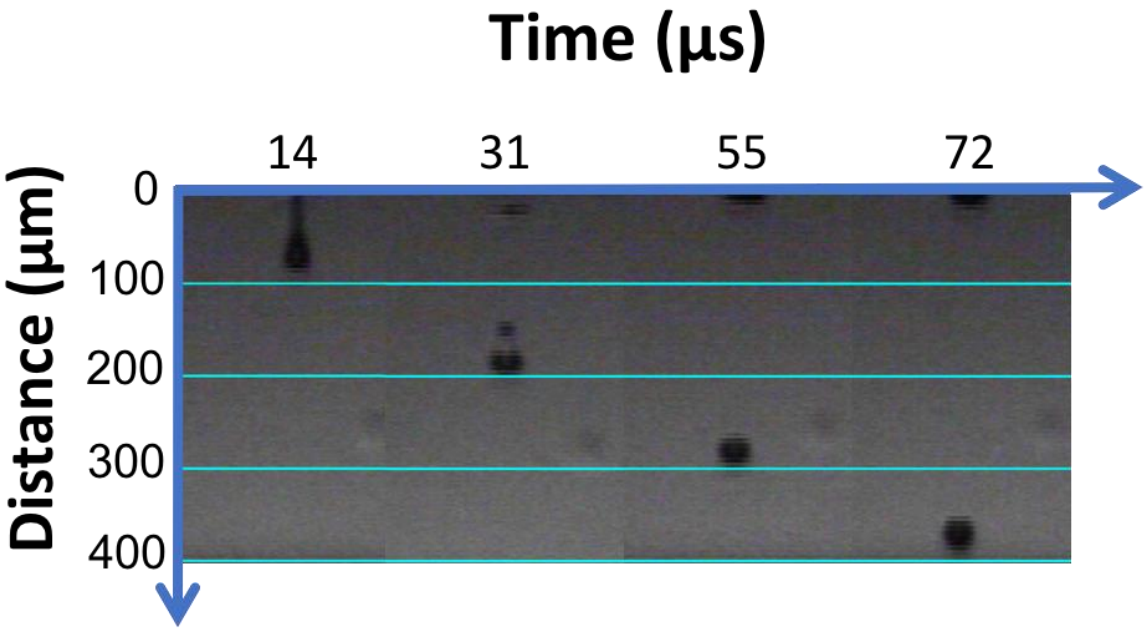

Figure S3. Stroboscopic images of 10 pL (nominal volume) droplets formation of an ink containing Ag NPs (1:10) and alizarin (10^{-5}M). The stroboscopic pictures are captured while a droplet pinches-off at nozzle exit (14 µs). Satellite recoil occurs after 55 µs, leading to reproducible production of spherical droplets without satellites.

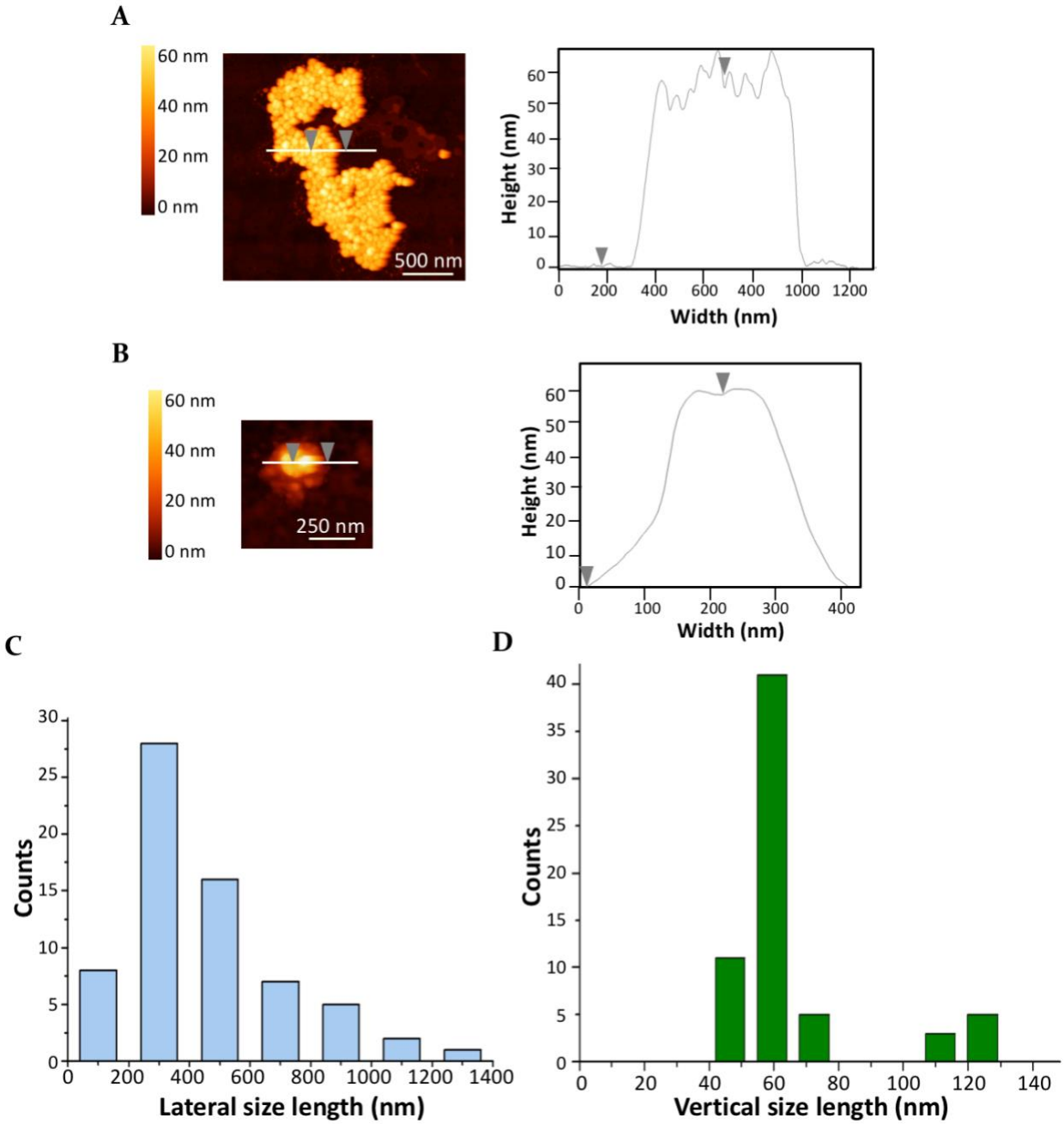

Figure S4. AFM characterization of: (A) A representative AgNPs aggregate on glass (left) with the section analysis along the line marked in the image (right); (B) A typical AgNPs aggregate in presence of alizarin (10^{-5} M) on glass with the relative section analysis. (C) Lateral size and (D) height distribution of AgNPs aggregates in presence of alizarin (about 65 measured aggregates from 100 inkjetted droplets).

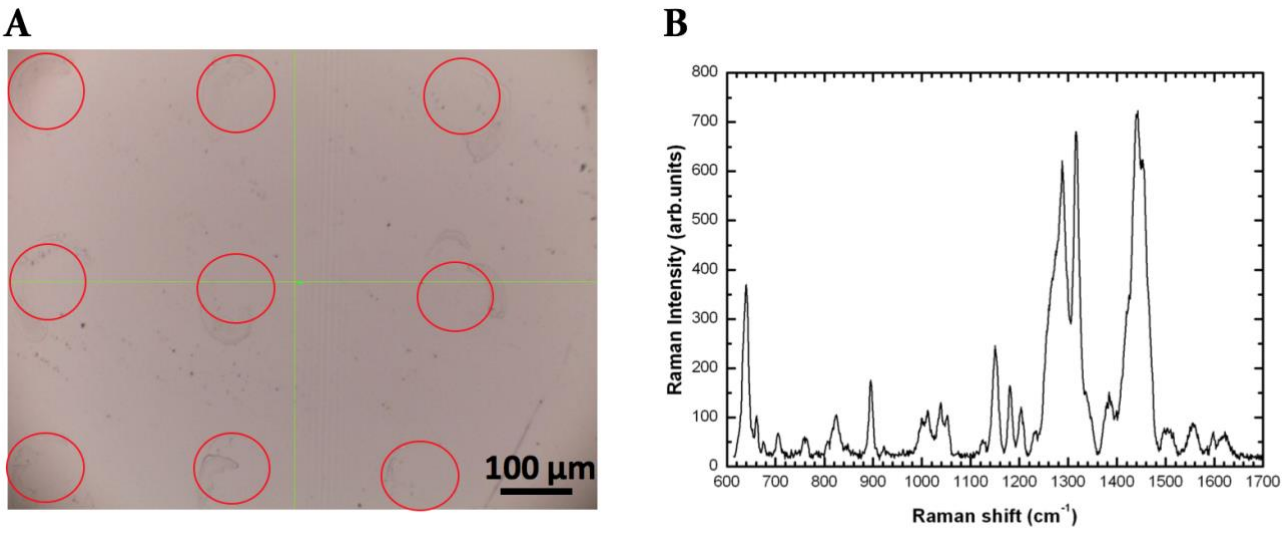

Figure S5. (A) Optical image of 9 dried droplets (marked by red circles) containing Ag NPs (1:10) and alizarin (10^{-5}M) at 1000 pL level, and (B) relative SERS spectra from a single hot spot.

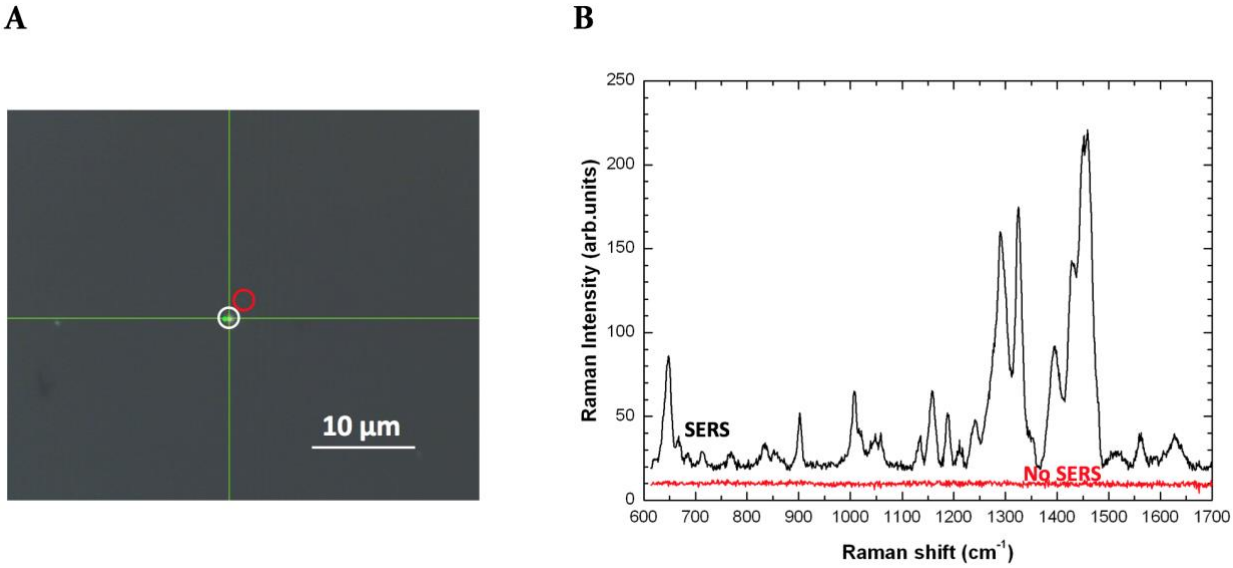

Figure S6. A single hot spot usable for SERS enhancement is visualized via optical microscope at 100 x magnification as a submicron sized bright dot inside dried 10 pL droplet. The white circle in panel A encompasses the bright dot (formed by aggregated AgNPs) onto which laser spot is focused. From the single bright dot, it is possible to extract a SERS spectrum with the typical peaks due to alizarin (**SERS** spectrum in panel B). On the other hand, no SERS effect is observable if laser spot is focused in nearby zones (red circle in panel A) and the resulting spectrum does not show typical any detectable peak (**no SERS** spectrum in panel B). For both spectra, laser power and acquisition time were, respectively, 0.01% and 20 seconds.

References

1. G. Arrabito, F. Cavaleri, V. Montalbano, V. Vetri, M. Leone, and B. Pignataro, *Lab Chip*, 2016, **16**, 4666–4676.
2. G. Arrabito, C. Galati, S. Castellano, and B. Pignataro, *Lab Chip*, 2013, **13**, 68–72.