Supporting Information

Real-time analysis of diaquat dibromide monohydrate in water with a SERS-based integrated microdroplet sensor

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Figure S6. (a) Concentration-dependent SERS spectra of DQ in a spiked drinking water; (b) variations of DQ peak intensity at 1579 cm^{-1} of SERS spectra as a function of DQ concentration. (correlation coefficient, R=0.996). All the measurements were performed in the microdroplet channel . Error bars indicate the standard deviations of three measurements.

Figure S7. (a) SERS spectra of 5×10^{-6} M DQ collected from three different different chips. (b) Magnified images for the dotted line zone in (a).

Figure S8. Mean spectra (solid lines) and double standard deviations (blue tubes) for three different chips. SERS measurements were carried out 50 times for each chip, and the concentration of DQ was 5×10^{-6} M.

Table S1. Vibrational assignments for the characteristic SERS peaks of DQ.

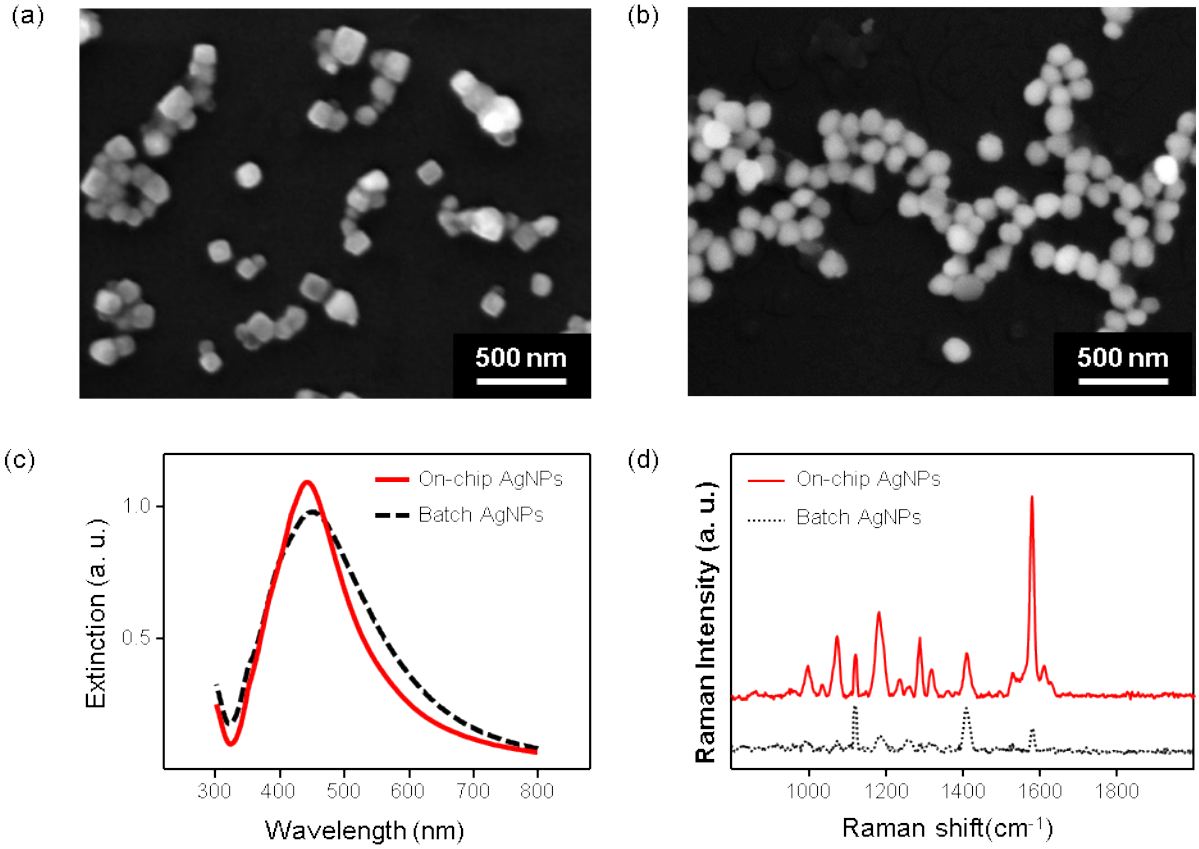


Figure S1 SEM images of (a) on-chip synthesized AgNPs (110±8 nm) and (b) batch-synthesized AgNPs (115 ± 11 nm). (c) UV/Vis spectra and (d) SERS spectra of 5×10^{-6} M DQ with two different types of AgNPs.

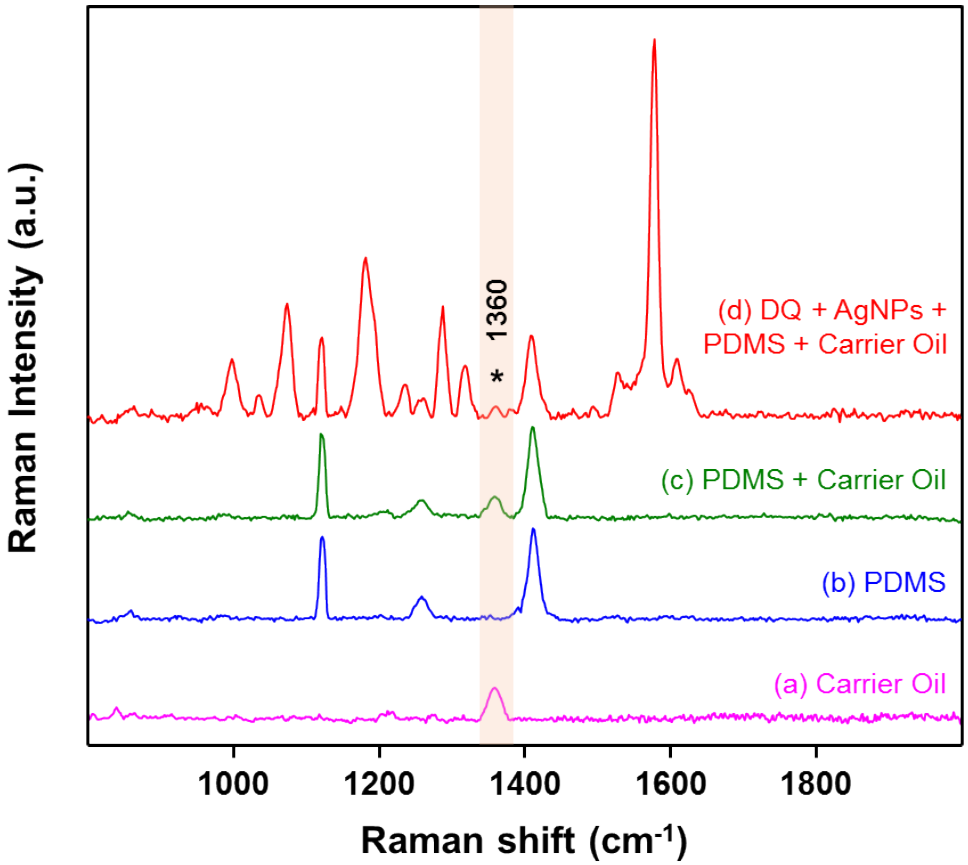


Figure S2. (a) Raman spectra of (a) carrier oil, (b) PDMS, and (c) PDMS + carrier oil. (d) SERS spectrum for 240 droplets including AgNPs and 2×10^{-5} M DQ solution in the microdroplet channel.

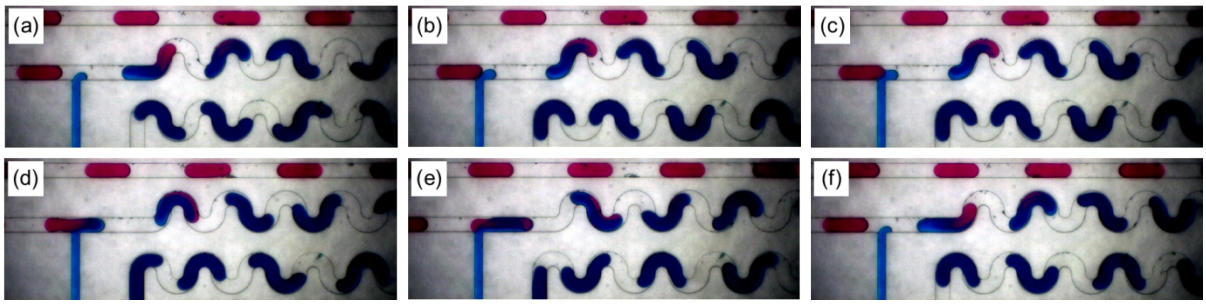


Figure S3. Droplet-merging process measured by high-speed camera.

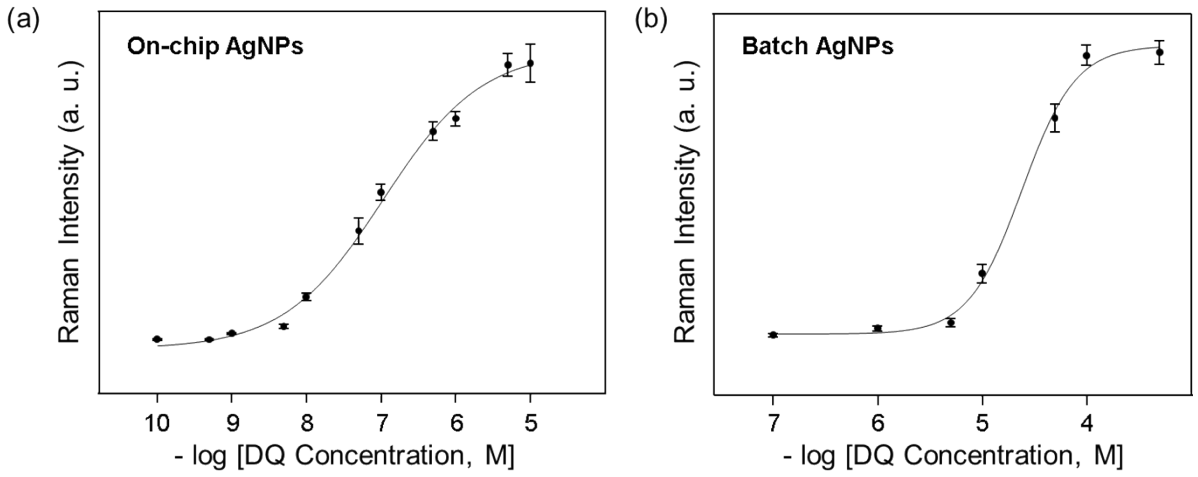


Figure S4. Variations of Raman intensity at 1579 cm^{-1} as a function of DQ concentration for (a) on-chip- and (b) batch-synthesized AgNPs. The range of concentrations constructed from SERS data was determined to be $10^{-5} \sim 10^{-10}$ M for on-chip AgNPs and $5\times10^{-4} \sim 10^{-7}$ M for batch AgNPs. Error bars denote the standard deviation resulting from three measurements.

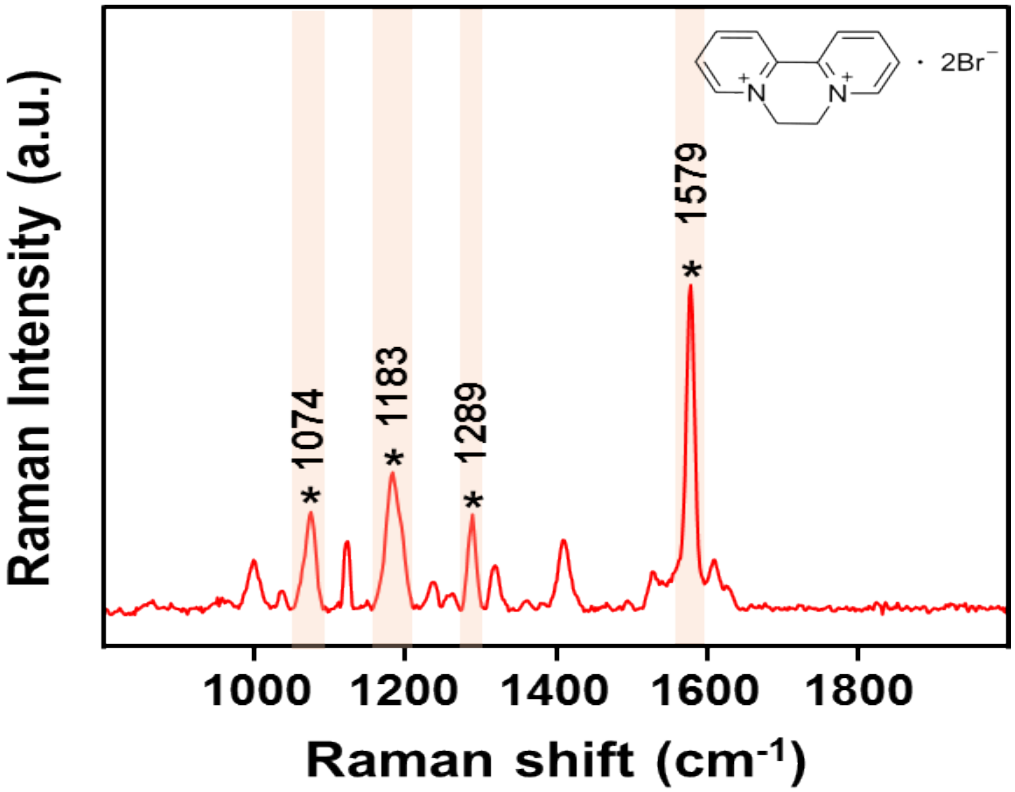
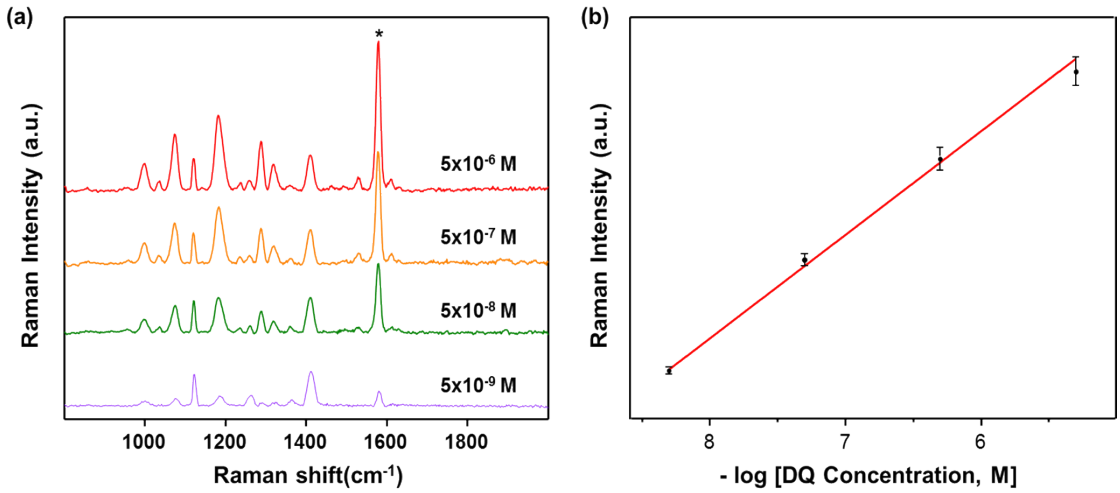


Figure S5. Observed SERS spectrum and the characteristic Raman peaks for 5×10^{-6} M DQ.



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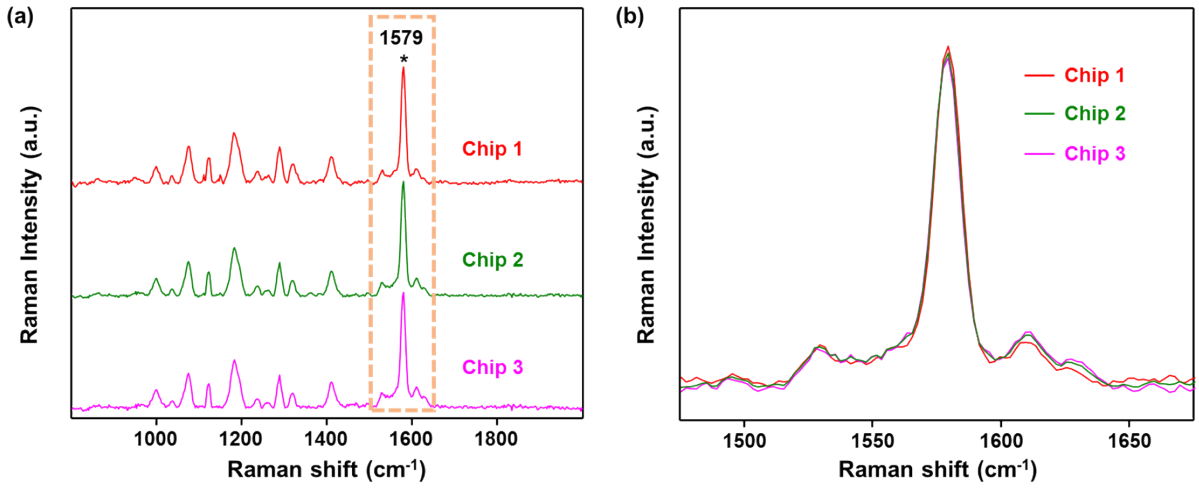

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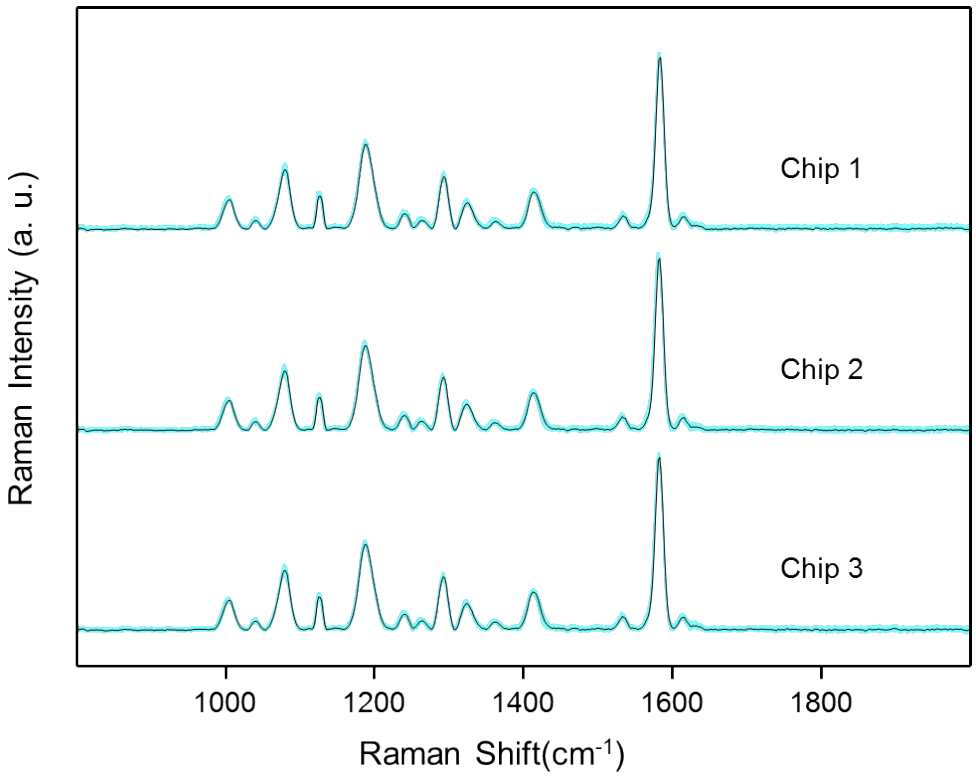

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Table S1 Vibrational assignments for the characteristic SERS peaks of DQ.

Bands (cm^{-1})	Assignment[a]
1579	ν_{ring} + ν(C=N)
1289	ν_{ring} + δ(CH) + $t_w(CH_2)$
1183	ν(H_2C-N) + δ(CH)
1074	δ_{ring} + δ(CH)

[a] ν, stretching; δ, in plane deformation; t_w, twisting.