ELECTRONIC SUPPLEMENTARY INFORMATION (E.S.I.)

Fusion of Microlitre Water-in-Oil Droplets for Simple, Fast and Green Chemical Assays

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Table S1. Intensities and wavelengths of different LED sources used in this study for colorimetric and fluorimetric detection. The intensities were measured above the Petri dish (*cf.* **Figure 1**). See **Figure S2** for full spectra.

Type	**Intensity / lux**	**λ_{max} / nm**	**Corresponding data**
Ultraviolet	41	397	Figs. S5A and S5B
Blue	1100	465	Figs. S5A and S5B
Green	480	525	Figs. S5A and S5B
Yellow	4	586	Fig. S5A
Orange	27	593	Figs. S5A and S5B
Bright red	500	633	Figs. S5A, S5B and S6
Red	2	691	Fig. S5A
White (array)	4000	448, 538	Figs. 2A, 3, S1, S2, S3A, and S4; Movie 1
Blue (array)	1660	475	Figs. 2B and S3B; Movie 2

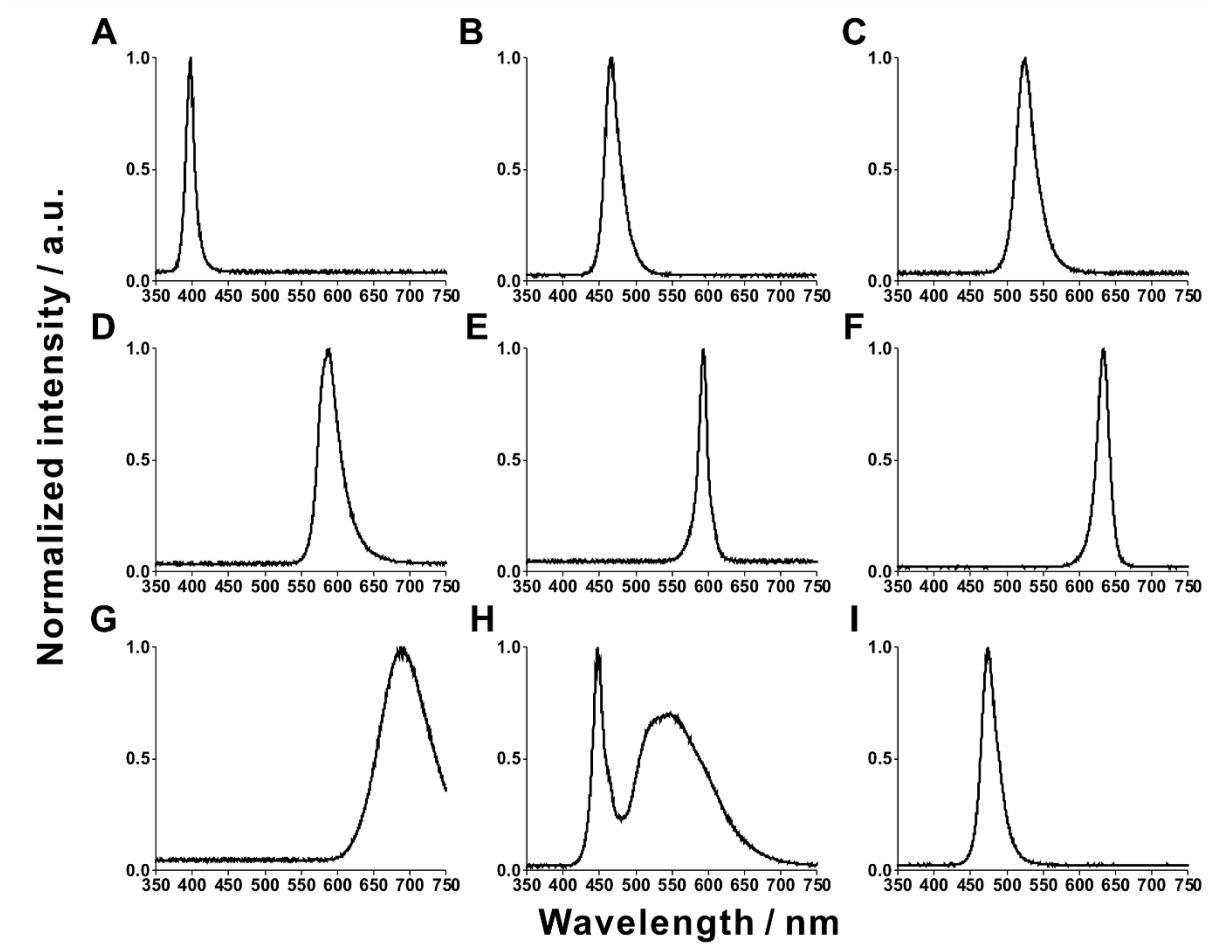

Figure S1. Spectral characteristics of the light sources used in this study: (A-G) Home-made LED light source (14 LEDs; 2 for each of 7 wavelengths). (H) White LED array (48). (I) Blue LED array (19). Emission maxima: (A) ultraviolet; (B) blue; (C) green; (D) yellow; (E) orange; (F) bright red; (G) red; (H) white; (I) blue. The measurement of wavelength was conducted using a portable spectrophotometer (USB4000-VIS-NIR; Ocean Optics, Dunedin, FL, USA).

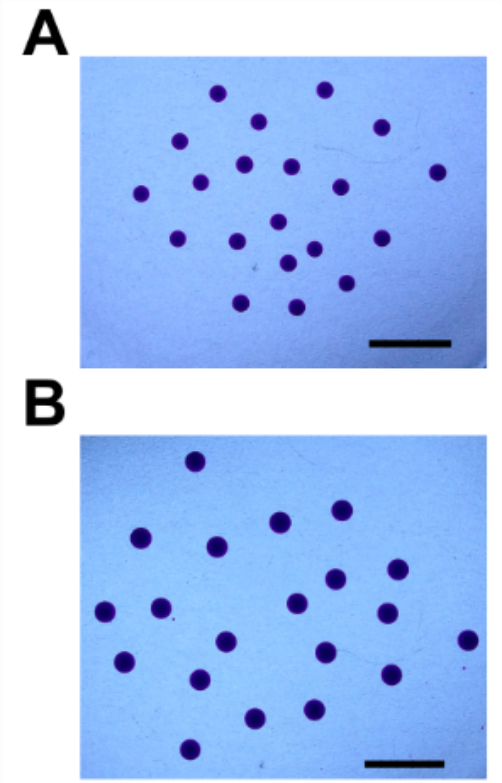

Figure S2. Droplet pipetting – repeatability test. In this experiment, 20 individual droplets ((A) 0.7 μL, (B) 1.4 μL), containing 1-M aqueous solution of potassium permanganate, were dispensed into the silicone oil matrix. Scale bar: 5 mm.

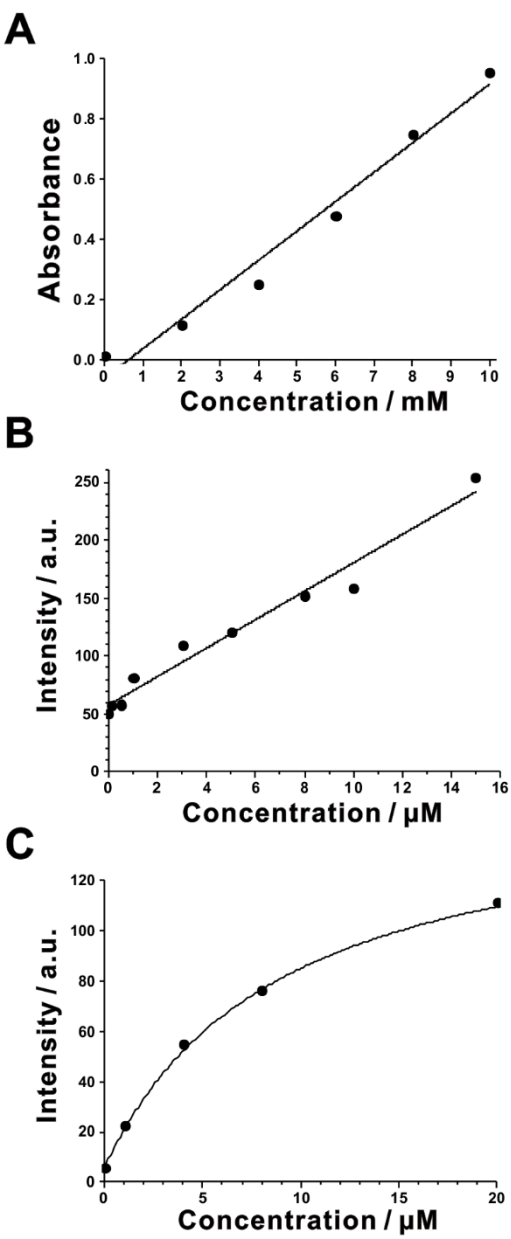

Figure S3. Calibration plots for quantitative analysis of droplet contents using (A) colorimetry (*cf.* **Figure 1B(i)**); (B) fluorimetry (*cf.* **Figure 1B(ii)**); (C) chemiluminescence (*cf.* **Figure 1B(iii)**). In (A), the standard volume was ~ 1.4 µL, while in (B) and (C), the standard volumes were ~ 5 µL. Every data point in (A) is obtained from average of ~ 30 pixels while in (B) and (C) ~ 65 pixels. Calibration equations: (A) *Absorbance* = (0.108±0.007) *C* - (0.138±0.043); (B) *Intensity* = (12.3±0.8) *C* + (57.8±5.6); (C) *Intensity* = 5.8 + ((151±5) × *C*) / (*C* + (0.009±0.001)). Concentration ranges used in the fits: (A) 0-100 mM potassium permanganate; (B) 0-15 µM fluorescein; (C) 0-20 mM sodium hypochlorite. LOD in colorimetry is 1.19 mM (~ 1.4 nmol), LOD in fluorimetry is 1.37 µM (~ 1.4 pmol), LOD in chemiluminescence is 112 nM (~ 580 fmol). The data presented in (C) has been obtained in the experiment illustrated in **Figure 2C**.

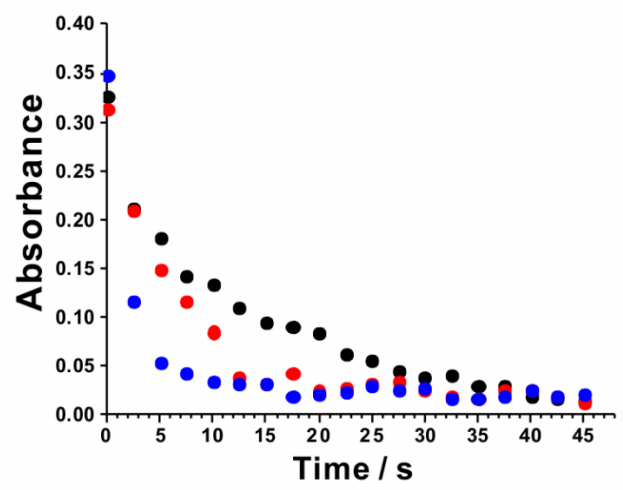

Figure S4. Comparison of silicone oil (●, black), soybean oil (●, red), and 1-octanol (●, blue) as assay matrix. Volume of every merged droplet was ~ 1.4 μL. The concentration of the initial droplets were: (i) 10 mM potassium permanganate; (ii) 222 mM glucose mixed with 167 mM sodium hydroxide (*cf.* **Figure 2A**). The data for silicone oil comes from a replicate of the experiment illustrated in **Figure 2A.**

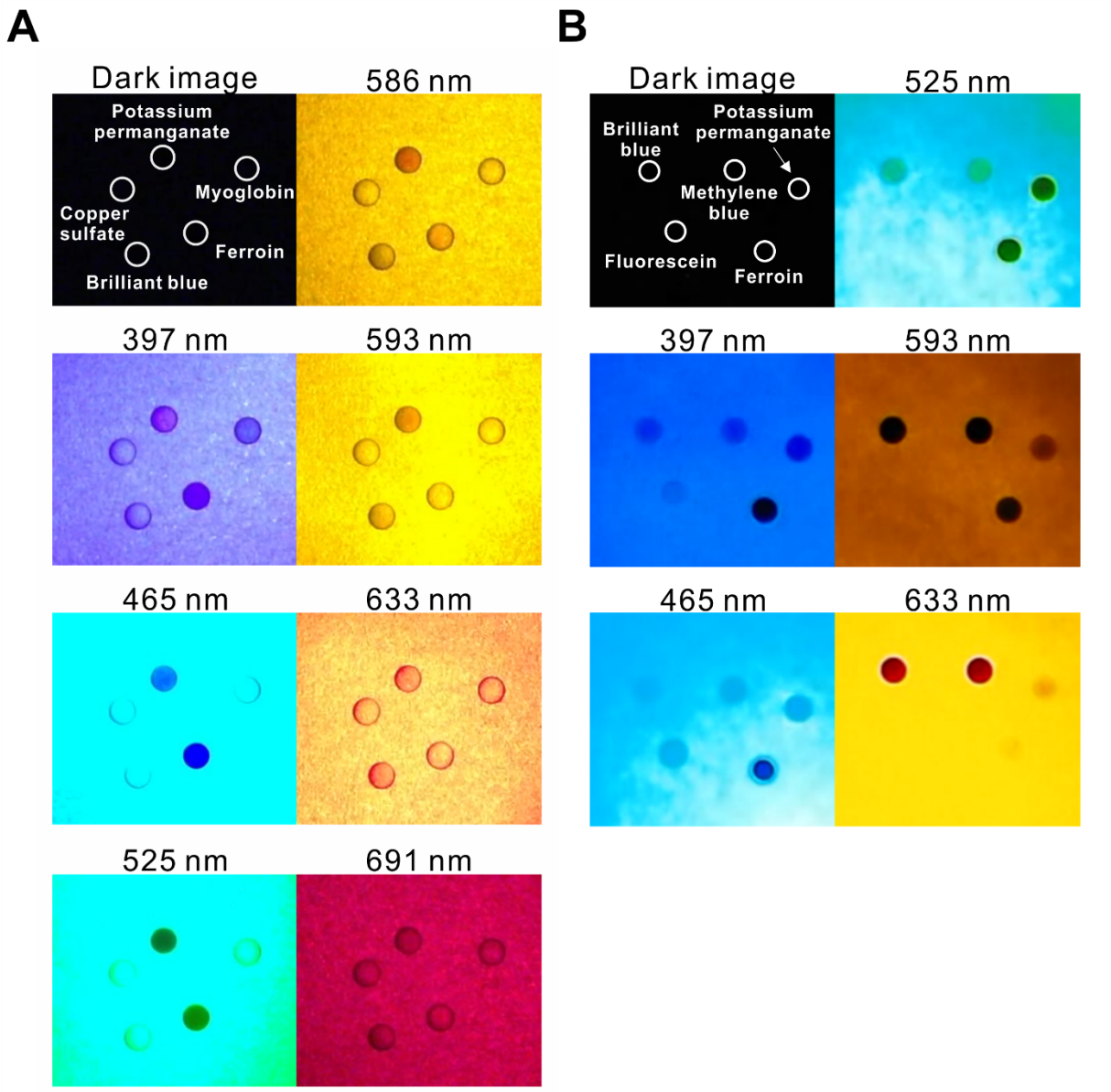

Figure S5. Possibility to carry out spectral analysis of multiple microdroplets in oil matrix. Volume of every droplet: ~ 1.4 µL. The Petri dish containing droplet suspension in silicone oil was illuminated using the home-made multi-wavelength LED source controlled by computer. Video sequences were recorded either by smartphone camera (A), or a professional reflex camera (B). The wavelength presentation time in (A) was either 4 nor 6 s (depending on wavelength), while the wavelength presentation time in (B) was fixed to 0.5 s. The droplets in (A) contain: 1 mM brilliant blue, 1 M copper sulphate, 25 mM ferroin, 0.1 mM myoglobin, and 1 mM potassium permanganate. The droplets in (B) contain: 1 mM brilliant blue, 25 mM ferroin, 6.92 mM fluorescein, 1 mM methylene blue, and 10 mM potassium permanganate.

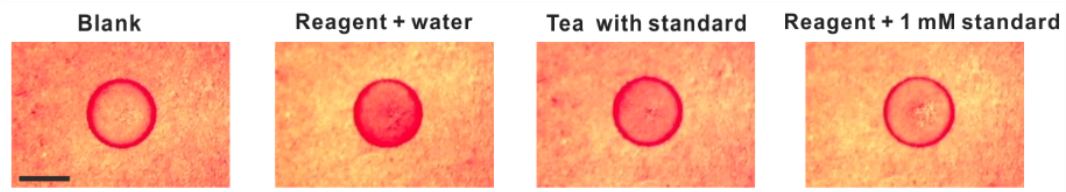

Figure S6. Semi-quantitative measurement of ascorbic acid. The images show the merged droplets 15 s after the merger. The blank was 5-μL 200 mM ammonium acetate droplet merged with 5-μL water droplet. The assay droplets originate from merging 5-μL Tillman's reagent (1 mM 2,6-dichloroindophenol sodium salt hydrate in aqueous 200 mM ammonium acetate) droplets with 5-μL sample droplets: water; 10× diluted mixture of oolong tea with ascorbic acid (final concentration of ascorbic acid, 0.5 mM); 1.0 mM ascorbic acid in water. The Petri dish was illuminated with red light source (λ = 633 nm; *cf.* **Figure S5A**). Scale bar: 2 mm.