Supplementary Information for

A microfluidic route to small CO_2 microbubbles with narrow size distribution

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Schematic of the devices

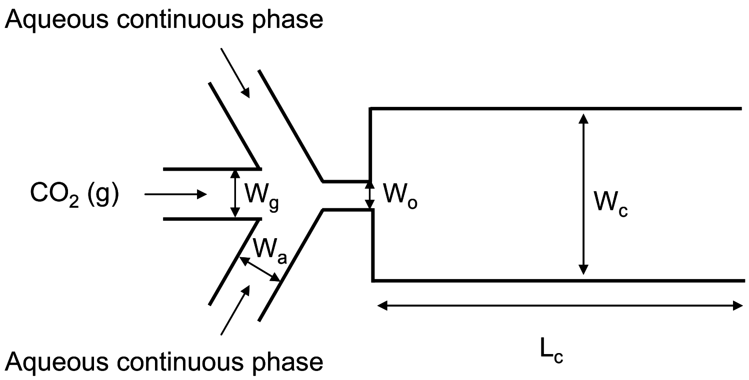

Figure S1. Schematics of microfluidic bubble generator. For the study of CO_2 bubble dissolution, W_g=50 µm, W_a=80 µm, W_o=33 µm, W_c=230 µm, and L_c=230 mm. Height of the channel is 115 µm ; for the production of small bubble (<10 µm), W_g=40 µm, W_a=70 µm, W_o=22 µm, W_c=60 µm (increased to 500 µm at the distance 500 µm away from the orifice), and L_c= 150 mm. The height of the channels is 40 µm

Estimation of the concentration of dissolved CO_2.

The dissolution of carbon dioxide $CO_2(g)\leftrightarrow CO_2(l)$ is described by Henry's law as

$$[CO_2]_l = k_H \times P_{CO_2} \tag{1}$$

where k_H is Henry's law constant and the following reactions between CO_2 and OH^- or H_2O[1,2]

$$\text{pH}<10\text{: } CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (K = 4.4 \times 10^{-7}) \tag{2}$$

$$\text{pH}>10\text{: } CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (K = 3.2 \times 10^{7}) \tag{3}$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \qquad (K = 3.5 \times 10^{3}) \tag{4}$$

where K is equilibrium constant.

The value of k_H depends on the concentration of the ionic species in water as $k_H = k_H^0 \times 10^{-0.138I}$ where k_H^0 is Henry's law constant for CO_2 in pure water ($k_H^0 = 3.3 \times 10^{-4}$ mol/(L kPa)) and I is the ionic strength, $I = 0.5\sum_i C_i z_i^2$ and C_i is the concentration of ions with charge z.[1]

At pH<5, the total concentration of dissolved CO_2 is determined by Henry's law,[3] whereas at pH ≥5, the total concentration of dissolved CO_2 can be estimated by adding the unreacted amount of CO_2 (determined by Henry's law) and reacted CO_2 (following eq. 2-4).[1]

Below we show the detailed calculation of the total concentration of dissolved CO_2 for pH=13.2, $k_H = 3.2 \times 10^{-4}$ mol/(L kPa) and P_{CO_2}=27.6 kPa. Based on eq. (1), $[CO_2]_l \approx 0.009$ mol/L and the reaction (2), we determined the concentration of reacted CO_2 as follows.

	$CO_2(l)$	+	OH^-	$\leftrightarrow$	HCO_3^-	$K = 3.2 \times 10^7$
Initial concentration	0.009		0.16			
Reacted concentration	$-x$		$-x$		x	
Final concentration	0.009-x		0.16-x		x	

$x \approx 0.009$ mol/L

The total amount of dissolved CO_2 (both reacted and unreacted) is $[CO_2]_l + x$, that is, ≈0.018 mol/L.

Using the same approach we found that for pH=11, the concentration of dissolved CO_2 was *ca.* 0.01 mol/L. For 5≤pH<10, by combining Henry's law (eq. 1) and reaction (2), we determined the total concentration of dissolved CO_2 to be approximately 0.009 mol/L.

For pH=1.5, we used Henry's law (eq. (1)) and found the total concentration of dissolved CO2 to be ca. 0.009 mol/L.

References

1. P. V. Danckwerts, *Gas-liquid Reactions*, McGraw-Hill Book Company, New York, 1970.
2. T. Madhavi, A. K. Golder, A. N. Samanta and S. Ray, *Chem. Eng. J.*, 2007, **128**, 95-104.
3. J. N. Butler, *Carbon dioxide equilibria and their applications*, Lewis Publisher, Michigan, 1981.