Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Liquid-gas dual phase microfluidic system for biocompatible $CaCO_3$ hollow nanoparticles generation and simultaneous molecule doping

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1. Experiment

Reagent

Sylgard 184 elastomer base and curing agent for polydimethylsiloxane (PDMS) were purchased from Dow Corning (Midland, MI). SG-2506 borosilicate glass (with 145 nm thick chrome film and 570 nm thick positive S-1805 type photoresist, Changsha Shaoguang Chrome Blank Co. Ltd) was applied as the initial glass wafer for glass mold fabrication. Bromothymol blue is provided by Shanghai Reagent Co., Ltd.. $CaCl_2$ and NaOH of analytical reagent grade are provided by Nanjing Chemical Reagent Co. Ltd. CO_2 gas is from Nanjing Special Gas Factory Co., Ltd.. Sodium fluorescein is from Sigma-Aldrich. Ultrapure water is from Milli-Q (Millipore, Inc., Bedford, MA).

Apparatus

Microfluidic pump (Model TS-2A, Longer pump Corp., Baoding, China) was applied for liquid manipulation. The gas flowmeter LOB-3WB from Changzhou KEDE thermo-technical instrument Co., Ltd. is applied for gas flow speed control. TL70000 optical system mounted with Olympus DP71 cooled CCD camera were applied for chip bright field image recording, results of which were analyzed by the Image-Pro Plus (IPP) 6.0 software. Confocal fluorescence microscopy is applied for imaging the shape of the $CaCO_3$ hollow nanoparticles. An S-4800 Field Emission Scanning Electron Microscope, by Hitachi, Ltd. (Japan) was applied for the $CaCO_3$ hollow nanoparticles characterization.

Chip design and fabrication

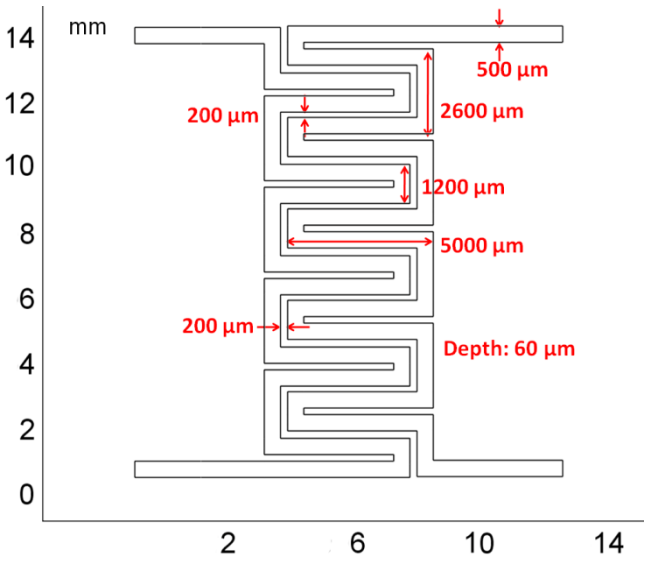

Figure S1. Detailed geometry of the chip.

The detailed geometry of the chip is depicted in **figure S1**. The large microchannels are both 500 μm for width, 60 μm for depth and 54 mm for length. They are interspaced by 200 μm. One of them is for gas phase and the other for liquid phase. The smaller microchannels bridging them are 35 μm for width, 10 μm for depth and 16 mm for length and interspaced for 100 μm.

To prepare PDMS chip with above structures, glass microlithography and its modified technique is applied for chip fabrication. Briefly, the glass molds for the cover sheet with liquid channel and gas channel and the bottom sheet with SMA are fabricated by firstly transferring the designed patterns to the SG-2506 borosilicate glass (with 145 nm thick chrome film and 570 nm thick positive S-1805 type photoresist). Then with 2 min of UV exposure, 1 min 0.5% NaOH solution soaking before another 1 min soaking in chromium etchant. After washing with pure water, all glass sheets with micropatterns are then baked at 80˚C for 10 min and etched by HF solution (HF : HNO_3 : NH_4F (1.0 M : 0.5 M : 0.5 M)) for 60 min. The SMA patterns start from an array of band pattern on the mask, with band width of 40μm. After 60 min HF etching, glass ridge structures with triangular cross sections are generated.

Micro-nanosphere particle preparation

The prepared $Ca(OH)_2$ suspension solution is injected to the chip by the pump at a predefined speed. A pipet tube is connected to the outlet for sample collection.

2. Dissolved CO_2 concentration modeling

For desolved gas concentration distribution modeling, the modeling technique is based on that reported in reference 1 but with different geometry and mesh numbers. The geometry of the modeled region are faithfully the same as that in figure S1. Comsol multiphysics 3.5 is applied with mesh number of 45172. The gradient system can be physically described by combining the steady state incompressible Navier-Stocks equation:

$$\rho((u\cdot\nabla)u) = -\nabla\cdot p + \eta(\nabla^2 u) \quad (1)$$

$$\nabla\cdot u = 0 \quad (2)$$

and ***the convection and diffusion equation:***

$$D\nabla^2 c = u\cdot\nabla c \quad (3)$$

ρ, u, p and η are the density, flow velocity field, pressure and the viscosity of the liquid. D and c are diffusion coefficient and dissolved gas concentration. The two equations are coupled together by sharing the 2D flow velocity field u. The detailed parameters and settings for the models share the following values.

Table S2. NS-equation boundary condition for Model S1

Boundary	Condition	Value
Inlet	Velocity	U_0
Outlet	Pressure	0
Gas-liquid interface	No slip	-
Wall	No slip	-

Table S3. Convection and diffusion boundary condition for Model S1

Boundary	Condition	Value
Inlet	Concentration	0 mol/m^3
Outlet	Convective flux	-
Gas-liquid interface	Concentration	1 mol/m^3

Wall	Insulation	-

Table S4. Physical data for subdomain settings for Model S1

Physical quantity	Value
Diffusion coefficient for CO_2 (isotropic) D	1.77e-9m^2/s
Initial concentration for CO_2 c_0	0 mol/m^3
x-velocity	u (the x direction component of u)
y-velocity	v (the y direction component of u)
Liquid density ρ	1 kg/m^3
Liquid Dynamic viscosity η	1 Pa*s
Liquid Volume force	0 N/ m^3

3. Biocompatibility of $CaCO_3$ hollow nanoparticles

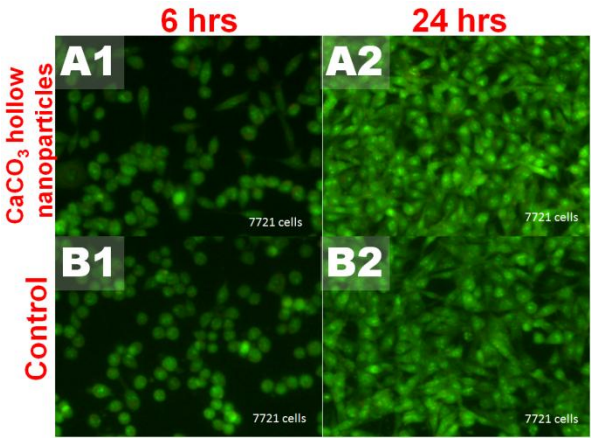

Figure S2. A. Combined AO-EB dye for 7721 cell culture in DMEM culture media with 30 mM doped $CaCO_3$ hollow particles. B. Control experiment： AO-EB dye for 7721 cell culture in DMEM culture media without the doped $CaCO_3$ hollow particles. A1 & B1 after 6 hrs. A2 & B2 after 24 hrs.