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Supporting Information

High-throughput and tunable synthesis of colloidal $CsPbX_3$ perovskite nanocrystals in a heterogeneous system by microwave irradiation

*Zi Long, Hong Ren, Jianghui Sun, Jin Ouyang, and Na Na**

Key Laboratory of Theoretical and Computational Photochemistry, College of Chemistry, Beijing Normal University, Beijing 100875, China

*Tel: +86-10-58805373. Fax: +86-10-58802075. E-mail: nana@bnu.edu.cn

Experimental Section

Chemical reagents. $PbCl_2$ (lead (II) chloride, ultra-dry, 99.999%), $PbBr_2$ (lead(II) bromide, ultra-dry, 99.999%), PbI_2 (lead(II) iodide, ultra-dry, 99.999%), Cs_2CO_3 (cesium carbonate, 99.994%), 1-octadecene (ODE, technical grade 90%), oleic acid (OA, technical grade 90%), and trioctylphosphine (TOP, 97%) were purchased from Alfa Aesar. Oleylamine (OAm, technical grade 70%) was purchased from Aladdin, and n-octylamine (OCT, grade ≥99%) was obtained from Acros, n-hexane (HPLC, grade ≥98.0%) was obtained from Damao Chemical Reagent Tianjin Company (Tianjin, China). In the fabricated films, poly(methyl methacrylate) (PMMA) from Acros was used. All solvents and reagents were used as received without further purification. All microwave syntheses in this work were performed in a Galanz household microwave oven made in China operating at 800 W.

Apparatus and software. Transmission electron microscopy (TEM) and scanning transmission electron microscope (STEM) images were obtained by a Tecnai G2 F20 transmission electron microscopy with an accelerating voltage of 200 kV. The chemical components were detected by energy-dispersive X-ray spectroscopy (EDS). The crystal structures were detected by high-angle annular dark-field STEM (HAADF-STEM). Dynamic light scattering (DLS) was carried out on a Nano-ZS Zetasizer ZEN3600 (Malvern Instruments Ltd., U.K.). UV-vis absorption spectra were measured using a UV2450 spectrophotometer (Shimadzu, Japan). Fluorescence spectra were recorded with an FS5 fluorescence spectrophotometer (Edingburgh Instruments, UK). The decay curves of colloidal suspensions were obtained by an FS980 fluorescence spectrophotometer using a monochromator equipped time-correlated single photon counting (TCSPC) system with 1 μs femtosecond laser pulses (Edingburgh Instruments, UK). X-ray diffraction measurements were carried out by a Maxima XRD-7000 (Shimadzu, Japan). An Advanced Microwave Digestion System (Milestone ETHOS 1, Italy) was applied to study the effect of the temperature and power on the property of the products.

Synthesis of the $CsPbX_3$ colloidal perovskite. Generally, 5 mL of ODE, 0.5 mL of dried OLA and 0.5 mL of dried OA, acting as solvents and stabilizers, were added into a round bottom flask and degassed by evacuation and stirred with a magnetic stirrer for approximately 5 min. The obtained degassed mixture was transferred into a 15-mL glass bottle, and 0.0926 g (0.2 mmol) of PbI_2 (0.0556 g for $PbCl_2$; 0.0738 g for $PbBr_2$) and 0.0217 g (0.0667 mmol) of Cs_2CO_3 were sequentially added. Another 1 mL of trioctylphosphine (TOP) was required for the synthesis of $CsPbCl_3$. Then, the obtained heterogeneous reaction system was placed into the microwave oven for the microwave irradiation for 4 min at 800 W. The working conditions of the microwave-assisted synthetic method were instrument-dependent, so the reactants and working conditions (power or time) must be optimized to each microwave system to acquire the highest-quality NCs. The amount of the reactants for the large-scale synthesis was increased to about 10 mmol.

Purification of the $CsPbX_3$ colloidal perovskite. The perovskite NCs were generated at the bottom of the reactor, which was dispersed in hexane after removing the supernatant. The obtained NCs were purified by centrifugation at a speed of 12500 rpm for 20 min to remove residual solvents and surfactant. The solid product was subsequently dispersed in hexane again and further purified by centrifugation at 3000 rpm for approximately 20 min to discard the large particles and solid remnants. Varisized NCs can be obtained by adjusting the centrifugation speed. Then, the obtained NCs were stored at 4 °C until use in subsequent experiments.

Synthesis of the $CsPbX_3$ perovskite NCs with different morphologies. In the preparation of $CsPbI_3$ perovskite NCs, nanorods were synthesized by decreasing the ratio of Cs_2CO_3 to PbI_2 (from 1: 3 to 1:6), nanowires were obtained by adding octylamine to replace the conventional oleic acid (0.5 mL for every 5 mL of ODE), and hexagonal nanoplates were generated by improving the amount of ODE, OAm and OA (two times than that used for $CsPbX_3$ cubes synthesis).

Preparations of the $CsPbX_3$ perovskite/PMMA film. The colloidal $CsPbX_3$ perovskite was dispersed into chloroform with poly(methyl methacrylate) (PMMA). The obtained mixed $CsPbX_3$ perovskite/PMMA solution was painted onto the clean surface of rectangular glasses. The chloroform volatilized quickly at room temperature (25 °C) and then $CsPbX_3$ perovskite/PMMA films formed.

Experimental Results

Fig. S1 Photographs of the $CsPbI_3$ NCs. (a) before and (b) after the reaction of the reactants; the $CsPbI_3$ NCs dispersed in hexane under (c) daylight and (d) UV light.

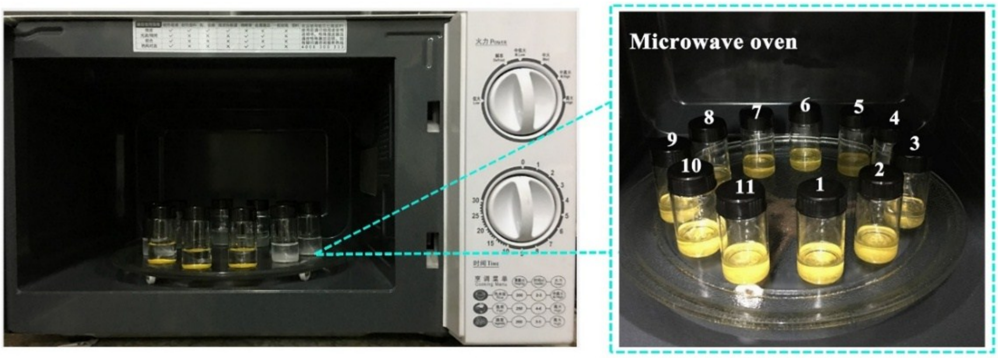

Fig. S2 Photographs of the synthetic process assisted by a microwave oven.

Table S1. The detailed PLQYs of the synthesized $CsPbX_3$ perovskite NCs with different components by microwave irradiation.

No.	**Sample**	**PLQY**
1	$CsPbCl_3$	10.98%
2	$CsPbCl_{2.4}Br_{0.6}$	15.85%
3	$CsPbCl_2Br_1$	50.94%
4	$CsPbCl_{1.5}Br_{1.5}$	70.74%
5	$CsPbBr_3$	91.89%
6	$CsPbBr_2I_1$	79.08%
7	$CsPbBr_{1.5}I_{1.5}$	80.53%
8	$CsPbBr_1I_2$	88.14%
9	$CsPbI_3$	92.17%

Table S2. The PLQYs of $CsPbX_3$ perovskite NCs synthesized by different methods.

No.	**PLQY**	**Protocols**	**Ref**
1	10.98-92.17%	Mircowave irradiation	This work
2	10-92%	Ultrasonication	1
3	50-90%	Hot injection	2
4	50–85%	Solution synthesis at RT	3
5	up to 80%	Solvothermal Synthesis	4
6	~ 80%	Photoinduced anion exchange	5
7	~ 70%	Hot injection	6
8	31-78%	Colloidal synthesis approach	7
9	44 and 38%	Solvent-free mechanosynthesis	8
10	70-95%	Supersaturated recrystallization	9

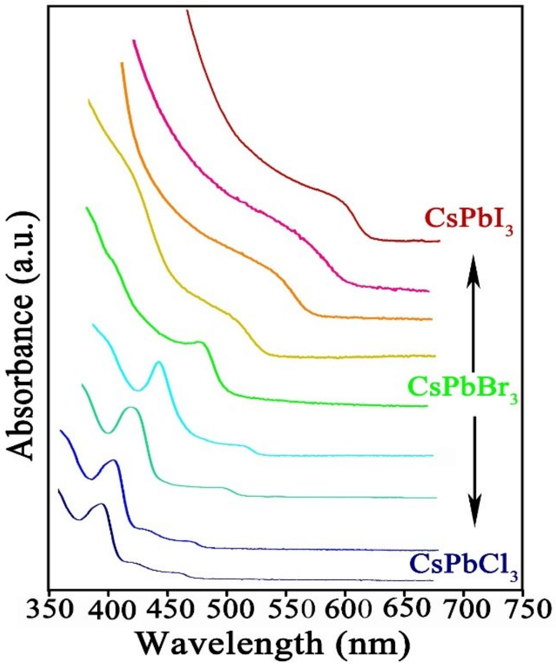

Fig. S3 UV-vis absorption spectra of the $CsPbX_3$ NCs simultaneously prepared in a single microwave oven.

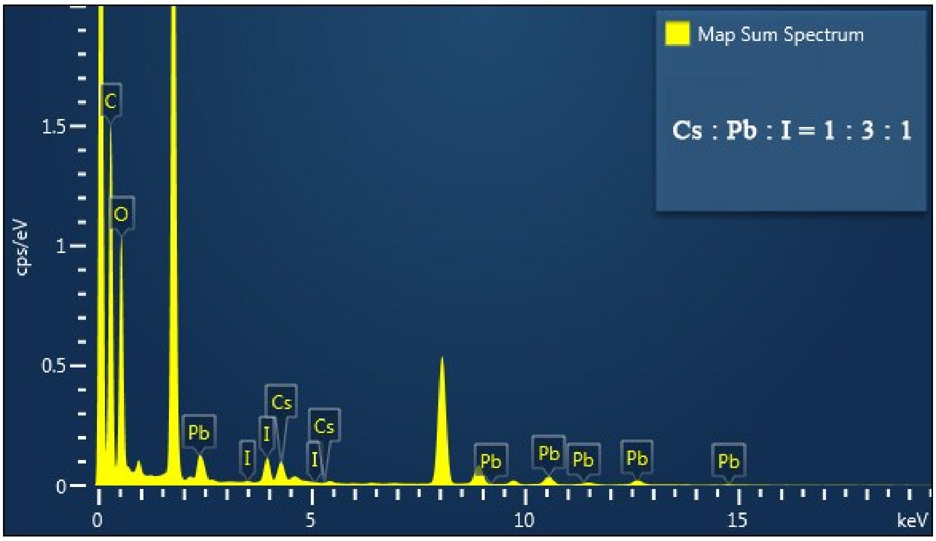

Fig. S4 Energy-dispersive X-ray spectroscopy (EDS) results of the $CsPbI_3$ perovskite NCs.

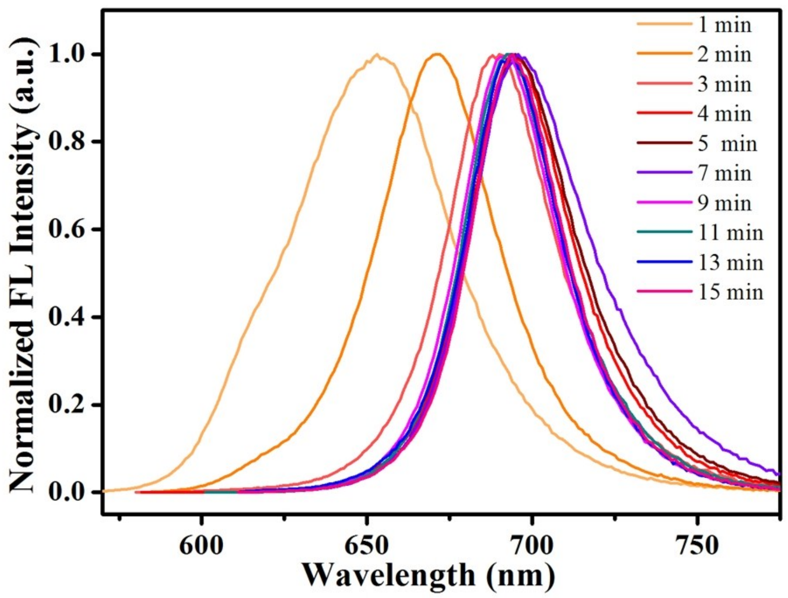

Fig. S5 FL spectra of the $CsPbI_3$ perovskite NCs synthesized by microwave irradiation for 1, 2, 3, 4, 5, 7, 9, 11, 13, and 15 min.

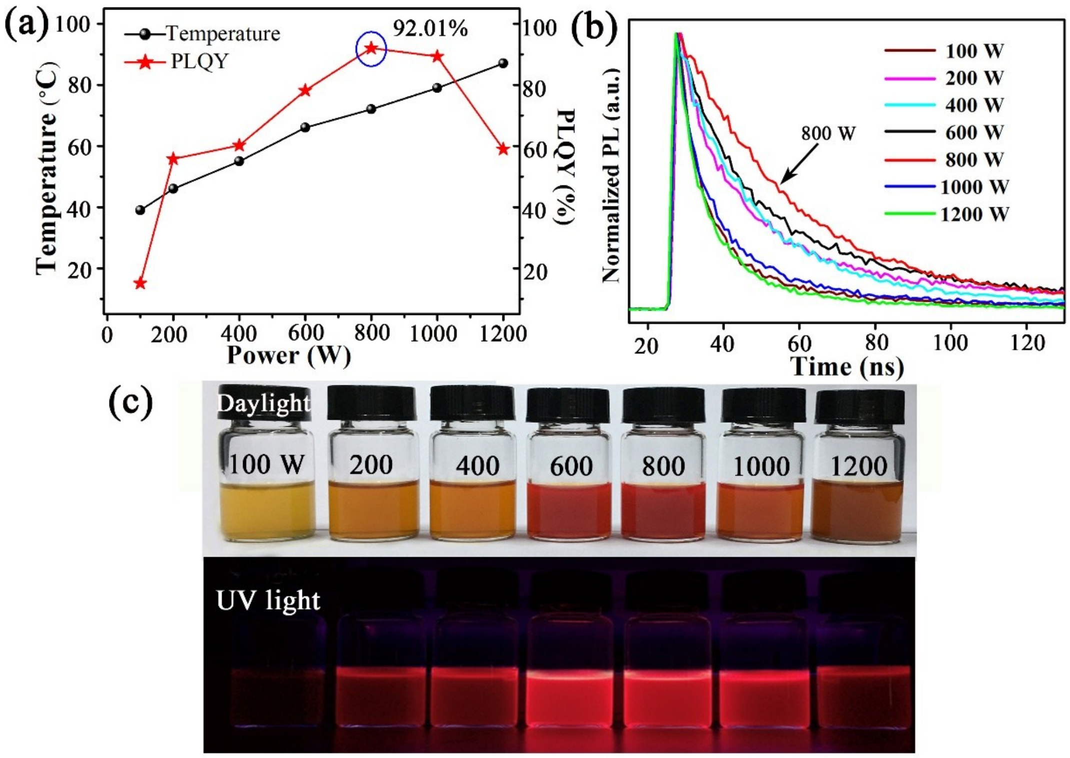

Fig. S6 (a) Temperatures of reaction systems irradiated by microwave digestion system at different powers and the corresponding PLQYs of the purified colloidal CsPbI3 NCs. (b) The PL dynamics and (c) Photographs of NCs dispersed in hexane under daylight (up) and UV light (down).

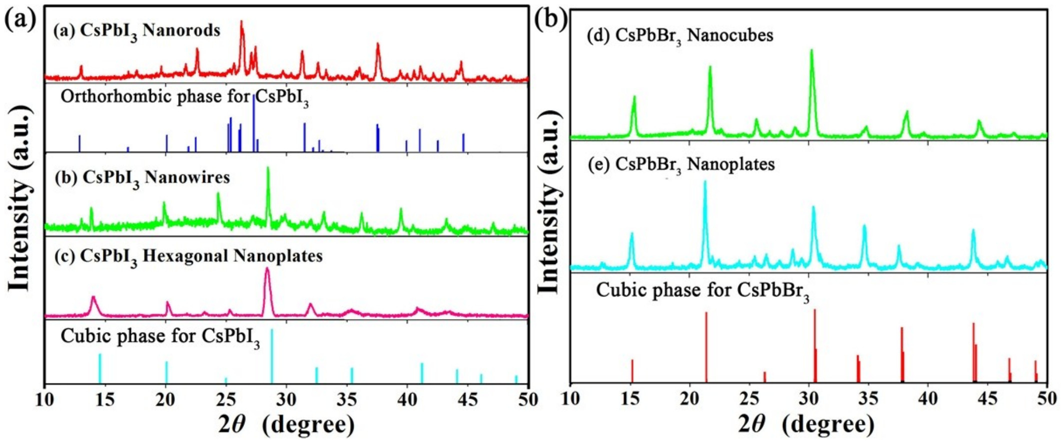

Fig. S7 XRD patterns of $CsPbI_3$ and $CsPbBr_3$ perovskite NCs with different morphologies and the standard diffraction pattern for orthorhombic, cubic $CsPbI_3$, and standard XRD patterns for cubic $CsPbBr_3$.

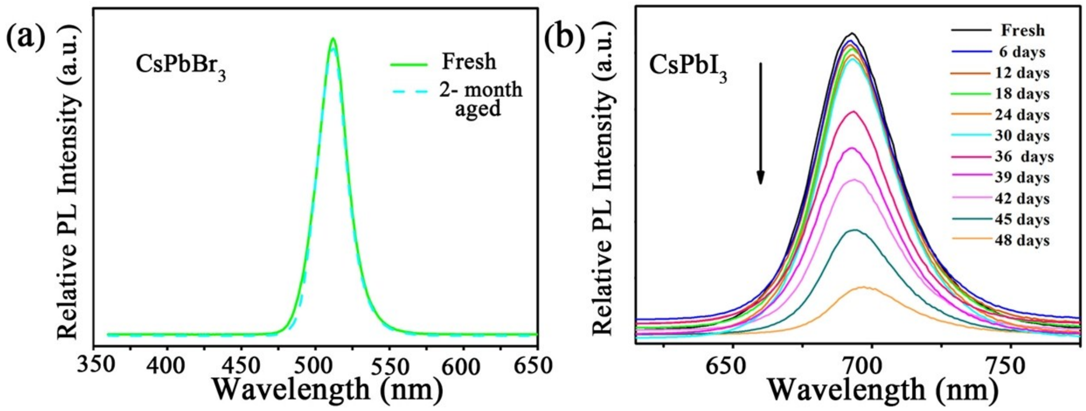

Fig. S8 FL spectra of fresh and different day-aged (a) $CsPbBr_3$ perovskite NCs and (b) $CsPbI_3$ perovskite NCs.

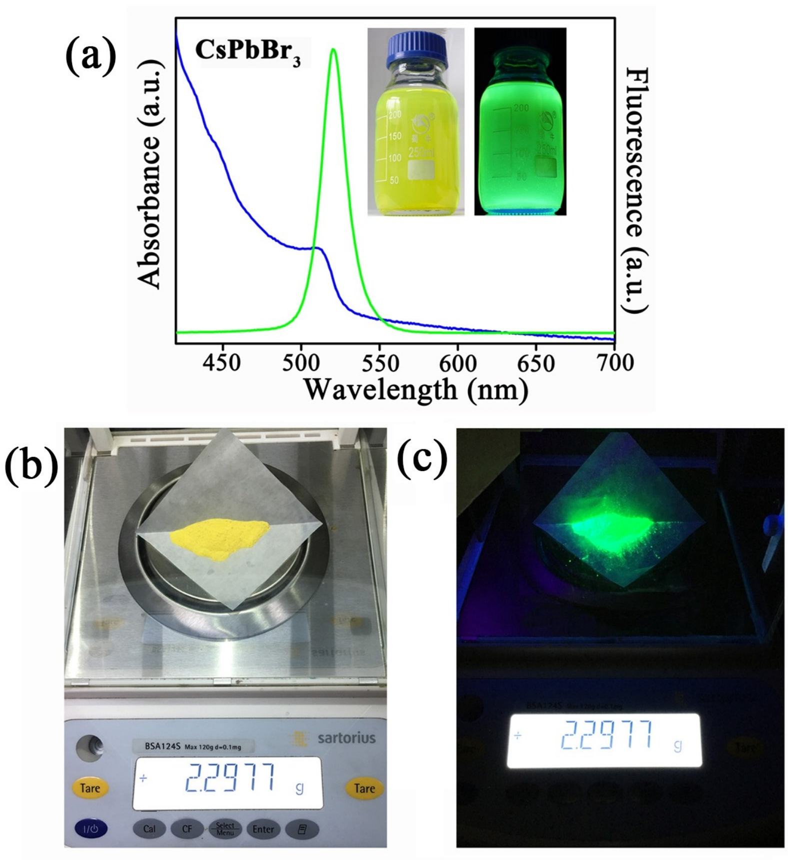

Fig. S9 Characterization on large-scale synthesized $CsPbBr_3$ NCs (reactants: 10 mmol of PbX_2: 3.698 g, 3.33 mmol of Cs_2CO_3: 1.0869 g). (a) FL and UV-vis absorption spectra in 300 mL. Photographs of the powder (b) under daylight and (c) UV light (365 nm) irradiation.

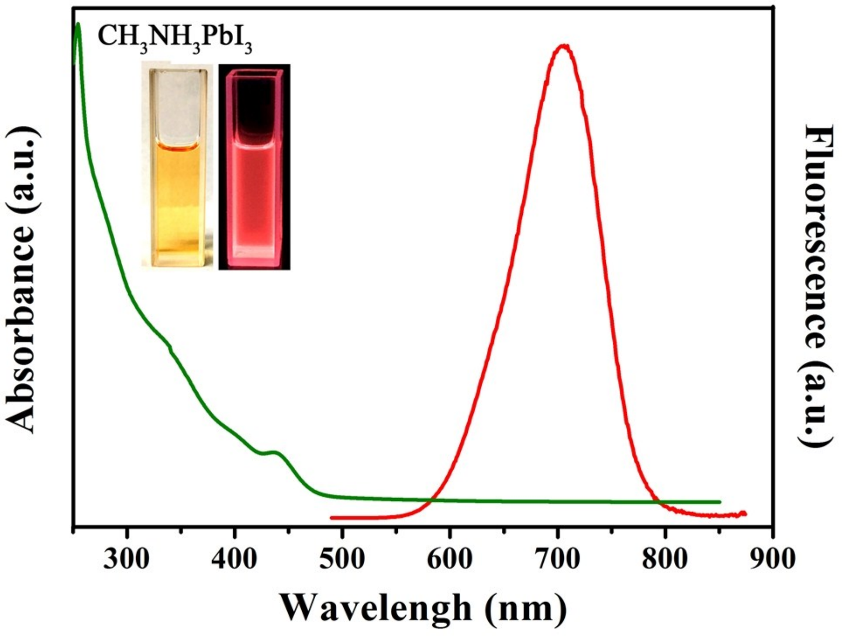

Fig. S10 FL and UV-vis absorption spectra of the $CH_3NH_3PbI_3$ perovskite NCs. Insets: Photographs of the NCs dispersed in hexane under daylight (left) and UV light (right).

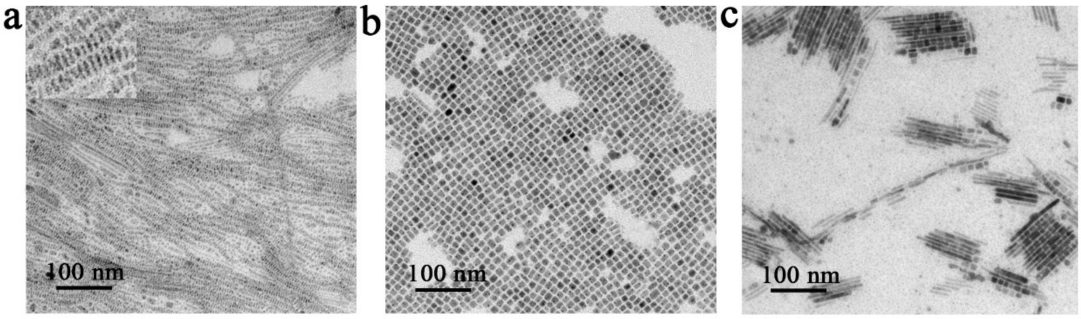

Fig. S11 TEM images of the $CsPbI_3$ perovskite NCs prepared by microwave irradiation with different amounts of oleylamine: (a) 50, (b) 500, and (c) 1500 μL. Inset of (a) is the magnifying image of one part of (a). The volume of ODE was ~5 mL.

Table S3. Temperatures of the solution phase under microwave irradiation for 4 min at different modes.

No.	Mode	Temperature / ^{o}C
1	Defrost	~31
2	Med-Low	~43
3	Medium	~55
4	Med-High	~67
5	High	~88

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