# Supporting Information for

# Spatiotemporal-Resolved Nanoparticle Synthesis via Simple Programmed Microfluidic Processes

Xiaomiao Shen[1], Yujun Song[2]*, Shuai Li[1], Runsheng Li[1], Shaoxia Ji[1], Qing Li[1], Huiping Duan[1], Riwei Xu[3], Wantai Yang[3], Kai Zhao[4], Rong Rong[4] and Xiaoying Wang[4]

[1] School of Materials Science and Engineering, Beihang University, Beijing 100191, China; [2] School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, China; [3] The State Key Laboratory of Chemical Resources Engineering, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China; [4] Department of Radiology, Peking University First Hospital, Beijing 100034, China

*Corresponding author: Y. S., songyj@ustb.edu.cn.

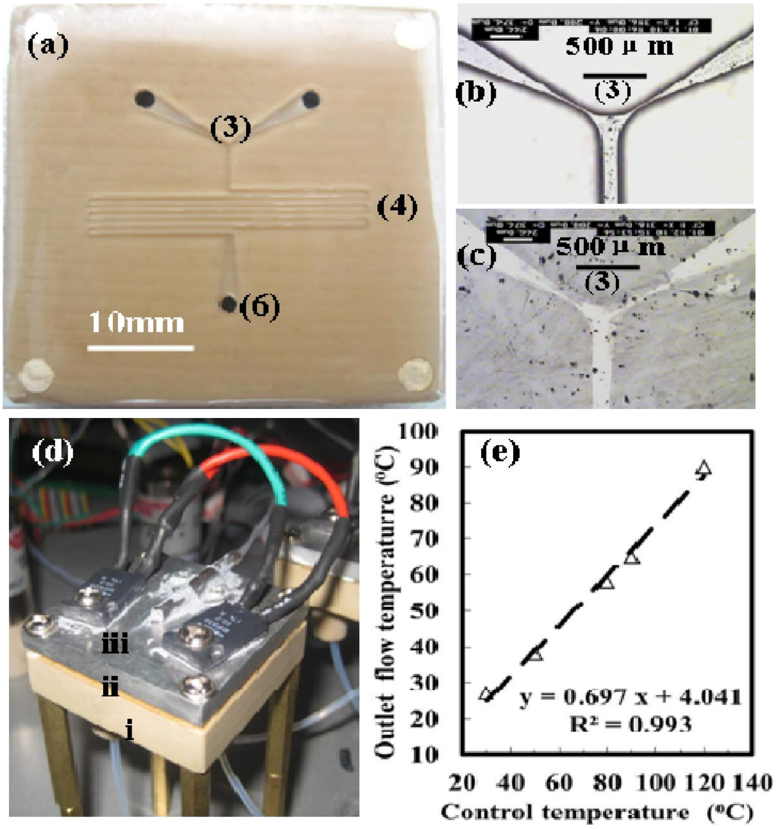


**Figure s1** (a) The full-viewed optical image of the sealed micro mixer and channel for the synthesis of NPs. (b) SEM images of the Y-mixer before sealed. (c) SEM images of the Y-mixer after sealed. (d) The optical image of the SU8 microfluidic chip coupled with a heating plate: (i) the bottom PEEK substrate; (ii) the middle SU-8 based microfluidic chip; (iii) the heating plates connecting with the temperature controller by electricity wires. (e) Temperature calibration curve of the fluid between the outlet of the microchannels and the control point in the heating plate.

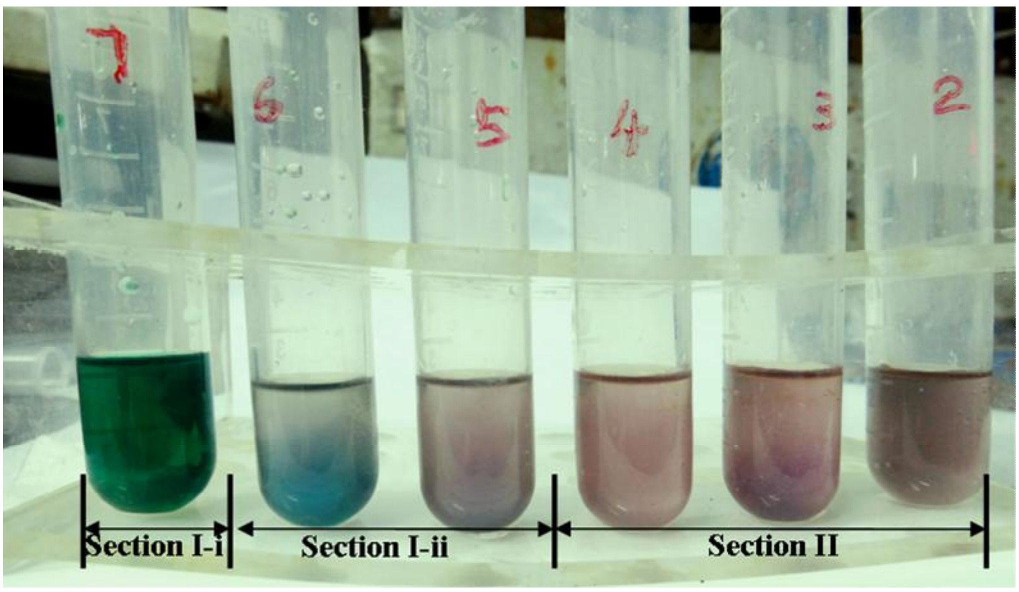


**Figure s2** Solution color changes of the first two sections with the reducing reaction to initiate nucleation.

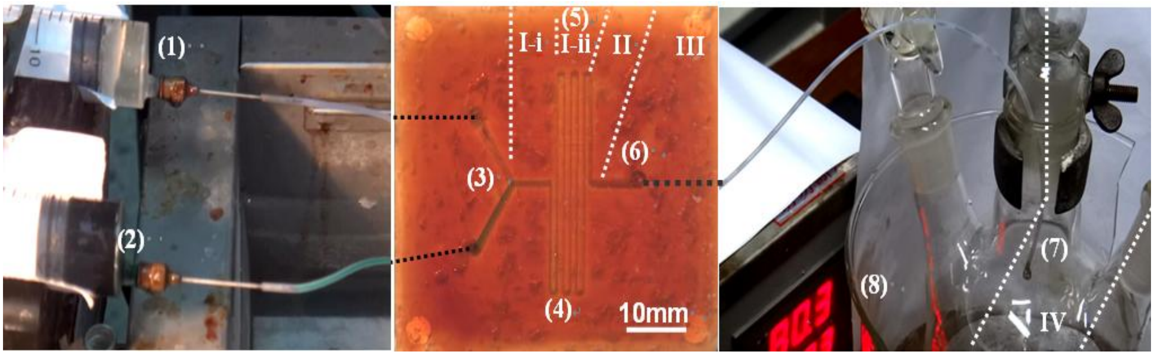


**Figure s3** The optical image of the real experiment to show the 4 sections of PTMP using CoFe nanoparticle synthesis as example via a SU-8 chip-based microfluidic reactor: one syringe pump for the reducing solution (1); another syringe pump for the metal salt solution (2); the chip-based microfluidic reactor (3) formed by Y mixer (4) and microchannels (120-200 μm wide, 200-500μm deep and 18-40 cm long) equipped with a heating plate (5) and temperature controller; a wide tubing (ID = 250-1000 μm; length = 15-25 cm) connecting the micro-channel outlet (6) to the receiver (7) controlled at 1-15$^{o}$C by a thermostatic bath (8). i, ii and iii in (a) are the substrate, the sealed SU-8 microchannel and the covered heating plate.

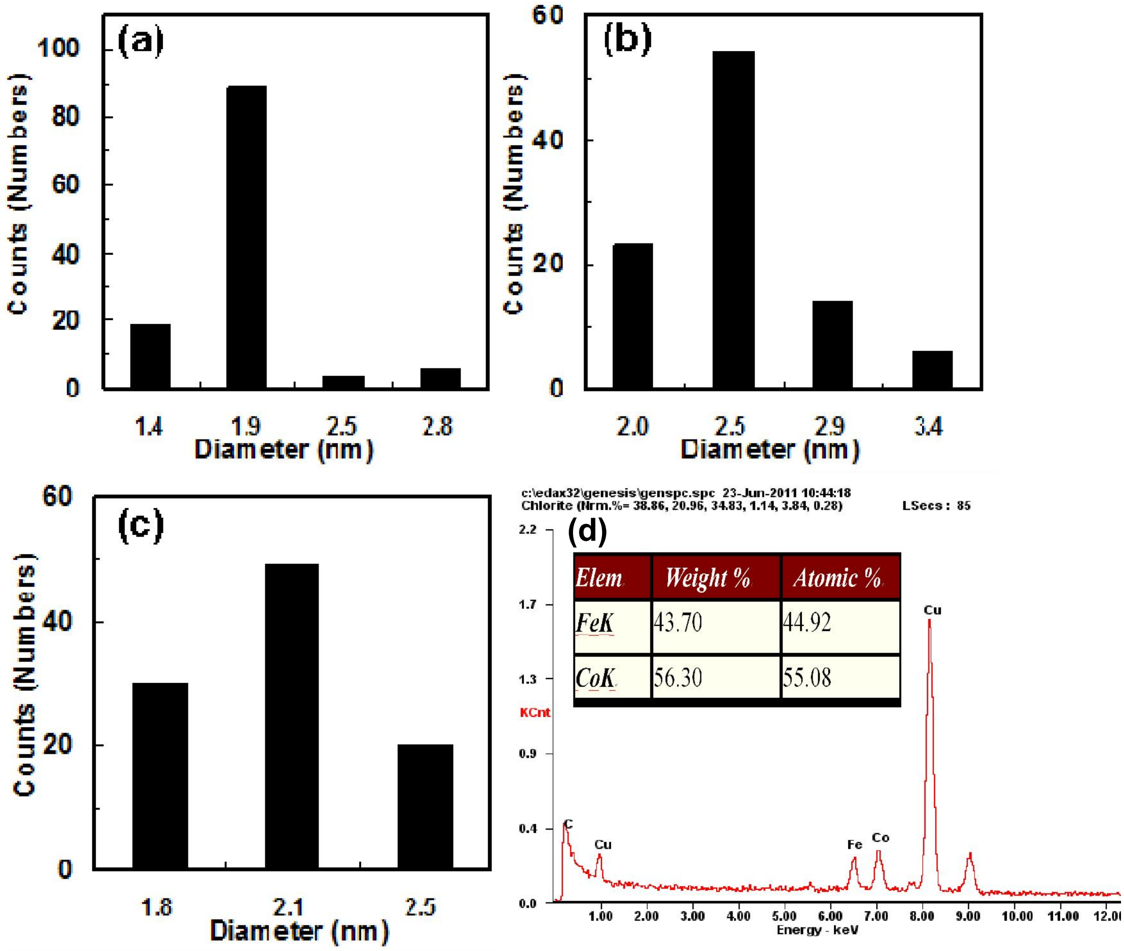


**Figure s4** Size histograms of CoFe NPs synthesized at 30$^{o}$C (a), 60$^{o}$C (b) and 80$^{o}$C (c). (d): the EDS spectrum of NPs synthesized at 60$^{o}$C.

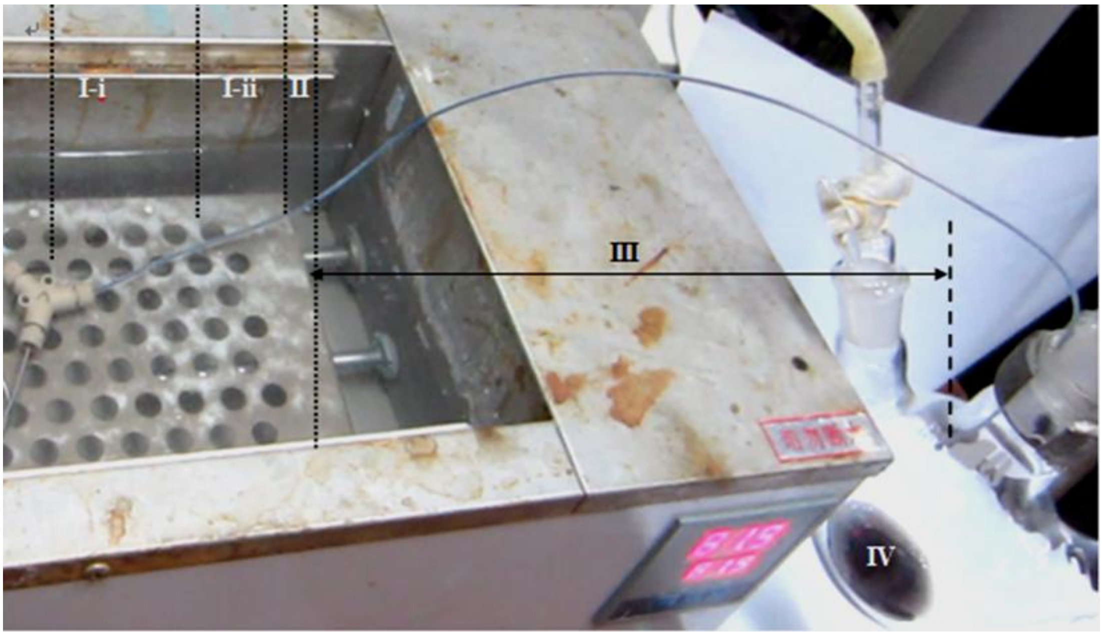


**Figure s5** the typical flow color change along the microtubing during the synthesis of CoFe NPs by microtubing-based simple programmed microfluidic processes (MT-SPMPs). Reaction conditions: the controlled highest reaction temperature, 80.5$^{o}$C; theconcentration of mixed salts, 55 mM (mmol/L); the flow rate, 0.2 mL/min.

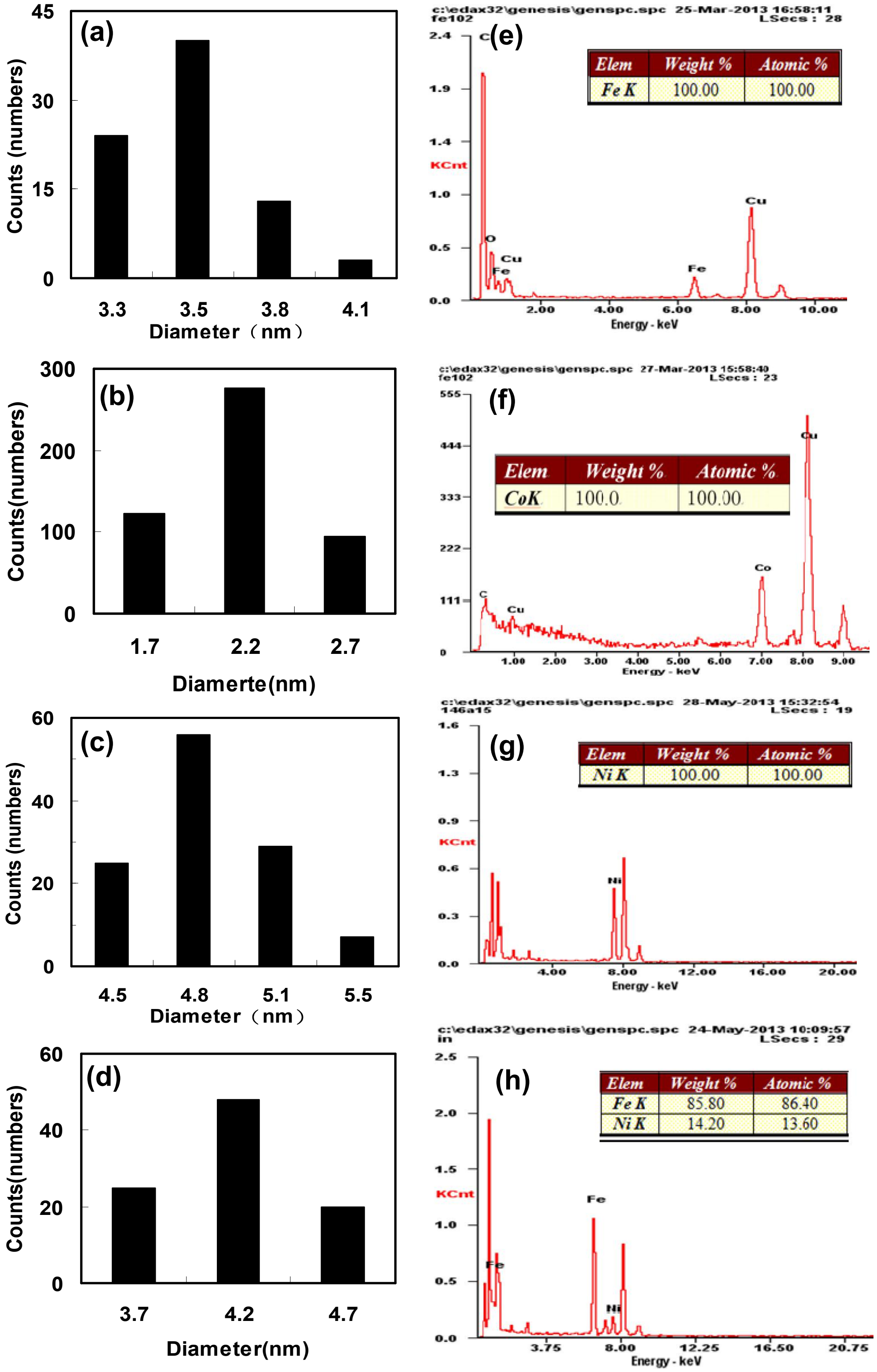


**Figure s6** (a)-(d): histograms of size distributions of Fe (a), Co (b), Ni (c) and NiFe (d) nanoparticles synthesized by MT-SPMPs; (e)-(h): EDX spectra of the related Fe (e), Co (f), Ni (g) and NiFe (h) nanoparticles.

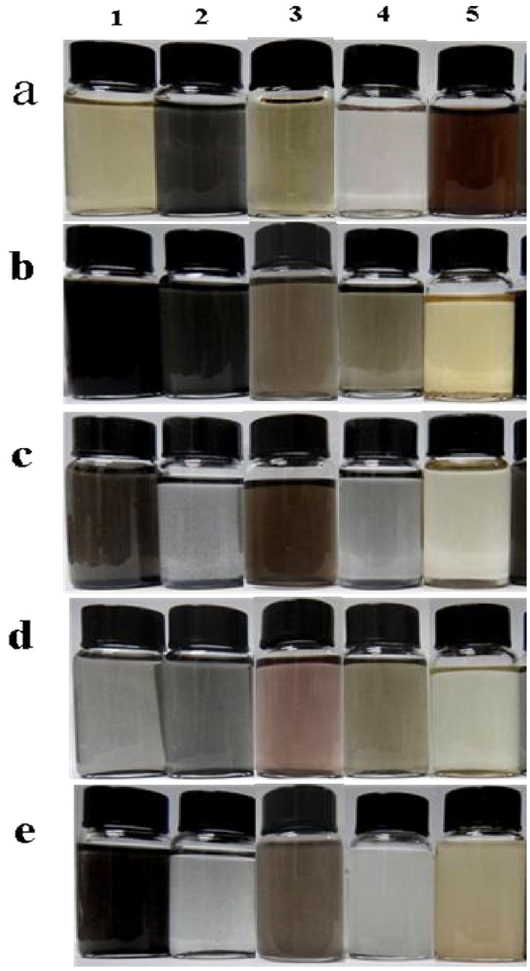


**Figure s7** Solubility investigation of these NPs in polar and non-polar solvents by directly re-dispersing their dry powders. (a) water; (b) NMP; (c) Chlorobenzene; (d) Chloroform; (e) cyclohexane. ×: aggregate. Types of the nanoparticles from 1-23 are listed in Table s3

**Table s1** Magnetic properties of magnetic NPs

| Samples | Size | $^{a}$ $H_c$, Oe | | $^{b}$ $T_f$ | $^{c}$ $T_m$ |
|---|---|---|---|---|---|
| | nm | left | right | K | K |
| CoFe synthesized at 30°C | 1.85 ± 0.28 | -2.5 | 3.0 | - | - |
| CoFe synthesized at 60°C | 2.74 ± 0.28 | -16 | 17 | 71 | 125 |
| CoFe synthesized at 80°C | 2.24 ± 0.22 | -9 | 10 | - | - |
| Fe | 3.52 ± 0.28 | -37 | 37 | 141 | 348 |
| Co | 2.22 ± 0.21 | -35 | 34 | 73 | 146 |
| Ni | 4.87 ± 0.27 | -32 | 31 | 10 | 105 |
| NiFe | 4.18±0.30 | -30 | 37 | 52 | 120 |

[a] Hc: coercivity; [b] $T_f$: the freezing temperature above which the NPs gradually shifts from clusters-glass (CG) like state to the ferromagnetic (FM) state; [c] Tm: the merging temperature for zero-field-cooling curves ($M_{ZFC}$(T)) and field-cooling curves ($M_{FC}$(T)), indicating that the NPs are in the same FM state for ZFC and FC processes above that temperature. If $T_f$ does not match with $T_m$ in the ZFC and FC magnetization curves, it means that the spontaneous magnetic state at low temperature of the nanoparticle system is a magnetic CG like state, and a low external magnetic field, such as 100 Oe here, can induce a long range FM order in the NPs system, and thus the crossover from CG to FM occurs[1, 2]. In our NPs, except for NPs synthesized by all NMP phase systems, the other magnetic NPs usually do not show the same temperature, indicating the presence of a mixed CG and FM state at low applied field (i.e., 100Oe), which are clearly from the enhanced surface canting, inter-particle and/or core-shell interaction effects in such small NPs. [c] The shape of FC-ZFC curves in the two NPs suggest the existence of superparamagnetic behavior associated with assembly of fine magnetic particles[3].

## References


1. X.-G. Li, X. J. Fan, G. Ji, W. B. Wu, K. H. Wong, C. L. Choy and H. C. Hu, *J. Appl. Phys.*, 2000, **85**, 1663-1666.
2. L. Wang, J. Ding, A. Roy, J. Ghose, Y. Li and Y. P. Feng, *J. Phys.: Condens. Matter.*, 2000, **12**, 9963–9972.
3. O. Santini, A. R. de Moraes, D. H. Mosca, P. E. N. de Souza, de Oliveria, Adilson J.A., R. Marangoni and F. Wypych, *Journal of Colloid and Interface Science*, 2005, **289**, 63-70.

**Table s2** Reaction conditions for each nanoparticle synthesis

| Particles | Process | Size nm | Metal salt concentration mM (mmol/L) | Reductant concentration mM | Stabilizers concentrations mM | Reaction Temperature (T) °C | Receiver Temperature °C | Flow rate mL/min | Channel length[a] cm |
|---|---|---|---|---|---|---|---|---|---|
| CoFe-30, | C-SPMPs | 1.85 ± 0.28 | $CoCl_2 \cdot 6H_2O$: 20.2; $FeCl_2 \cdot 4H_2O$: 15.0 | $NaBH_4$: 36.6 | PVP: 0.80 | 30 | 2 | 0.5 | 35 |
| CoFe-60, | C-SPMPs | 2.74 ± 0.32 | $CoCl_2 \cdot 6H_2O$: 20.2; $FeCl_2 \cdot 4H_2O$: 15.0 | $NaBH_4$: 36.6 | PVP: 0.80 | 60 | 2 | 0.8 | 35 |
| CoFe-80 | C-SPMPs | 2.24 ± 0.22 | $CoCl_2 \cdot 6H_2O$: 20.2; $FeCl_2 \cdot 4H_2O$: 15.0 | $NaBH_4$: 36.6 | PVP: 0.80 | 80 | 2 | 1.2 | 35 |
| CoFe | MT-SPMPs | 4.40 ± 0.36 | $CoCl_2 \cdot 6H_2O$: 37; $FeCl_2 \cdot 4H_2O$: 28 | $NaBH_4$: 36.6 | PVP: 0.80 | 80 | 2 | 0.2 | 35 |
| CoFe | MT-SPMPs | 2.98 ± 0.29 | $CoCl_2 \cdot 6H_2O$: 37; $FeCl_2 \cdot 4H_2O$: 28 | $NaBH_4$: 36.6 | PVP: 0.80 | 80 | 2 | 3.0 | 40 |
| Fe | Mt-SPMPs | 3.52 ± 0.26 | $FeCl_2 \cdot 4H_2O$: 30.6 | $NaBH_4$: 116 | PVP: 0.80 | 80 | 15 | 1.0 | 37 |
| Co | MT-SPMPs | 2.22 ± 0.22 | $CoCl_2 \cdot 6H_2O$: 30.2 | $NaBH_4$ : 205 | PVP: 2.00 | 80 | 10 | 0.8 | 35 |
| Ni | MT-SPMPs | 4.87 ± 0.27 | $NiCl_2 \cdot 6H_2O$: 30.8 | $NaBH_4$: 163 | PVP: 0.80 | 80 | 15 | 1.0 | 37 |
| NiFe | MT-SPMPs | 4.18 ± 0.30 | $NiCl_2 \cdot 6H_2O$: 6; $FeCl_2 \cdot 4H_2O$ : 15 | $NaBH_4$ of 105 | PVP: 0.44 | 80 | 10 | 7.7 | 37 |

[a]: The channel length includes the length of the chip-based channel (19 cm) and the microtubing connecting the outlet of the chip to the receiver (about 16-21 cm) for C-SPMPs, and totally 30-40 cm for MT-SPMPs. PVP：polyvinylpyrrolidone**.**

**Table s3** Solubility of NPS in different solvents by directly re-dispersing their dry powder

| No. | Nanoparticles | Solvents | | | | |
|---|---|---|---|---|---|---|
| | | $H_2O$ (a) | NMP (b) | Chloro-benzene (c) | Chloroform (d) | Cyclohexane (e) |
| 1 | Fe | √√ | √√√ | √√√ | √√√ | √√√ |
| 2 | Co | √√√ | √√√ | √√√ | √√√ | √√√ |
| 3 | Ni | √√ | √√√ | √√ | √√√ | √√√ |
| 4 | CoFe | √√√ | √√√ | √√√ | √√ | √√√ |
| 5 | NiFe | √√√ | √ | √√√ | √√√ | √√√ |
| Solubility symbols, √√√: excellent, >10 g/L; √√: good, 5-10g/L; √: fine, 2-5g/L; ×: difficult or aggregate. | | | | | | |

* Synthesized using all NMP-phased reaction systems.

[#] synthesized using aqueous-phased metal salts.

**Movie 1:** CoFe NPs synthesis using SU-8 chip based microfluidic reactor at 80°C and a flow rate of 1.2 mL/min.