

Supporting Information

Structure-dependent Magnetoelectric and Magnetothermal Effects of MOF-derived Zero-valence Cobalt and Iron Oxide Nanoparticles on Carbonaceous Matrix

Jing-Guan Liang,^{1,2,7} Wei-Xiang Gao,^{1,3,7} Chieh-Wei Chung,¹ Loise Ann Dayao,¹ Ho-Hsiu Chou,³ Zong-Hong Lin,⁴ Dehui Wan,¹ Jen-Huang Huang,³ Ying-Chieh Chen,^{1*} Tsai-Te Lu^{1,5,6*}

Affiliations:

¹Institute of Biomedical Engineering, National Tsing Hua University, Hsinchu, 30013 Taiwan.

²Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, 30013 Taiwan.

³Department of Chemical Engineering, National Tsing Hua University, Hsinchu, 30013 Taiwan.

⁴Department of Biomedical Engineering, National Taiwan University, Taipei, 106319 Taiwan.

⁵Department of Chemistry, National Tsing Hua University, Hsinchu, 30013 Taiwan.

⁶Department of Chemistry, Chung Yuan Christian University, Taoyuan 32023, Taiwan.

⁷These authors contributed equally: Mr. Jing-Guan Liang and Mr. Wei-Xiang Gao.

*Corresponding author:

Ying-Chieh Chen, Ph.D., Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, 30013 Taiwan. E-mail: yisschen@mx.nthu.edu.tw

Tsai-Te Lu, Ph.D., Institute of Biomedical Engineering and Department of Chemistry, National Tsing Hua University, Hsinchu, 30013 Taiwan. E-mail: ttlu@mx.nthu.edu.tw

Experimental Section.

Materials. Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%, AENCORE), 1,4-benzenedicarboxylic acid (99%, ACROS), 2-methylimidazole (ACROS), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Showa), graphite flake (Alfa Aesar), and alginic acid sodium salt (Sigma-Aldrich) were used as received without further purification.

Preparation of Fe-MIL-88B. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.404 g, 1 mmol) and 1,4-benzenedicarboxylic acid (0.166 g, 1 mmol) were dissolved in 6 mL of ethanol. After this solution was stirred at room temperature overnight, this ethanol solution was centrifuged at 6000 rpm for 10 min, which resulted in the precipitation of orange Fe-MIL-88B. After removing the supernatant solution, the obtained crude Fe-MIL-88B was washed with ethanol for three times and dried at 80 °C overnight. Then, the obtained Fe-MIL-88B was suspended in 60 mL of ethanol and stirred at 60 °C overnight. After this ethanol solution was centrifuged at 6000 rpm for 10 min and the supernatant solution was removed, the prepared Fe-MIL-88B was dried at 80 °C in a vacuum oven (yield 0.110 g).

Preparation of MIL-88B-derived $\text{Fe}_3\text{O}_4\text{:C}$ Microrod. 0.100 g of Fe-MIL-88B was placed in a ceramic boat within a tube furnace and calcined under a $\text{N}_2(\text{g})$ gas flow (200 mL/min). During the calcination process, the temperature was gradually raised from room temperature to 150 °C at a rate of 5 °C/min and then increased from 150 °C to 500 °C at a rate of 2 °C/min. Subsequently, the temperature was maintained at 500 °C for 3 h before decreased from 500 °C to room temperature at a rate of 5 °C/min, which resulted in the formation of MIL-88B-derived $\text{Fe}_3\text{O}_4\text{:C}$ microrod (yield 0.035 g).

Preparation of ZIF-67. A solution of 2-methylimidazole (1.180 g, 14.4 mmol) in 12 mL of methanol was added into a 100-mL flask loaded with a methanol solution (36 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.047 g, 3.6 mmol). This mixture solution was stirred at room temperature for 3 min and incubated at room temperature overnight before the purple precipitates of ZIF-67 were obtained by centrifugation at 8000 rpm for 10 min. After the supernatant solution was

removed, the purple precipitates of ZIF-67 were washed with methanol for three times and dried in a vacuum oven at 80 °C overnight (yield, 0.155 g).

Preparation of ZIF-67-derived Co@C Microparticle. ZIF-67 (0.100 g) was loaded into a ceramic boat within a tube furnace and calcined under a N_{2(g)} gas flow (200 mL/min). During the calcination process, the temperature was slowly increased from ambient temperature to 200 °C at a rate of 5 °C/min and maintained at 200 °C for 2 h. Then, the temperature was elevated from 200 °C to 600 °C at the same rate and kept at 600 °C for 2 h before the temperature was gradually lowered to room temperature at a rate of 5 °C/min, which resulted in the formation of ZIF-67-derived Co@C microparticles (yield 0.051 g).

Materials Characterization. The scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) images of MIL-88B-derived Fe₃O₄:C microrod and ZIF-67-derived Co@C microparticles were captured using a field-emission scanning electron microscope (JEOL JSM-7000F), a transmission electron microscope (Hitachi H-7100), and a transmission electron microscope (JEM2100), respectively. PXRD patterns of MIL-88B-derived Fe₃O₄:C microrod and ZIF-67-derived Co@C microparticles were recorded with an X-ray diffractometer (Bruker D2 Phaser) using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). Besides, the SPXRD patterns of MIL-88B-derived Fe₃O₄:C microrod and ZIF-67-derived Co@C microparticles were acquired using a position-sensitive detector (MYTHEN 24K) with 20-keV X-ray ($\lambda = 0.61992 \text{ \AA}$) at Taiwan Photon Source (TPS) 19A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The magnetic properties of MIL-88B-derived Fe₃O₄:C microrod and ZIF-67-derived Co@C microparticles were measured using a superconducting quantum interference device (SQUID, Quantum Design, US) at 300 K. The conductivity of MIL-88B-derived Fe₃O₄:C microrod and ZIF-67-derived Co@C microparticles was determined using a four-point probe measurement system (Sadhudesign, Taiwan). To determine the Co content in ZIF-67-derived Co@C microparticles, the ZIF-67-derived Co@C microparticles (2.5 mg) were

digested in the aqua regia (1 mL) and diluted with 9 mL of ddH₂O before the Co content was analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 725, USA). Fe content in the MIL-88B-derived Fe₃O₄:C microrod was determined in a similar manner.

Magnetothermal Properties of ZIF-67-derived Co@C Microparticle, MIL-88B-derived Fe₃O₄:C Microrod, and Graphite under Alternating Magnetic Field (AMF) in the Aqueous Solution with Different Viscosity. The aqueous solution with different viscosity was prepared through loading 40 mg, 80 mg, 160 mg, and 200 mg of alginic acid sodium salt, respectively, into 2 mL of ddH₂O. Then, the viscosity of 2/4/8/10 wt% sodium alginate aqueous solution was determined as 17.3/123.2/1423.9/3211.9 mPa•S using a rheometer (Anton paar, MR302e, Austria). After addition of 3 mg of ZIF-67-derived Co@C microparticle into 2 mL of 2 wt% sodium alginate_(aq), 0.5 mL of this mixture solution was transferred into a 4-mL glass tube. Using a cylindrical solenoid with a 1.1-cm diameter, an alternating magnetic field (AMF) at an output intensity of 1.60 kW (50%), generated from a high frequency generator (Power Cube 32/900), was applied to the 2 wt% sodium alginate_(aq) solution loaded with 1.5 mg/mL of ZIF-67-derived Co@C microparticle. The temperature was then recorded every second over a span of 400 sec (or 480 sec and 600 sec) using an IR thermal imaging camera (Thermo Shot F30S, NEC). Magnetothermal properties of ZIF-67-derived Co@C microparticle (1.5 mg/mL), MIL-88B-derived Fe₃O₄:C microrod (1.5 mg/mL), and graphite (1.5 mg/mL) in the aqueous solution with different concentrations of sodium alginate (10/8/4/2 wt%) under different output intensities of AMF (1.60 kW, 50%; 0.96 kW, 30%; 0.32 kW, 10%) were measured in a similar manner.

Magnetoelectric Properties of ZIF-67-derived Co@C Microparticle, MIL-88B-derived Fe₃O₄:C Microrod, and Graphite under AMF. 40 mg of ZIF-67-derived Co@C microparticle (or MIL-88B-derived Fe₃O₄:C microrod and graphite) was pressed into pellet (0.9 cm in diameter) at 2000 psi using a manual hydraulic press. As shown in Figure S7, using a cylindrical

solenoid with a 1.1-cm diameter, an alternating magnetic field (AMF) at an output intensity of 1.60 kW (50%), generated from a high frequency generator (Power Cube 32/900), was applied to the pellet of ZIF-67-derived Co@C microparticle. During the intermittent application of AMF, the generated electric current was measured using a digital multimeter (PROVA 803), whereas a digital bench oscillator (Tektronix MSO44 4-BW-350, 4 Series MSO Mixed Signal Oscilloscope, 4 Channel, 350MHz) was utilized to measure the generated voltage upon application of AMF to the pellet of ZIF-67-derived Co@C microparticle. To the original V-t curve obtained upon application of AMF to the pellet of ZIF-67-derived Co@C microparticle (Figure S8a), a fast Fourier transform (FFT) process was applied using the MATLAB software to obtain the frequency spectrum. In the obtained frequency spectrum, the peak at 937330-941920 Hz lying within the range of 0.75-1.15 MHz generated by the high frequency generator was further processed using a sequential inverse fast Fourier transform (IFFT) followed by cosine function fitting by the MATLAB software, which resulted in the processed and simulated V-t curve. Magnetoelectric properties of ZIF-67-derived Co@C microparticle, MIL-88B-derived Fe₃O₄:C microrod, and graphite under different output intensities of AMF (1.60 kW, 50%; 0.96 kW, 30%; 0.32 kW, 10%) were measured in a similar manner.

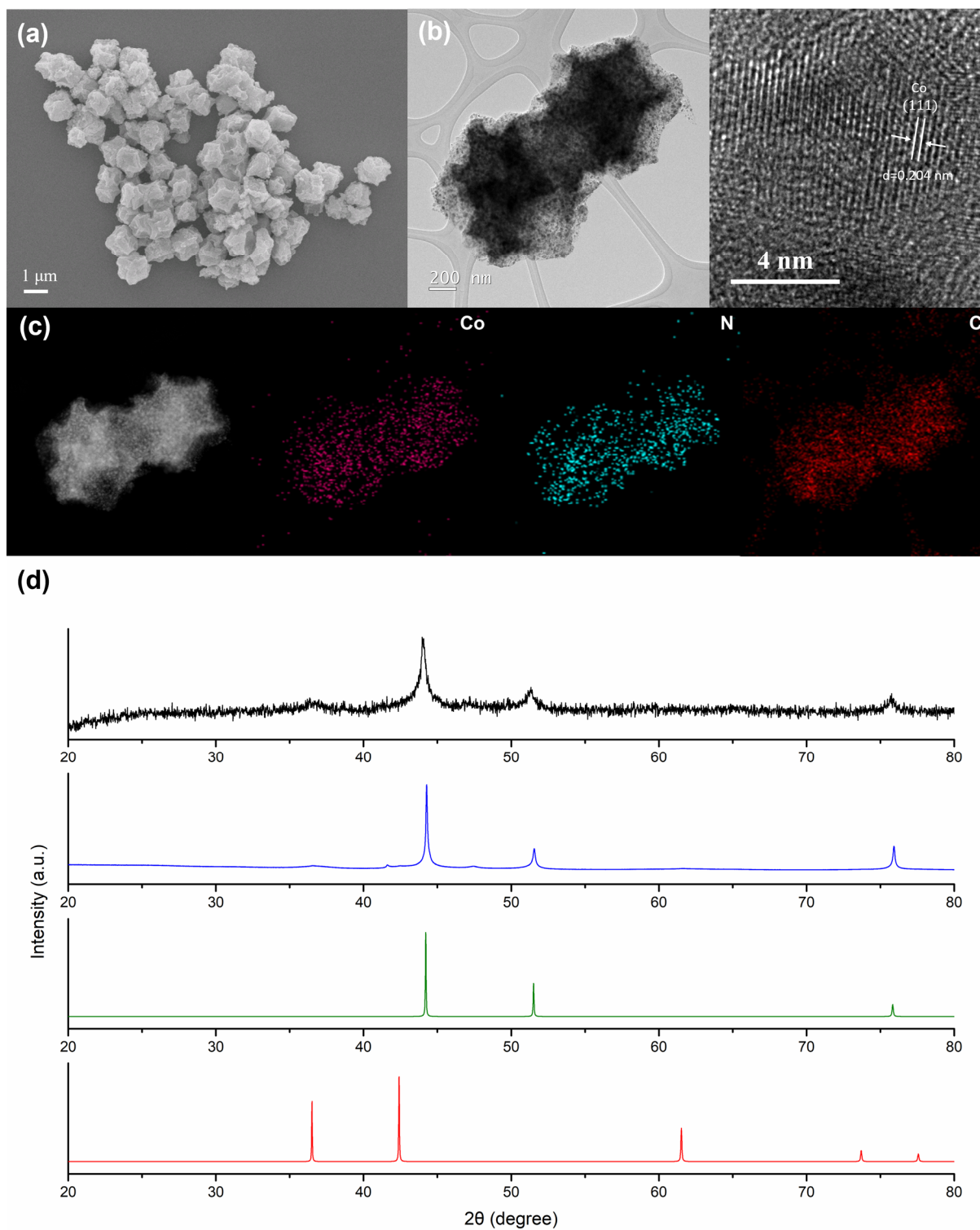


Figure S1. (a) SEM, (b) TEM/HRTEM, and (c) TEM together with the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of Co (pink), N (light blue), and C (red) of ZIF-67-derived Co@C microparticle. (d) PXRD (black) and SXRPD (blue) patterns of ZIF-67-derived Co@C microparticle. Simulated PXRD patterns of fcc-Co (COD #9008466) and fcc-CoO (COD #1533087) are shown in green and red, respectively.

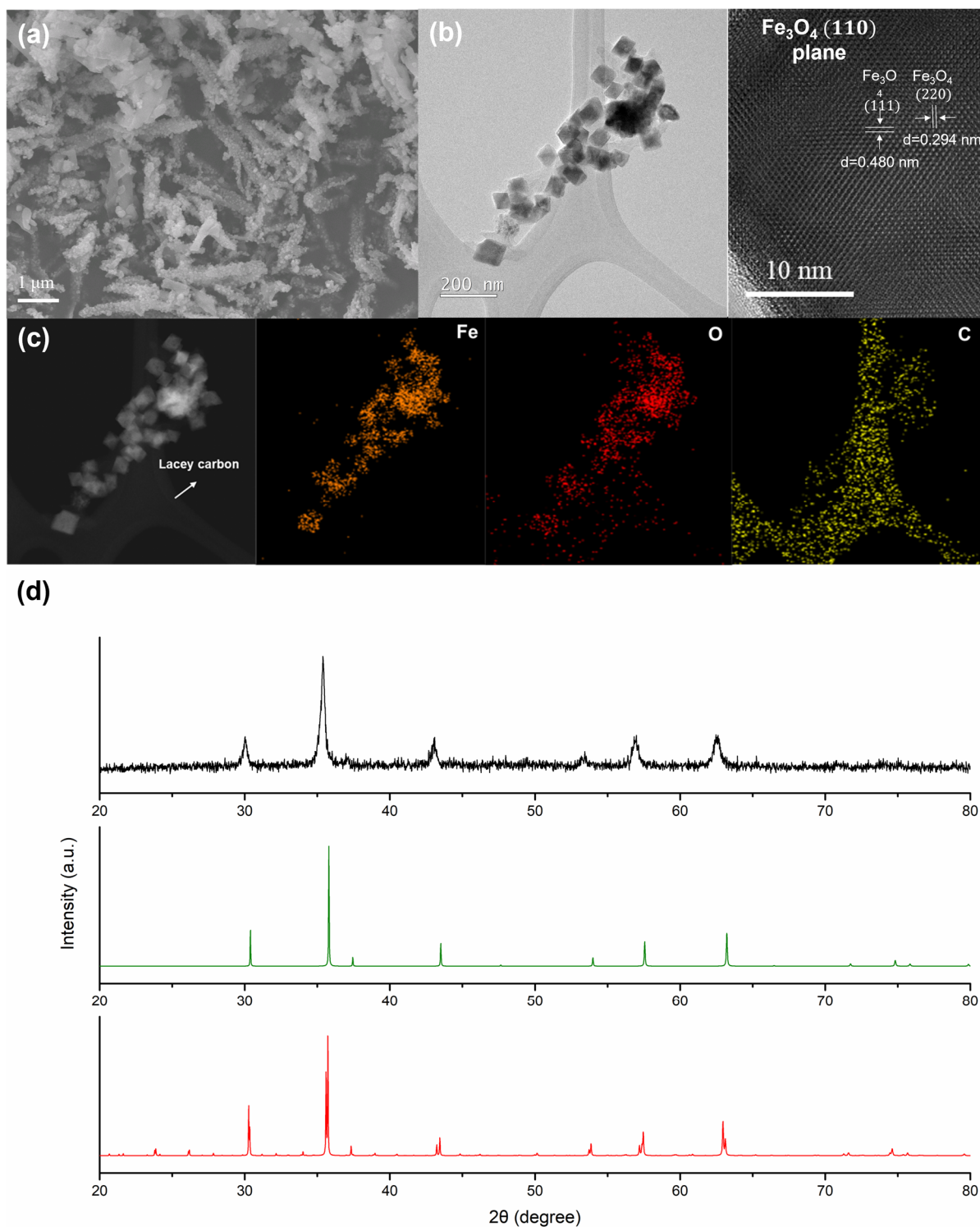


Figure S2. (a) SEM, (b) TEM/HRTEM, and (c) TEM together with the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images of Fe (orange), O (red), and C (yellow) of MIL-88B-derived $\text{Fe}_3\text{O}_4\text{:C}$ microrod. (d) PXRD patterns of MIL-88B-derived $\text{Fe}_3\text{O}_4\text{:C}$ microrod (black). Simulated PXRD patterns of Fe_3O_4 (COD #1011032) and $\gamma\text{-Fe}_2\text{O}_3$ (COD #1528612) are shown in green and red, respectively.

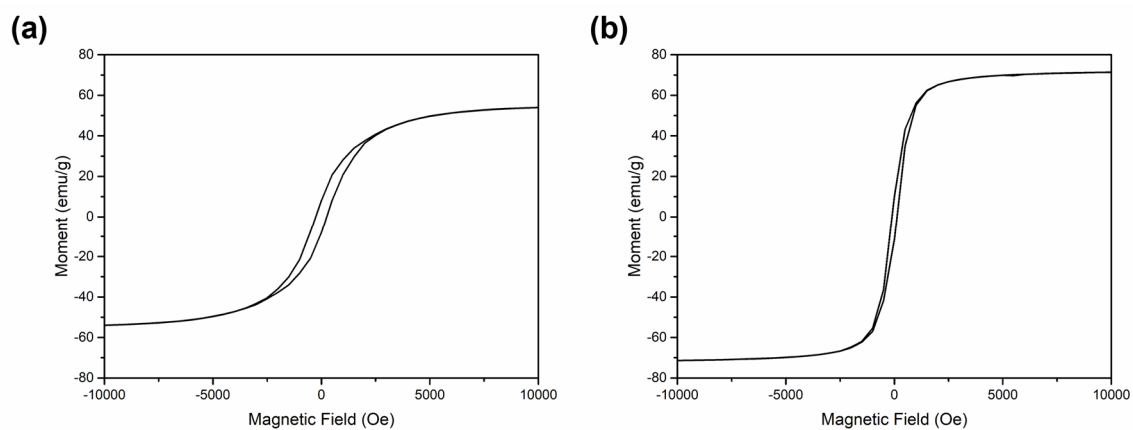


Figure S3. Magnetization diagrams of (a) ZIF-67-derived Co@C microparticle and (b) MIL-88B-derived Fe₃O₄:C microrod normalized to the weight of whole hybrid materials.

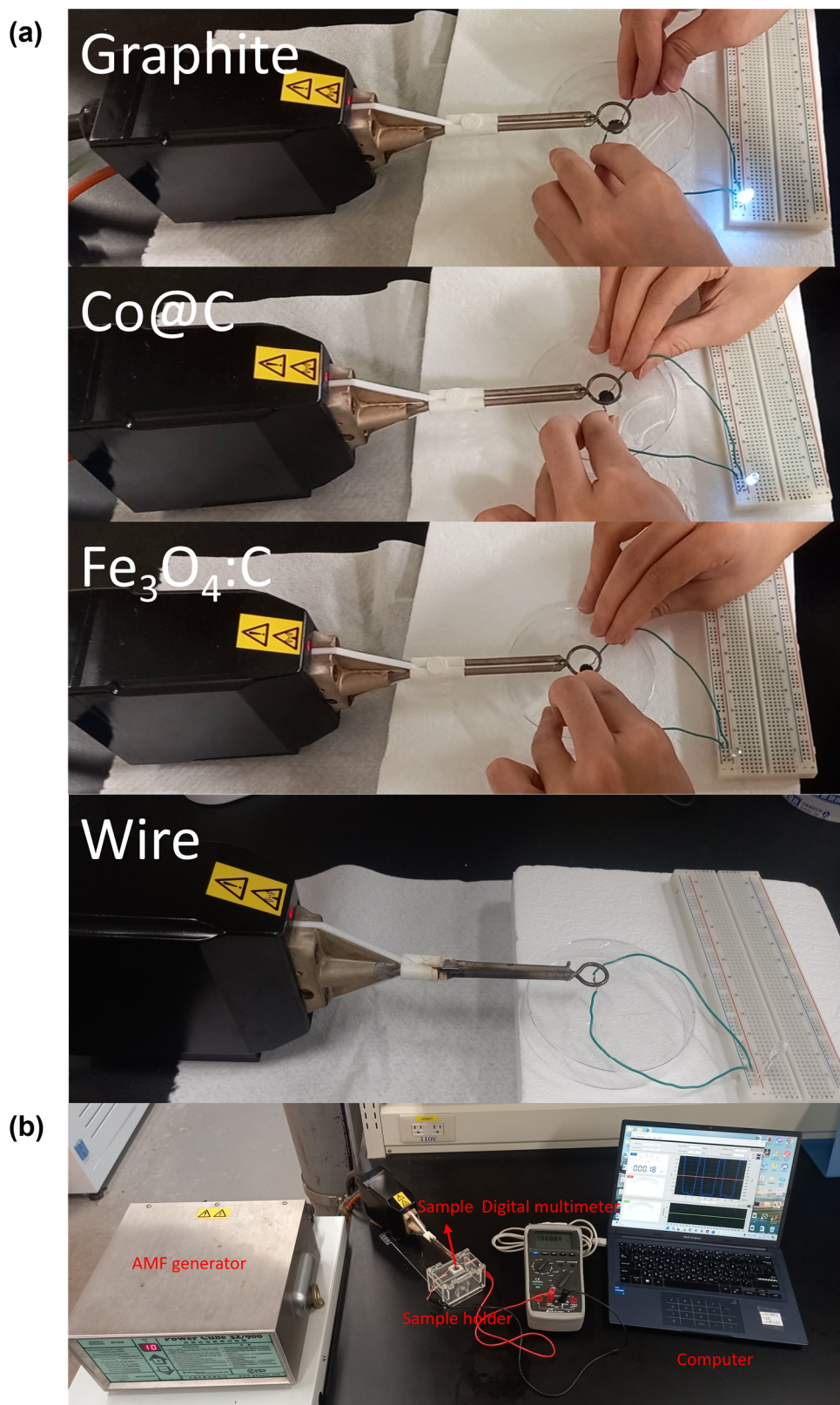


Figure S4. Representative images illustrating the setup for measurements on AMF-induced (a) luminous light-emitting diode (LED) and (b) I-t curves.

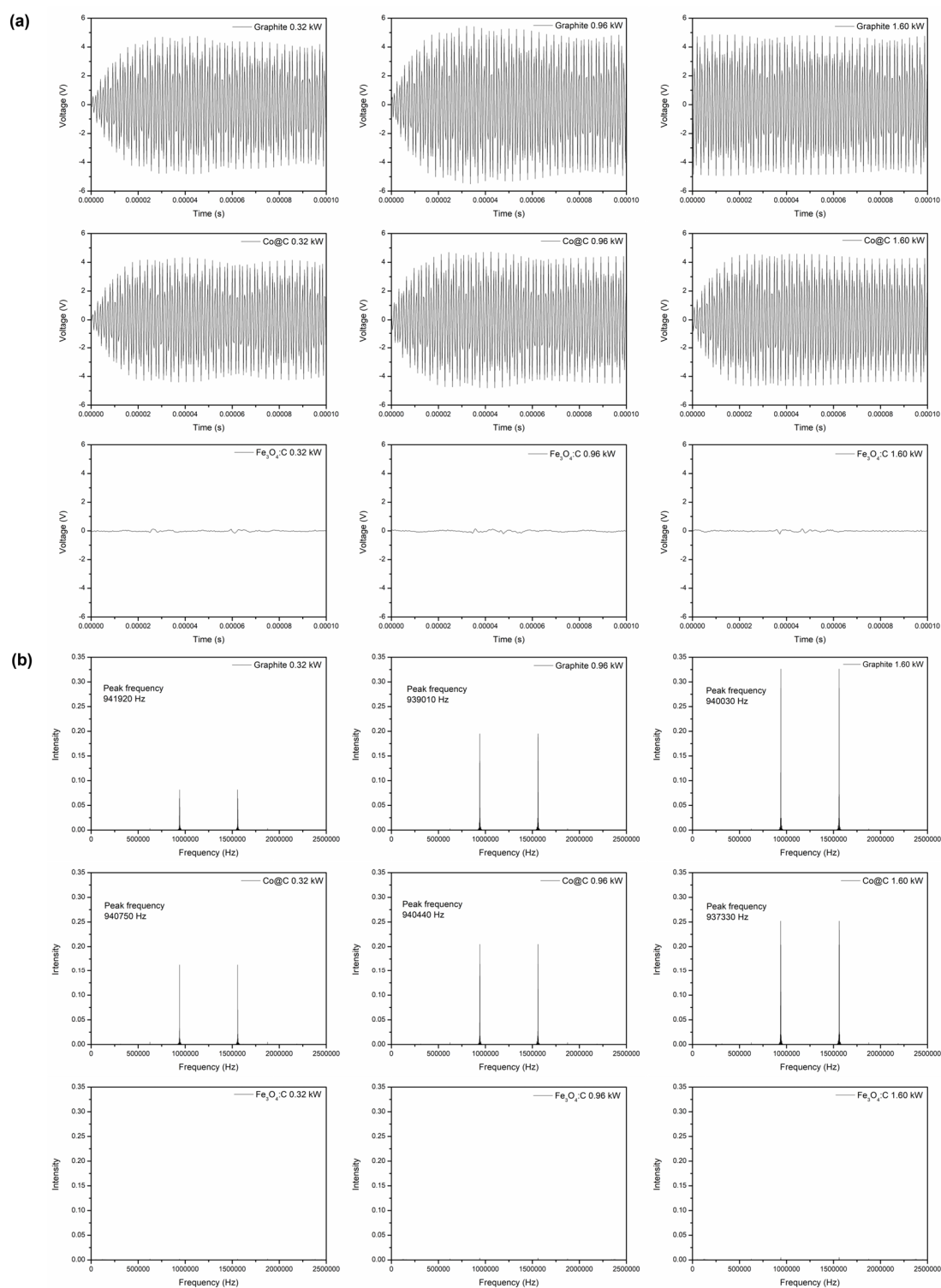


Figure S5. Representative (a) original V-t curves and (b) frequency spectra derived from Fast Fourier-transformed V-t curves for graphite, ZIF-67-derived Co@C microparticle, and MIL-88B-derived Fe₃O₄:C microrod under application of AMF at 0.32 kW, 0.96 kW, and 1.60 kW. In the frequency spectra, the peaks at 1558080-1562670 Hz are the mirror images of those at 937330-941920 Hz due to the symmetric nature of Fast Fourier transform.

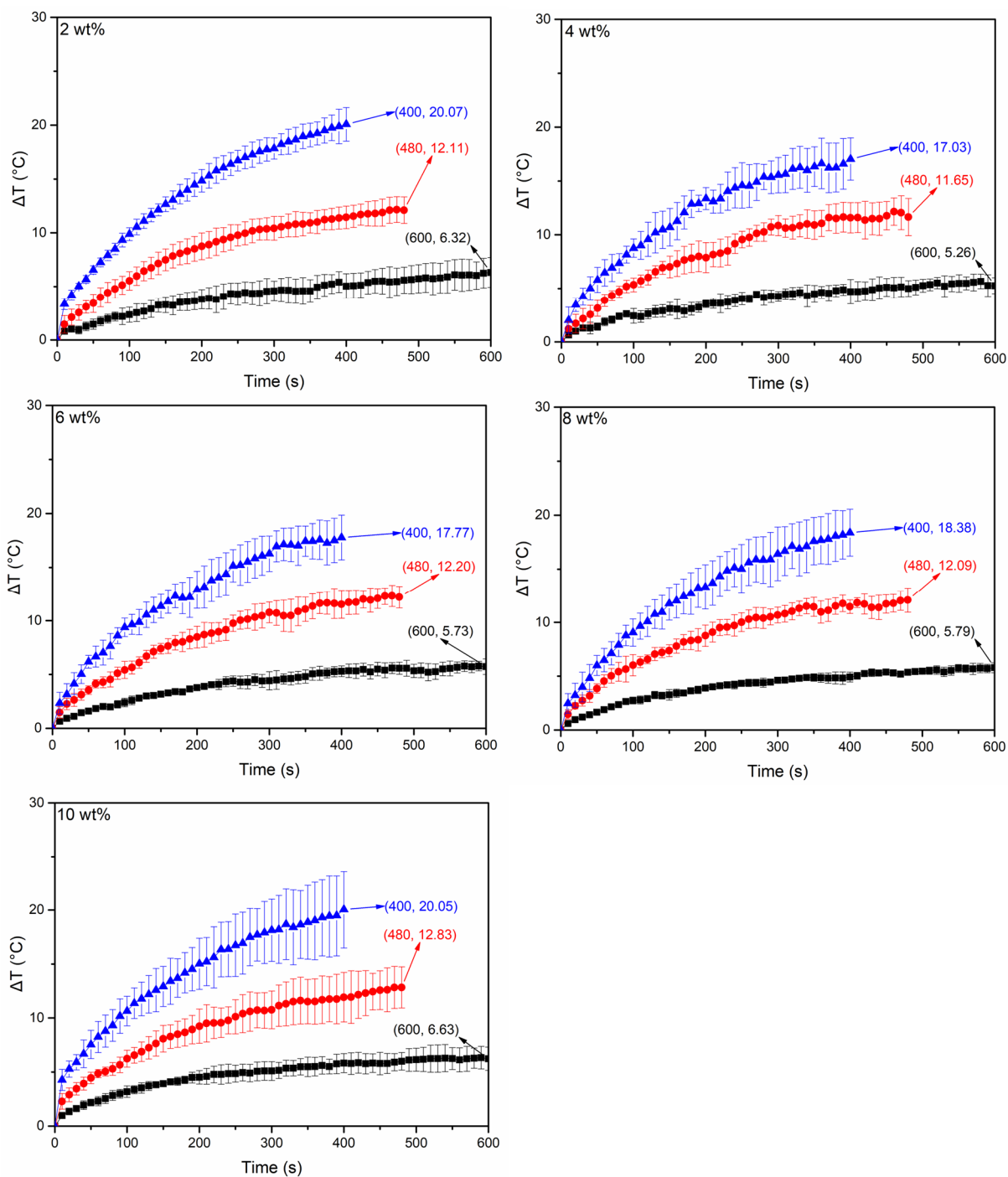


Figure S6. Time-dependent change of temperature upon application of AMF (10% intensity/0.32 kW, black; 30% intensity/0.96 kW, blue; 50% intensity/1.60 kW) to graphite in the aqueous solution with different concentration of sodium alginate.

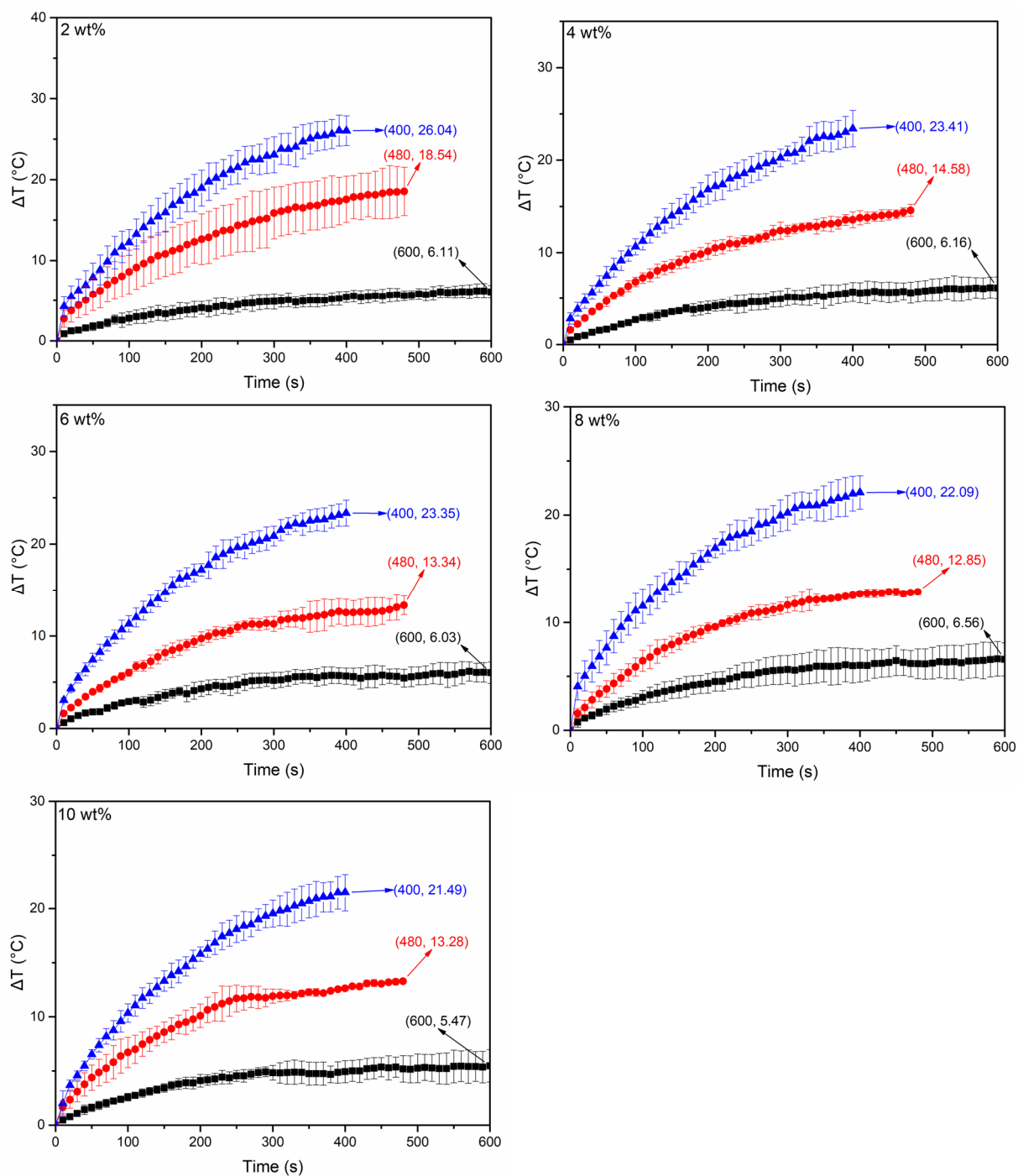


Figure S7. Time-dependent change of temperature upon application of AMF (10% intensity/0.32 kW, black; 30% intensity/0.96 kW, blue; 50% intensity/1.60 kW) to ZIF-67-derived Co@C microparticle in the aqueous solution with different concentration of sodium alginate.

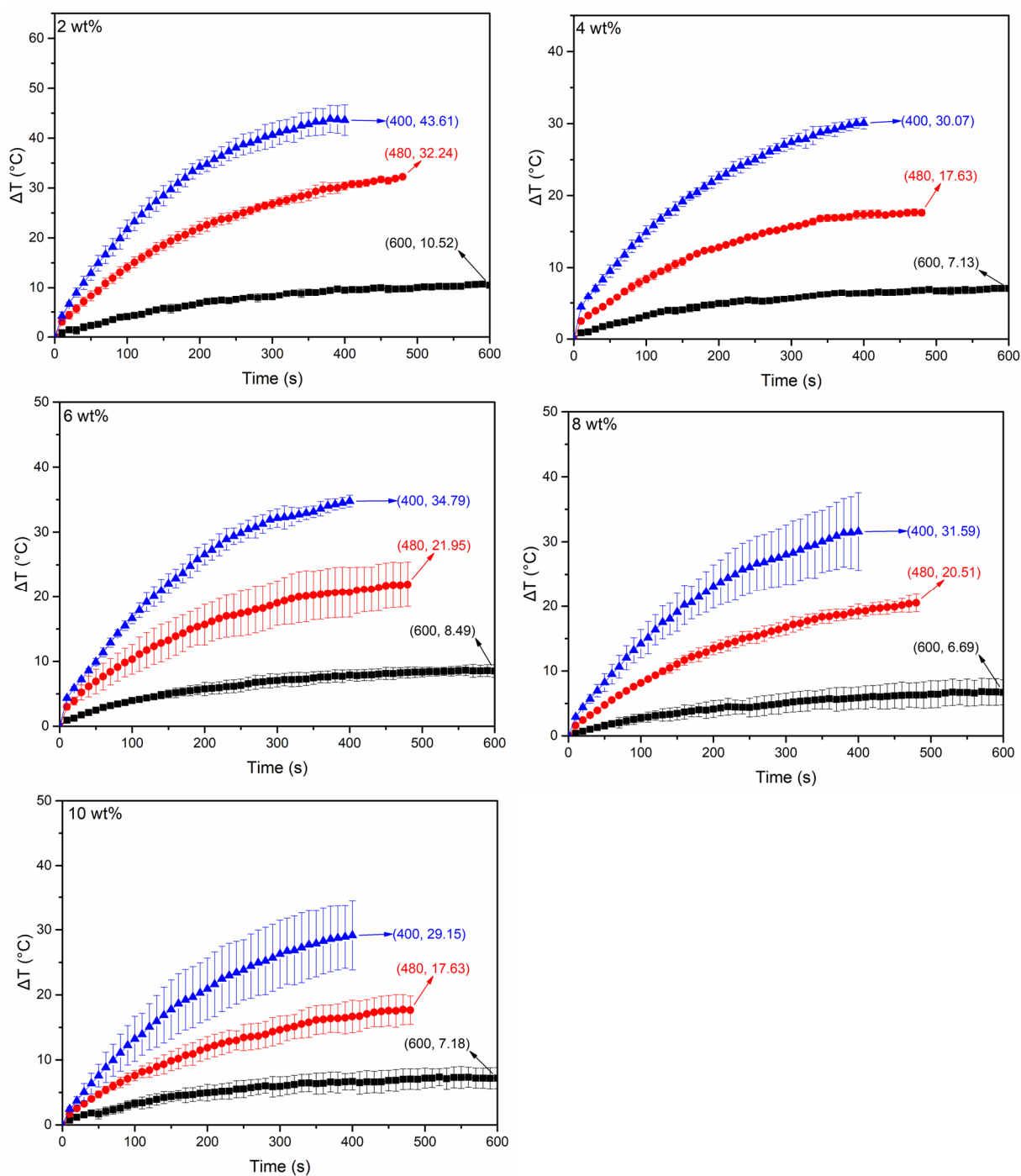


Figure S8. Time-dependent change of temperature upon application of AMF (10% intensity/0.32 kW, black; 30% intensity/0.96 kW, blue; 50% intensity/1.60 kW) to MIL-88B-derived $\text{Fe}_3\text{O}_4\text{:C}$ microrod in the aqueous solution with different concentration of sodium alginate.