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Supporting Information

A general strategy for facile synthesis of ultrathin transition metal hydroxide nanosheets

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Experimental Section

Chemicals. All chemicals were commercially available and were used without additional purification. $Fe(acac)_3$, $Co(acac)_3$ and $Ni(acac)_2$ were purchased from Alfa Asear. $Mn(acac)_2$ was purchased from J&K Chemicals. EDTAFeNa and $Zn(acac)_2$ were purchased from Shanghai Baidi Chemical Factory Co., Ltd.. CH_3COONa and NaOH were purchased from Xilong Chemical Factory Co., Ltd. Na_2CO_3 and $NaHCO_3$ were purchased from Beijing Chemical Works.

Synthesis of FeOOH nanosheets. In a typical synthesis, 70 mg of $Fe(acac)_3$ were dissolved in 200 mL of Na_2CO_3 and $NaHCO_3$ solution with pH of approximately 10.5 at room temperature and stirred for 6 h. The products at different reaction times were collected by filtering and washed several times with water and ethanol, and finally freeze-dried.

Synthesis of $Co(OH)_2$ nanosheets. 5 mg of $Co(acac)_3$ were dissolved in 200 mL of CH_3COONa and NaOH solution with pH of approximately 10.7 at room temperature and stirred for 6 h. The products were collected by filtering and washed several times with water and ethanol, and finally freeze-dried.

Synthesis of $Ni(OH)_2$ nanosheets. 30 mg of $Ni(acac)_2$ were dissolved in 200 mL of Na_2CO_3 and $NaHCO_3$ solution with pH of approximately 10.5 at room temperature and stirred for 8 h. The product is obtained by following the same procedure as that for $Co(OH)_2$ nanosheets.

Synthesis of Fe-Mn hydroxide nanosheets. 70 mg of EDTAFeNa and 5 mg of $Mn(acac)_2$ were dissolved in 200 mL of CH_3COONa and NaOH solution with pH of approximately 10.7 at room temperature and stirred for 6 h. The product is obtained by following the same procedure as that for $Co(OH)_2$ nanosheets.

Synthesis of Co-Zn hydroxide nanosheets. 15 mg of $Co(acac)_3$ and 15 mg of $Zn(acac)_2$ were dissolved in 200 mL of Na_2CO_3 and $NaHCO_3$ solution with pH of approximately 10.5 at room temperature and stirred for 8 h. The product is obtained by following the same procedure as that for $Co(OH)_2$ nanosheets.

Synthesis of Ni-Zn hydroxide nanosheets: The preparation of Ni-Zn hydroxide nanosheets follows the same procedure as that of Co-Zn hydroxide nanosheets except for the use of $Ni(acac)_2$ as the precursor

Materials characterization. The conventional bright-field images were performed utilizing FEI Tecnai T20 microscope (200 kV), and HRTEM images and element mapping analyses results were obtained on an FEI Tecnai F30 microscope (300 kV) with an Energy Dispersive Spectrometer (EDX). SEM images were taken on a Merlin Compact scanning electron microscope. Powder X-ray diffraction (PXRD) patterns were obtained using a Rigaku X-ray diffractometer equipped with Cu-Kα radiation at 40 kV and 100 mA, respectively. The topography of the shattered samples was observed by atomic force microscopy (AFM, Bruker INNOVA). The nitrogen adsorption and desorption isotherms were measured with the Quantachrome Autosorb-IQ instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on Imaging Photoelectron Spectrometer (Axis Ultra DLD, Kratos Analytical Ltd.) using monochromatized Al Kα anode (Al Ka, hv=1486.7 eV). All the collected spectra were calibrated with contaminated C 1s peak at 284.8 eV. Magnetization was measured by Physical Property Measurement System (PPMS-9, Quantum Design, USA). The concentrations of Fe and Mn were quantified using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Prodigy 7, Leeman, USA). The pH of solutions was monitored via a Mettler Toledo FE20 pH meter.

In vitro MRI. Measurement of relaxation parameters of Fe-Mn nanosheets was conducted in test tubes with a 3 T clinical MRI scanner (SIEMRNS, Germany). The nanosheets with various concentrations of iron (0-1.4 mM) were dissolved in water with 1 % agarose. After acquiring MR images, the signal intensity was measured with selected region of interests for each sample.

Relaxation rates r_1 ($1/T_1$) and r_2 ($1/T_2$) were measured from the relaxation time (T_1 and T_2) at various iron concentrations. T_1-mapping image sequence is TR = 15 ms, TE = 2.6 ms, FOV=180 × 180 mm^2, slice = 5, slice thickness = 3 mm. T_2-mapping image sequence is TR =1000 ms, TE = 13.8 ms, FOV=180 × 180 mm^2, slice = 5, slice thickness = 3 mm.

Cell culture. KB cells were obtained from Hospital Chinese Academy of Medical Science and cultured at 37 °C under 5 % CO_2. All cell culture related reagents were purchased from Invitrogen. KB cells were grown in DMEM culture medium with 10 % fetal bovine serum (FBS) and 1 % penicillin/streptomycin. Cells were plated in cell culture flasks under 100 % humidity.

Cytotoxicity by CCK-8 assay. The *in vitro* cytotoxicity of Fe-Mn hydroxide nanosheets was evaluated colorimetrically by the Cell Counting Kit-8 (CCK-8) from Dojindo Laboratories (Tokyo, Japan). Briefly, all cells were seeded on 96-well cell culture plates with 5 × 10^3 cells per well and incubated overnight. After removing the culture medium, fresh culture medium with Fe-Mn hydroxide nanosheets in different concentrations were added and incubated for 24h. CCK-8 assay was performed after washing cells with Dulbecco's phosphate buffered saline (DPBS). The WST-8[2-(2-methoxy-4-nitrophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2H-tetrazolium, monosodium salt] solution was added and cells were incubated for 4 h at 37 °C under 5 % CO_2. The absorbance of each well was measured with a luminescence microplate reader (SoftMax Pro 5) at 450 nm.

Tumor mice model. All animal studies were kept in the environment of SPF with 12 h light and 12 h darkness. They were raised in compliance with standard laboratory guidelines. KB cells (1×10^7, in 100 μL PBS solution) were subcutaneously injected into the right back of 7-week old female Balb/c mice weighting 18-20 g.

In Vivo MRI. When the tumor volume reached about 100-200 mm^3, 10 μL of 400 μg/ml Fe-Mn nanosheets was injected intratumorally. MR images were acquired before and 2 h after injection. The T_1-weighted and T_2-weighted images were obtained in a clinic 3 T MRI scanner (SIEMRNS, Germany). The T_1-weighted sequence was TR = 1000 ms, TE = 13.8 ms, slice thickness = 3.0 mm, and the T_2-weighted sequence was TR = 15 ms, TE = 2.6 ms, slice thickness = 3.0 mm.

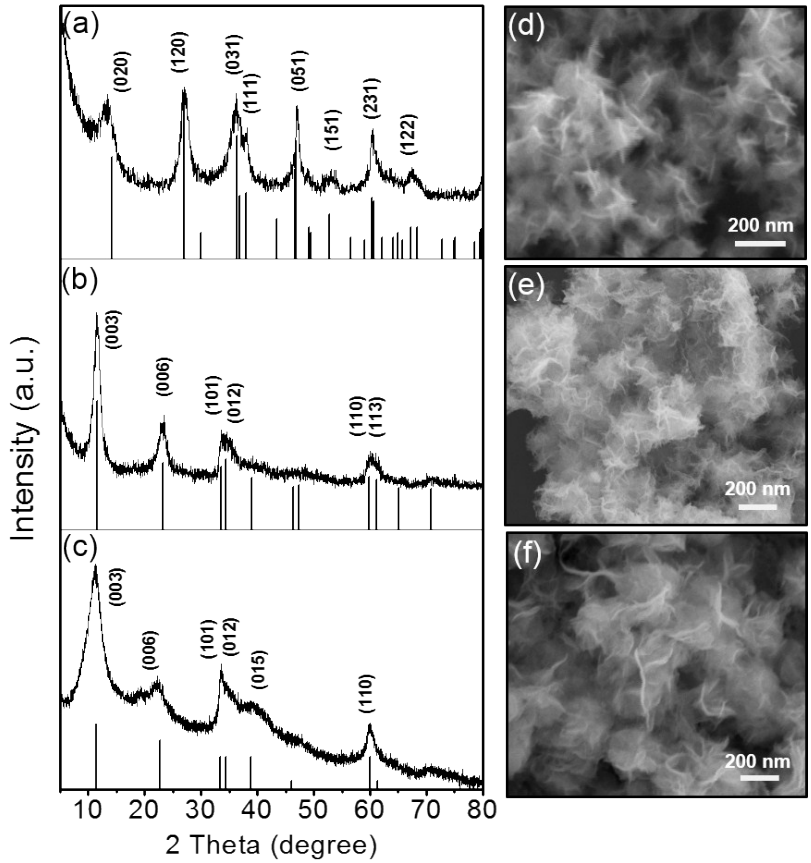

Fig. S1 PXRD patterns (left) and SEM (right) images of (a), (d) FeOOH, (b), (e) $Co(OH)_2$ and (c), (f) $Ni(OH)_2$ ultrathin nanosheets.

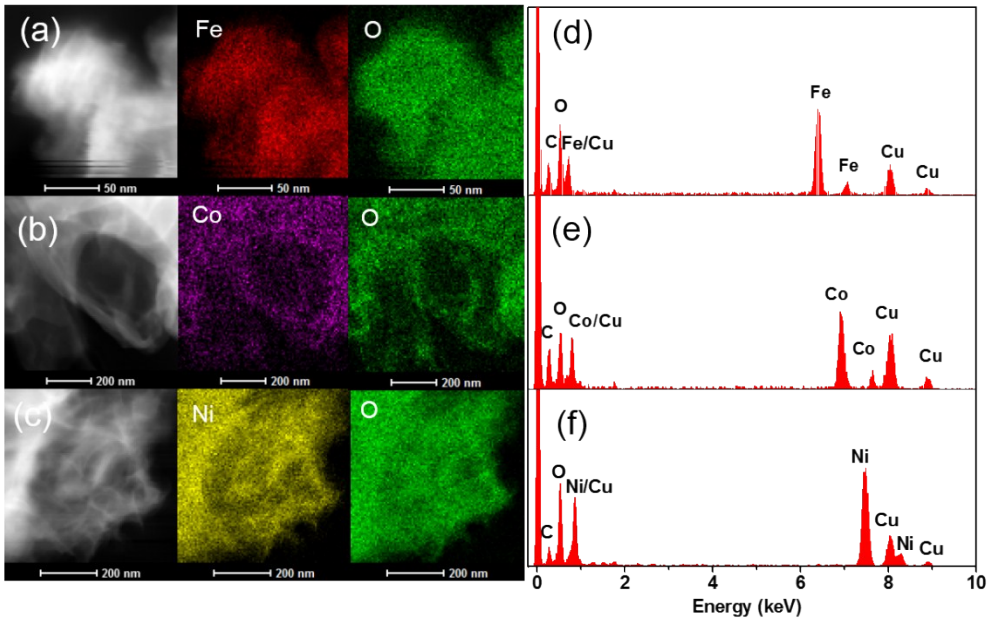

Fig. S2 HAADF-STEM images, elemental mapping and EDX spectra of (a), (d) FeOOH, (b), (e) $Co(OH)_2$ and (c), (f) $Ni(OH)_2$ ultrathin nanosheets.

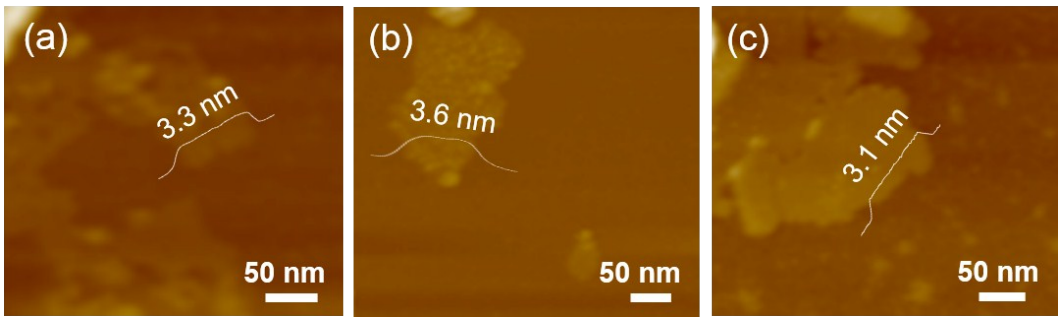

Fig. S3 AFM images of (a) Fe-Mn hydroxide, (b) Co-Zn hydroxide and (c) Ni-Zn hydroxide nanosheets.

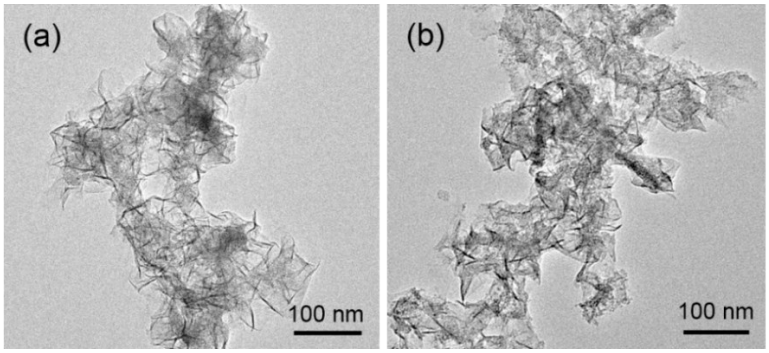

Fig. S4 TEM images of the obtained Fe-Mn hydroxides with Mn/Fe atom ratio of (a) 1:2 and (b) 1:1 in the raw materials.

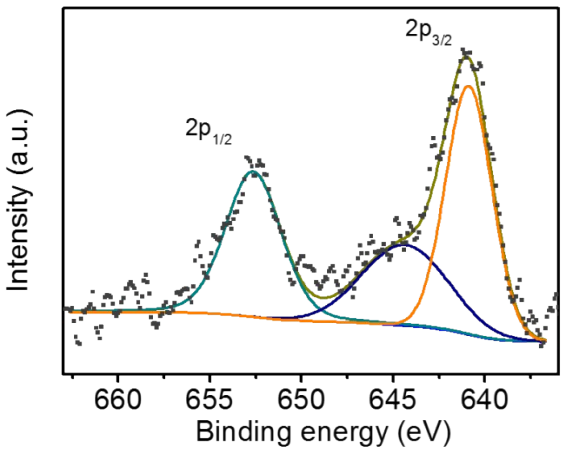

Fig. S5 XPS spectrum of Mn 2p of the Fe-Mn hydroxide nanosheets.

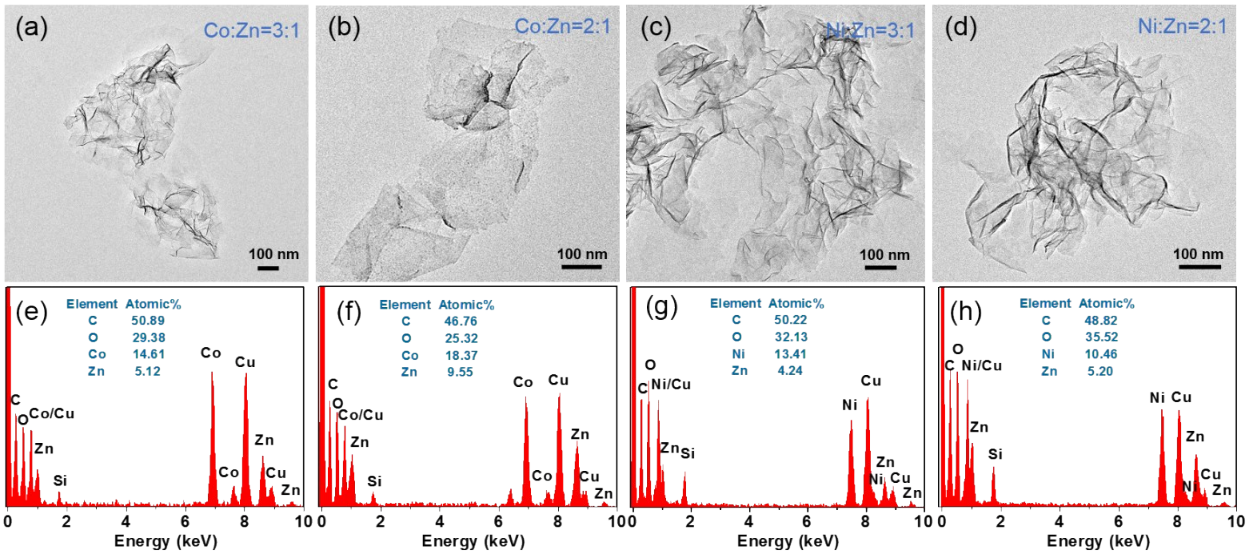

Fig. S6 TEM images (top) and EDX spectra (bottom) of (a), (b), (e) and (f) Co-Zn hydroxides and (c), (d), (g) and (h) Ni-Zn hydroxides with different atomic ratios.

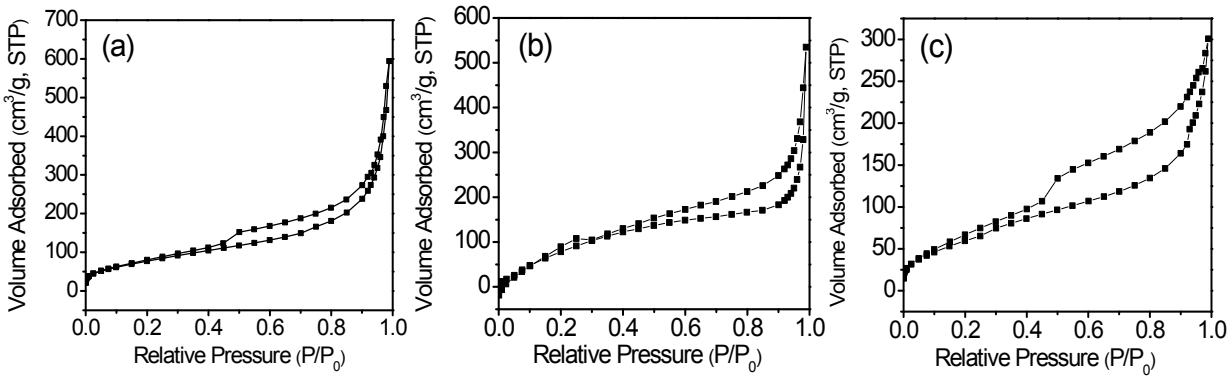

Fig. S7 N_2 adsorption and desorption isotherms of (a) Fe-Mn hydroxide, (b) Co-Zn hydroxide and (c) Ni-Zn hydroxide nanosheets.

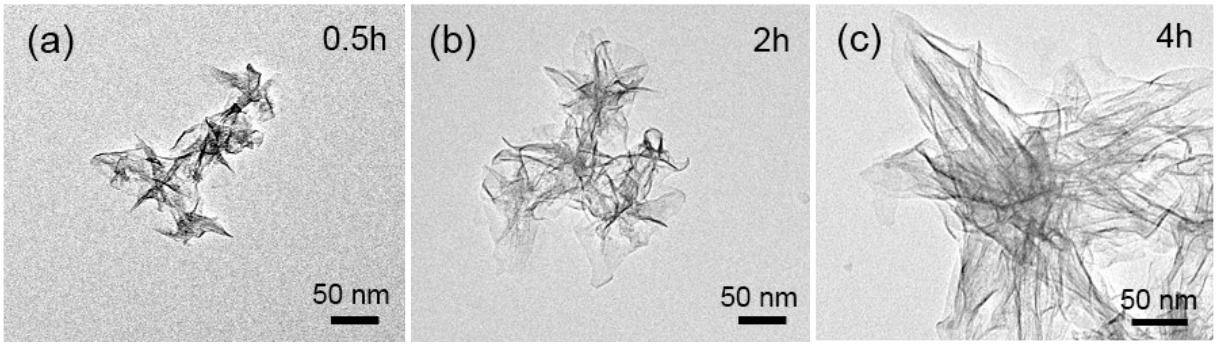

Fig. S8 TEM images of the Fe-Mn hydroxide nanosheets obtained at different time.

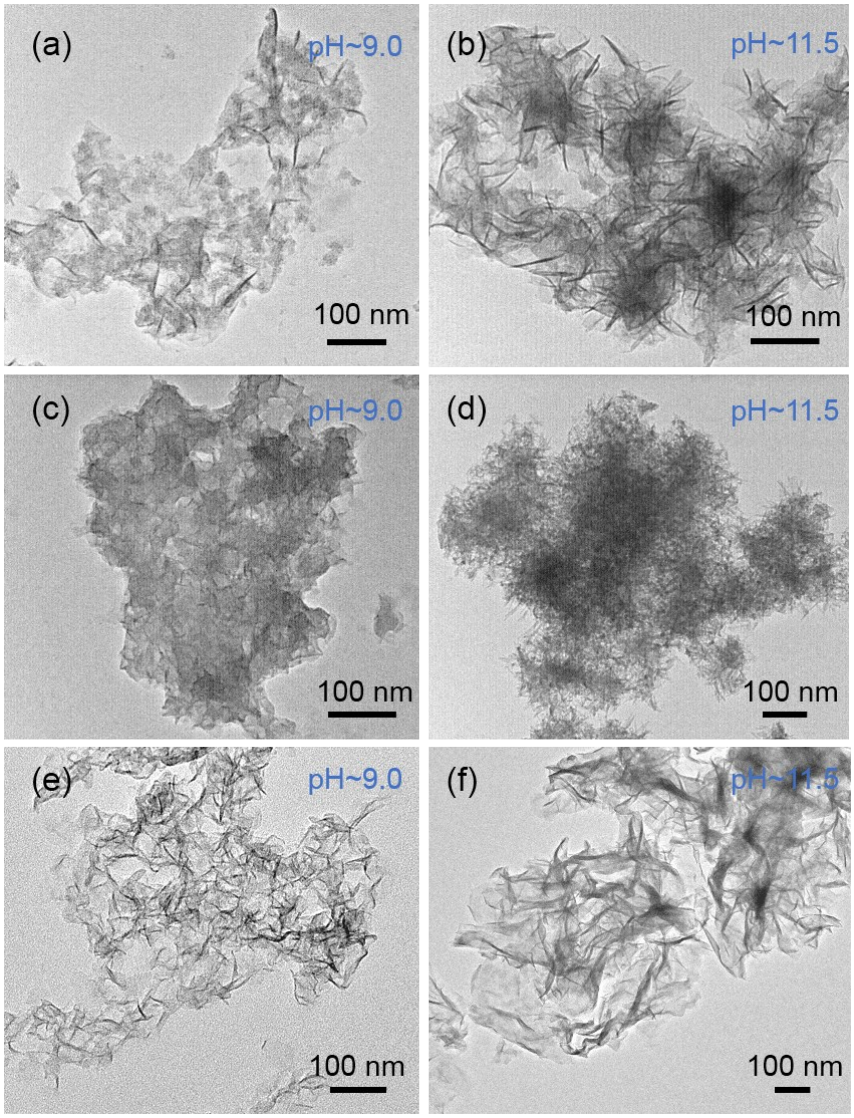

Fig. S9 TEM images of the obtained (a), (b) FeOOH, (c), (d) $Co(OH)_2$ and (e), (f) $Ni(OH)_2$ in the solution with different pH.

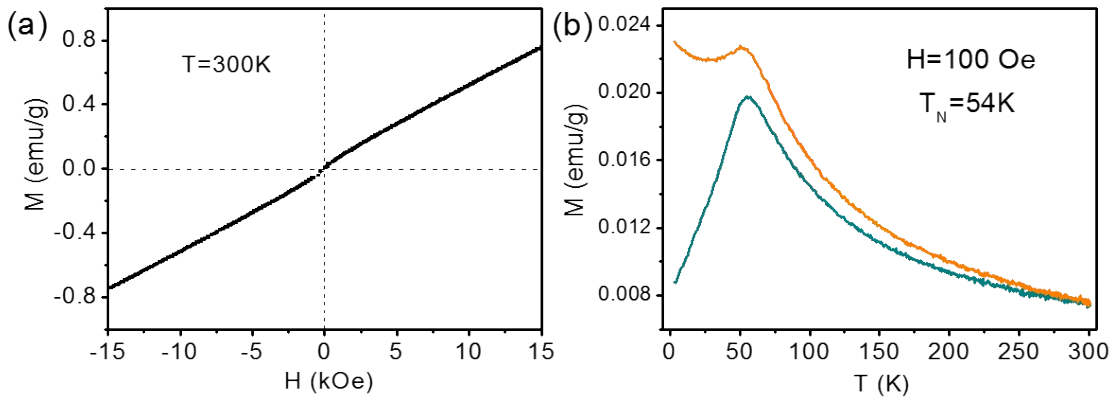

Fig. S10 (a) Hysteresis loops and (b) magnetization curves of FeOOH nanosheets.

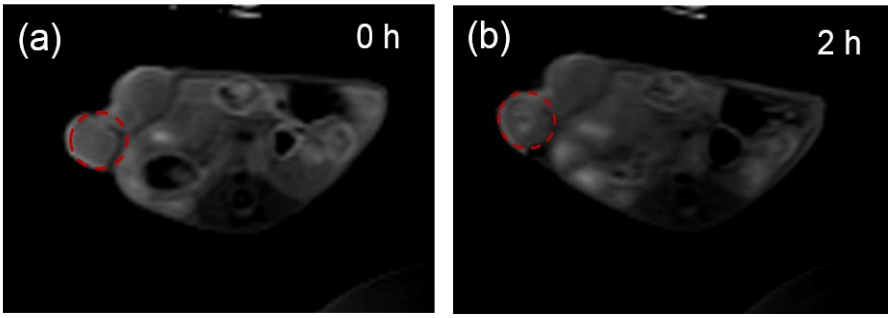

Fig. S11 T_1-weighted MR images of KB tumor-bearing mice (a) before and (b) after intratumoral injection of FeOOH nanosheets to tumor tissues.

Table S1. Atomic ratio of Fe-Mn hydroxide nanosheets obtained from EDX analysis.

Element	Weight %	Atomic %
C	22.40	47.51
O	15.08	24.00
Fe	57.33	26.08
Mn	5.19	2.41
Total	100	100

Table S2. Atomic ratio of Co-Zn hydroxide nanosheets obtained from EDX analysis.

Element	Weight %	Atomic %
C	27.93	52.94
O	19.56	27.82
Co	26.06	10.06
Zn	26.45	9.18
Total	100	100

Table S3. Atomic ratio of Ni-Zn hydroxide nanosheets obtained from EDX analysis.

Element	Weight %	Atomic %
C	6.93	16.21
O	31.86	56.01
Ni	29.69	14.22
Zn	31.52	13.56
Total	100	100

Table S4. Relaxation properties comparison with references.

Sample	r_1 (mM^{-1} s^{-1})	r_2 (mM^{-1} s^{-1})	Magnetic field (T)	Reference
γ-FeOOH nanosheets	0.76	21.2	3.0	This work
α-FeOOH clusters	0.4	0.54	1.41	1
β-FeOOH Nanoparticles	4.0	4.8	0.47	2
β-FeOOH nanospindles	3.06	5.06	1.5	3
α-FeOOH/WMSN	4.03	7.94	0.47	4
FeOOH/HMSS	4.11	10.85	7	5
FeOOH/HMSS	4.73	11.3	0.47	5
GO-PEG-β-FeOOH	-	303.81	7	6

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