Supporting Information

Dual metal centers within a water-stable Co/Ni bimetallic metal-triazolate framework contribute to durable photocatalysis for water treatment

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Contents:

Experimental Section

1. Chemicals

1H-1,2,3-triazole (98%), CoCl$_2$ (97%), NiCl$_2$ (99%), Mn(NO$_3$)$_2$ (98%), N, N-dimethylformamide (DMF, 99.9%), N,N-diethylformamide (DEF, 99%), methanol (99.5%), ethanol (99.7%), deionized water, Nafion® perfluorinated resin-aqueous dispersion (10 wt.% in water), 2', 7'-Dichlorodihydrofluorescein (DCFH),

2. Synthesis of MOFs

CoNi-MET-T140(CoNi-1:1): 0.518 g of CoCl$_2$ and 0.519 g of NiCl$_2$ were dissolved in 48 mL of DMF by stirring in a three-neck flask. The solution was flushed with 100 sccm N$_2$ gas for 30 min to remove air. 1390.67 μL of 1H-1,2,3-triazole was then added to the solution drop wise. Then, the solution was further flushed with 100 sccm N$_2$ for 60 min. The mixture was heated up to 140 ℃ and retained reaction for 24 h. A brownish-yellow solid was formed. The sample was thoroughly washed 3 times with DMF to remove the excess of unreacted reactant. Next, the sample was immersed in 150 mL of methanol for 5 days and exchanging the solvent 5 times during this time. The solvent was removed by centrifugation. Finally, the sample was dried in a vacuum oven at 60 ℃ for 2 hours. Yield: 53% based on CoCl$_2$ and NiCl$_2$. Elemental analysis for CoNi-MET. Calculated: C 24.6%, N 43.1% and H 2.1 %; tested results: C 27.3 %, N 44.4% and H 3.0%.

The synthesis of other samples with different Co:Ni ratio (sample CoNi-3:1 and CoNi-1:3) were similar with CoNi-1:1, except 779 and 259.2 mg CoCl$_2$ and NiCl$_2$ were used for sample CoNi-3:1, respectively; 259.6 and 777.6 mg CoCl$_2$ and NiCl$_2$ were used

for sample CoNi-1:3, respectively.

CoNi-MET-T180(CoNi-1:1-1): 1.554 g of $CoCl_2$ and 1.557 g of $NiCl_2$ were dissolved in 48 mL of DEF by stirring in a three-neck flask. The solution was flushed with 100 sccm N_2 gas for 30 min to remove air. 4172.01 µL of 1H-1,2,3-triazole was then added to the solution drop wise. Then, the solution was further flushed with 100 sccm N_2 for 60 min. The mixture was heated up to 180 °C and retained reaction for 24 h. A brownish-yellow solid was formed. The sample was thoroughly washed 1 time with DEF and 2 times with DMF to remove the excess of unreacted reactant. Next, the sample was immersed in 150 mL of methanol for 5 days and exchanging the solvent 5 times during this time. The solvent was removed by centrifugation. Finally, the sample was dried in a vacuum oven at 60 °C for 2 hours.

Ni-MET-T140: 0.972 g $NiCl_2$ were dissolved in 45 mL of DMF by stirring in a three-neck flask. The solution was flushed with 100 sccm N_2 gas for 30 min to remove air. Then, 1303.75 µL of 1H-1,2,3-triazole was added to the solution drop wise and further flushed with 100 sccm N_2 for 60 min. The mixture was heated up to 140 °C and retained reaction for 48 h. A purple solid was formed. The sample was washed 3 times with DMF. Next, the sample was immersed in 150 mL of methanol for 5 days and exchanging the solvent 5 times during this time. The solvent was removed by centrifugation. Finally, the sample was dried in a vacuum oven to obtain a purple and dry powder.

Ni-MET-T180: 2.916 g $NiCl_2$ were dissolved in 45 mL of DEF by stirring in a three-neck flask. The solution was flushed with 100 sccm N_2 gas for 30 min to remove air.

Then, 3911.25 μL of 1H-1,2,3-triazole was added to the solution drop wise and further flushed with 100 sccm N_2 for 60 min. The mixture was heated up to 180 °C and retained reaction for 48 h. A purple solid was formed. The sample was washed 1 time with DEF and 2 times with DMF. Next, the sample was immersed in 150 mL of methanol for 5 days and exchanging the solvent 5 times during this time. The solvent was removed by centrifugation. Finally, the sample was dried in a vacuum oven to obtain a purple and dry powder.

Co-MET was synthesized similar to Ni-MET.

3. The test of water stability

Around 50 mg samples were stirred in 50 mL of deionized water for 0.05 h, 1 h, 24 h, 48 h, 72 h, respectively. Then the solvent was removed by centrifugation. Next, the sample was thoroughly washed 2 times with 50 mL of methanol. Finally, the sample was dried at 60 °C for 2 hours.

4. Electrochemical measurements

Cyclic voltammetry was studied in a standard three-electrode system in O_2-saturated 0.5 M Na_2SO_4 solution (pH=6.54). A Ag/AgCl electrode and a Platinum coil electrode were used as the reference electrode and counter electrode, respectively. Cyclic voltammetry tested by a CHI 760 instrument.

Preparation of working electrodes: 5 mg of each active materials and 10 μl of Nafion solution (10 wt.% in water) were uniformly dispersed in a mixture of 490 μL of H_2O and 500 μl of ethanol with the assistance of ultrasonication for 1-2 h until no visible solid in the dispersion. 12 μL of the dispersion was then dropped onto to a 1*1 cm Ni

foam and dried in air.

5. <u>Reactive oxygen species (ROS) detection</u>

2', 7'-Dichlorodihydrofluorescein (DCFH) was used as the index to investigate the ROS generation ability. The aqueous solution containing 50 μM DCFH was added to the sample (stock solution: 5 mg mL^{-1} in DMSO), and the final concentration was 50 μg mL^{-1}. Then the white light (50 mW cm^{-2}) was irradiated for 5 min at a time interval of 1 min. The change of fluorescence intensity of the indicator was monitored by fluorescence spectrometer. The indicator was excited at 480 nm and the luminescence at 525 nm was recorded.

6. <u>Superoxide anion radical detection.</u>

Dihydrorhodamine 123 (DHR123) was used to monitor superoxide anion radical production. An aqueous solution containing 20 μM DHR123 (stock solution: 10 mM in DMSO) was added to the sample (stock solution: 5 mg mL^{-1} in DMSO), and the final concentration was 50 μg mL^{-1}. Then the white light (50 mW cm^{-2}) was irradiated for 5 min at a time interval of 1 min. The change of fluorescence intensity of the indicator was monitored by fluorescence spectrometer. The indicator was excited at 480 nm and the luminescence at 525 nm was recorded.

7. <u>Singlet oxygen detection.</u>

9,10-Anthracenediyl-bis(methylene)-dimalonic acid (ABDA) was used as the indicator. An aqueous solution containing 100 μM ABDA (stock solution: 10 mM in DMSO) was added to the sample (stock solution: 5 mg mL^{-1} in DMSO) for a final concentration of 50 μg mL^{-1}. The white light (50 mW cm^{-2}) was then irradiated for 5

min at a time interval of 1 min. The absorbance of ABDA in the range of 300-450 nm was monitored with Shimazu UV-2600 spectrophotometer.

8. Hydroxyl radical detection.

Hydroxyphenyl fluorescein (HPF) was used to monitor Hydroxyl radical production. An aqueous solution containing 10 μM HPF (stock solution: 5 mM in DMSO) was added to MOF (stock solution: 5 mg mL^{-1} in DMSO) for a final concentration of 50 μg mL^{-1}. Then the white light (50 mW cm^{-2}) was irradiated for 5 min at a time interval of 1 min. The change of fluorescence intensity of the indicator was monitored by fluorescence spectrometer. The excitation wavelength was 480 nm, and the fluorescence intensity of HPF at 515 nm was recorded.

9. Photostability test of CoNi-MET

The photostability of CoNi-MET-T140 (50 μg mL^{-1}) in water under white light (50 mW cm^{-2}) was investigated by detecting changes in the absorption spectrum. The solution was exposed to white light (50 mW cm^{-2}) for different times (0, 2, 4, 6, 8, 10, 15, 20, 25, 30 min) and the change of absorbance was monitored with Shimadzu UV-2600 spectrophotometer.

10. Bacteria culture

Individual colonies of E. coli on Luria-Bertani (LB) broth solid agar plates were transferred to 5 mL LB liquid broth medium and grown at 37 °C for 16 h. Then the bacteria were harvested via centrifugation (7100 rpm, 2 min) and washed three times with phosphate-buffered saline (PBS). The supernatant was removed and the remaining E. coli was resuspended in PBS and its OD$_{600}$ value was adjusted to 1 (approximately

1×10^9 CFU mL^{-1}).

11. <u>Antibacterial Experiments</u>

E. coli bacterial suspension (1×10^7 CFU mL^{-1}, 1 mL) was incubated with a certain concentration METs for 30 min at 37 °C and then treated in dark or with white light irradiation (100 mW cm^{-2}) for 1 h. And then the suspension was serially diluted with suitable folds (10^4 or 10^3). Then 200 μL suspension was spread on LB agar plate and incubation at 37 °C for 24 h (each group with three parallel independent plates). Then the number of colony-forming units was counted. The number of survived bacterial in suspension before dilution is calculated according to the following equation: $C = C_{plate} \times 5 \times 10^A$ (Where C is the actual CFU of colony number before dilution, C_{plate} is the average number of colony-forming units on the agar plate, and A is diluted magnitude).

12. <u>Characterizations</u>

The samples were analyzed using Powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), synchrotron XRD, scanning electron microscopy (SEM), inductively coupled plasma-optical emission spectrometer (ICP-OES), N_2 adsorption isotherms at 78 K, Thermal gravimetric analysis (TGA). XRD patterns were obtained using a SmartLabTM 9 kW X-ray diffractometer (Cu Kα radiation, λ=1.541 Å). Pawley refinement was carried out with crystal structures derived from that of Ni-MET-T180 and CoNi-MET-T180 by using GSAS-II. GSAS-II, a software for crystal determination from PXRD pattern, implemented by means of the Rietveld refinement method. The results of the Rietveld refinements are summarized in Table S1. TEM images were conducted using a Thermofisher Talos F200S. Elemental analysis was conducted by

using ICP-OES (Agilent 720ES). TGA was done using a SDT Q600. N_2 adsorption isotherms at 78 K were tested by Micromeritics ASAP 2460.

Tables

Table S1. The lattice parameters of the Co-MET. The refined parameters of Ni-MET-T180 and CoNi-MET-T180.

Name	Co-MET[1]	Ni-MET-T180	CoNi-MET-T180
Crystal system		Cubic	
Space Group		$Fd\overline{3}m$ (No. 227)	
a (Å)	17.3423	17.1653	17.081(3)
V (Å³)	5215.79	5057.71	4983.73
$M - N_1$ (Å)	2.06239(0)	2.04134(0)	2.0313(4)
$M - N_2$ (Å)	2.08038(0)	2.05915(0)	2.0490(4)
$M \cdots M$ (Å)	3.75472(0)	3.71640(0)	3.6981(7)
R_p (%)		1.073	0.784
R_{wp} (%)		1.395	3.374

Table S2. The ICPES results of the Co and Ni in the CoNi-MET.

Material	Co (µg L⁻¹)	Ni (µg L⁻¹)
CoNi-MET-T140	13.1282	24.1400
	13.0629	23.8778

13.4710	24.7245

Table S3. The BET surface area ($m^2 \ g^{-1}$) of the METs and after stirred in water.

	As-synthesized	0.05 h	72 h
Co-MET-T140	419	360	284
CoNi-3:1	585	622	480
CoNi-1:1	769	784	569
CoNi-1:3	665	716	
Ni-MET-T140	820	390	

Table S4. The changes of the mass.

	m_0 (mg)	m_1 (mg)	Δm (mg)
CoNi-3:1-1 h	52.9	35.6	17.3(32.7%)
CoNi-1:1-1 h	16.6	11.59	5.01(30.2%)
CoNi-1:3-1 h	35.8	12.1	23.7(66.2%)
CoNi-3:1-48 h	50.7	34.9	15.8(31.2%)
CoNi-1:1-48 h	50.7	22.9	27.8(54.8%)
CoNi-1:3-48 h	50.9	10.2	40.7(79.9%)
CoNi-3:1-72 h	60.7	45.6	15.1(24.9%)
CoNi-1:1-72 h	60.7	32.0	28.7(47.3%)
CoNi-1:3-72 h	60.9	0.8	60.1(98.7%)

m_0 : The mass of the initial sample. m_1: The mass after stirring in water.

Figures
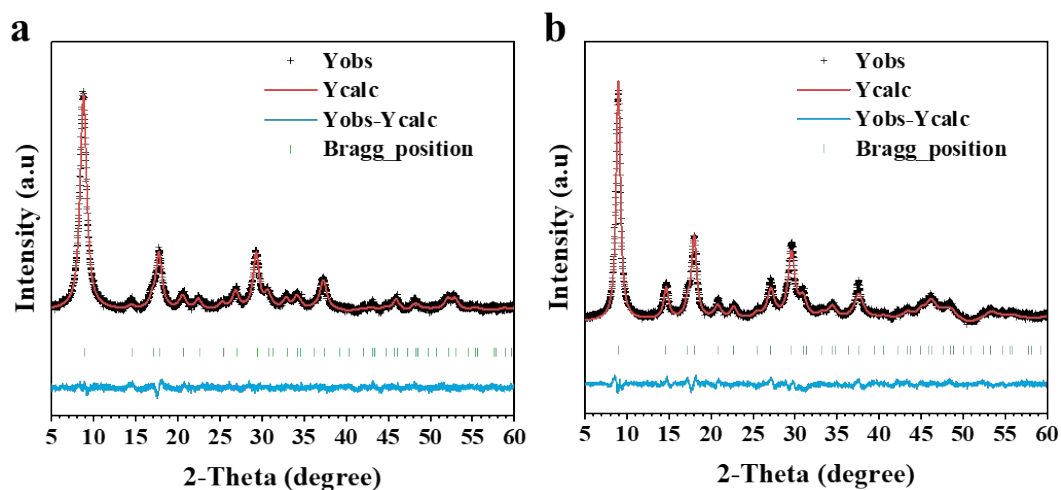
Figure S1. The Pawley refinement of the PXRD result of the (a) Ni-MET-T180 and (b) CoNi-MET-T180.

Area	Co fraction (%)	Ni fraction (%)
#1	31.23	68.77
#2	32.01	67.99
#3	32.29	67.71
#4	32.40	67.60
#5	32.29	67.71
#6	34.80	65.20
#7	50.43	49.57
#8	57.46	42.54
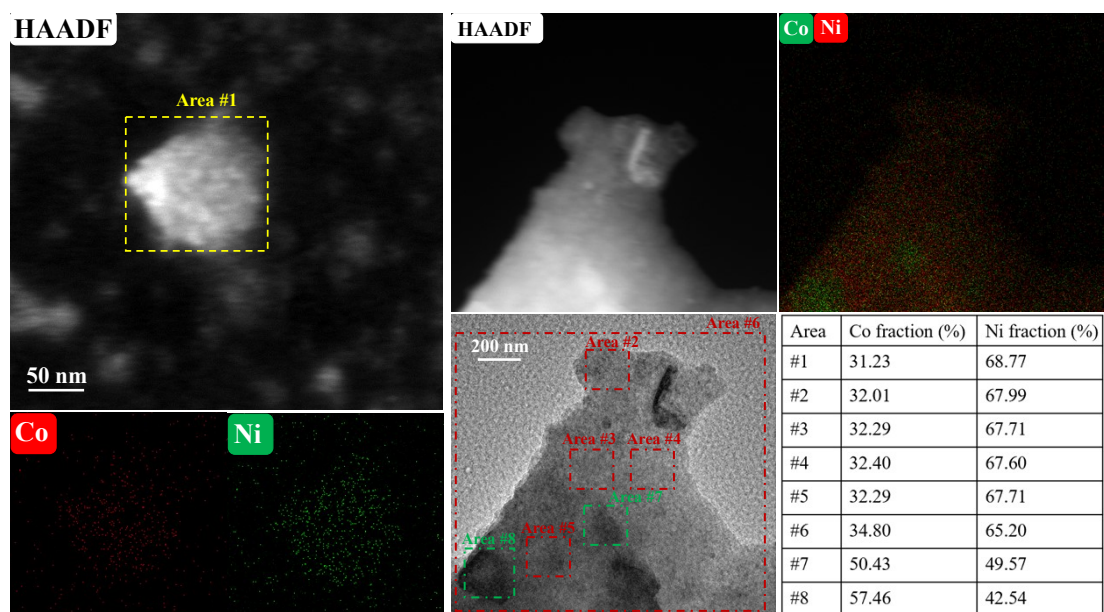
Figure S2. The EDS element mapping result of the CoNi-MET-T140.
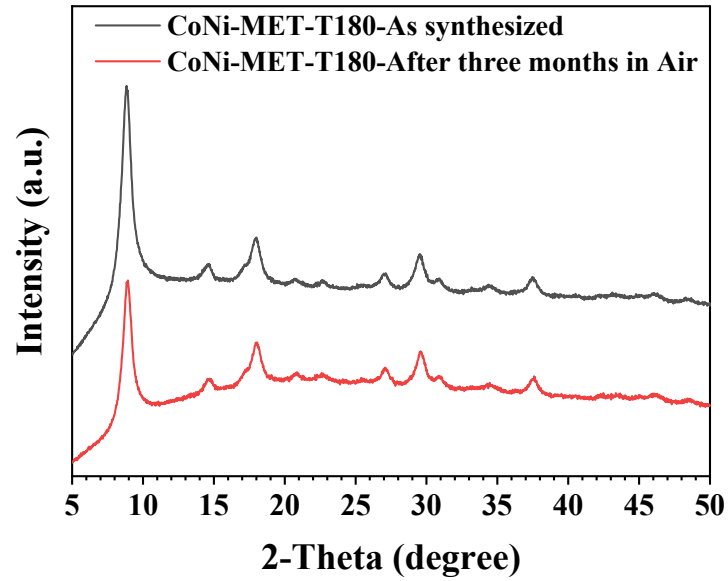
Figure S3. PXRD results of the as synthesized CoNi-MET-T180 and the one left three months in humid environment.
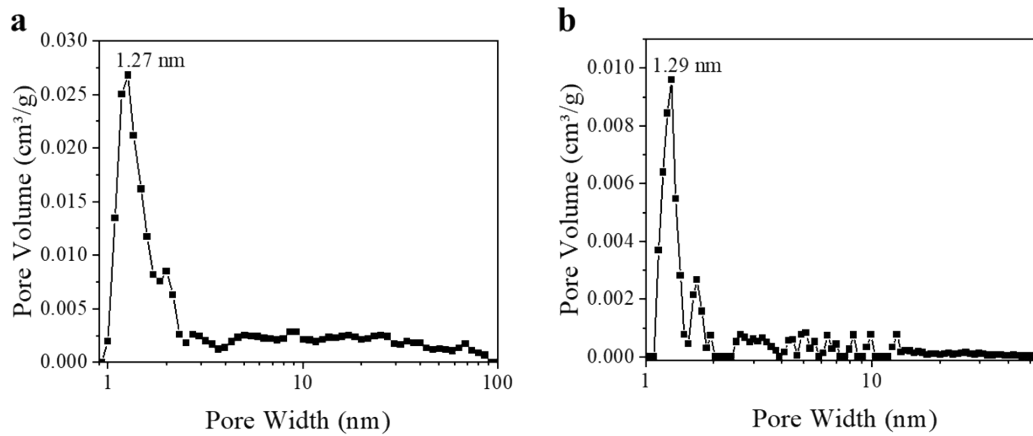
Figure S4. DFT(density function theory) pore size distribution of (a) Ni-MET-T140 and (b) CoNi-MET-T140, calculated based on the N_2 adsorption test.
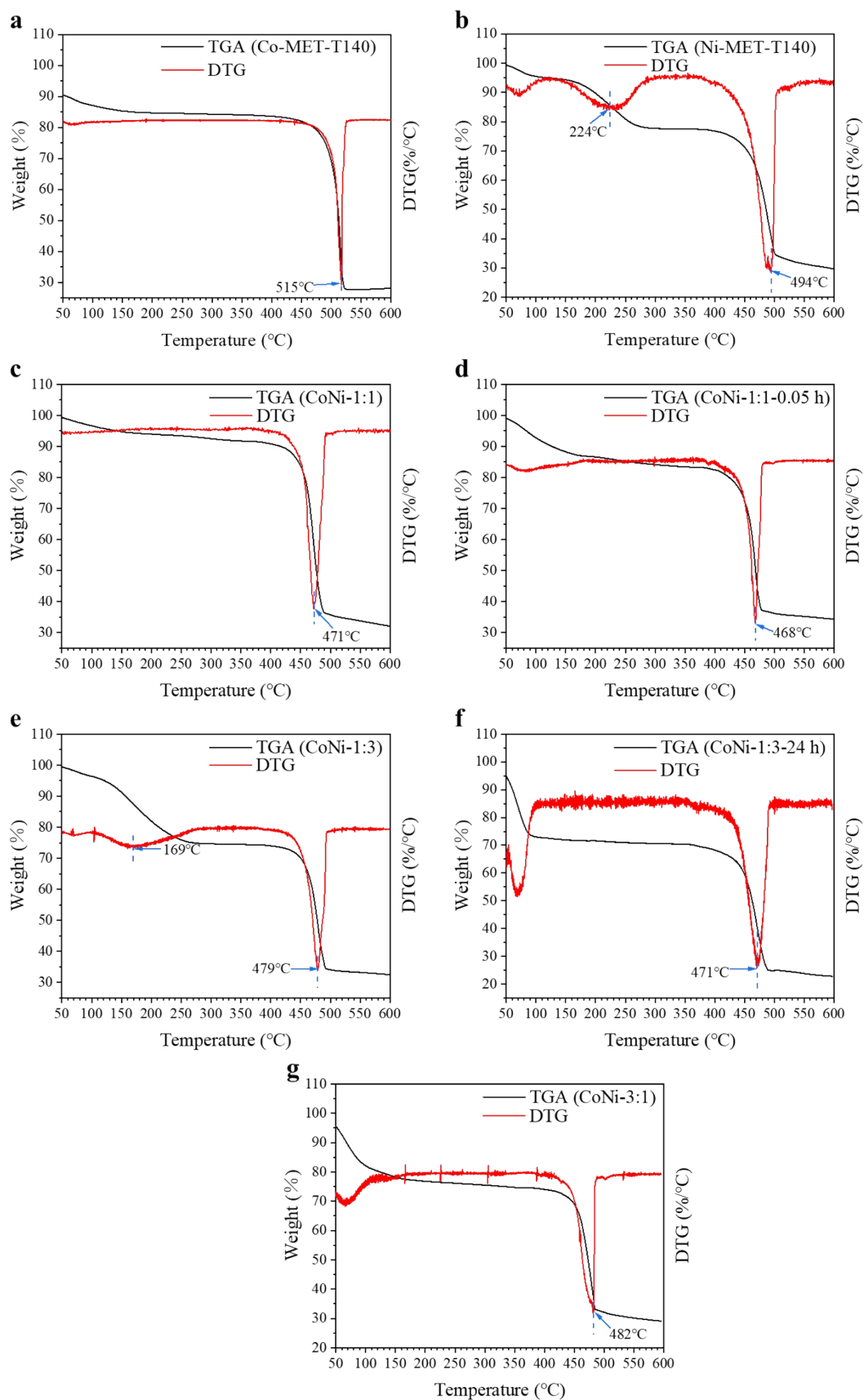
Figure S5. TGA and DTG curve of (a) Co-MET-T140 (b) Ni-MET-T140 (c) CoNi-1:1 (d) CoNi-1:1-0.05 h (e) CoNi-1:3 (f) CoNi-1:3-24 h and (g) CoNi-3:1.
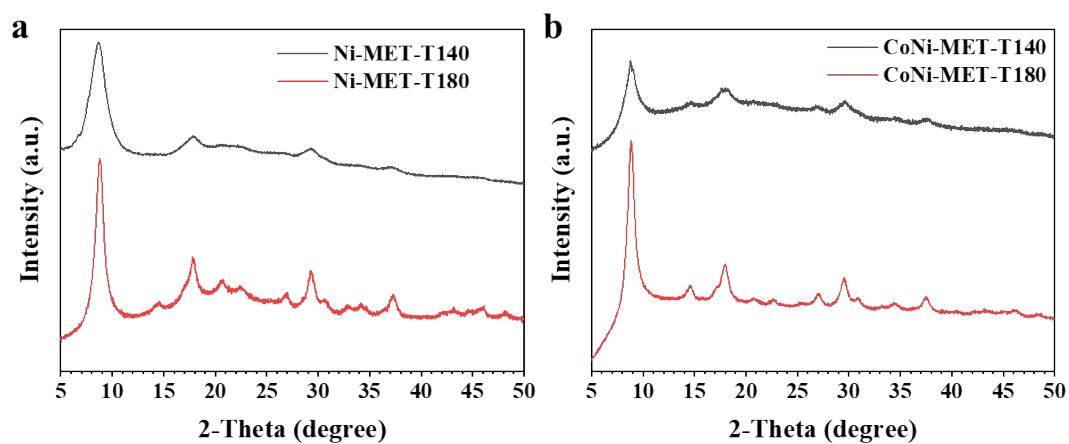
Figure S6. The PXRD results of (a) Ni-MET-T140 and (b) CoNi-MET-T140 after improving the synthesis condition.
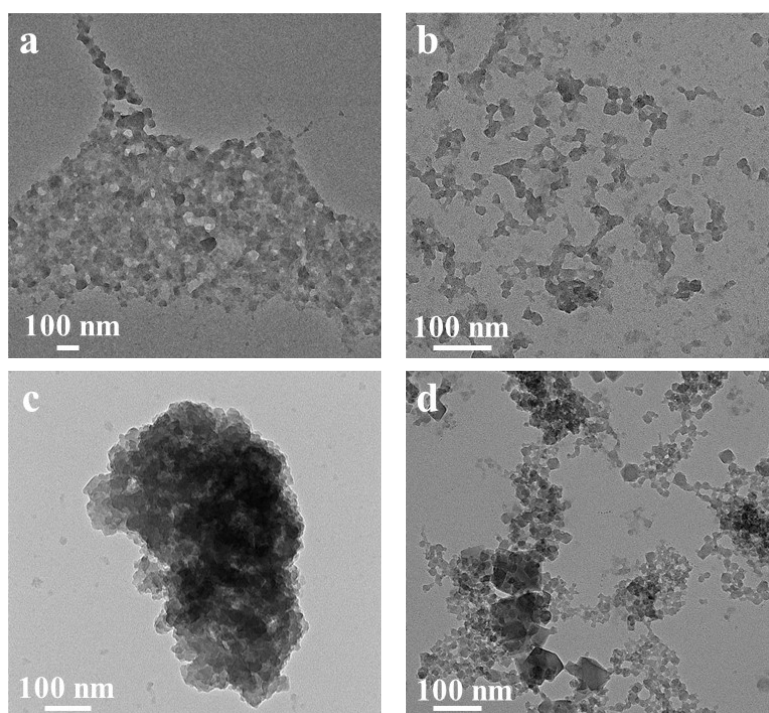
Figure S7. TEM images of (a) Ni-MET-T140, (b) Ni-MET-T180, (c) CoNi-MET-T140, (d) CoNi-MET-T180.
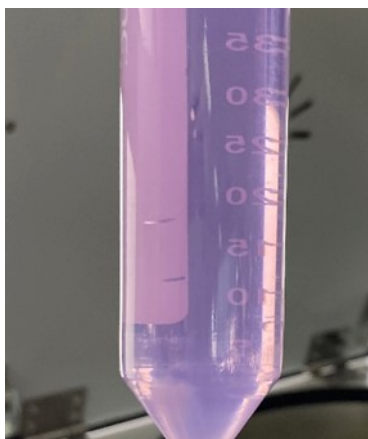
Figure S8. Picture showing that the Ni-MET-T140 disperse very well in water.
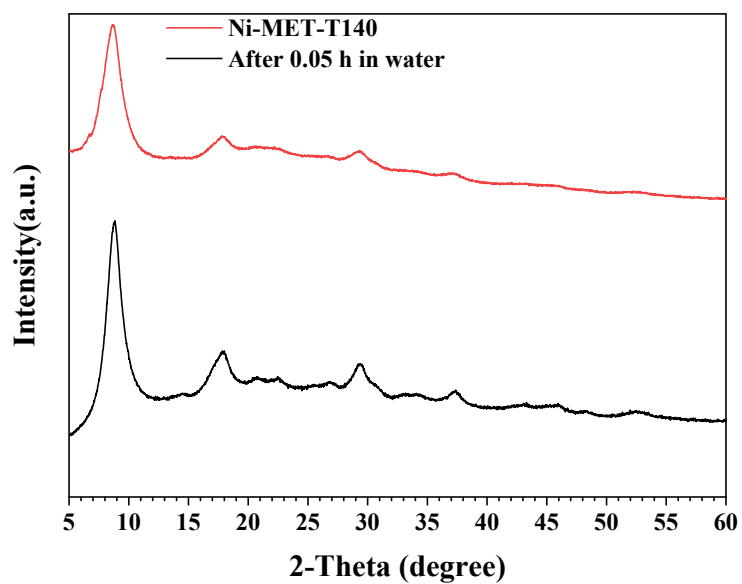
Figure S9. PXRD results of the as-synthesized Ni-MET-T140 and the one stirred in water for 0.05 h and dried at 100 °C.
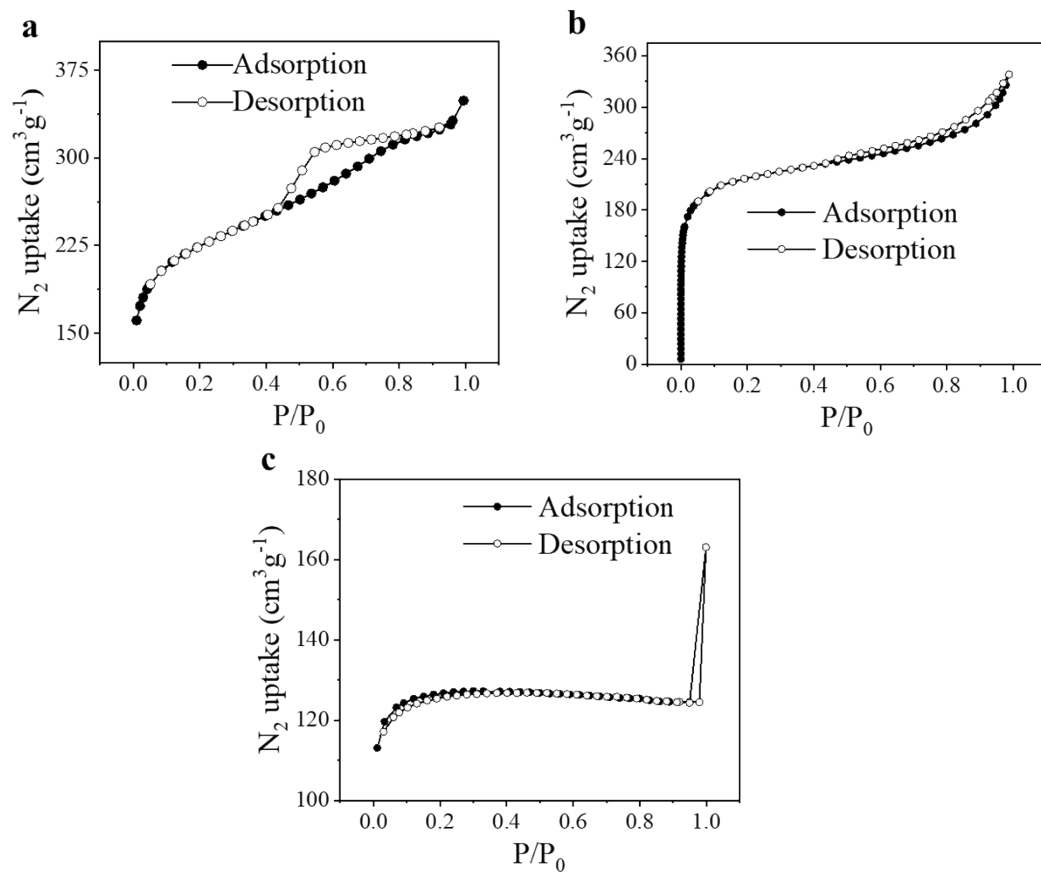
Figure S10. N_2 adsorption isotherms of (a) Ni-MET-T180 and Ni-MET-T140 stirred in water for (b) 0 h and (c) 0.05 h.
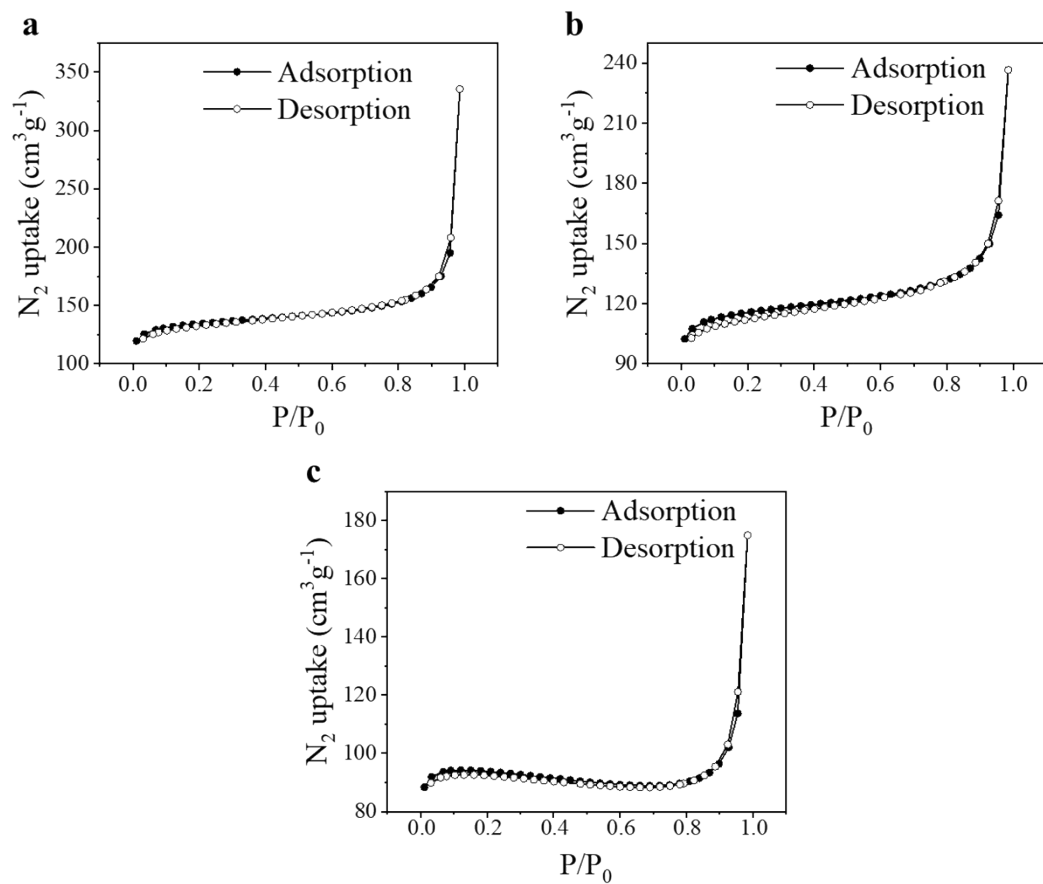
Figure S11. N_2 adsorption isotherms of Co-MET-T140 stirred in water for (a) 0 h (b) 0.05 h and (c) 72 h.
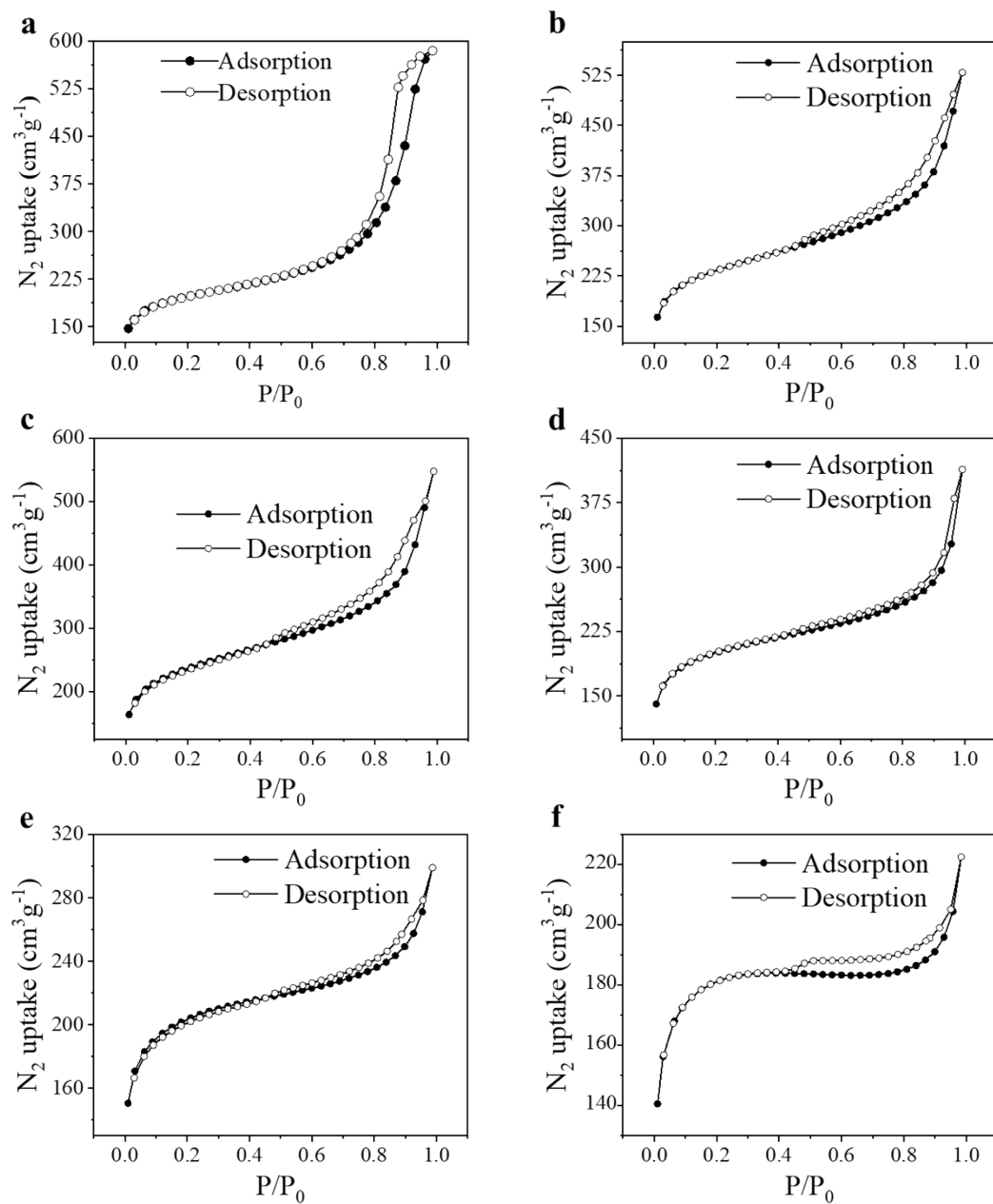
Figure S12. N_2 adsorption isotherm of CoNi-1:1 (a) CoNi-MET-T180 and CoNi-MET-T140 stirring in water for (b) 0 h (c) 0.05 h (d) 1 h (e) 24 h and (f) 72 h.
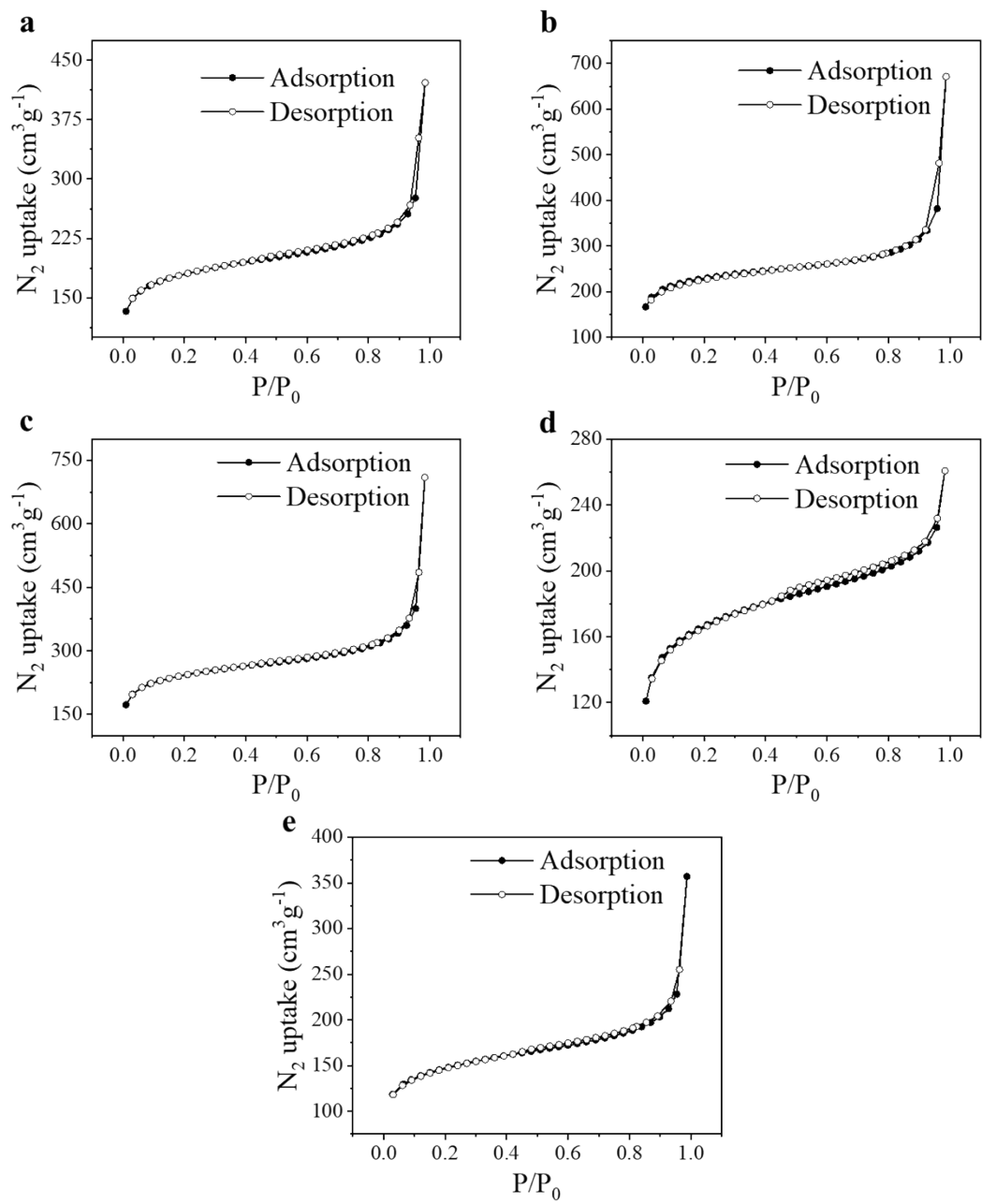
Figure S13. N_2 adsorption isotherms of CoNi-3:1 stirring in water for (a) 0 h (b) 0.05 h (c) 1 h (d) 24 h and (e) 72 h.
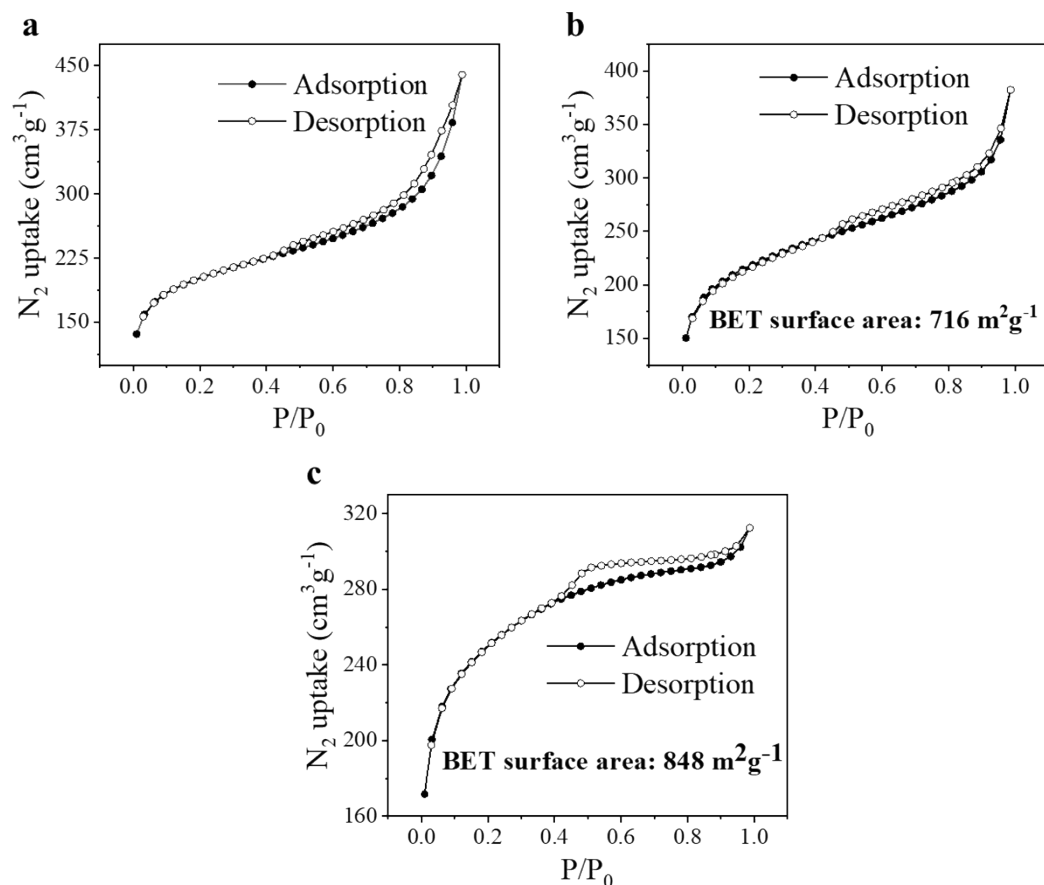
Figure S14. N_2 adsorption isotherms of CoNi-1:3 in water for (a) 0 h (b) 0.05 h and (c) 1 h (BET: Brunauer-Emmett-Teller).
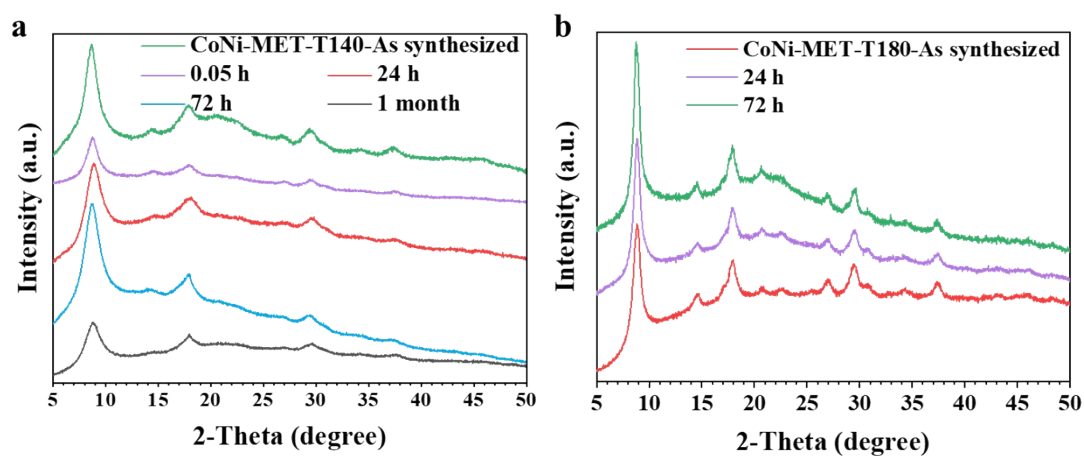
Figure S15. The PXRD result of (a) CoNi-MET-T140 and (b) CoNi-MET-T180 stirred in water for different time.
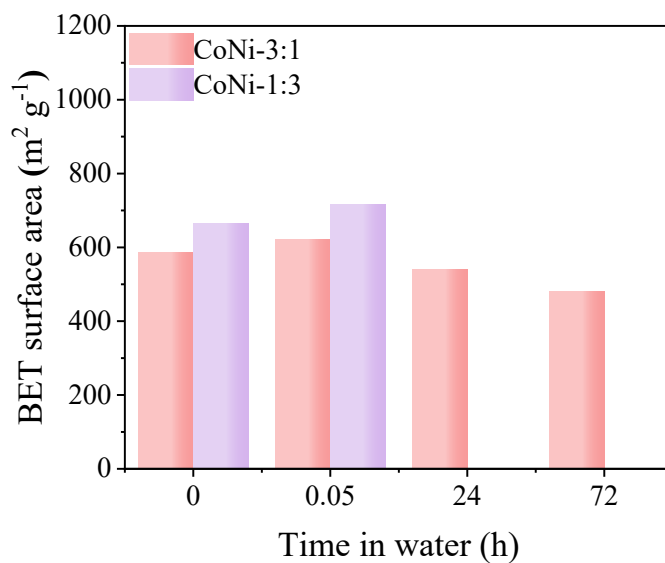
Figure S16. The changes of the BET surface area after stirring in water: CoNi-3:1 and CoNi-1:3.
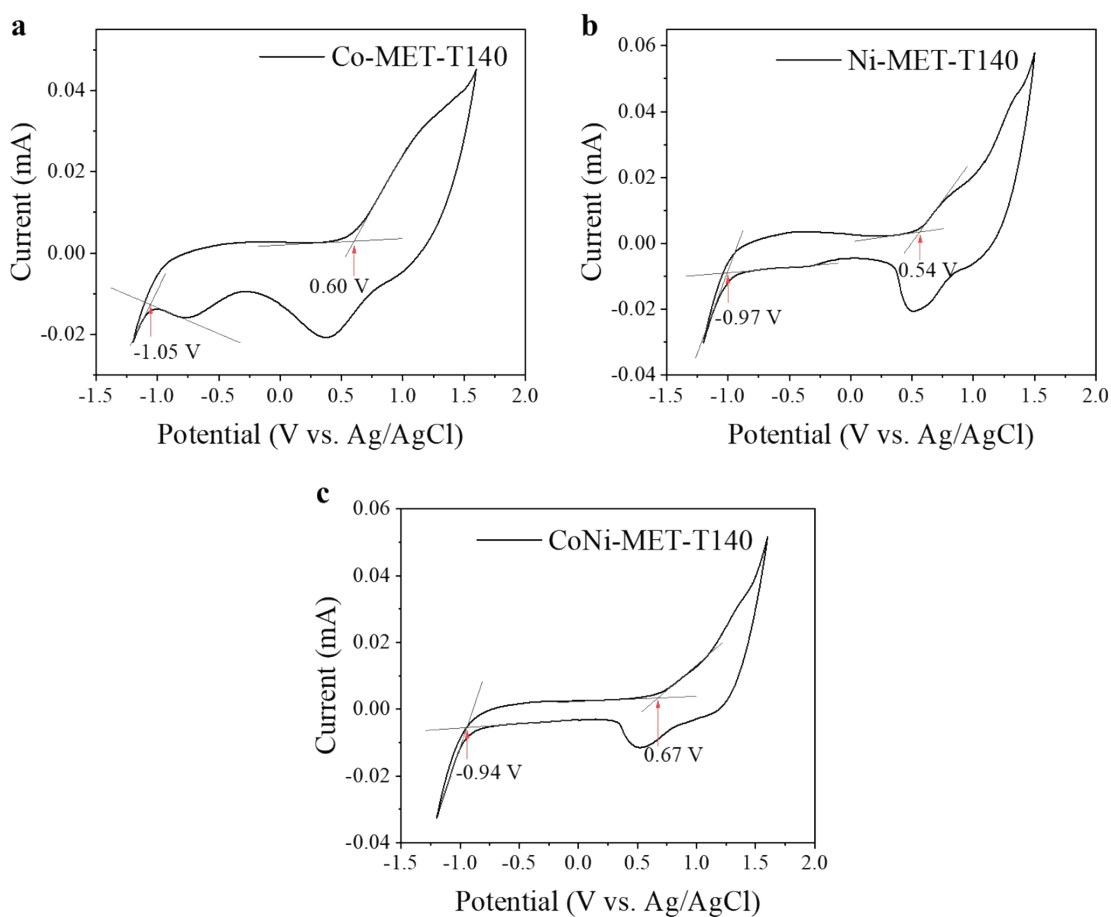
Figure S17. Cyclic voltammetry curves of (a) Co-MET-T140, (b) Ni-MET-T140 and (c) CoNi-MET-T140. The energetic levels of these METs are determined as follows: $E_{HOMO} = -(eE_{ox\_onset} + 4.4)$ V and $E_{LUMO} = -(eE_{red\_onset} + 4.4)$ V[2, 3].
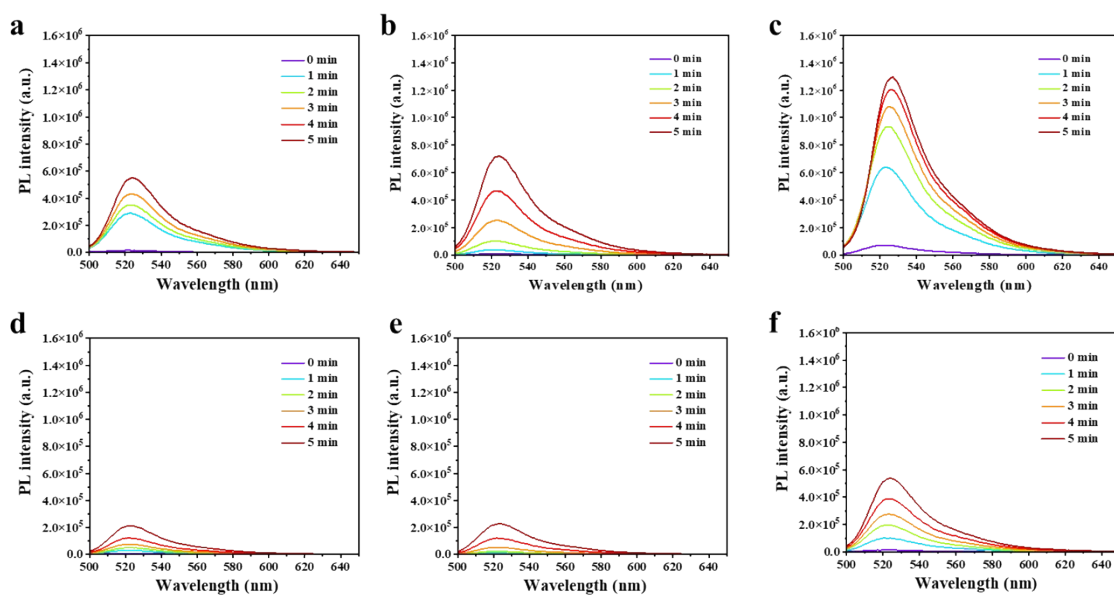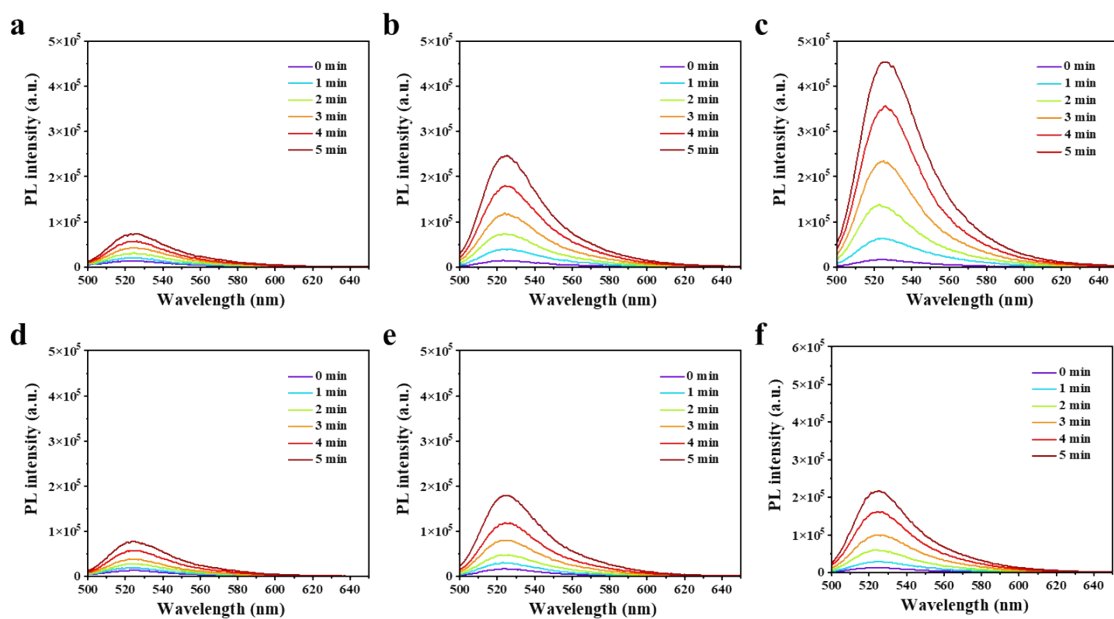
Figure S18. PL spectra of DCFH in the presence of (a) Co-MET-T140, (b) Ni-MET-T140, (c) CoNi-MET-T140, (d) Co-MET-T180, (e) Ni-MET-T180 and (f) CoNi-MET-T180 under white light irradiation (50 mW cm^{-2}).
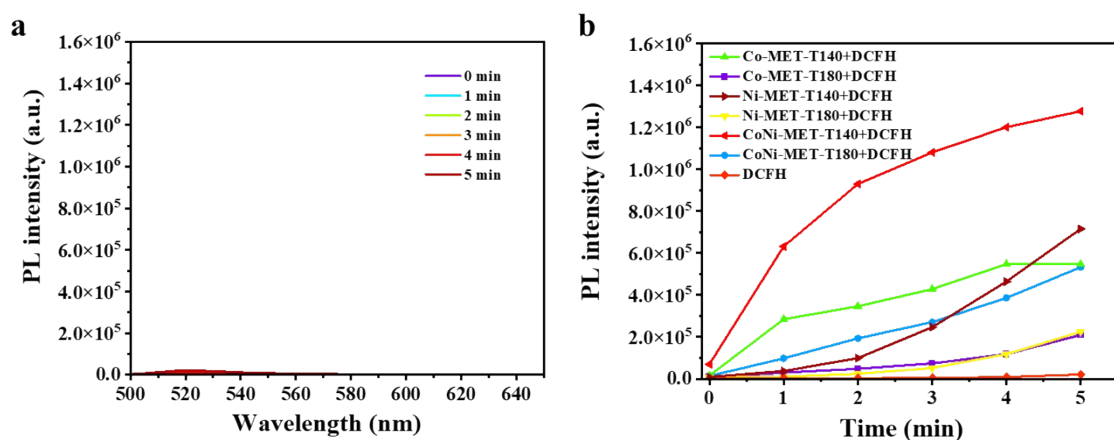
Figure S19. (a) PL spectra of DCFH in the presence of blank under white light irradiation (50 mW cm^{-2}), (b) ROS generation of these METs (50 μg mL^{-1}) under white light irradiation (50 mW cm^{-2}) accessed with DCFH (50 μM) enhancement factors.

Figure S20. PL spectra of DHR123 in the presence of (a) Co-MET-T140, (b) Ni-MET-T140, (c) CoNi-MET-T140, (d) Co-MET-T180, (e) Ni-MET-T180 and (f) CoNi-MET-T180 under white light irradiation (50 mW cm^{-2}).
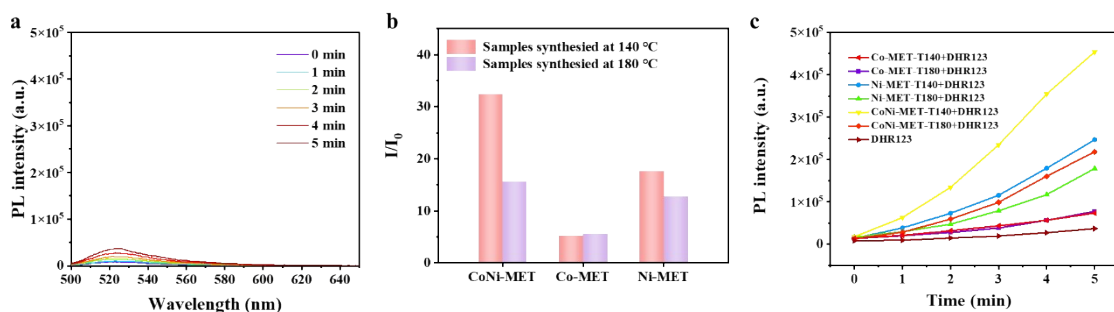

Figure S21. (a) PL spectra of DHR123 in the presence of blank under white light irradiation (50 Mw cm^{-2}), (b) •O_2^- generation of samples that synthesized at different condition, (c) •O_2^- generation of these METs (50 μg mL^{-1}) under white light irradiation (50 mW cm^{-2}) accessed with DHR123 (20 μM) enhancement factors.
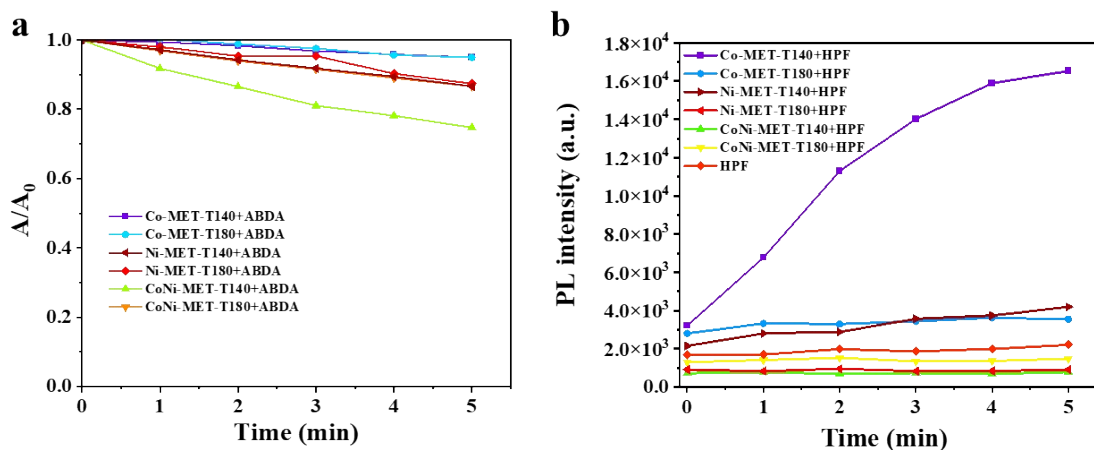
Figure S22. (a) $^1O_2$ generation of these METs (50 µg mL^{-1}) under white light irradiation (50 mW cm^{-2}) accessed with ABDA (100 µM) enhancement factors, (b) •OH generation of these METs (50 µg mL^{-1}) under white light irradiation (50 mW cm^{-2}) accessed with HPF (10 µM) enhancement factors.
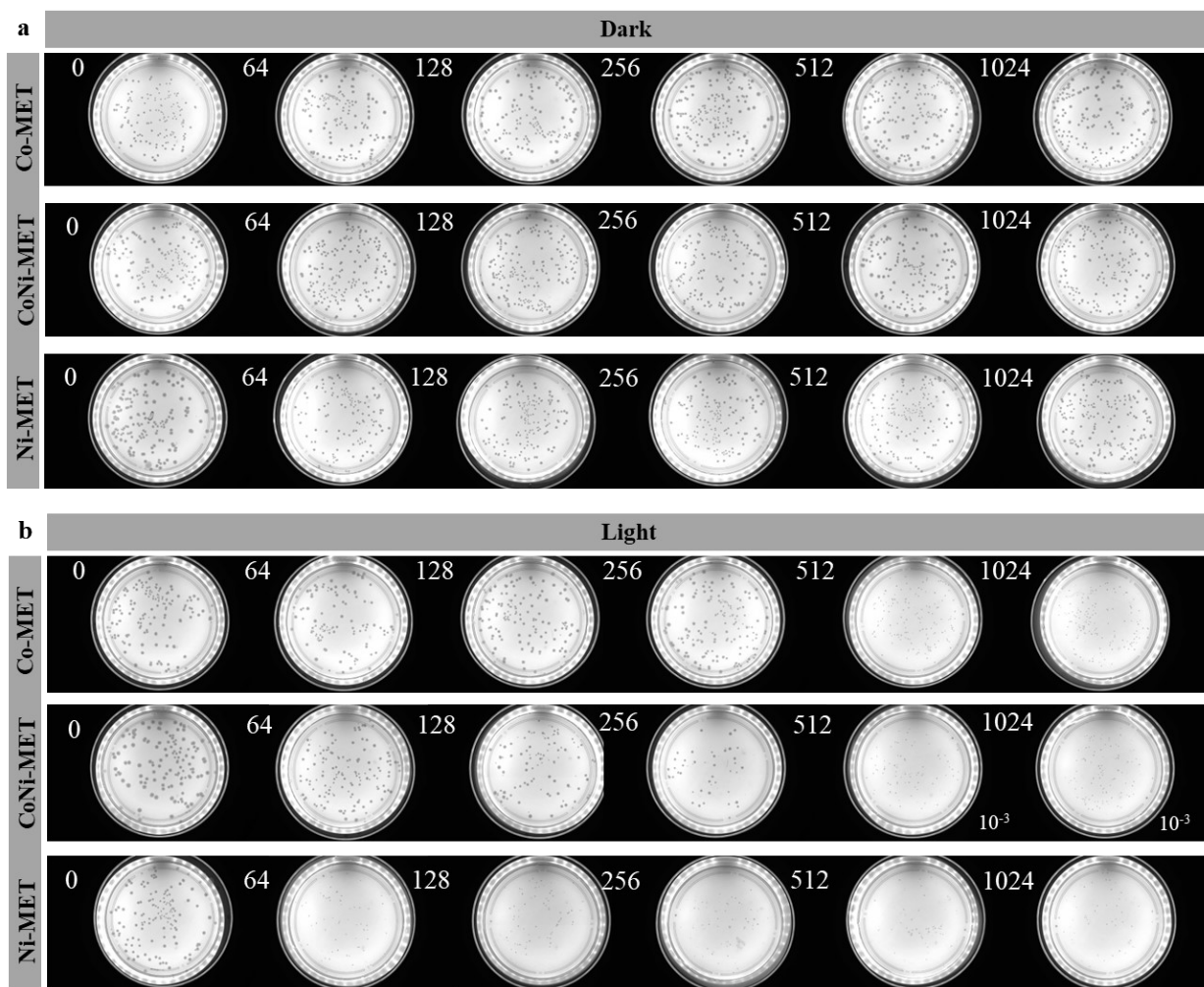
Figure S23. Photographs of agar plate containing E coli clonies after treatment with different METs (a) without or (b) with white light irradiation (100 mW cm^{-2}). Except for labeled 10^{-3}, the rest are diluted 10^{-4}.
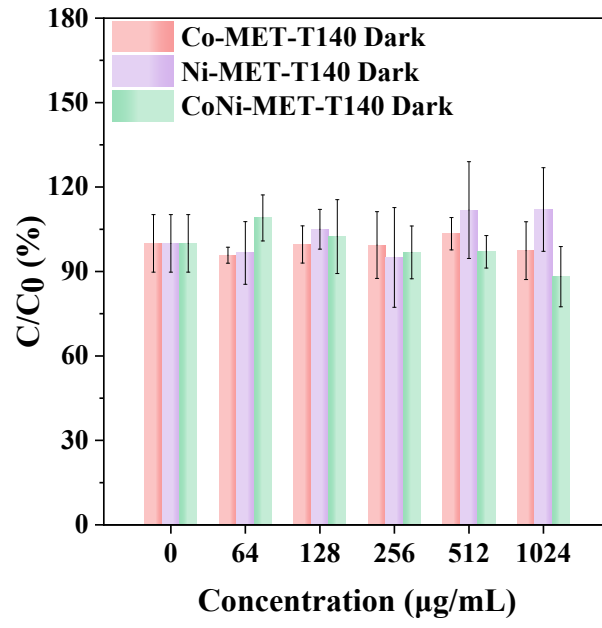
Figure S24. Survival rate of E coli. upon incubation with these METs at varied concentrations under dark condition.

References

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