Electronic Supplementary Material (ESI) for Green Chemistry.

Water nanodomain for efficient photocatalytic CO_2 reduction to CO

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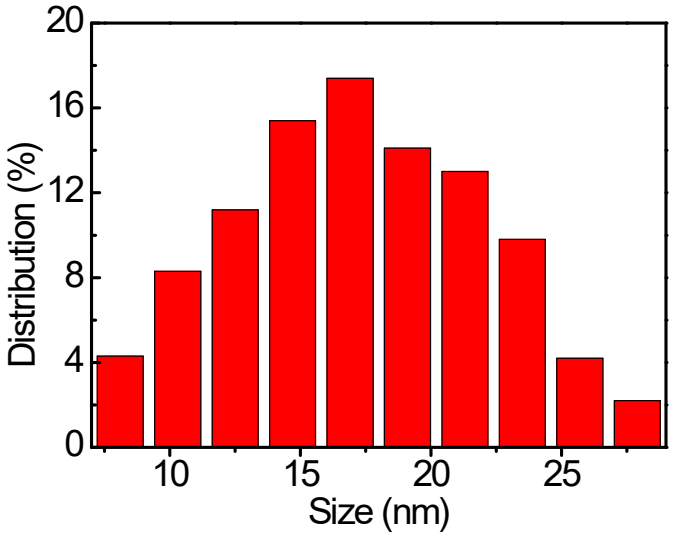


Fig. S1 Droplet size distribution of water-in-oil microemulsion (W_0=30).

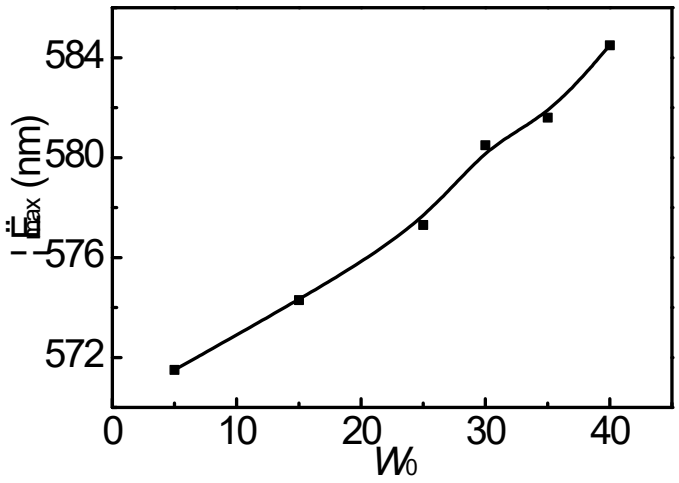


Fig. S2 Maximum absorption wavelength changes with W_0 of water-in-oil microemulsions.

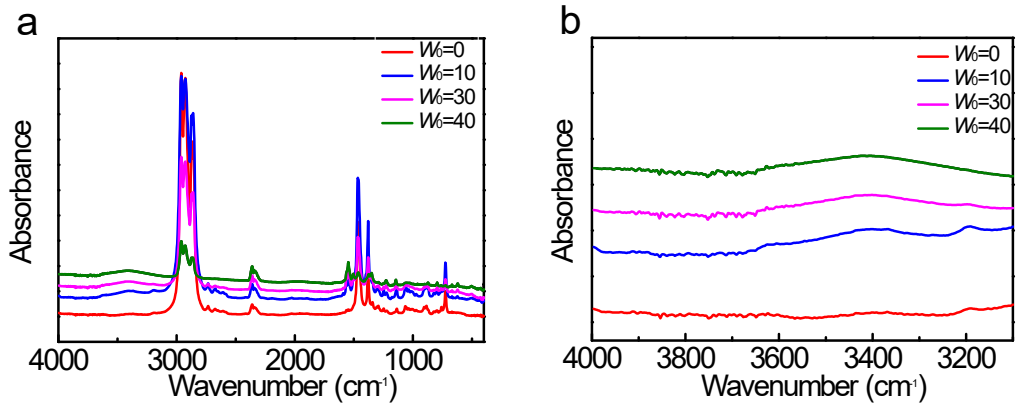


Fig. S3 FT-IR spectra of Fe(tmhd)$_3$/*n*-hexane solution and microemulsions with W_0=10, 30 and 40 in wavenumber range of 400-4000 cm^{-1} (a) and 3100-4000 cm^{-1} (b).

In Fe(tmhd)$_3$/*n*-hexane binary system, the absorptions at 2955, 2927 and 2858 cm^{-1} correspond to the stretching vibration of C-H. The absorptions at 1466 and 1385 cm^{-1} can be assigned to the bending vibration of C-H. For the water-in-oil microemulsion, the absorptions around 3200-3500 cm^{-1} appear and become stronger with increasing W_0, indicating that more and more water molecules are dissolved in Fe(tmhd)$_3$/*n*-hexane system to form microemulsion.

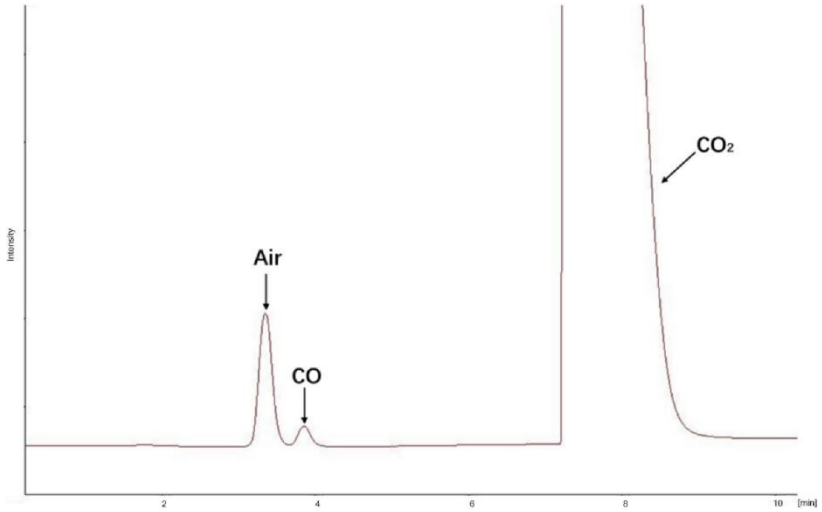


Fig. S4 GC spectrum of gaseous mixture of the photocatalytic reaction.

Retention time: 3.345 min (Air), 3.849 min (CO) and 7.265 min (CO_2).

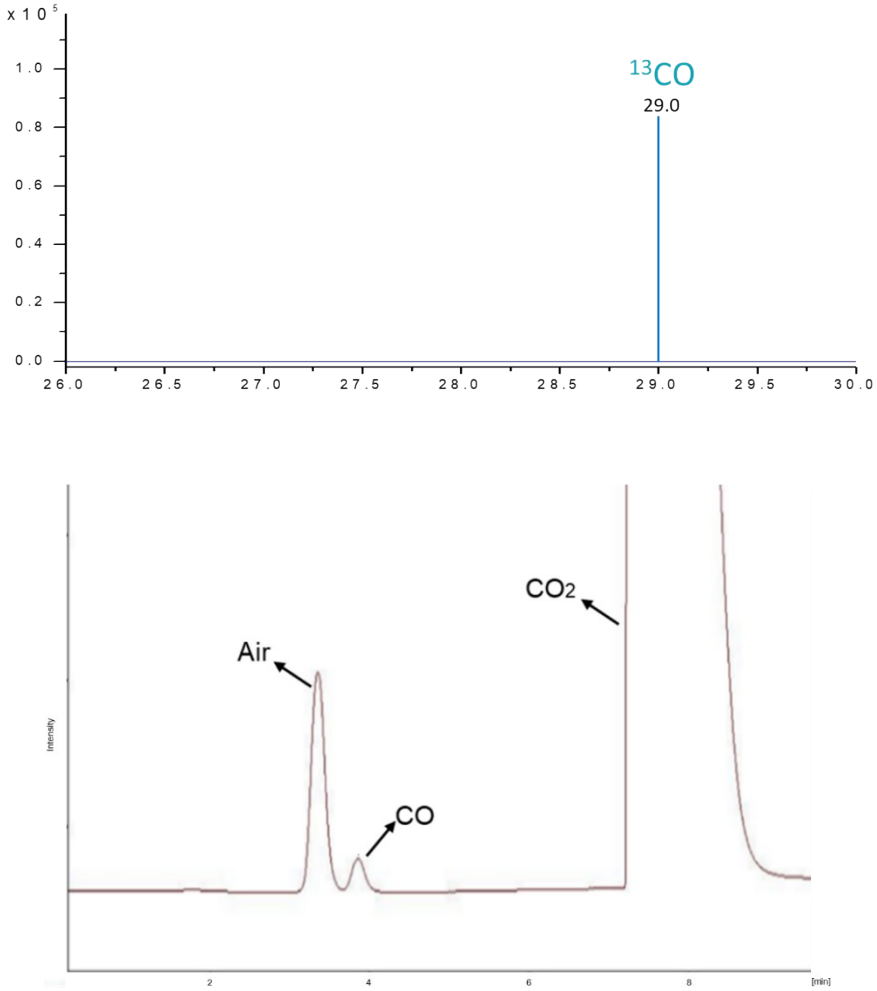


Fig. S5 Mass spectrometry signal and GC spectrum of the CO_2 reduction product using $^{13}CO_2$ as the feedstock.

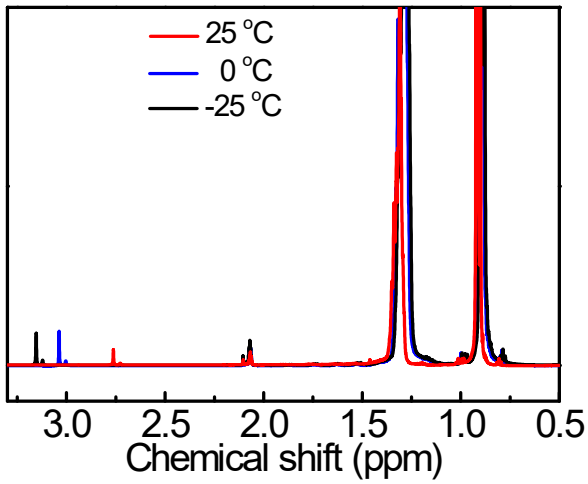


Fig. S6 ^{1}H NMR spectra of water-in-oil microemulsion (W_0=30) at different temperatures.

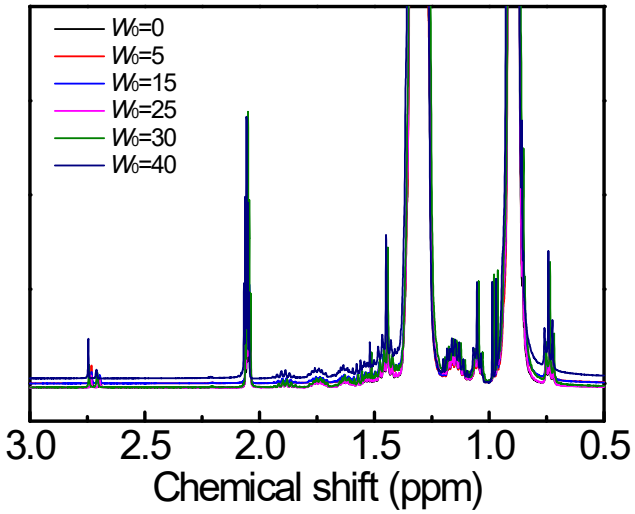


Fig. S7 ^{1}H NMR spectra of the water-in-oil microemulsions with different W_0 values.

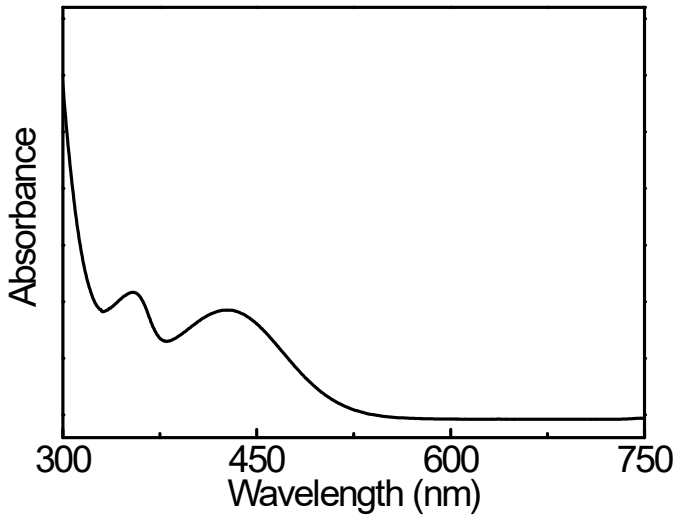
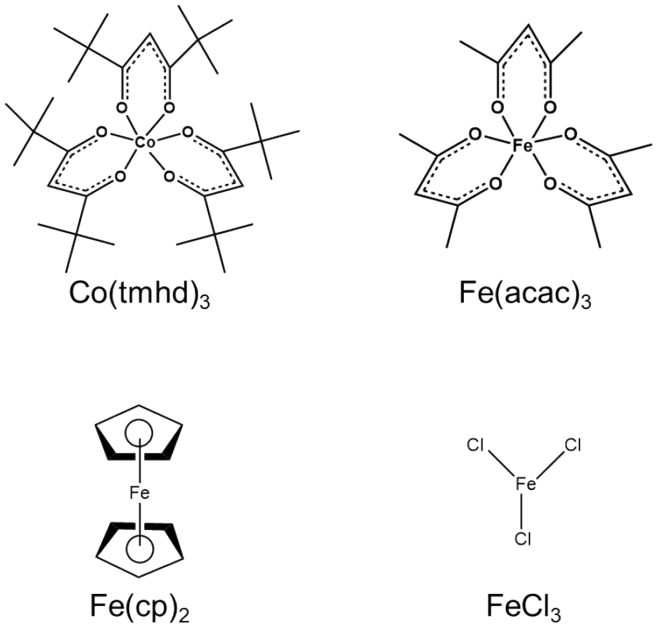


Fig. S8 UV-Vis spectrum of $Fe(tmhd)_3$ in *n*-hexane.

The absorption with λ_{max} of 356 nm is caused by charge transition and belongs to M→L transition. The valence electron layer of the central ion Fe^{3+} is configured with d5 electrons, and its anti-orbital π* orbital is filled with 5 electrons, which can only accept electrons from the ligand π-orbital transition, and excess electrons can transit to the π orbital of ligand. The absorption with λ_{max} of 428 nm is caused by the transition of the conjugated π electron in the ligand $tmhd^-$ and belongs to π→π* transition.

Fig. S9 Reaction mixture before (left) and after reaction for 12 h (right).



$Co(tmhd)_3$ $Fe(acac)_3$ $Fe(cp)_2$ $FeCl_3$

Fig. S10 Molecular structures of $Co(tmhd)_3$, $Fe(acac)_3$, $Fe(cp)_2$ and $FeCl_3$.

Table S1 Control experiments of photocatalytic CO_2RR to CO.

Control Conditions	CO evolution rate ($\mu mol\ g^{-1}\ h^{-1}$)	Selectivity (%)
Normal[a]	682	> 99%
No CO_2	0	0
No $Fe(tmhd)_3$	0	0
No light	0	0

[a]Reactions conditions: 6.0 mg of $Fe(tmhd)_3$, 8.0 mL of *n*-hexane, CO_2 0.1 MPa, W_0=30, 300 W Xe lamp, wavelength > 360 nm, reaction time 12 h.

Table S2 Performances of the reported photocatalytic CO_2RR to CO and this work.[a]

Catalysts	Solvent	Light	CO evolution rate (μmol g^{-1} h^{-1})	Selectivity (%)	Ref.
Co-ZIF-9/TiO_2	H_2O	>200 nm	17.58	90.0	1
CPO-27-Mg/TiO_2	H_2O	~365 nm	4.09	63.5	2
$ZnIn_2S_4$	H_2O	400 nm	33.2	-	3
BiOBr atomic layers	H_2O	visible light	87.4	-	4
$Bi_{12}O_{17}C_{l2}$ nanotubes	H_2O	300 W Xe lamp	48.6	-	5
HKUST-1/Cu_2O/TiO_2	H_2O	>320 nm	85	35.4	6
ZIF-67/$CsPbBr_3$	H_2O	>420 nm	29.6	24.2	7
MOF-74-Mg/Zn_2GeO_4	MeCN/H_2O (v:v=4:1)	>200 nm	12.94	100	8
NH_2-UiO-66/$CsPbBr_3$	EtOAC/H_2O (v:v=300:1)	>420 nm	8.21	97.0	9
Eosin Y-functionalized COP	H_2O	>420 nm	33	92	10
porphyrin-tetra thiafulvalene COF-Zn	H_2O	420-800	~20	100	11
polymer-TiO_2-graphene composite	H_2O	>420 nm	~22	-	12
CT-COF	H_2O	>420 nm	102.7	98	13
Hypercrosslinked polymer	H_2O	UV-vis	~16	-	14
$Fe(tmhd)_3$	*n*-hexane/H_2O (v:v=667:1)	>360 nm	682	>99	This work

[a]For all these reactions, water was used as only sacrificial, involving no additional sacrificial donor.

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