Supporting Information

Iron Sulfur Clusters in Protein Nanocages for Photocatalytic Hydrogen Generation in Acidic Aqueous Solutions

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Experimental Section
Chemicals and Materials

All commercially available reagents were used as received without further purification unless otherwise noted. Horse spleen ferritin (apo-HSF) was obtained from Sigma-Aldrich Co. LLC. Solutions were prepared in Milli-Q water (18.2 MΩ) purified by the Millipore system.

Methods

NMR spectra were recorded on a Bruker AMX 400 spectrophotometer. Transmission electron microscopy (TEM) images were taken with a JEM-2100 TEM (JEOL, Ltd., Japan). Circular dichroism (CD) spectra were collected using a Chirascan CD (Applied Photophysis, U.K.). Hydrodynamic diameters of nanoparticles were determined on Zetasizer nanoseries (Nano zs90, Malvern Instruments Ltd., U.K.). Ultraviolet-visible (UV-vis) spectra were collected on a Shimadzu UV-2600 spectrophotometer. Steady state fluorescence was detected on a Hitachi F-7000 fluorimeter. Fourier transform infrared (FT-IR) spectra were acquired on a ThermoFisher Nicolet iS50 FT-IR spectrometer further equipped with an iS50 ATR unit. Cyclic voltammetric measurements were carried out on a CHI-600E electrochemical workstation (CH Instruments, Inc. China). The photocatalytic water splitting measurements were performed in a 100-mL air-tight reactor connected to an inline closed gas circulation system (CEL-SPH2N, Beijing China Education Au-light Co., Ltd). The amounts of evolved hydrogen were determined by gas chromatography (GC-7920, Beijing China Education Au-light Co., Ltd) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column. The CO products were monitored using gas chromatography (GC-9860, Luchuang Instrument, China) equipped with an FID detector with a methane conversion oven to convert CO and CO₂ into CH₄ before entering FID detector. The temperature for TCD, FID, column and methane converter were 100, 150, 100 and 360 °C, respectively. The retention times of H₂ and CO were about 0.7 min and 1.3 min, respectively. Calibration curves
for gases were established separately. Protein concentrations were examined by BCA assay.

**Synthesis of [Fe₂{(μ-SC₂H₄)(μ-SCH)(CH₂)₄COOH}₆] (FeFe-COOH)**

FeFe-COOH was synthesized according to the reported procedure with minor modifications.¹ In brief, the mixture of Fe₃(CO)₁₂ (0.220 g, 0.437 mmol) and DL-thiolic acid (0.082 g, 0.4 mmol) in dry THF (20 mL) was refluxed under argon atmosphere at 75 °C for 3 h. After removal of solvent under vacuum, the resulted red residue was purified by column chromatography on silica gel (eluent: ethyl acetate/dichloromethane 1:2, v/v) to afford the product as a dark red solid (0.132 g, yield: 68%).¹¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm): 2.56 (1H, d, CH), 2.42 (2H, m, CH₂), 2.10 (H, m, CH₂), 1.84 (2H, m, CH₂), 1.48 - 1.63 (6H, m, CH₂), 1.26 (1H, m, CH₂). TOF-ESI-MS: m/z Calcd for C₁₄H₁₄Fe₂O₈S₂: 485.88; Found: 484.9(M-H⁺).

**Synthesis of poly(L-glutamic acid) (L-PGA)**

Synthesis of N-carboxyanhydrides (NCA)
α-pinene (5.74 g, 42.1 mmol) and γ-benzyl-L-glutamate (5 g, 21.1 mmol) were dissolved in distilled ethyl acetate (40 mL) in a three-neck round-bottomed flask. The mixture was stirred and heated to reflux. Then a solution of triphosgene (3.13 g, 10.5 mmol) in ethyl acetate (20 mL) was added dropwise. After reaction mixture became clear, the mixture was condensed to ~ 30 mL in vacuo and n-heptane (30 mL) was
added. The mixture was allowed to cool down to room temperature and then placed in a freezer overnight. After filtration, the solid was washed three times with a solution of 1:4 ethyl acetate/n-heptane and freeze dried. The NCA was recovered as a white powder and stored in a freezer over P₂O₅. ¹H NMR: (400 MHz, CDCl₃, 298 K) δ (ppm): 7.36 (m, 5H), 6.67 (s, 1H), 5.14 (s, 1H), 4.38 (q, 1H), 2.59 (t, 2H), 2.14 (m, 2H).

Synthesis of Azide-Terminated PBLG (PBLG-N₃)

An oven-dried Schlenk tube was charged with a stir bar and γ-benzyl-L-glutamate NCA (510 mg, 1.94 mmol), and dissolved with anhydrous DMF (4.5 mL). The solution was stirred for 10 min at room temperature, and 1-azido-3-aminopropane (0.05 M, 0.02 mmol) in anhydrous DMF (0.40 mL) was added with a nitrogen flushed syringe. The mixture was stirred under an atmosphere of nitrogen for 40 h at room temperature, and was poured into diethyl ether. The precipitated solid was recovered by filtration, washed with diethyl ether, and dried under vacuum to afford 322 mg (76% yield) of the desired polymer. GPC (THF): $M_n = 11.5$ kDa, PDI = 1.05. ¹H NMR (400 MHz, CDCl₃ containing 5% trifluoroacetic acid, 298 K) δ (ppm): 8.00-8.61 (br, NH), 7.10-7.65 (br, Ar), 4.68-5.30 (br, CO₂CH₂), 3.63-4.21 (br, CH), 2.81-2.42 (br, CHCH₂), 2.40-1.78 (br, COCH₂CH₂CH).

Synthesis of poly(L-glutamic acid) (L-PGA)
PBLG (100 mg) was dissolved in dichloroacetic acid (1 mL) at 25 °C in a flask. A solution (1.2 mL) of HBr/HOAc (33 wt.%) was added. The solution was slowly stirred at 30 °C for additional 1 h and poured into excess diethyl ether. The precipitated solid was recovered by filtration, washed with diethyl ether, and dried under vacuum to afford L-PGA. ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.00-8.61 (br, NH), 3.63-4.21 (br, CH), 2.81-2.42 (br, CHCH₂), 2.40-1.78 (br, COCH₂CH₂CH).
**Preparation of apoferritin (apo-HSF)**
Horse spleen apoferritin was prepared according to the reported procedure, and was stored in PBS (pH 7.4) at 4 °C before use.

**Preparation of FeFe NPs**
To a solution of apoferritin (0.3 μM, 2.7 mg, 0.14 mg/mL) in diluted PBS (20.0 mL) was added an aqueous solution of FeFe-COOH (16 mM, 750 μL) at 4 °C and stirred for 1 h. The mixture was dialyzed against successive 10% acetonitrile-PBS (pH 7.4) and PBS with a molecular weight cutoff of 10000 Da to remove nonspecific small molecules, followed by purification on a PD-10 column (GE, USA) and passing through a 0.22 μm filter to collect FeFe NP solution in yellow-orange color. The NP1, NP2, NP3, NP4, and NP5 were prepared in feed molar ratios of 300:1, 600:1, 1000:1, 2000:1, and 5000:1, respectively, and stored with protection from light at 4 °C.

**Complexation of L-PGA by FeFe-COOH**
A solution of L-PGA (2.7 mg, 0.27 mg/mL) in diluted PBS (10.0 mL) was mixed with an aqueous solution of FeFe-COOH (16 mM, 750 μL) at 4 °C and stirred for 1 h. The mixture was dialyzed against successive 10% acetonitrile-PBS (pH 7.4) and PBS with a molecular weight cutoff of 10000 Da. The L-PGA/FeFe-COOH complex was stored with protection from light at 4 °C.

**FT-IR measurements**
FT-IR measurements were performed on a ThermoFisher Nicolet iS50 FT-IR spectrometer further equipped with an iS50 ATR unit. As the vast amounts of water molecules strongly interfered with IR signals, the liquid samples were lyophilized before IR analysis. Therefore, the lyophilized samples about 2 mg were placed onto the ATR crystal each time. Spectral data were collected after 32 scans at a range of 400 ~ 4000 cm⁻¹ with a resolution of 4 cm⁻¹ using an OMNIC 9.0 (Thermo Fisher Scientific Inc.) software.
TEM imaging
For imaging NP4, drops of NP4 (protein concentration of 0.14 mg/mL determined by BCA assay) were adsorbed on 400-mesh carbon-coated copper grids (Electron Microscopy Services). After 4 min, excess fluid was removed from the edge of grid with filter paper, and the grid was air dried at room temperature before being subjected to TEM imaging. L-PGA/FeFe-COOH nanoparticles were imaged in the same manner except using uranyl acetate as the staining agent.

Dynamic light scattering (DLS) analysis
Pre-filtered protein solutions (0.14 mg/mL) in diluted PBS buffer (pH = 7.4) were pre-equilibrated for 10 ~ 20 min at 298 K in a disposable polystyrene cell, and then subjected to DLS analysis. The scanning cycled for 3 × 30 times.

Circular dichroism (CD) measurements
CD spectra were recorded in the far-ultraviolet wavelength range of 180 ~ 260 nm in a quartz cell (0.1 cm) using following parameters: bandwidth, 1 nm; step resolution, 0.1 nm; scan speed, 10 nm min⁻¹; and response time, 1 s. The data of each spectrum were collected as the average of three scans. All samples were at the same protein concentration (0.14 mg/mL in diluted PBS).

Fe content analysis
The Fe content in NPs was determined according to the previous report with minor modifications.⁶ (NH₄)₂Fe(SO₄)₂ was used to obtain a standard calibration curve at a Fe concentration range from 0.05 to 3.2 µg/mL. Iron detection solution was prepared by a series of ferrozine (6.5 mM), neocuproine hemihydrate (6.5 mM), ammonium acetate (1.0 mM) and sodium ascorbate (2.5 mM) in 10 mL de-ionized water. Oxidizing solution was prepared by mixing KMnO₄ (27 mg) and HCl solution (0.75 M, 6 mL). The mixture of NPs (400 µL) and oxidizing solution (600 µL) was shaken at 60 °C for 1 h. Then, iron detection solution (240 µL) was added and shaken at room
temperature for 30 min. The absorption intensity at 562 nm was measured on the microplate reader and Fe content was calculated using the standard calibration curve.

**Electrochemical measurements**
Cyclic voltammetry experiments were performed on an electrochemical analyzer (CHI600E, CH Instrument Inc., Shanghai) in a one-compartment three electrode cell, using gold working electrode, platinum counter electrode and Ag/AgCl as reference electrode under nitrogen. The gold working electrode was polished with a 0.05 mm alumina paste and sonicated for 15 min. The electrolyte solution containing varied concentration of HOAc (0, 0.4, 0.8, 1.2 mM) was prepared in 0.1 M of Na$_2$SO$_4$. To the electrolyte solution (final volume 5 mL) was added FeFe-COOH (final concentration 51 μM) or NP4 (final concentration 51 μM incorporated FeFe-COOH), degassed with dry argon for 30 min, and sealed with parafilm. The potentials for the cyclic voltammetry experiment were in the range of −1.0 V to 0 V versus Ag/AgCl at a scan rate of 50 mV s$^{-1}$.

To verify the produced H$_2$ in the process of electrochemical reaction, a fixed volume (1 mL) of gas in the head space of the electrolyte solution was extracted by a syringe when one cycle of cyclic voltammetric scan was finished (one CV cycle about 40 s from −1.0 V to 0 V then to −1 V). The gas sample was injected immediately into a GC instrument (GC-7920) and the H$_2$ produced during each CV cycle was detected by a TCD detector.

**Photocatalysis experiment**
Typically, 20 mL of the solution containing various components was irradiated from the top by a 300 W xenon lamp (200 mW cm$^{-2}$) with a cutoff filter (λ > 400 nm). At each given time interval, the amounts of evolved hydrogen were automatically determined according to the external standard method by gas chromatography (GC-7920) equipped with a TCD detector and a 5 Å molecular sieve column, using N$_2$ as carrier gas. All photochemical reactions were carried out at room temperature.
Measurements of catalyst decomposition

Typically, 20 mL of FeFe-COOH or NP4 solution at pH 5.3 with or without the presence of Ru(bpy)$_3^{2+}$ (1 mM)/ascorbic acid (50 mM) was irradiated from the top by a 300 W xenon lamp (200 mW cm$^{-2}$) with a cutoff filter ($\lambda > 400$ nm). At each given time interval, the amounts of evolved hydrogen and carbon monoxide were automatically determined according to the external standard method by gas chromatography (GC-9860, Luchuang Instrument, China) equipped with FID and TCD detector, using N$_2$ as carrier gas. In parallel to GC analysis, the solution was also collected and lyophilized for FT-IR analysis. All photochemical reactions were carried out at room temperature.
<table>
<thead>
<tr>
<th>Scaffold</th>
<th>Catalyst</th>
<th>PS</th>
<th>Electron donor/proton source</th>
<th>Solvent</th>
<th>Light source</th>
<th>TON (based on catalyst)</th>
<th>Enhancement</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>cytochrome b562</td>
<td>CoPPIX</td>
<td>(10.8 μM)</td>
<td>Ru(bpy)_2^(2+,(1 mM))</td>
<td>sodium ascorbate (100 mM)</td>
<td>potassium phosphate buffer (1 M)</td>
<td>Lumileds LXS8-PW27-0024(N) lamp (1100 W m⁻², λ &gt; 410 nm)</td>
<td>310</td>
<td>−3.0</td>
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<tr>
<td>helical peptide</td>
<td>(μ-S-(CH₂)₃-S) [Fe₂(CO)₆] (9.33 μM)</td>
<td>Ru(bpy)_2^(2+,(150 μM))</td>
<td>ascorbate (50 mM)</td>
<td>citrate buffer (50 mM)</td>
<td>450 W Xe (1100 W m⁻², λ &gt; 410 nm)</td>
<td>84</td>
<td>N.A.</td>
<td>8</td>
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<td>nitrobindin, β-barrel protein</td>
<td>(μ-S-Cys)₂[Fe₆(CO)₁₈] (7.8 μM)</td>
<td>Ru(bpy)_2^(2+,(140 μM))</td>
<td>ascorbate (100 mM)</td>
<td>Tris/HCl buffer (50 mM)</td>
<td>500 W Xe (λ &gt; 410 nm)</td>
<td>130</td>
<td>−1.0</td>
<td>9</td>
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<td>myoglobin scaffold</td>
<td>CoPPIX</td>
<td>(5 μM)</td>
<td>Ru(bpy)_2^(2+,(1 mM))</td>
<td>sodium ascorbate (100 mM)</td>
<td>potassium phosphate buffer (1 M)</td>
<td>450 W Xe (1100 W m⁻², λ &gt; 400 nm)</td>
<td>518</td>
<td>4.32</td>
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<tr>
<td>cytochrome c₅₅₆</td>
<td>[Fe₂(CO)₆] core (140 μM)</td>
<td>[Ru(bpy)_3^(2+,(140 μM))</td>
<td>ascorbate (100 mM)</td>
<td>Tris/HCl buffer (50 mM)</td>
<td>500 W Xe</td>
<td>9</td>
<td>N.A.</td>
<td>11</td>
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<tr>
<td>cycloextrin</td>
<td>[(μ-S(CH₂)₃)₂NC₅H₃SO₃][Fe₂(CO)₆] (0.5 M)</td>
<td>Eosin Y</td>
<td>(0.5 mM)</td>
<td>triethylamine (TEA)</td>
<td>10 vol% TEA</td>
<td>500 W Xe (λ &gt; 450 nm)</td>
<td>75</td>
<td>9.38</td>
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<tr>
<td>MOF (ZnPF)</td>
<td>[[(μ-S(CH₂)₃)₂NC(O)C₅H₃N][Fe₂(CO)₆] (2 μM)</td>
<td>ZnTCPP</td>
<td>(0.5 M)</td>
<td>ascorbic acid (20 mM)</td>
<td>acetate buffer (1 M)</td>
<td>300 W Xe lamp (λ &gt; 420 nm)</td>
<td>3.5 μmol H₂</td>
<td>N.A.</td>
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<tr>
<td>MOF (UiO-66)</td>
<td>[FeFe]-[(dcbdt)²(CO)₆] (0.5 μM)</td>
<td>Ru(bpy)_2^(2+,(140 μM))</td>
<td>ascorbic acid (100 mM)</td>
<td>acetate buffer (1 M)</td>
<td>LED lamp (λ = 470 nm, 850 μE)</td>
<td>3.6 μmol H₂</td>
<td>−3.5</td>
<td>14</td>
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<tr>
<td>cytochrome c</td>
<td>H-apocyt complex</td>
<td>(μ-S-Cys)₃[Fe₇(CO)₆] (14 μM)</td>
<td>Ru(bpy)_2^(2+,(140 μM))</td>
<td>ascorbate (100 mM)</td>
<td>Tris/HCl buffer (50 mM)</td>
<td>500 W Xe (189 mW cm⁻², λ &gt; 410 nm)</td>
<td>82</td>
<td>6.83</td>
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<td>SDS micelles</td>
<td>[Fe₂(m-bdt)²(CO)₆] (0.1 mM)</td>
<td>Eosin Y</td>
<td>(0.2 mM)</td>
<td>TEA</td>
<td>10 vol% TEA</td>
<td>LED lamp (λ = 455 nm, 0.3 W)</td>
<td>117</td>
<td>−4</td>
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Table S1. Comparison of reported artificial hydrogenases.
<table>
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<tr>
<th>vesicular membranes</th>
<th>[FeFe]-H$_2$ase subunit mimic (C$<em>3$H$</em>{16}$NO$_3$S;Fe$_2$) (0.1 mM)</th>
<th>ruthenium polypyridine complexes (0.1 mM)</th>
<th>ascorbic acid (100 mM)</th>
<th>aqueous solution</th>
<th>LED lamp ($\lambda = 455$ nm, 91 mW/cm$^2$)</th>
<th>57</th>
<th>5.7</th>
<th>17</th>
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<tbody>
<tr>
<td>chitosan</td>
<td>[Fe$_2$(CO)$_6$(m-adt)CH$_2$C$_6$H$_5$] (1.00 $\mu$m)</td>
<td>MPA-CdTe QDs (1.71 $\mu$m)</td>
<td>ascorbic acid (200 mM)</td>
<td>methanol/water (1:3 v/v)</td>
<td>LED lamp ($\lambda = 410$ nm)</td>
<td>52800</td>
<td>4130</td>
<td>18</td>
</tr>
<tr>
<td>Amphiphilic polymeric micelles</td>
<td>(μ-S-(CH$_2$)$_2$-S)$_2$ [Fe$_3$(CO)$_6$] (30 $\mu$m)</td>
<td>Ru(bpy)$_3^{2+}$ (0.3 mM)</td>
<td>ascorbic acid (45 mM)</td>
<td>CH$_3$CN/water (4:1, v/v)</td>
<td>LED lamp ($\lambda = 450$ nm)</td>
<td>133</td>
<td>32.4</td>
<td>19</td>
</tr>
<tr>
<td>SDS micelles</td>
<td>[Fe$_3$(CO)$_6$(μ-adt)C$_2$H$_4$C$_6$H$_5$] (180 $\mu$m)</td>
<td>Re(I)(4,4’-dim ethylbpy) (CO)$_3$Br (180 $\mu$m)</td>
<td>ascorbic acid (100 mM)</td>
<td>aqueous solution</td>
<td>500 W high-pressure Hanovia mercury lamp ($\lambda &gt; 400$ nm)</td>
<td>0.13</td>
<td>N.A.</td>
<td>20</td>
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<tr>
<td>apo-HSF</td>
<td>FeFe-COOH (51 $\mu$m)</td>
<td>Ru(bpy)$_3^{2+}$ (1 $\mu$m)</td>
<td>ascorbic acid (50 mM)</td>
<td>acetate buffer (0.2 M)</td>
<td>300 W Xe (200 mW cm$^2$, $\lambda &gt; 400$ nm)</td>
<td>30.6</td>
<td>-8.5</td>
<td>This work</td>
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**Table S2.** Comparison of NP4-1, NP4 and NP4-2.

<table>
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<tr>
<th>Composite</th>
<th>Number of catalyst$^{[a]}$</th>
<th>LE, %$^{[b]}$</th>
<th>LC, %$^{[c]}$</th>
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<tr>
<td>NP4-1</td>
<td>81</td>
<td>4.1</td>
<td>8.0</td>
</tr>
<tr>
<td>NP4</td>
<td>169</td>
<td>8.4</td>
<td>15.4</td>
</tr>
<tr>
<td>NP4-2</td>
<td>203</td>
<td>10.2</td>
<td>17.9</td>
</tr>
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</table>

$^{[a]}$ The numbers represent the average amount of incorporated FeFe-COOH per apo-HSF.  
$^{[b]}$ The LEs of FeFe-COOH nanoparticles were calculated as the weight ratio of incorporated FeFe-COOH to feded FeFe-COOH.  
$^{[c]}$ The LCs of FeFe-COOH nanoparticles were calculated as the weight ratio of incorporated FeFe-COOH to FeFe NP. Apo-HSF has a molecular weight of *approx.* 450 kDa.
**Fig. S1**  The $^1$H NMR spectrum of FeFe-COOH in CDCl$_3$.

**Fig. S2**  (a) The UV-vis absorption spectra of apo-HSF and NP4 in PBS at pH 7.4.

**Fig. S3**  DLS analysis of apo-HSF in PBS buffer.
Fig. S4  The UV-Vis spectra of NP4 before and after 1-week storage at 4 °C.

Fig. S5  (a) DLS and (b) CD spectra of NP4 before and after 1-week storage at 4 °C.

Fig. S6  The UV-vis absorption spectra of NP4-1, NP4 and NP4-2 at pH 7.4.
Fig. S7  The $^1$H NMR spectrum of (a) NCA in CDCl$_3$, (b) PBLG-N$_3$ in CDCl$_3$ containing 5% trifluoroacetic acid and (c) L-PGA in DMSO-d6.
Fig. S8  (a) DLS spectrum and (b) TEM image of L-PGA/FeFe-COOH complex in PBS buffer. The scale bar indicates 200 nm.

Fig. S9  (a) The emission spectra and (b) corresponding Stern-Volmer plot of \( I_0/I - 1 \) against \( C_{NaHA} \) by successive addition of sodium ascorbate into a solution of Ru(bpy)_3^{2+} (5 \( \mu \)M). Ru(bpy)_3^{2+} was excited at 453 nm and luminesced at 629 nm.
Fig. S10  (a) Cyclic voltammograms of FeFe-COOH (51 μM) in the presence of varied concentration of HOAc (0 ~ 1.2 mM) in 0.1 M Na$_2$SO$_4$ solution. (b) GC spectra of the gas phase collected during electrochemical reaction of FeFe-COOH, with H$_2$ detected at ~ 0.7 min.

Fig. S11  The photocatalytic H$_2$ production with FeFe-COOH (51 μM) in water or a mixed solution of CH$_3$CN/H$_2$O (v/v = 1/1), pH 5.3. The concentration of Ru(bpy)$_3^{2+}$ and ascorbic acid were 1 mM and 50 mM, respectively. The optical power was 200 mW cm$^{-2}$. 
Fig. S12  The 3-h Photocatalytic H₂ production by irradiation of solution containing NP4, Ru(bpy)₃²⁺ and ascorbic acid at pH 5.3. As controls, experiments were performed in the absence of one of photochemical reaction components.

Fig. S13  Photocatalytic H₂ production of NP3 solutions containing Ru(bpy)₃²⁺ (0.5 mM) and ascorbic acid (50 mM) at different pH values. The optical power was 200 mW cm⁻².

Fig. S14  The CD spectra of apo-HSF and NP3 at pH 5.3.
Fig. S15  Photocatalytic H₂ production at different Ru(bpy)₃²⁺ concentration of NP3 solutions containing ascorbic acid (50 mM). The optical power was 200 mW cm⁻².

Fig. S16  Photocatalytic H₂ production of NP4 before and after 1-week storage at 4 °C.

Fig. S17  (a) DLS and (b) CD spectra of NP4 before and after photocatalytic H₂ evolution by a 300 W xenon lamp (200 mW cm⁻²).
Fig. S18  Photocatalytic H$_2$ evolution from solution (pH 5.3) containing Ru(bpy)$_3^{2+}$ (1 mM), ascorbic acid (50 mM) and FeFe-COOH (51 μM). The optical power was 200 mW cm$^{-2}$. Reaction was re-performed at 3 h after adding another portion of Ru(bpy)$_3^{2+}$ (1 mM) or FeFe-COOH (51 μM).

Fig. S19  FT-IR spectroscopy of FeFe-COOH after varied time of photochemical reaction under the same condition described in Fig. S18.
Fig. S20 FT-IR spectroscopy of (a) FeFe-COOH (51 μM) and (b) NP4 (51 μM incorporated FeFe-COOH) after varied time of irradiation in the absence of Ru(bpy)$_3^{2+}$ and ascorbic acid. The optical power was 200 mW cm$^{-2}$.

Fig. S21 The volumes of released CO and percentages of the loss of CO ligands after varied time of irradiation under the same condition described in Fig. S20 and FeFe-COOH (51 μM) was used for comparison. CO was detected by an FID detector in GC analysis.

References


(2) Knoop, R. J.; Habraken, G. J.; Gogibus, N.; Steig, S.; Menzel, H.; Koning, C. E.;


