Supporting Information

Photoinduced morphology transformation of a self-assembled iron(II) coordination polymer: non-precious, high-performance, and self-enhancing photocatalytic CO₂ reduction

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1. Experimental Section

1.1 Materials and instruments

All reagents including solvents and starting materials for synthesis were purchased from commercial suppliers and used as received. Ligand N3tpy was synthesized as we previously reported[1] Scanning electron microscope (SEM) were obtained on a Hitachi S4800 Field-Emission Scanning Electron Microscope at an accelerating voltage of 15.0 kV. Powder X-ray diffraction (XRD) patterns were obtained using D8 Advance Xray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was carried out using Kratos Axis Ultra DLD with Al Kα X-ray source (hv = 1486.6 eV). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 670 FT-IR spectrometer with KBr. High-resolution Transmission Electron Microscopy (HRTEM) image was obtained on Tecnai F20 with an accelerating voltage of 200 kV. UV-Vis absorption studies were carried on a LAMBDA 850+ spectrophotometer. 1H-NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz). Photoluminescence experiments were accomplished using Shimadzu RF-6000 Luminescence spectrometer. The UV-vis diffuse reflectance spectra (DRS) were recorded on Lambda 950 Scan Spectrophotometers (Perkin Elmer).

1.2 Synthesis of coordination polymer FeN3tpy

Ligand N3tpy (500 mg, 0.38 mmol) dissolved in DMF (30 mL) at room temperature. Then, Fe(BF₄)₂•6H₂O (73 mg, 0.19 mmol) was carefully added into the solution. The mixed solution was further stirred with a magnetic stirrer at 100 °C overnight. Purple precipitate was generated and then collected by filtration and washing with CH₂Cl₂, C₂H₅OH, and H₂O, respectively. The collected precipitate was dried under vacuum to afford coordination polymer FeN3tpy (309 mg).

1.3 Photocatalytic CO₂ reduction

General procedure: FeN3tpy (2.0 mg), 4CzIPN (0.2 mM), and TEA (0.28 M) were mixed in 5.0 mL DMA/H₂O (v/v = 4:1) solution in a glass tube sealed up with a rubber septum. Before light irradiation, the mixed solution was bubbled with CO₂ for 20 min. Then, the reaction suspension was stirred with a stirrer under blue LED light irradiation for 6 h at room temperature. The light source is a blue LED instrument at 420 nm with a light intensity of 0.2 W (3STECH, Shanghai). Gaseous products (CO and H₂) were analyzed by injection of 250 µL aliquots from headspace to GC instrument. Liquid product was analyzed by recording 1H NMR spectrum of reaction solution.

Apparent quantum yiled (AQY) was determined by the following equation.

\[
\text{AQY} = \frac{\text{Number of CO molecules} \times 2}{\text{Number of incident photons}} \times 100\% \quad (\text{eq S1})
\]

The number of incident photons was obtained using a chemical actinometer K₃Fe(C₂O₄)₃ as reported.[2, 3] Fe(II) can be generated when K₃Fe(C₂O₄)₃ irradiated in buffer solution (HAc/Ac⁻). As
Fe(II) is easily coordinated to 1,10- phenanthroline (phen), a new complex \([\text{Fe}^{II}(\text{phen})]^{2+}\) is therefore formed in buffer solution containing phen. The newly formed complex \([\text{Fe}^{II}(\text{phen})]^{2+}\) is well-known and its amount is can be quantitatively determined through UV-vis absorption spectroscopy due to typical absorption at 510 nm. In our experiment, the \(K_3\text{Fe(C}_2\text{O}_4)_3\) solution (5.0 mL) was irradiated for 5 seconds. Then the solution was diluted to 17.5 mL for UV-vis absorption measurement. The absorbance at 510 nm of the diluted solution (3.0 mL) was recorded to be 0.28. According to Beer-Lambert’s equation \(A = \varepsilon c l\), the moles of generated Fe(II) can be obtained. For Beer-Lambert’s equation, \(\varepsilon (11100 \text{ L mol}^{-1} \text{ cm}^{-1})\) is the molar coefficient of \([\text{Fe}^{II}(\text{phen})]^{2+}\) at 510 nm, \(c\) is the concentration of generated \([\text{Fe}^{II}(\text{phen})]^{2+}\) and \(l (1 \text{ cm})\) is the width of quartz cuvette. Concentration of generated Fe(II) in the quartz cuvette: \(c(\text{Fe}^{II}) = \frac{A}{\varepsilon l} = \frac{0.28}{(11100 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1\text{cm})} = 2.52 \times 10^{-5} \text{mol L}^{-1}\).

Moles of generated Fe(II) every second in the irradiated solution: \(n(\text{Fe}^{II}) = c(\text{Fe}^{II}) \times 17.5 \text{ mL} / 5 \text{s} = 8.82 \times 10^{-8} \text{mol s}^{-1}\).

Numbers of generated Fe(II) every second: \(n(\text{Fe}^{II}) \times N_A. N_A \text{ is } 6.02 \times 10^{23} \text{ mol}^{-1}. \) As the quantum yield for Fe\(^{2+}\) generation at 420 nm is about 1.0, the incident photons are then calculated to be \(1.91 \times 10^{20} \text{ h}^{-1}\).

The AQY of \text{FeN}_3\text{tpy} was determined to be 11.7% by using the generated amount of CO (73.6 μmol) in the first 4 hours at the fifth cycle.

### 1.4 Photoelectrochemical measurements

All photoelectrochemical measurements were conducted in a three–electrode electrochemical cell with a platinum plate as the counter electrode, Ag/AgCl as the reference electrode, and FTO glass loaded with sample \text{FeN}_3\text{tpy} (nanoplate-like or and nanosphere-like) as the working electrode.

FTO glass working electrode was prepared as follows: \text{FeN}_3\text{tpy} (2 mg) was added to \(\text{C}_2\text{H}_5\text{OH}\) (2 mL) solution containing Nafion (10 μL). The mixture was then treated by sonication for 20 min to obtain the ink of \text{FeN}_3\text{tpy}. The ink (200 μL) was carefully dropped onto the conductive surface of FTO glass. Next, the FTO glass was left to dry naturally under air and used as a working electrode.

Mott-Schottky plots, transient photocurrent responses and electro-chemical impedance spectra were all obtained in the aqueous \(\text{Na}_2\text{SO}_4\) solution (0.5 M). For Mott-Schottky plots, the open circuit voltage was 0.36 V. The initial potential was −1.5 V and the final potential is 0 V (at 800,1000,1200 Hz). The increment of potential was set as 0.05 V. For transient photocurrent responses, run time was 300 s with an interval of 20 s. The light source was white LEDs equipment (SMPC–LVWT, 420–650 nm, 3 W LEDs, Technical Institute of Physics and Chemistry & Chinese Academy of Sciences). The potential for transient photocurrent test was set at open circuit potential. For electrochemical impedance spectra, the potential was set at open circuit potential and the frequency was set from 0.1 Hz to 100 kHz.

Linear sweep voltammetry (LSV) curves were obtained in a H-cell with a platinum plate as the counter electrode, Ag/AgCl as the reference electrode, and carbon paper loaded with \text{FeN}_3\text{tpy} (1 mg cm\(^{-2}\)). The electrolyte is aqueous KHCO\(_3\) solution (0.5 M). The scan rate is 20 mV s\(^{-1}\). The potentials vs Ag/AgCl are transformed to values vs RHE. \(E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.197 V + 0.0591 V \times \text{pH}\).
2. Supplementary Figures and tables

**Fig. S1** SEM image of FeN3tpy with a scale bar of 200 nm.

**Fig. S2** PXRD result of FeN3tpy.

**Fig. S3** FT-IR spectra of FeN3tpy and ligand N3tpy.
**Fig. S4** XPS survey spectrum of FeN3tpy.

![XPS spectrum](image)

**Table S1.** Binding energy (BE) of C 1s, O 1s, N 1s, B 1s, F 1s, and Fe 2p for FeN3tpy and N3tpy

<table>
<thead>
<tr>
<th>Sample</th>
<th>C 1s BE (eV)</th>
<th>O 1s BE (eV)</th>
<th>N 1s BE (eV)</th>
<th>B 1s BE (eV)</th>
<th>F 1s BE (eV)</th>
<th>Fe 2p1/2 BE (eV)</th>
<th>Fe 2p3/2 BE (eV)</th>
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</thead>
<tbody>
<tr>
<td>C=C</td>
<td>284.6 (76)</td>
<td>285.6 (21)</td>
<td>284.5 (3)</td>
<td>531.8 (66)</td>
<td>399.8 (25)</td>
<td>194.0</td>
<td>685.9</td>
</tr>
<tr>
<td>N3tpy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>285.2 (21)</td>
<td>285.5 (4)</td>
<td>531.7 (70)</td>
<td>398.4 (70)</td>
<td>399.6 (23)</td>
<td>194.0</td>
<td>685.9</td>
</tr>
<tr>
<td>FeN3tpy</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>285.6 (21)</td>
<td>285.5 (3)</td>
<td>531.8 (66)</td>
<td>399.8 (25)</td>
<td>398.6 (9)</td>
<td>194.0</td>
<td>721.2</td>
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**Fig. S5** SEM image of FeN3tpy with a scale bar of 150 nm.
Fig. S6 UV-vis-DRS spectrum of FeN3tpy.

Fig. S7 Tauc plot of FeN3tpy.

Fig. S8 Mott-Schottky plots of FeN3tpy.
**Fig. S9** $^1\text{H}$ NMR spectrum of reaction solution (400 μL) by addition of D$_2$O (100 μL) and DMSO (15 μL) as the internal standard.

**Table S2.** Control experiments of photocatalytic CO$_2$ reduction using FeN3tpy

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>CO (μmol)</th>
<th>H$_2$ (μmol)</th>
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</thead>
<tbody>
<tr>
<td>1[a]</td>
<td>FeN3tpy, 4CzIPN, TEA, light irradiation, and CO$_2$</td>
<td>55</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>Without FeN3tpy</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Without 4CzIPN</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Without TEA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Ar instead of CO$_2$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>In the dark</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

[a] Conditions: FeN3tpy (2.0 mg), 4CzIPN (0.2 mM), TEA (0.28 M), light irradiation at 420 nm, DMA (4.0 mL), H$_2$O (1.0 mL), 6 h, under CO$_2$.

**Fig. S10** GC-MS result of labeling experiment with $^{13}$CO$_2$.
**Fig. S11** XPS survey spectrum of nanosphere-like FeN3tpy.

**Table S3.** Binding energy (BE) of C 1s, O 1s, N 1s, B 1s, F 1s, and Fe 2p for nanosphere-like FeN3tpy

<table>
<thead>
<tr>
<th>Sample</th>
<th>C=C BE (eV)</th>
<th>C=N- BE (eV)</th>
<th>C=O BE (eV)</th>
<th>O=C BE (eV)</th>
<th>=N- BE (eV)</th>
<th>NH- BE (eV)</th>
<th>Fe 2p 1/2 BE (eV)</th>
<th>Fe 2p 3/2 BE (eV)</th>
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<tr>
<td>Nanosphere-like FeN3tpy</td>
<td>284.8 (75)</td>
<td>285.8 (22)</td>
<td>284.5 (3)</td>
<td>531.2 (69)</td>
<td>399.7 (23)</td>
<td>398.5 (8)</td>
<td>194.0</td>
<td>685.8</td>
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**Fig. S12** High resolution XPS spectra of Fe 2p, N 1s, C 1s, and F 1s for nanosphere-like FeN3tpy.
**Fig. S13** FT-IR spectrum of nanosphere-like FeN3tpy.

**Fig. S14** Comparison of PXRD patterns of nanoplate-like FeN3tpy and nanosphere-like FeN3tpy.

**Fig. S15** PL quenching of 4CzIPN (5 μM) by (a) nanosphere-like FeN3tpy, (b) nanoplate-like FeN3tpy in DMF (λex = 450 nm). Excitation and emission slits are 5 and 10 nm, respectively.
**Fig. S16** UV-vis absorption spectra of nanosphere-like FeN3tpy (0.1 mg mL⁻¹) in DMF/H₂O (v/v = 4:1) solution containing 4CzIPN (50 μM) and TEA (70 mM) before and after irradiation of 120 s under N₂ at room temperature.

**Fig. S17** (a) CVs of nanosphere-like FeN3tpy at different scan rates. (b) CVs of nanoplate-like FeN3tpy at different scan rates. Experiments were conducted in aqueous KHCO₃ solution (0.5 M).

References

