Visible-Light-Driven Selective Oxidation of Benzyl Alcohol and Thioanisole by Molecular Ruthenium Catalysts Modified Hematite

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Experimental Section

Materials

Ultra pure water (18.2 MΩ cm-1) for reactions was obtained from a Milli-Q system (Millipore, Direct-Q 3 UV). Organic solvents were chromatographically pure and used without further purification. RuCl3·3H2O, SnCl4·5H2O, FeCl3·6H2O, bpy (2,2′-bipyridine), bpy-COOH (2,2′-bipyridine-4,4′-dicarboxylic acid), tpy (2,2′:6′,2′′-terpyridine), α-Fe2O3 particles (particle size: 30 nm, spherical) were purchased from Aladdin, [Co(NH3)5Cl]Cl2 (98 %) were purchased from Sigma Aldrich. Other reagents were commercially available and used as received. Mebimpy (2,6-bis(1-methylbenzimidazol-2-yl)pyridine) were prepared as previously reported. FTO substrates were purchased from Dalian Heptachroma SolarTech Co., Ltd. (thickness of ~2.2 mm, transmittance of >90%, resistance <15 Ω/cm²).

Instruments for Analysis

1H NMR spectra were collected at 298 K using a Bruker DRX-500 instrument. Electrospray ionization mass spectra were recorded on a LTQ Orbitrap XL micromass spectrometer (Thermo Scientific). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. UV–vis diffuse reflectance spectra (DRS) of the samples were measured using a Hitachi UV-3010PC UV–vis spectrophotometer. Electrochemical measurements were carried out on a CHI630E electrochemical workstation (Shanghai Chenhua, China). Powdered X-ray
Diffraction (PXRD) was collected with a D/max-2400 diffractometer (Japan Rigaku Rotaflex) using Cu Kα radiation (154.1 nm). Scanning electron microscopy (SEM) was carried out by FEI Nova NanoSEM 450 instrument with an accelerating voltage of 3.0 kV. ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) analysis was conducted by an Optima 2000DV instrument (America PerkinElmer Corp.).

Preparation of ruthenium complexes

The Ru1 and Ru2 were prepared according to published procedures. The synthetic route was depicted as Scheme S1.

**Scheme S1 Synthetic route of [Ru(tpy)(bpy-R)(H₂O)](ClO₄)₂.**

**Ru(tpy)Cl₃.** RuCl₃·3H₂O (0.70 mmol) and tpy (0.70 mmol) were combined in 50 mL of EtOH and refluxed for 4 h. The mixture was cooled, and the product was collected as a brown solid upon filtration. The obtained solid was washed with EtOH and Et₂O and then dried in the air. The compound was used to next reaction without further purification.

**[Ru(tpy)(bpy-R)(Cl)](Cl).** Ru(tpy)Cl₃ (0.70 mmol) and bpy-R (0.70 mmol) were combined with LiCl (7.0 mmol) and N-ethylmorpholine (0.5 mL) in 30 mL of MeOH/H₂O (5:1). The mixture was then heated at reflux for 3 h under nitrogen. The solvent was evaporated and the crude product was loaded onto silica. The product was collected as a deep purple-colored band using acetone/methanol/water (3:1:1) saturated with LiCl as the eluent (typical R_f values for the purple band were 0.6-0.7). The product fractions were combined, and the solvent removed to near dryness (~15 mL), and then 1 mL of concentrated HCl was added and let stand for overnight. The purple solid was then collected and washed with 10 mL of 1 M HCl and left to air-dry.

**[Ru(tpy)(bpy-R)(H₂O)](ClO₄)₂.** [Ru(tpy)(bpy-R)Cl][Cl] (0.34 mmol) was combined with AgClO₄ (0.74 mmol) and refluxed in 50 mL water for 3 h under nitrogen. The mixture was filtered through Celite. The volume of the filtrate was reduced to near dry followed by the addition of 5 mL of 1 M HClO₄ to precipitate the product. The purple solid was collected and then washed with 10 mL of 1 M HClO₄ and left to air-dry. The final product was characterized by ESI-MS and 1H NMR as Figure S1-S4.
Figure S1 ESI-MS of Ru1 in H$_2$O.

Figure S2 $^1$H NMR spectrum of Ru1 in DMSO-d$_6$. 
Figure S3 ESI-MS of Ru2 in H2O.

Figure S4 1H NMR spectrum of Ru2 in DMSO-d6.
The Ru3 and Ru4 were prepared according to published procedures. The synthetic route was depicted as Scheme S2.

[Ru(Mebimpy)(bpy-R)(OTf)](OTf). A mixture of [Ru(Mebimpy)(bpy-R)(Cl)](Cl) (0.50 mmol) and AgOTf (1.05 mmol; OTf = triflate anion) in MeOH (40 mL) was stirred under nitrogen at room temperature overnight. The silver chloride was filtered by Celite, and the filtrate was taken to dryness by rotary evaporation. Et$_2$O was added, the formed solid was filtered, washed with ether,
and air-dried. The aquo complexes were generated in situ by dissolving the triflate complexes in water. The final product was characterized by ESI-MS and $^1$H NMR as Figure S5-S8.

Figure S5 ESI-MS of Ru3 in CH$_3$CH$_2$OH.

Figure S6 $^1$H NMR spectrum of Ru3 in CD$_3$CN.
Figure S7 ESI-MS of Ru4 in CH3OH.

Figure S8 ¹H NMR spectrum of Ru4 in CD3CN.
Preparation of Sn-doped α-Fe₂O₃ films

Sn-doped α-Fe₂O₃ films were prepared according to previously reported literature with a little modification.³ To a 20 mL de-ionized water (pH was adjusted to 1.5 with concentrated HCl), 811 mg FeCl₃.6H₂O, 1.700 g NaNO₃, and 1 mL tin (IV) chloride (SnCl₄) ethanol solution (10 mg/mL) were added. A teflon-lined stainless steel autoclave was then filled with above mixture. A piece of FTO glass slide, successively washed with acetone, ethanol, and then de-ionized water, was put into the autoclave and heated at 95 °C for 4 h. A uniform layer of iron oxyhydroxides (FeOOH) film (yellow color) was formed on the FTO substrate. The FeOOH film was thoroughly rinsed with de-ionized water then sintered in air at 550 °C for 2 h, and subsequently 750 °C for 15 min. During this process, the FeOOH film was converted to hematite film.

Preparation of α-Fe₂O₃/molecular catalyst hybrid photocatalyst

35 mg α-Fe₂O₃ particles were added to 25 mL methanol solution of the catalyst (0.2 mM) and stirred for 12 h at room temperature in dark. The suspended solid was collected by centrifugation and dried under vacuum overnight. UV-vis spectra of the initial solution and the supernate were measured. The difference of the absorption maximum at visible-light region between two samples was calculated for quantifying the loading of catalysts. For Ru² and Ru⁴, the absorption maximums at 490 nm and 492 nm respectively (Figure S9 and S10).

Preparation of α-Fe₂O₃/molecular catalyst hybrid photoanode

A piece of α-Fe₂O₃ electrode was immersed in 25 mL methanol solution of the catalyst (0.2 mM) for 4 h at room temperature in dark. The as-prepared electrode was washed with methanol to remove any unbounded molecules and then dried under nitrogen before use. ICP-AES was used for quantifying the loading of catalysts. (The modified hematite photoanode was put into 10 mL 1 M NaOH solution, the adsorbed molecules desorbed and then dissolved. The Ru content of the NaOH solution was quantified by ICP-AES. The content based on Ru atom is 0.0921 and 0.0876 μg/cm² for Ru² and Ru⁴ respectively.)

General procedure for photocatalytic oxidation in sacrificial system

0.1 M phosphate buffer solution (10 mL, pH 4.7) containing α-Fe₂O₃ powder (15 mg), organic substrate (10 mM), [Co(NH₃)₅Cl]Cl₂ (20 mM) was charged in a custom built glass reactor with jacketed cooler and then degassed with argon for 30 min. The reactor was irradiated with a 300 W Xe lamp equipped with a cutoff filter (λ > 400 nm) for 5 h. The light intensity was measured by an EAULIGHT CEL-NP2000 photometer and then adjusted to 400 mW/cm². The gas of the headspace was analyzed and quantified by gas chromatography (Techcomp GC 7890T, Ar carrier gas, Thermo Conductivity Detector). The resulted solution was extracted with 3×10 mL CH₂Cl₂ and dried with anhydrous Na₂SO₄. Dodecane was added as an internal standard. After evaporation of solvent to nearly dryness (ca. 2 mL) by vacuum, the products were analyzed and quantified by gas chromatography (Agilent GC 6890N, N₂ carrier gas, Flame Ionization Detector). ¹H NMR spectroscopy was also adopted for characterizing and quantifying the organic products. For ¹H NMR
analysis, the extracted solution was evaporated to dryness and the residue was redissolved in CDCl$_3$.

Two representative $^1$H NMR spectra used for product quantification in the oxidation of benzyl alcohol and sulfide were shown in Figure S11 and S12.

**Photo-generation of Ru(IV)=O complexes in sacrificial system**

A phosphate buffer solution (10 mL, 0.1 M, pH = 4.7) containing ruthenium catalyst (Ru1 or Ru3, 0.04 mM), α-Fe$_2$O$_3$ powder (15 mg), and [Co(NH$_3$)$_5$Cl]$Cl_2$ (5 mM) was irradiated for 15 min at 25°C ($\lambda$ > 400 nm, 400 mW/cm$^2$). A portion of the reaction mixture was taken out through a syringe-driven filter and then analyzed by UV-Vis.

**General procedure for photoelectrochemical cells (PECs) measurements**

0.05 M phthalate buffer solution (25 mL, pH = 3) was added with LiClO$_4$ (0.45 M) and 20 mM substrate. The resulting solution was charged in a home-made cell and purged with argon before measurement. In a three-electrode system, hematite film with and without catalyst modification was served as the working electrode. Ag/AgCl (3 M KCl) was the reference electrode and Pt wire was the counter electrode. The working electrode was irradiated with a 300 W Xe lamp equipped with an AM 1.5G filter and the light intensity was adjusted to 100 mW/cm$^2$. All samples were irradiated from the frontside due to the poor performance of backside illumination for hematite films (Figure S6b). The working area of the electrode exposed to electrolyte was 1 cm$^2$. J-V curves were obtained by linear sweeping voltammetry (LSV) at a scan rate of 10 mV/s. I-t curves were acquired under a constant bias (1.0 V vs. RHE) at ambient pressure and room temperature. All potentials were reported with respect to reversible hydrogen electrode (RHE) by $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.20 \text{ V} + 0.059 \text{pH}$. For the measurement of Faradaic efficiency, the gas of the headspace and the extracted solution was quantified by gas chromatography as the similar method described in sacrificial system. The Faradaic efficiency was calculated by integrated charge (Q) and amount of product (Eq. S1).

$$\text{FE(\%)} = \frac{n_{\text{(product)}}}{\frac{Q}{2}} \times 100\%$$

(S1)
Figure S9 UV-vis spectra of 0.2 mM Ru2 solution in methanol before (black) and after (red) stirred with α-Fe2O3 particles. According to the change of the spectra, the loading of Ru2 was evaluated to be $6.58 \times 10^{-8}$ mol/mg on α-Fe2O3 particles.

Figure S10 UV-vis spectra of 0.2 mM Ru4 solution in methanol before (black) and after (red) stirred with α-Fe2O3 particles. According to the change of the spectra, the loading of Ru4 was evaluated to be $3.23 \times 10^{-8}$ mol/mg on α-Fe2O3 particles.
Figure S11 ¹H NMR spectrum of the residue extracted by DCM from the resulted solution of photocatalytic dehydrogenation of benzyl alcohol (solvent CDCl₃), the marked values of chemical shift represent methylene of benzyl alcohol (4.61) and aldehyde of benzaldehyde (9.94), respectively. Reaction conditions: Ru₄ modified Fe₂O₃ (15 mg), benzyl alcohol (10 mM), and [Co(NH₃)₅Cl]Cl₂ (20 mM) in a 0.1 M (pH 4.7) phosphate buffer solution irradiated under visible light for 5 h.

Figure S12 ¹H NMR spectrum of the residue extracted by DCM from the resulted solution of photocatalytic oxygenation of thioanisole (solvent CDCl₃), the marked values of chemical shift represent methyl of thioanisole (2.42) and benzyl methyl sulfoxide (2.66), respectively. Reaction conditions: Ru₁ (9.87×10⁻⁷ mol), Fe₂O₃ (15 mg), thioanisole (10 mM), and [Co(NH₃)₅Cl]Cl₂ (20 mM) in a 0.1 M (pH 4.7) phosphate buffer solution irradiated under visible light for 5 h.
Figure S13 UV-vis spectra of 0.1 M phosphate buffer (pH 4.7) containing 0.04 mM Ru1 and 5 mM [Co(NH$_3$)$_5$Cl]Cl$_2$ before (black) and after (red) 15 mins light-irradiation. After addition of 5 mM thioanisole, the spectra change within 5 mins is showed as blue curve.

Figure S14 UV-vis spectra of 0.1 M phosphate buffer (pH 4.7) containing 0.04 mM Ru3 and 5 mM [Co(NH$_3$)$_5$Cl]Cl$_2$ before (black) and after (red) 15 mins light-irradiation. After addition of 5 mM thioanisole, the spectra change within 5 mins is showed as blue curve.
Figure S15  Kubelka-Munk function converted UV-vis diffuse reflectance spectra of Sn-doped α-Fe₂O₃ film. Kubelka-Munk function: \( f(R) = (1 - R)^2 (2R)^{-1} \), \( R \) = reflectance. Reflectance was converted to Kubelka-Munk as \( f(R) \) versus wavelength to correct for scattering.⁴

Figure S16 PXRD spectra of Sn-doped α-Fe₂O₃ film. Red and blue vertical lines highlight the diffraction peaks of α-Fe₂O₃ (JCPDS 33-0664) and SnO₂ (JCPDS 41-1445), respectively. The SnO₂ was originated from the FTO substrate.
Figure S17  FE-SEM images of Sn-doped hematite sintered at 750 °C.

Figure S18 (a) LSVs of pristine $\alpha$-Fe$_2$O$_3$ film in 1 M NaOH (pH = 13.6) and 0.05 M potassium hydrogen phthalate buffer solution containing 0.45 M LiClO$_4$ (pH = 3). The LSVs of $\alpha$-Fe$_2$O$_3$ film in the dark were also shown. (b) LSVs of pristine $\alpha$-Fe$_2$O$_3$ film in 1 M NaOH illuminated from front side (red) and back side (blue).
Figure S19 Cyclic Voltammograms of α-Fe$_2$O$_3$ films without (black) and with Ru$_2$ (red) or Ru$_4$ (blue) modification in pH 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.45 M LiClO$_4$. Scan rate: 10 mV/s, CE: Pt, RE: Ag/AgCl.

Figure S20 LSVs of pristine α-Fe$_2$O$_3$ film in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole (blue) or benzyl alcohol (red) and 0.45 M LiClO$_4$. The LSV of α-Fe$_2$O$_3$ film in the buffer solution without adding substrates (black) were also shown.
Figure S21 LSVs of α-Fe₂O₃ films with (red) and without (black) Ru₂ modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M LiClO₄. The LSVs of α-Fe₂O₃ films with (orange) and without (blue) Ru₂ modification in the dark conditions were also shown.

Figure S22 I-t curves of α-Fe₂O₃ films with (red) and without (black) Ru₂ modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M LiClO₄ with chopped light.
Figure S23 LSVs of α-Fe₂O₃ films with (red) and without (black) Ru² modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole and 0.45 M LiClO₄. The LSVs of α-Fe₂O₃ films with (orange) and without (blue) Ru² modification in the dark conditions were also shown.

Figure S24 I-t curves of α-Fe₂O₃ films with (red) and without (black) Ru² modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole and 0.45 M LiClO₄ with chopped light.
Figure S25 LSVs of α-Fe$_2$O$_3$ films with (red) and without (black) Ru4 modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M LiClO$_4$. The LSVs of α-Fe$_2$O$_3$ films with (orange) and without (blue) Ru4 modification in the dark conditions were also shown.

Figure S26 I-t curves of α-Fe$_2$O$_3$ films with (red) and without (black) Ru4 modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole and 0.45 M LiClO$_4$ with chopped light.
### Table S1 Products distribution for the oxidation of thioanisole

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Benzylic sulfoxide (μmol/yield)</th>
<th>Benzylic sulphone (μmol/yield)</th>
<th>CO₂ (μmol/yield)</th>
<th>O₂ (μmol/yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-Fe₂O₃</td>
<td>0.8/0.8 %</td>
<td>-</td>
<td>-</td>
<td>0.9/1.8 %</td>
</tr>
<tr>
<td>2</td>
<td>α-Fe₂O₃/Ru₁</td>
<td>64.7/64.7 %</td>
<td>-</td>
<td>-</td>
<td>0.4/0.8 %</td>
</tr>
<tr>
<td>3</td>
<td>α-Fe₂O₃/Ru₂</td>
<td>99.1/99.1 %</td>
<td>-</td>
<td>-</td>
<td>0.3/0.6 %</td>
</tr>
<tr>
<td>4</td>
<td>α-Fe₂O₃/Ru₃</td>
<td>17.6/17.6 %</td>
<td>-</td>
<td>-</td>
<td>0.4/0.8 %</td>
</tr>
<tr>
<td>5</td>
<td>α-Fe₂O₃/Ru₄</td>
<td>31.6/31.6 %</td>
<td>-</td>
<td>-</td>
<td>0.4/0.8 %</td>
</tr>
</tbody>
</table>

a. The reaction condition was same as Table 1 in the main text.
b. Yields were calculated as (mol of organic products) × 2 / (mol of sacrificial reagents).
c. Yields were calculated as (mol of evolved oxygen) × 4 / (mol of sacrificial reagents).

### Table S2 Products distribution for the oxidation of benzyl alcohol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Benzaldehyde (μmol/yield)^a</th>
<th>Benzoic acid (μmol/yield)</th>
<th>CO₂ (μmol/yield)</th>
<th>O₂ (μmol/yield)^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-Fe₂O₃</td>
<td>2.0/2.0 %</td>
<td>-</td>
<td>-</td>
<td>0.7/1.4 %</td>
</tr>
<tr>
<td>2</td>
<td>α-Fe₂O₃/Ru₁</td>
<td>7.5/7.5 %</td>
<td>-</td>
<td>-</td>
<td>0.6/1.2 %</td>
</tr>
<tr>
<td>3</td>
<td>α-Fe₂O₃/Ru₂</td>
<td>35.2/35.2 %</td>
<td>-</td>
<td>-</td>
<td>0.5/1.0 %</td>
</tr>
<tr>
<td>4</td>
<td>α-Fe₂O₃/Ru₃</td>
<td>4.9/4.9 %</td>
<td>-</td>
<td>-</td>
<td>0.5/1.0 %</td>
</tr>
<tr>
<td>5</td>
<td>α-Fe₂O₃/Ru₄</td>
<td>24.9/24.9 %</td>
<td>-</td>
<td>-</td>
<td>0.5/1.0 %</td>
</tr>
</tbody>
</table>

a. The reaction condition was same as Table 1 in the main text.
b. Yields were calculated as (mol of organic products) × 2 / (mol of sacrificial reagents).
c. Yields were calculated as (mol of evolved oxygen) × 4 / (mol of sacrificial reagents).

### Table S3 Faradaic efficiency measurements for the oxidation of benzyl alcohol using Ru₄ modified hematite.

<table>
<thead>
<tr>
<th>Name of product</th>
<th>Yield of product (μmol)</th>
<th>Passed charge (C)</th>
<th>Faradaic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>1.40</td>
<td>0.33</td>
<td>82</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.78</td>
<td>0.17</td>
<td>88</td>
</tr>
</tbody>
</table>

### Table S4 Faradaic efficiency measurements for the oxidation of thioanisole using Ru₄ modified hematite.

<table>
<thead>
<tr>
<th>Name of product</th>
<th>Yield of product (μmol)</th>
<th>Passed charge (C)</th>
<th>Faradaic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl methyl sulfoxide</td>
<td>12.5</td>
<td>2.58</td>
<td>93</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8.38</td>
<td>1.70</td>
<td>95</td>
</tr>
</tbody>
</table>

### References