Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

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. $RuCl_3 \cdot 3H_2O$, $SnCl_4 \cdot 5H_2O$, $FeCl_3 \cdot 6H_2O$, bpy (2,2′-bipyridine), bpy-COOH (2,2’-bipyridine-4,4’-dicarboxylic acid), tpy (2,2′:6′,2″-terpyridine), α-Fe_2O_3 particles (particle size: 30 nm, spherical) were purchased from Aladdin, $[Co(NH_3)_5Cl]Cl_2$ (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.[1] FTO substrates were purchased from Dalian Heptachroma SolarTech Co., Ltd. (thickness of ~2.2 mm, transmittance of >90%, resistance <15 Ω/cm^2).

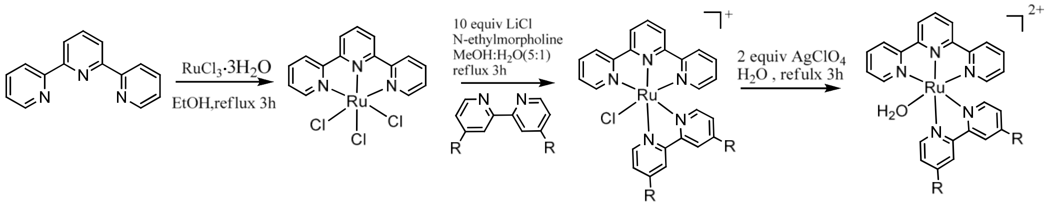
Instruments for Analysis

^{1}H 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.[2] The synthetic route was depicted as Scheme S1.



R = H (Ru1), COOH (Ru2)

Scheme S1 Synthetic route of [Ru(tpy)(bpy-R)(H_2O)](ClO_4)$_2$.

Ru(tpy)Cl$_3$. $RuCl_3 \cdot 3H_2O$ (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 Et_2O and then dried in the air. The compound was used to next reaction without further purification.

[Ru(tpy)(bpy-R)(Cl)](Cl). Ru(tpy)Cl$_3$ (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/H_2O (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)(H_2O)](ClO_4)$_2$. [Ru(tpy)(bpy-R)Cl]Cl (0.34 mmol) was combined with $AgClO_4$ (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 $HClO_4$ to precipitate the product. The purple solid was collected and then washed with 10 mL of 1 M $HClO_4$ and left to air-dry. The final product was characterized by ESI-MS and ^{1}H NMR as Figure S1-S4.

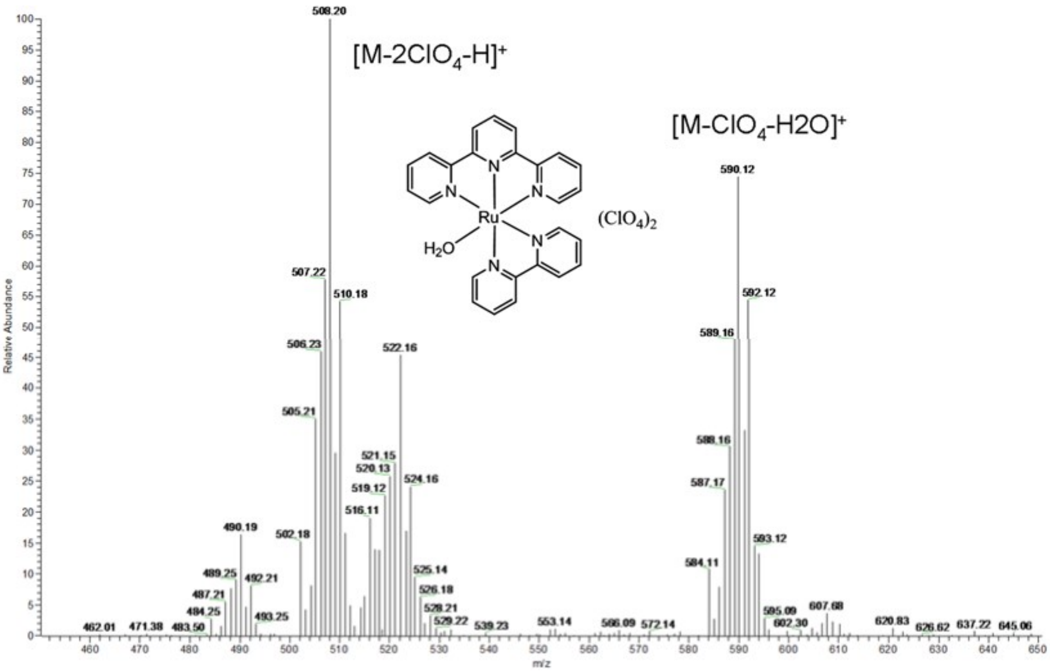


Figure S1 ESI-MS of **Ru1** in H_2O.

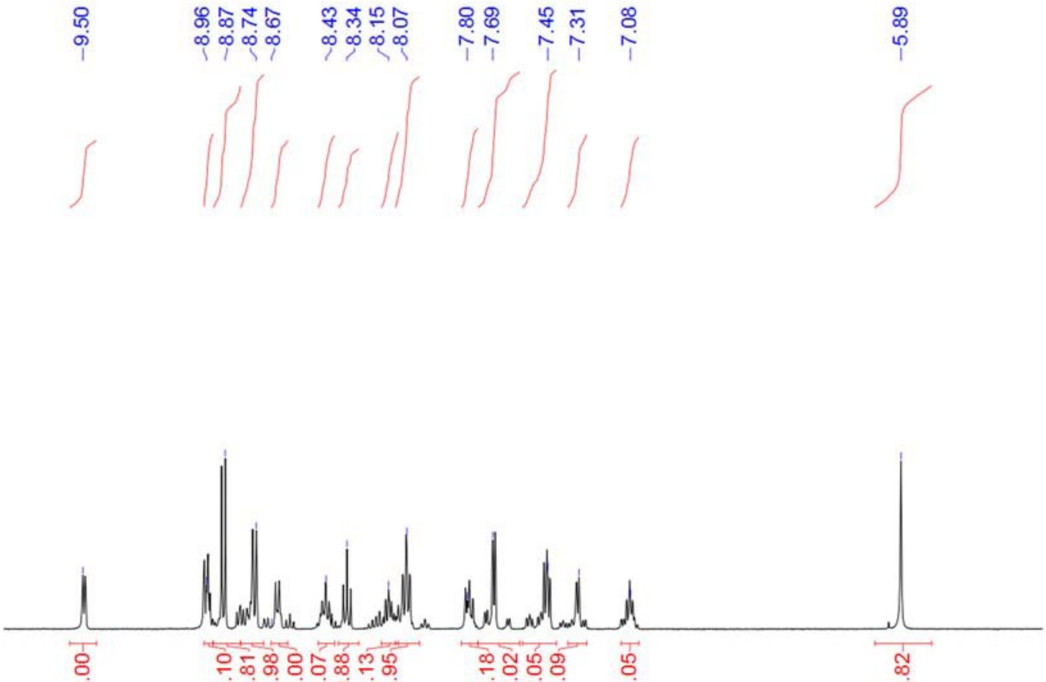


Figure S2 ^{1}H NMR spectrum of **Ru1** in DMSO-d6.

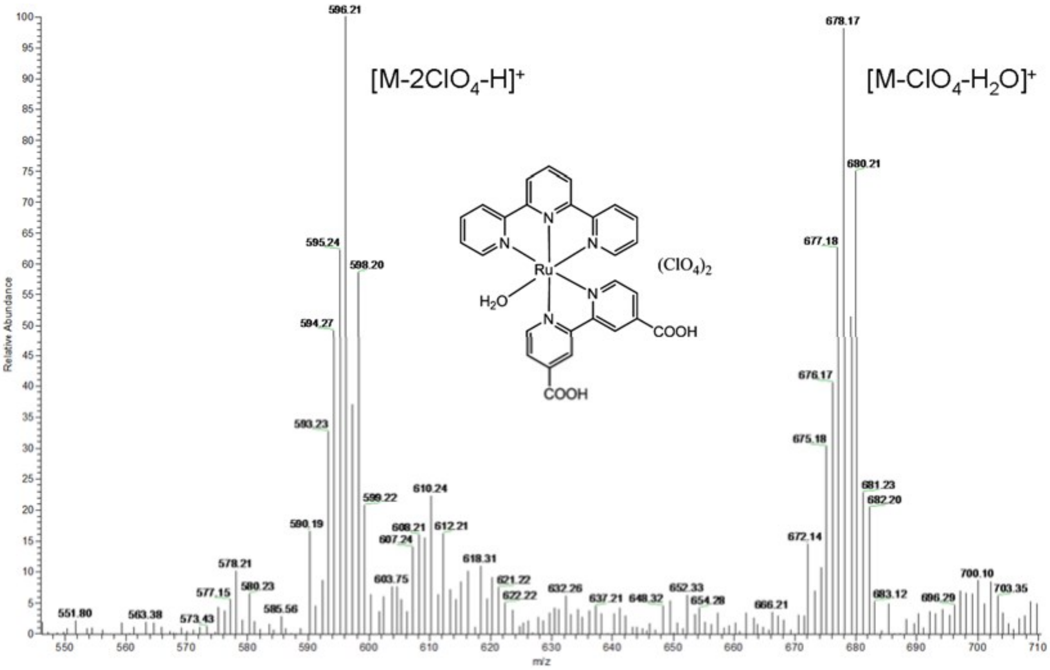


Figure S3 ESI-MS of **Ru2** in H_2O.

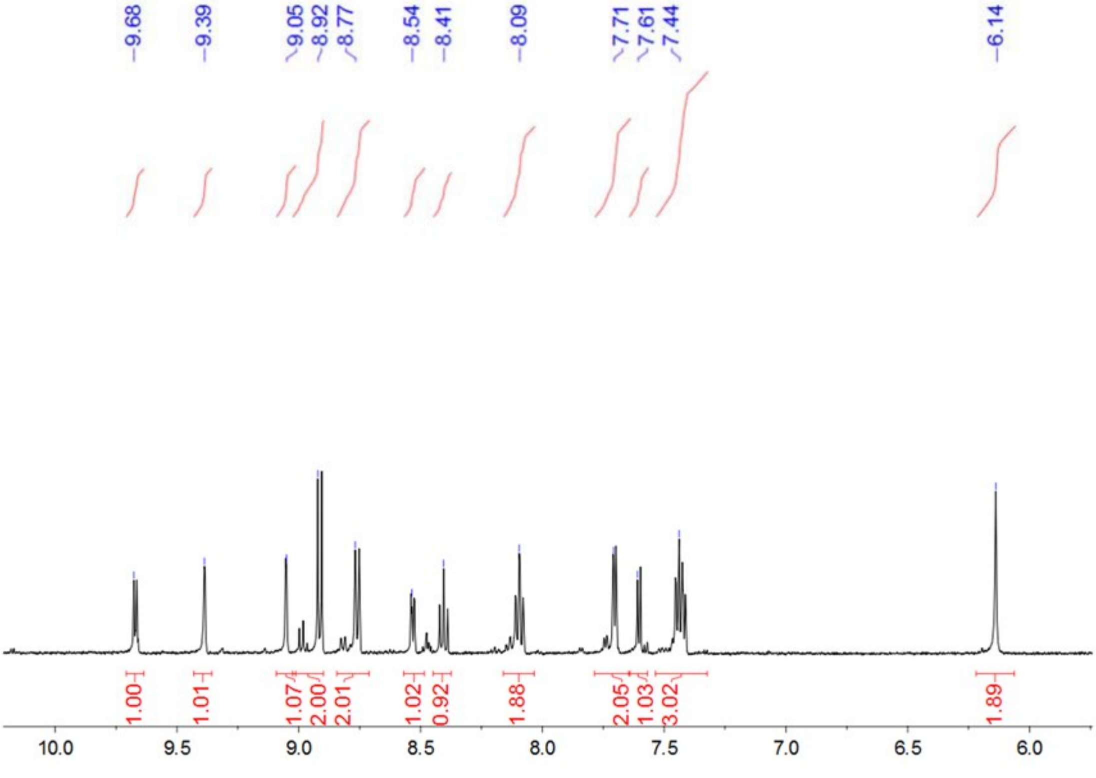
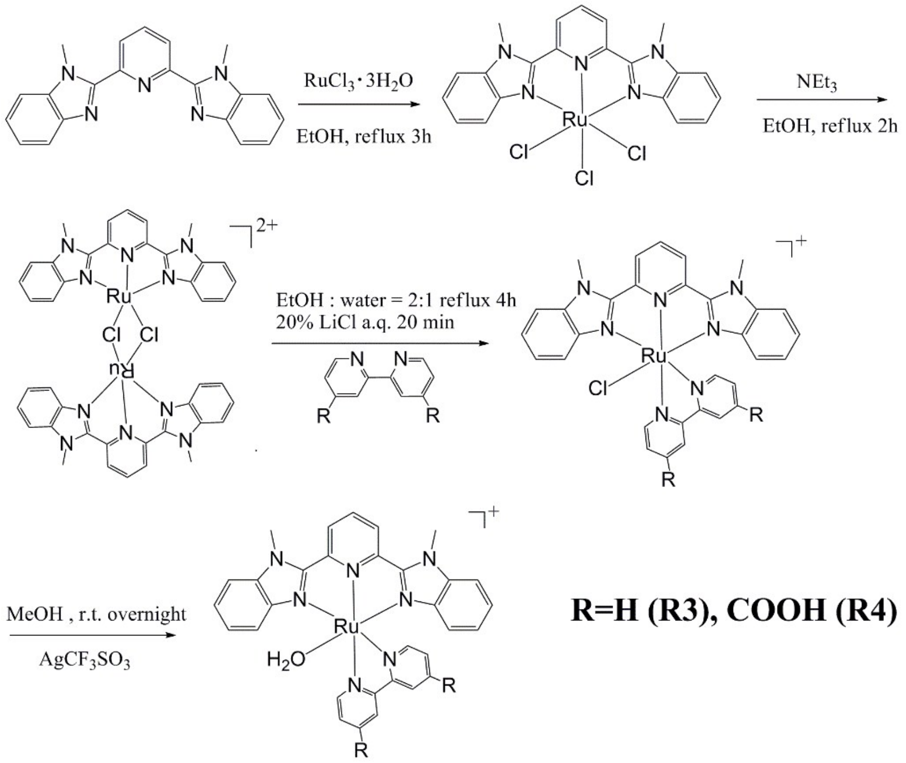


Figure S4 ^{1}H NMR spectrum of **Ru2** in DMSO-d6.

The **Ru3** and **Ru4** were prepared according to published procedures.[1] The synthetic route was depicted as Scheme S2.



Scheme S2 Synthetic route of [Ru(Mebimpy)(bpy-R)(OTf)](OTf).

[Ru(Mebimpy)Cl$_3$]. In a typical experiment, RuCl$_3$·3H$_2$O (262 mg, 1 mmol) and Mebimpy (340 mg, 1 mmol) were mixed in 100 mL of ethanol, and the mixture was refluxed for 3 h. Upon cooling the mixture to room temperature, a brown solid was filtered, which was successively washed with ethanol and ether. The product was air-dried and used without further purification.

[((Mebimpy)(Cl)Ru)$_2$Cl$_2$]. [Ru(Mebimpy)Cl$_3$] (500 mg) was suspended in ethanol (40 mL) and the mixture degassed by nitrogen bubbling. NEt$_3$ (1.5 mL) was added and the mixture was refluxed for 2 h and filtered hot. The purple solid obtained was washed with ethanol and ether. The product was air-dried and used without further purification.

[Ru(Mebimpy)(bpy-R)(Cl)](Cl). [((Mebimpy)(Cl)Ru)$_2$Cl$_2$] (0.29 mmol) and bpy-R (0.59 mmol) were suspended in 45 mL of 2:1 EtOH:H$_2$O, and the suspension was heated at reflux for 4 h under nitrogen. 10 mL of 20% aqueous LiCl was added. After an additional 20 min, the mixture was filtered hot, and the filtrate was allowed to cool overnight. The brown microcrystalline solid formed was isolated by filtration and washed successively with water and ether.

[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.

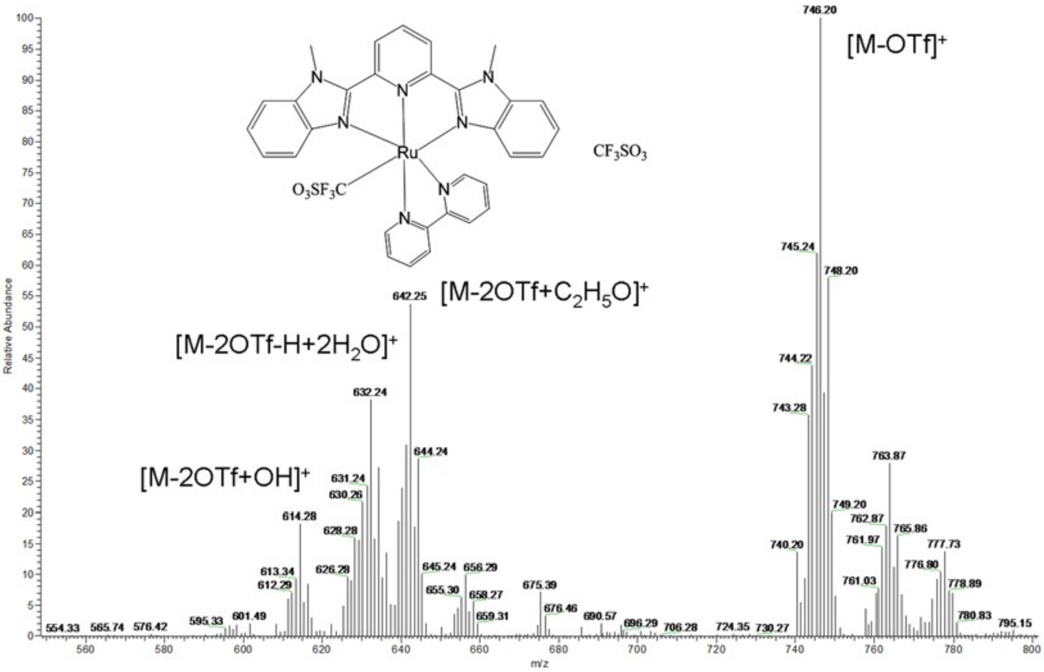


Figure S5 ESI-MS of **Ru3** in CH_3CH_2OH.

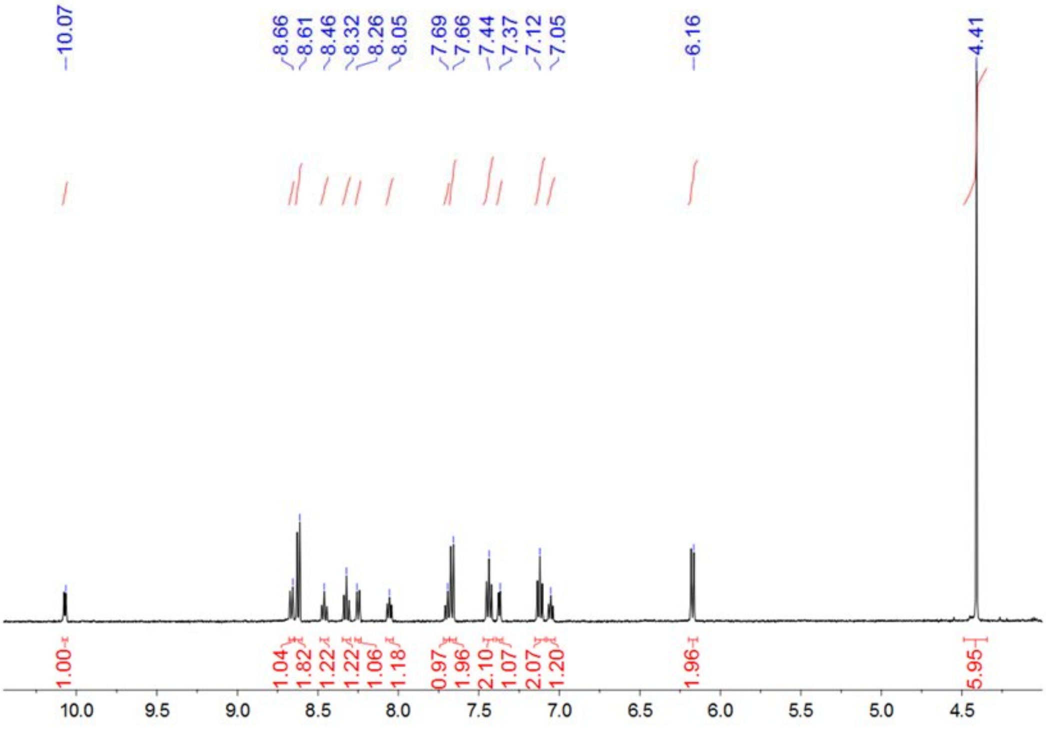


Figure S6 ^{1}H NMR spectrum of **Ru3** in CD_3CN.

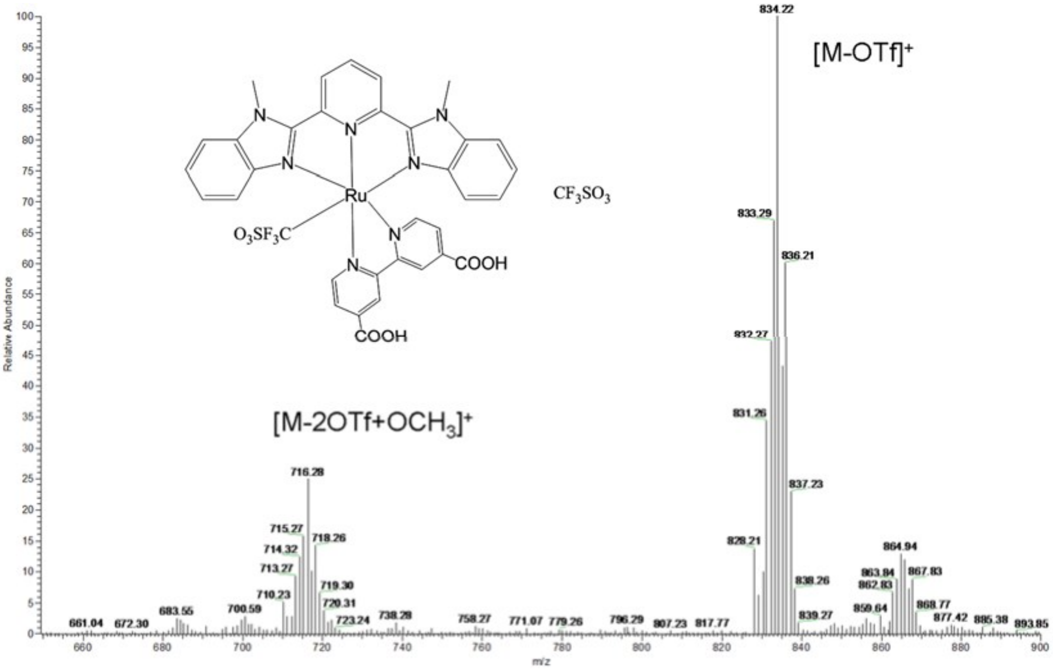


Figure S7 ESI-MS of **Ru4** in CH$_3$OH.

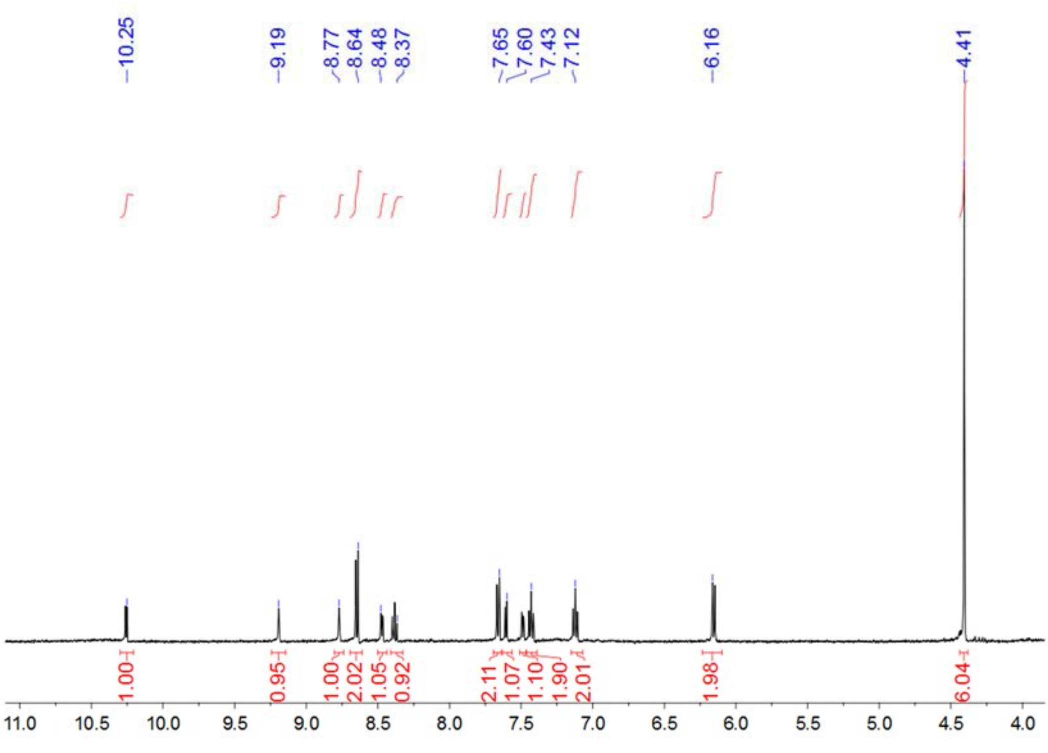


Figure S8 ^{1}H NMR spectrum of **Ru4** in CD$_3$CN.

Preparation of Sn-doped α-Fe_2O_3 films

Sn-doped α-Fe_2O_3 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 $FeCl_3.6H_2O$, 1.700 g $NaNO_3$, and 1 mL tin (IV) chloride ($SnCl_4$) 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-Fe_2O_3/molecular catalyst hybrid photocatalyst

35 mg α-Fe_2O_3 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-Fe_2O_3/molecular catalyst hybrid photoanode

A piece of α-Fe_2O_3 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/cm^2 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-Fe_2O_3 powder (15 mg), organic substrate (10 mM), $[Co(NH_3)_5Cl]Cl_2$ (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 ($\lambda > 400$ nm) for 5 h. The light intensity was measured by an EAULIGHT CEL-NP2000 photometer and then adjusted to 400 mW/cm^2. 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 CH_2Cl_2 and dried with anhydrous Na_2SO_4. 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, N_2 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_2O_3 powder (15 mg), and $[Co(NH_3)_5Cl]Cl_2$ (5 mM) was irradiated for 15 min at 25 °C (λ > 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 (RHE) = E (Ag/AgCl) + 0.20 V + 0.059 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).

$$\mathrm{FE}(\%) = \frac{n_{(\mathrm{product})}}{\left(\frac{Q/2}{96485}\right)} \times 100\,\% \qquad \text{(S1)}$$

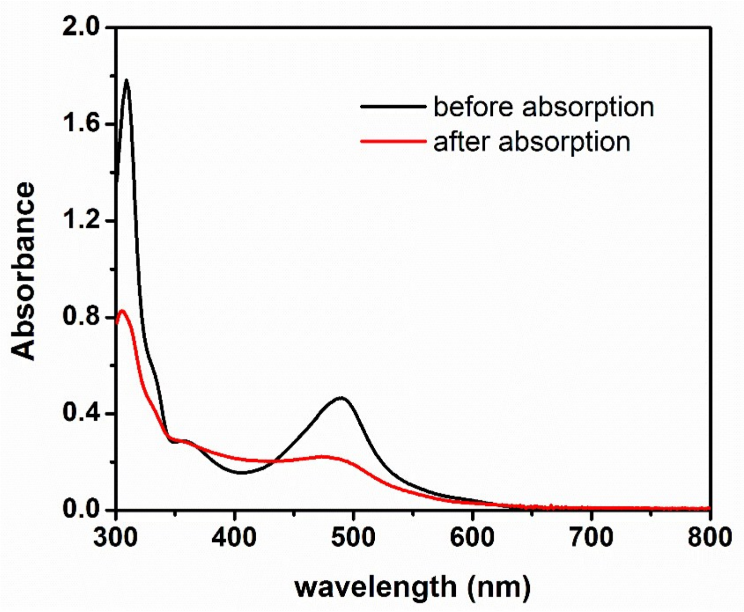


Figure S9 UV-vis spectra of 0.2 mM **Ru2** solution in methanol before (black) and after (red) stirred with α-Fe_2O_3 particles. According to the change of the spectra, the loading of **Ru2** was evaluated to be 6.58×10^{-8}mol / mg on α-Fe_2O_3 particles.

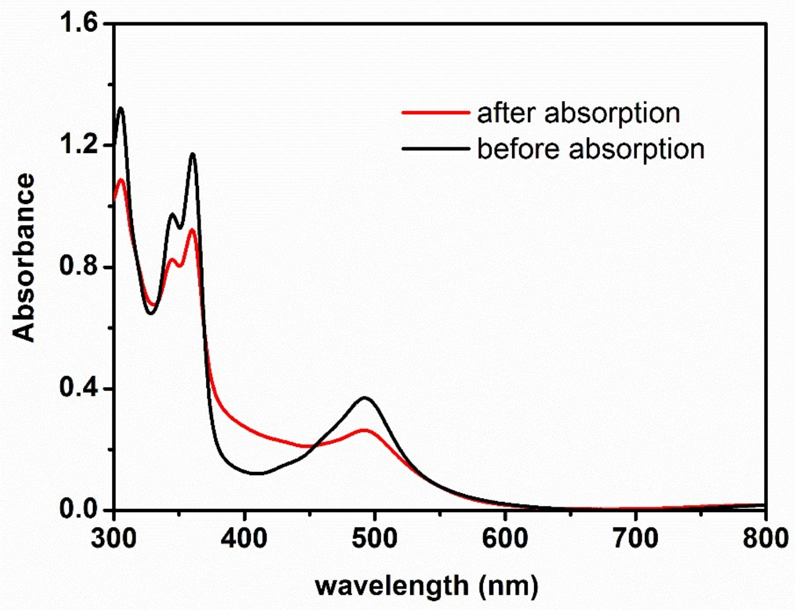


Figure S10 UV-vis spectra of 0.2 mM **Ru4** solution in methanol before (black) and after (red) stirred with α-Fe_2O_3 particles. According to the change of the spectra, the loading of **Ru4** was evaluated to be 3.23×10^{-8} mol/mg on α-Fe_2O_3 particles.

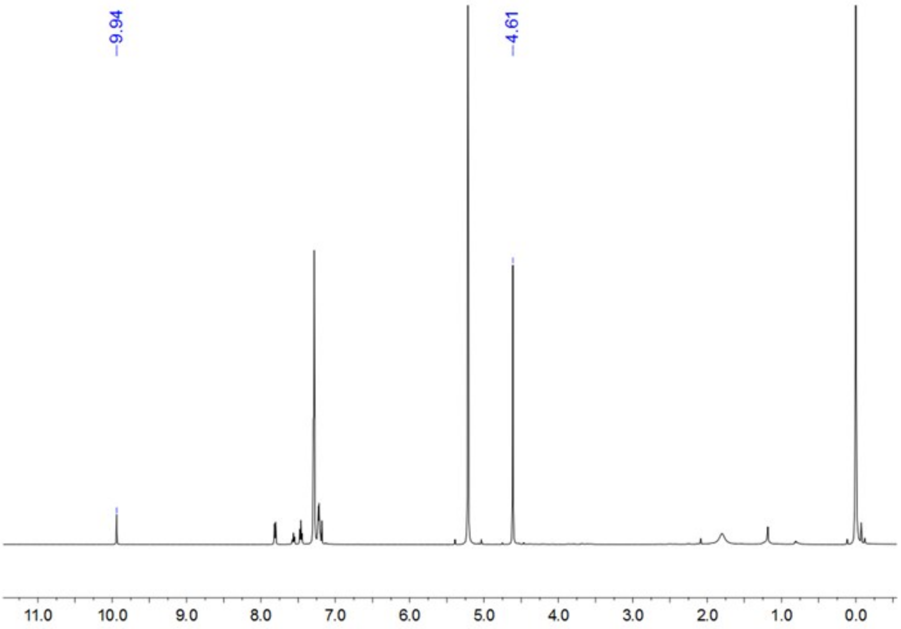


Figure S11 ^{1}H NMR spectrum of the residue extracted by DCM from the resulted solution of photocatalytic dehydrogenation of benzyl alcohol (solvent $CDCl_3$), the marked values of chemical shift represent methylene of benzyl alcohol (4.61) and aldehyde of benzaldehyde (9.94), respectively. Reaction conditions: **Ru4** modified Fe_2O_3 (15 mg), benzyl alcohol (10 mM), and $[Co(NH_3)_5Cl]Cl_2$ (20 mM) in a 0.1 M (pH 4.7) phosphate buffer solution irradiated under visible light for 5 h.

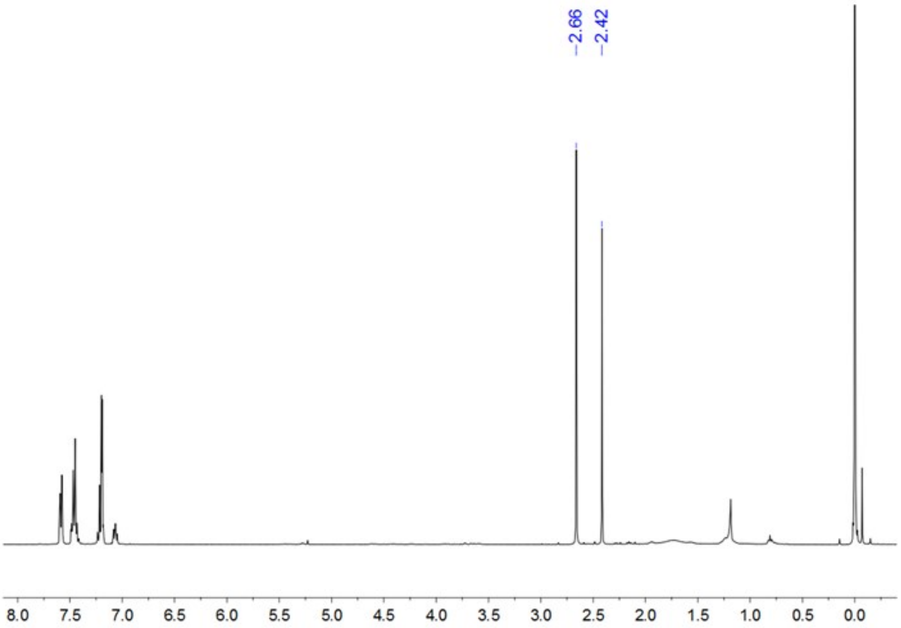
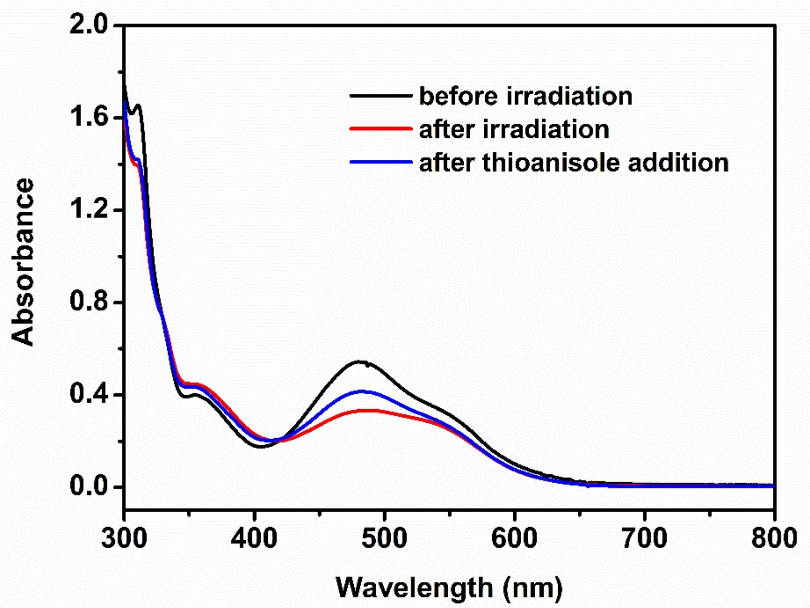
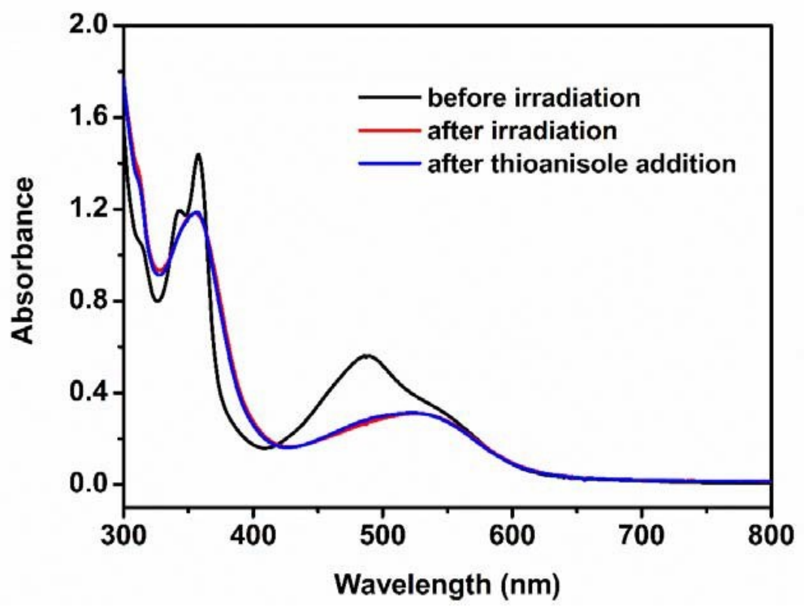


Figure S12 ^{1}H NMR spectrum of the residue extracted by DCM from the resulted solution of photocatalytic oxygenation of thioanisole (solvent $CDCl_3$), the marked values of chemical shift represent methyl of thioanisole (2.42) and benzyl methyl sulfoxide (2.66), respectively. Reaction conditions: **Ru1** (9.87×10^{-7} mol), Fe_2O_3 (15 mg), thioanisole (10 mM), and $[Co(NH_3)_5Cl]Cl_2$ (20 mM) in a 0.1 M (pH 4.7) phosphate buffer solution irradiated under visible light for 5 h.



FigureS13 UV-vis spectra of 0.1 M phosphate buffer (pH 4.7) containing 0.04 mM **Ru1** and 5 mM $[Co(NH_3)_5Cl]Cl_2$ 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.



FigureS14 UV-vis spectra of 0.1 M phosphate buffer (pH 4.7) containing 0.04 mM **Ru3** and 5 mM $[Co(NH_3)_5Cl]Cl_2$ 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.

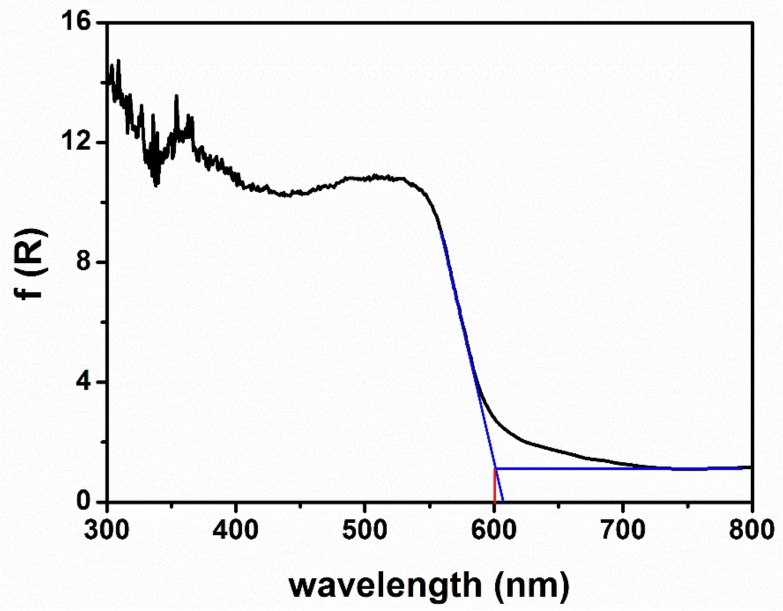


Figure S15 Kubelka-Munk function converted UV-vis diffuse reflectance spectra of Sn-doped α-Fe_2O_3 film. Kubelka-Munk function: $f(R) = (1-R)^2(2R)^{-1}$, R= reflectance. Reflectance was converted to Kubelka-Munk as f(R) versus wavelength to correct for scattering.[4]

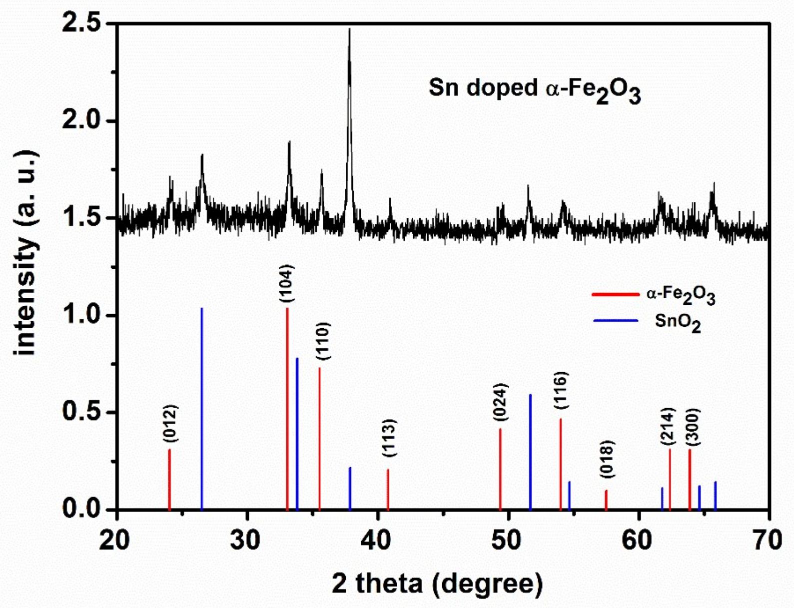


Figure S16 PXRD spectra of Sn-doped α-Fe_2O_3 film. Red and blue vertical lines highlight the diffraction peaks of α-Fe_2O_3 (JCPDS 33-0664) and SnO_2 (JCPDS 41-1445), respectively. The SnO_2 was originated from the FTO substrate.

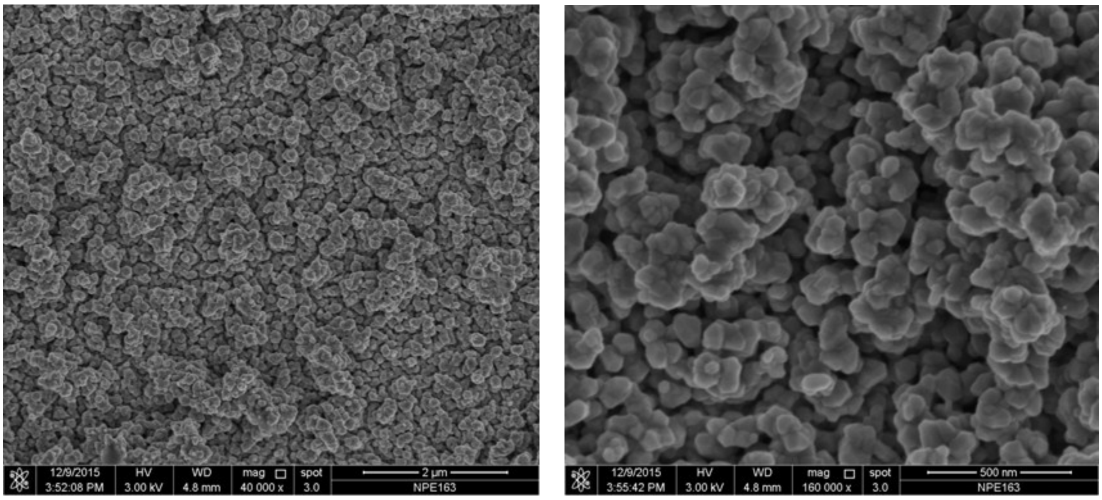


Figure S17 FE-SEM images of Sn-doped hematite sintered at 750 ℃.

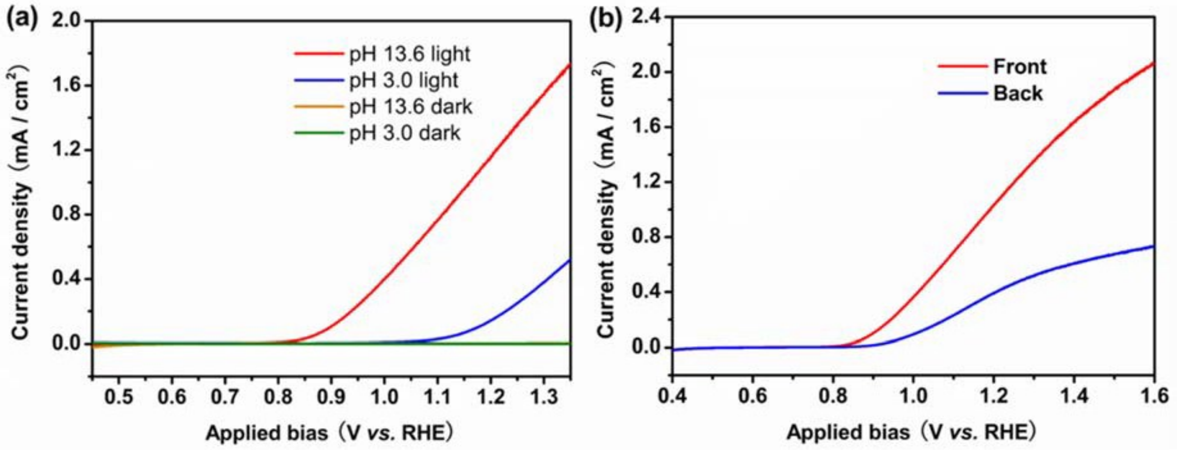


Figure S18 (a) LSVs of pristine α-Fe_2O_3 film in 1 M NaOH (pH = 13.6) and 0.05 M potassium hydrogen phthalate buffer solution containing 0.45 M $LiClO_4$ (pH = 3). The LSVs of α-Fe_2O_3 film in the dark were also shown. (b) LSVs of pristine α-Fe_2O_3 film in 1 M NaOH illuminated from front side (red) and back side (blue).

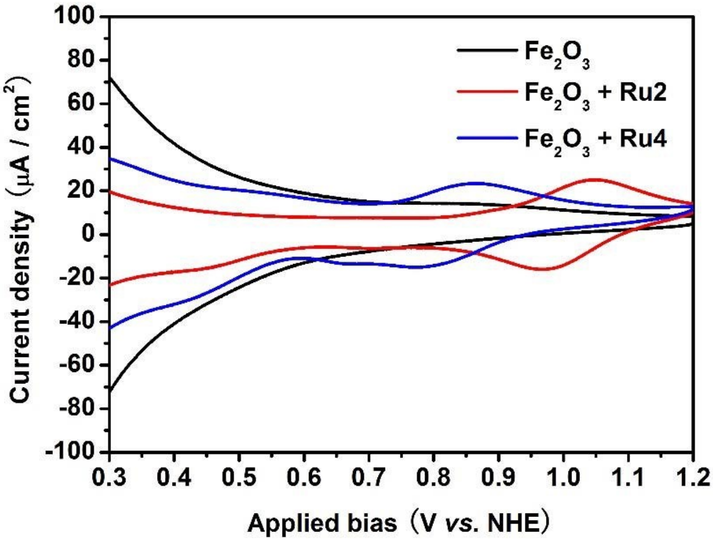


Figure S19 Cyclic Voltammograms of α-Fe_2O_3 films without (black) and with **Ru2** (red) or **Ru4** (blue) modification in pH 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.45 M $LiClO_4$. Scan rate: 10 mV/s, CE: Pt, RE: Ag/AgCl.

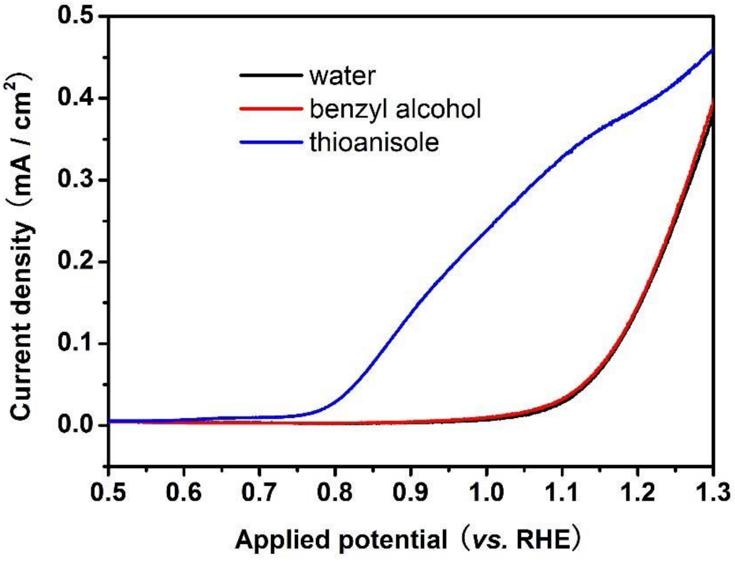


Figure S20 LSVs of pristine α-Fe_2O_3 film in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole (blue) or benzyl alcohol (red) and 0.45 M $LiClO_4$. The LSV of α-Fe_2O_3 film in the buffer solution without adding substrates (black) were also shown.

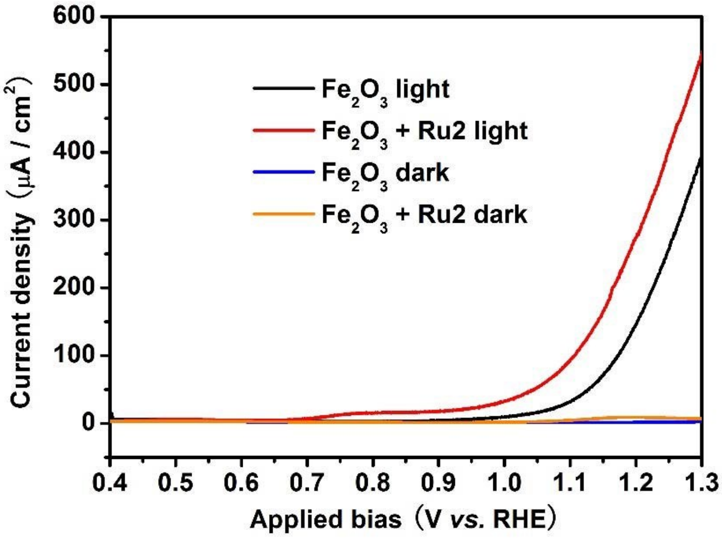


Figure S21 LSVs of α-Fe_2O_3 films with (red) and without (black) **Ru2** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M $LiClO_4$. The LSVs of α-Fe_2O_3 films with (orange) and without (blue) **Ru2** modification in the dark conditions were also shown.

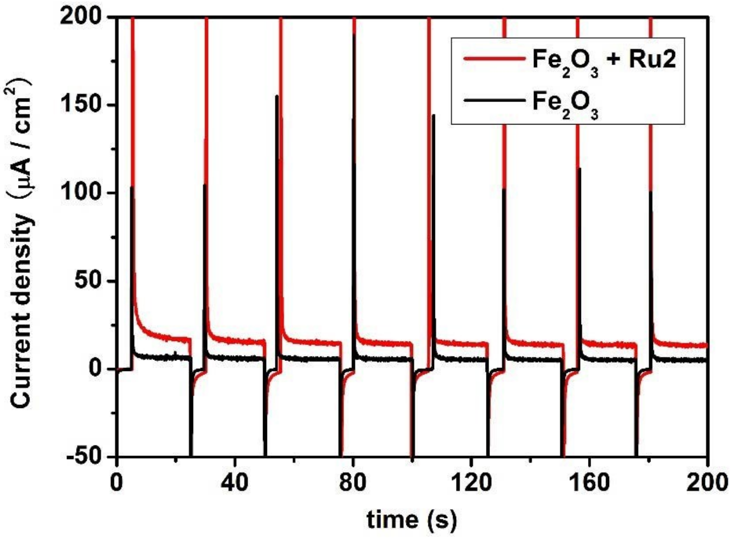


Figure S22 I-t curves of α-Fe_2O_3 films with (red) and without (black) **Ru2** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M $LiClO_4$ with chopped light.

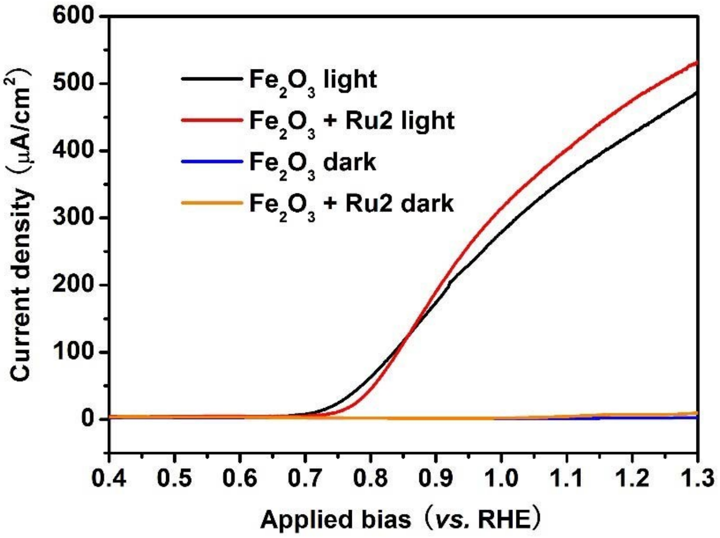


Figure S23 LSVs of α-Fe_2O_3 films with (red) and without (black) **Ru2** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanisole and 0.45 M $LiClO_4$. The LSVs of α-Fe_2O_3 films with (orange) and without (blue) **Ru2** modification in the dark conditions were also shown.

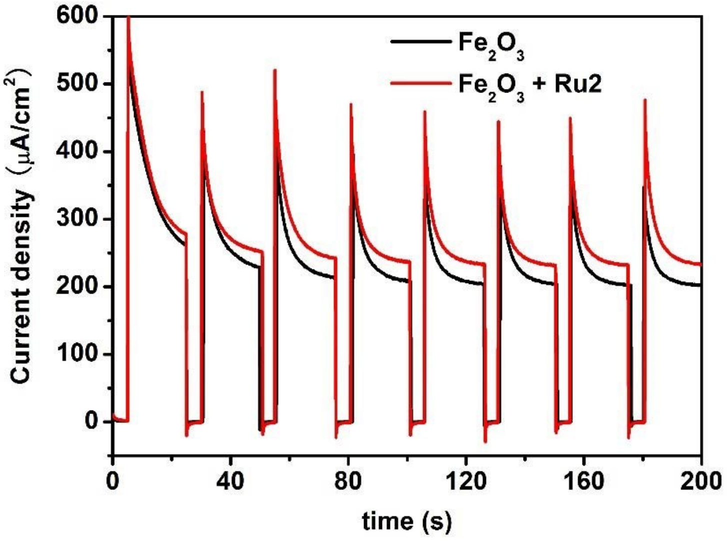


Figure S24 I-t curves of α-Fe_2O_3 films with (red) and without (black) **Ru2** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanosole and 0.45 M $LiClO_4$ with chopped light.

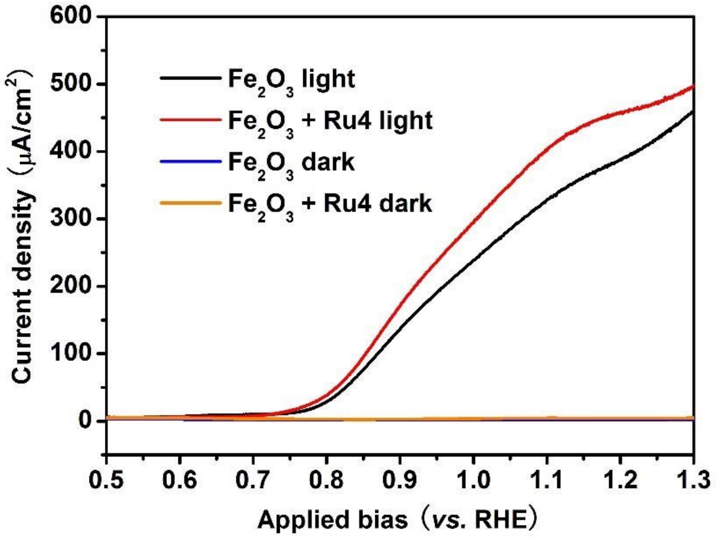


Figure S25 LSVs of α-Fe_2O_3 films with (red) and without (black) **Ru4** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M benzyl alcohol and 0.45 M $LiClO_4$. The LSVs of α-Fe_2O_3 films with (orange) and without (blue) **Ru4** modification in the dark conditions were also shown.

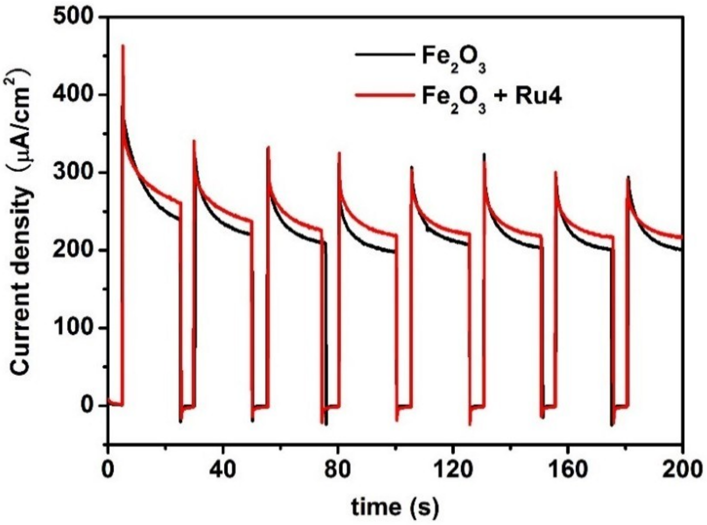


Figure S26 I-t curves of α-Fe_2O_3 films with (red) and without (black) **Ru4** modification in pH = 3 0.05 M potassium hydrogen phthalate buffer solution containing 0.02 M thioanosole and 0.45 M $LiClO_4$ with chopped light.

TableS1 Products distribution for the oxidation of thioanisole[a]

Entry	Catalysts	Benzyl methyl sulfoxide (μmol/yield)[b]	Benzyl methyl sulphone (μmol/yield)	CO_2 (μmol/yield)	O_2 (μmol/yield)[c]
1	α-Fe_2O_3	0.8/0.8 %	-	-	0.9/1.8 %
2	α-Fe_2O_3/**Ru1**	64.7/64.7 %	-	-	0.4/0.8 %
3	α-Fe_2O_3/**Ru2**	99.1/99.1 %	-	-	0.3/0.6 %
4	α-Fe_2O_3/**Ru3**	17.6/17.6 %	-	-	0.4/0.8 %
5	α-Fe_2O_3/**Ru4**	31.6/31.6 %	-	-	0.4/0.8 %

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).

TableS2 Products distribution for the oxidation of benzyl alcohol[a]

Entry	Catalysts	Benzaldehyde (μmol/yield)[b]	Benzoic acid (μmol/yield)	CO_2 (μmol/yield)	O_2 (μmol/yield)[c]
1	α-Fe_2O_3	2.0/2.0 %	-	-	0.7/1.4 %
2	α-Fe_2O_3/**Ru1**	7.5/7.5 %	-	-	0.6/1.2 %
3	α-Fe_2O_3/**Ru2**	35.2/35.2 %	-	-	0.5/1.0 %
4	α-Fe_2O_3/**Ru3**	4.9/4.9 %	-	-	0.5/1.0 %
5	α-Fe_2O_3/**Ru4**	24.9/24.9 %	-	-	0.5/1.0 %

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.

Name of product	Yield of product (μmol)	Passed charge (C)	Faradaic efficiency (%)
Benzaldehyde	1.40	0.33	82
Hydrogen	0.78	0.17	88

TableS4 Faradaic efficiency measurements for the oxidation of thioanisole using **Ru4** modified hematite.

Name of product	Yield of product (μmol)	Passed charge (C)	Faradaic efficiency (%)
Benzyl methyl sulfoxide	12.5	2.58	93
Hydrogen	8.38	1.70	95

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