

Electronic Supplementary Information for

Lignin as a quasi-homogenous electron mediator enables efficient photocatalytic H₂ evolution in molecular systems

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1. Experimental

1.1 Chemicals and materials

All chemicals were of analytical grade and used as received without further purification. Triethanolamine (TEOA, >99.8%) was purchased from Xilong Scientific. Erythrosin B (ErB, >97%) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Eosin Y (EY, >80%) was purchased from Tianjin Dingsheng Xin Chemical Co., Ltd. Rose Bengal (RB, >99.5%) was purchased from Shanghai Zhongqin Chemical Reagent Co., Ltd. Lignosulfonate (LS, $\geq 98\%$, $M_w=4347$, $M_n=3542$, $M_w/M_n=1.227$) was purchased from Hefei Qiansheng Biotechnology and used without any supplementary treatments (for example, filtering off insoluble residues of the lignin). $H_2PtCl_6 \cdot 6H_2O$ (99.9%), $Co(NO_3)_2 \cdot 6H_2O$ (99%), and $Ni(NO_3)_2 \cdot 6H_2O$ (98%) were purchased from Shanghai Titan Scientific Co. Ltd. $FeSO_4 \cdot 7H_2O$ (99%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Commercial Pt/C (20 wt.% Pt, average size of Pt: 3~5 nm) catalyst was purchased from Alfa Aesar (Shanghai, China). All solutions used throughout the experiments were prepared with ultrapure water (18.2 M Ω cm).

1.2 Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken with a FEI Talos F200x field emission transmission electron microscope. X-ray diffraction (XRD) measurements were performed on a Rigaku Smartlab diffractometer using a nickel filtrated Cu *K* α radiation source at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using a monochromatic Al *K* α X-ray source (1486.6 eV). The binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp^2 hybridized (C=C) carbon from the sample. The weight-average

(M_w) and number-average (M_n) molecular weights of the LS were measured with a gel permeation chromatography (Agilent 1260 Infinity II). Photoluminescence (PL) spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. Fourier transform infrared spectroscopy (FTIR) spectra of the samples were collected by using a Thermo Nicolet Avatar 380 FT-IR spectrometer. UV-vis absorption spectra were taken with a Thermo Scientific Evolution 220 spectrophotometer.

1.3 Photocatalytic H₂ evolution experiments

Photocatalytic H₂ evolution experiments were performed in a sealed Pyrex reactor (315 mL) with a top flat quartz window (38.47 cm²) for light irradiation and a silicone rubber septum was fixed on its side for sampling the produced H₂. In a typical procedure, ErB, lignosulfonate, and a certain amount of aqueous solution containing metal salts (H₂PtCl₆·6H₂O, FeSO₄·7H₂O, Co(NO₃)₂·6H₂O, or Ni(NO₃)₂·6H₂O) were added to the reaction cell containing 100 mL of 10 vol.% TEOA (pH 8) under vigorous stirring (600 rpm). Upon mixing Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, or FeSO₄·7H₂O with TEOA solution, the Fe-, Co-, or Ni-TEOA complexes ([M(TEOA)₂]²⁺, M=Fe, Co, and Ni) can be in-situ generated and serve as the H₂ evolution catalysts.¹⁻⁵ Then, the reaction solution was thoroughly degassed by repeated evacuation-N₂ filling, and finally refilled with N₂ to reach ambient pressure. After that, the reaction solution was irradiated by a 30-W white LED lamp equipped with a 420 nm cut-off filter. During the reaction, the mixture solution was continuously stirred (300 rpm) and it was noted that the temperature of the solution during photocatalytic HER processes increased from room temperature (24 °C) to 37 °C after 1 h irradiation and then keeps unchanged afterward. The amount of H₂ produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column,

and with N₂ as carrying gas.

1.4 UPS analysis

Ultraviolet photoelectron spectrum (UPS) of LS was measured by Thermo Scientific Escalab-250xi X-ray photoelectron spectrometer with Photon Energy of 21.2 eV (He I radiation). We estimated a work function (W) in the unit of eV (vs. vacuum) using Equation (1):

$$W = -h\nu + E_{cutoff,high} - E_F \quad (1)$$

where $h\nu$ is the energy of incident light (21.2 eV), $E_{cutoff,high}$ is the high-binding-energy cutoff, and E_F is the fermi level, which is set to be zero binding energy. A HOMO level was calculated according to Equation (2):

$$E_{HOMO} = W - (E_{cutoff,low} - E_F) \quad (2)$$

where $E_{cutoff,low}$ is the low-binding-energy cutoff. The unit conversion from eV (vs. vacuum) to V_{NHE} is in accordance with Equation (3):

$$E_{eV} = (-e) \times (E_{NHE} + 4.5 V) \quad (3)$$

2. Additional data and discussion

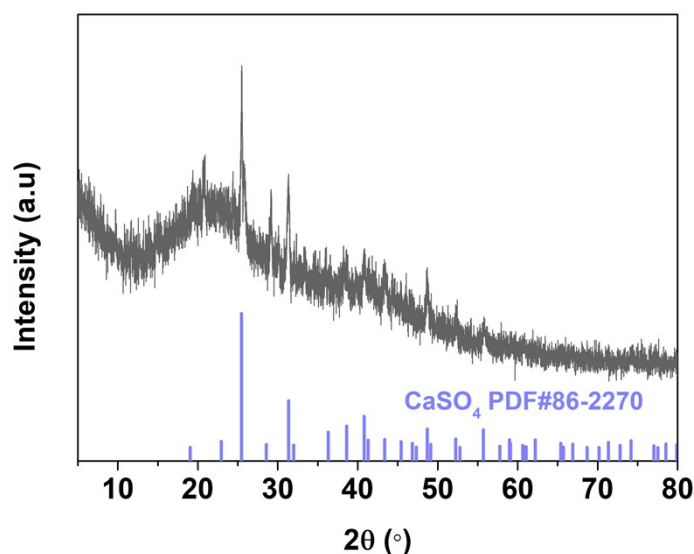


Fig. S1 XRD pattern of LS. The observed diffraction peaks can be well-indexed into the residual CaSO_4 during the production of LS *via* the calcium bisulfite process, indicating that the LS itself is in the amorphous form.

To study the possible effect of residual CaSO_4 in the LS on the photocatalytic HER performance of ErB/LS/Pt system, two control experiments were conducted. First, the same amount of commercial CaSO_4 as that in the LS was used to perform the photocatalytic HER experiments. The results showed that the presence of CaSO_4 (8.8 mg) cannot enhance even slightly reduce the HER activity of the system, suggesting that the presence of CaSO_4 can hardly affect the role of LS as an electron mediator. Second, the commercial LS was first treated with diluted H_2SO_4 (0.5 or 2 M) to remove the CaSO_4 followed by dialysis (1000 Da) to further remove the acid and soluble organic molecules. The purified LS was then used to replace commercial LS to construct the photocatalytic systems and their photocatalytic HER activities were tested under the same conditions. The results also showed that the purified LS shows a comparable similar HER activity to commercial LS, also indicating that neither the residual CaSO_4 nor the soluble impurities can play a significant role affecting the electron transfer properties of LS.

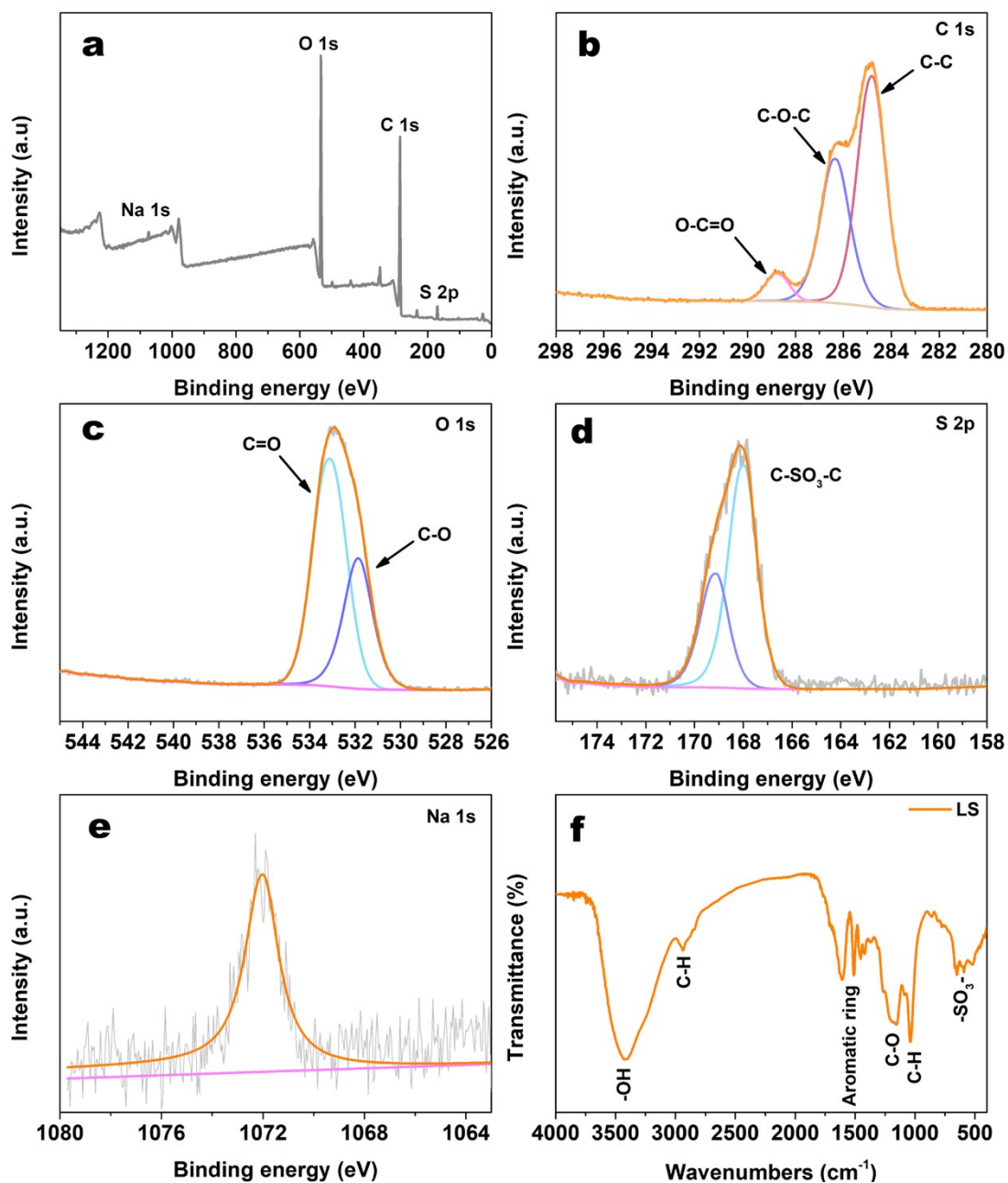


Fig. S2 (a) XPS survey spectrum of LS. (b) C 1s, (c) O 1s, (d) S 2p, and (e) Na 1s

XPS spectra of LS. (f) FTIR spectrum of LS.

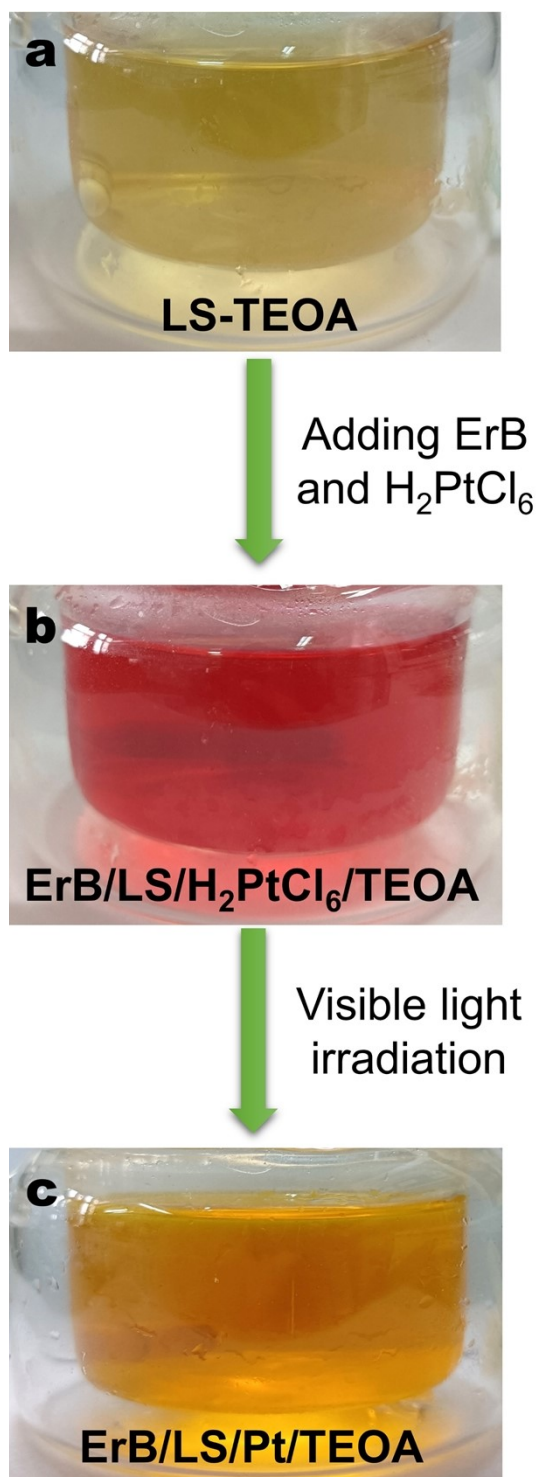


Fig. S3 Schematic diagram of the construction of ErB/LS/Pt system for photocatalytic H_2 evolution under visible light irradiation.

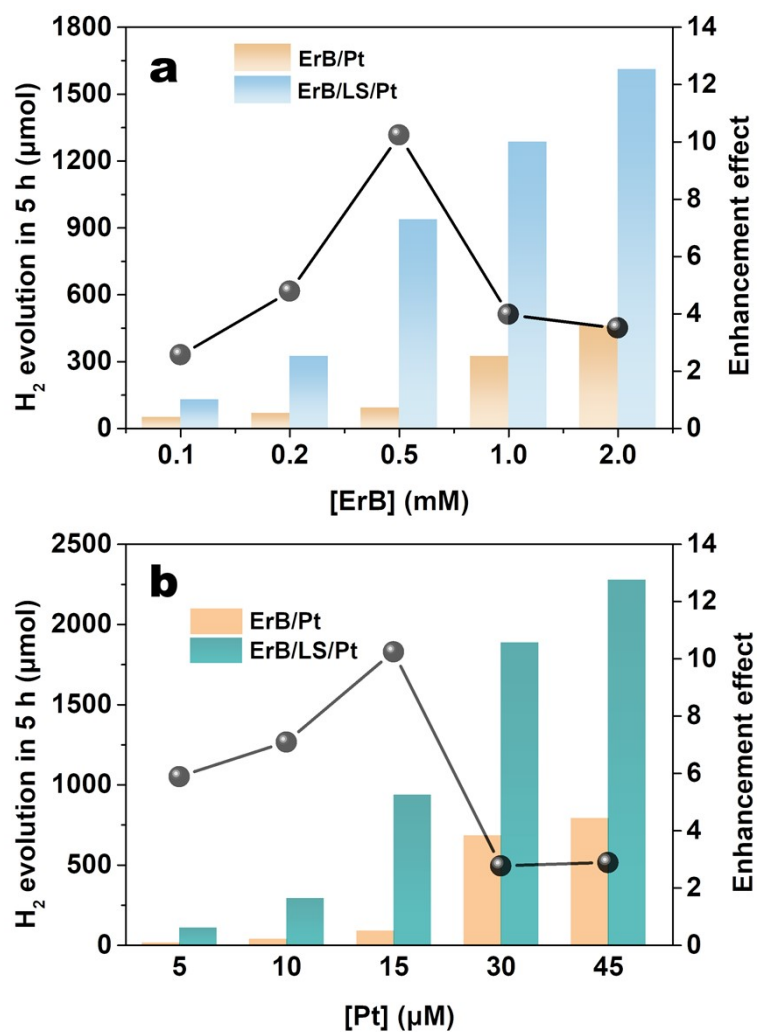


Fig. S4 Photocatalytic H₂ evolution from ErB/LS/Pt and ErB/Pt systems as a function of (a) ErB concentration (Pt: 15 μM) and (b) Pt in a 5 h reaction (ErB: 0.5 mM). Light source: 30-W white LED lamp, λ_≥420 nm; TEOA: 10 vol.%, 100 mL, pH 8; LS: 1.0 mg mL⁻¹.

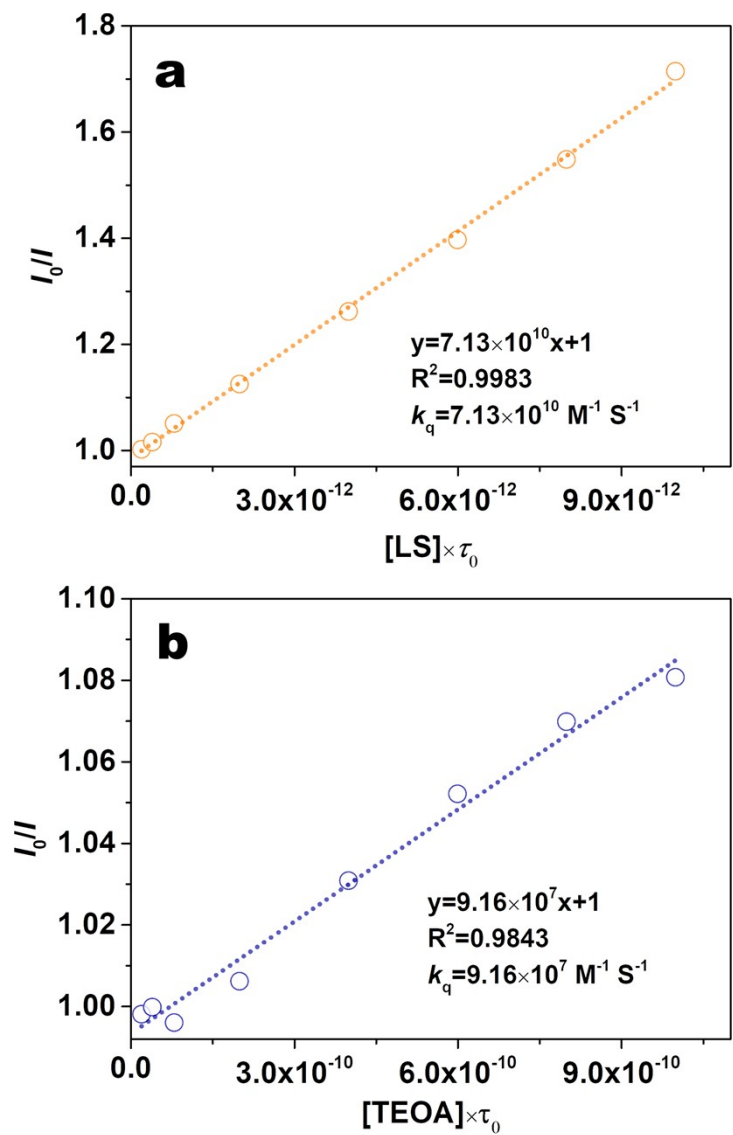


Fig. S5 Stern–Volmer plots for PL mission quenching of ErB solution (10 mM) with (a) LS and (b) TEOA ($\tau_{\text{ErB}}=0.15$ ns).

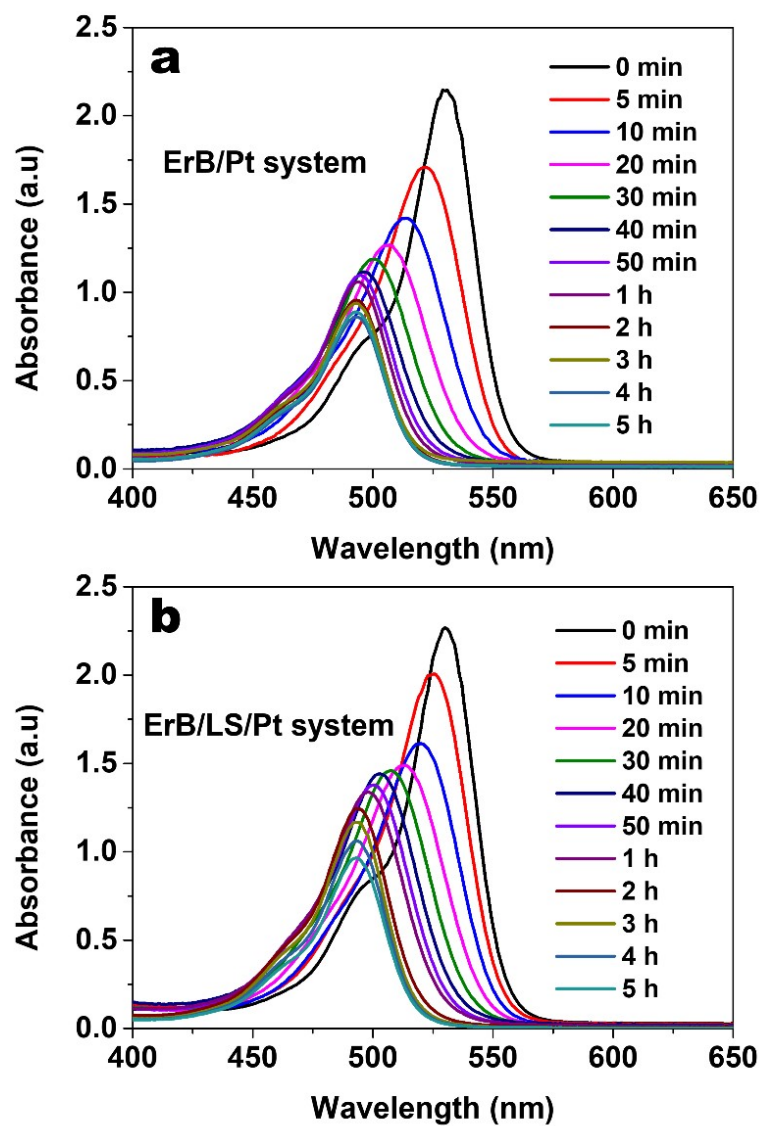


Fig. S6 UV-vis absorption spectra of (a) ErB/Pt and (b) ErB/LS/Pt reaction systems as a function of irradiation time. Prior to measurements, the reaction solution was diluted by 10 times.

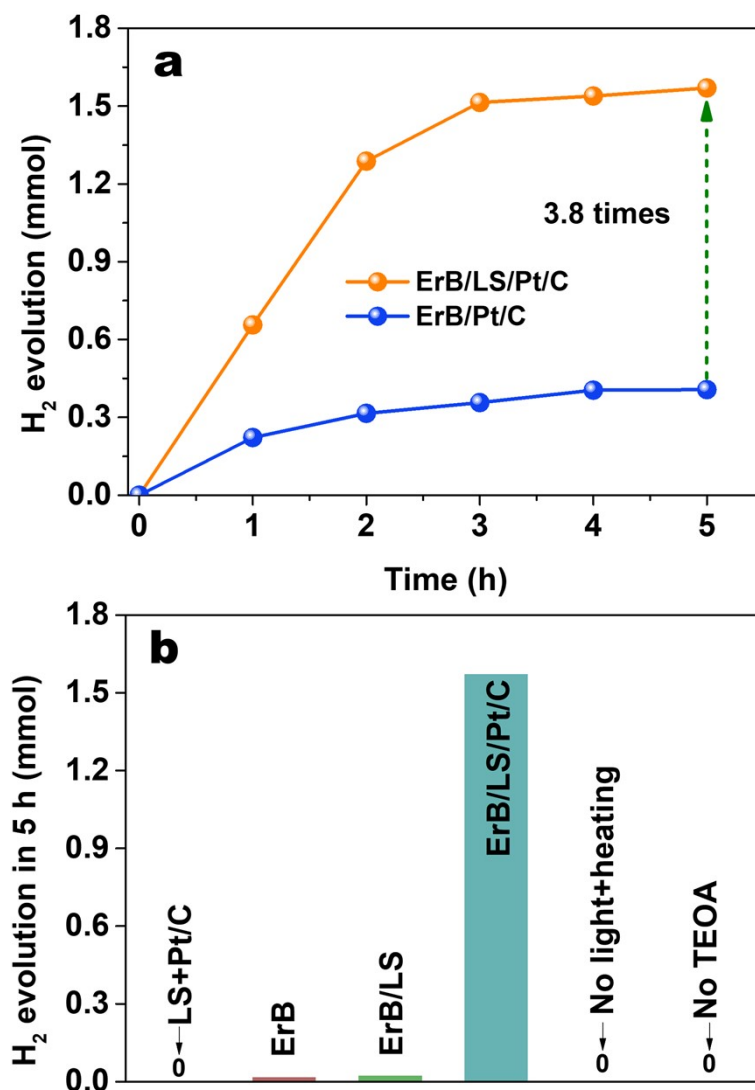


Fig. S7 (a) Time courses of photocatalytic H₂ evolution from ErB-sensitized Pt/C system with and without adding LS. (b) Photocatalytic H₂ evolution from different systems. Light source: 30-W white LED lamp, $\lambda \geq 420$ nm; ErB: 0.5 mM; Pt/C: 1.5 mg; TEOA: 10 vol.%, 100 mL, pH 8; LS: 1.0 mg mL⁻¹.

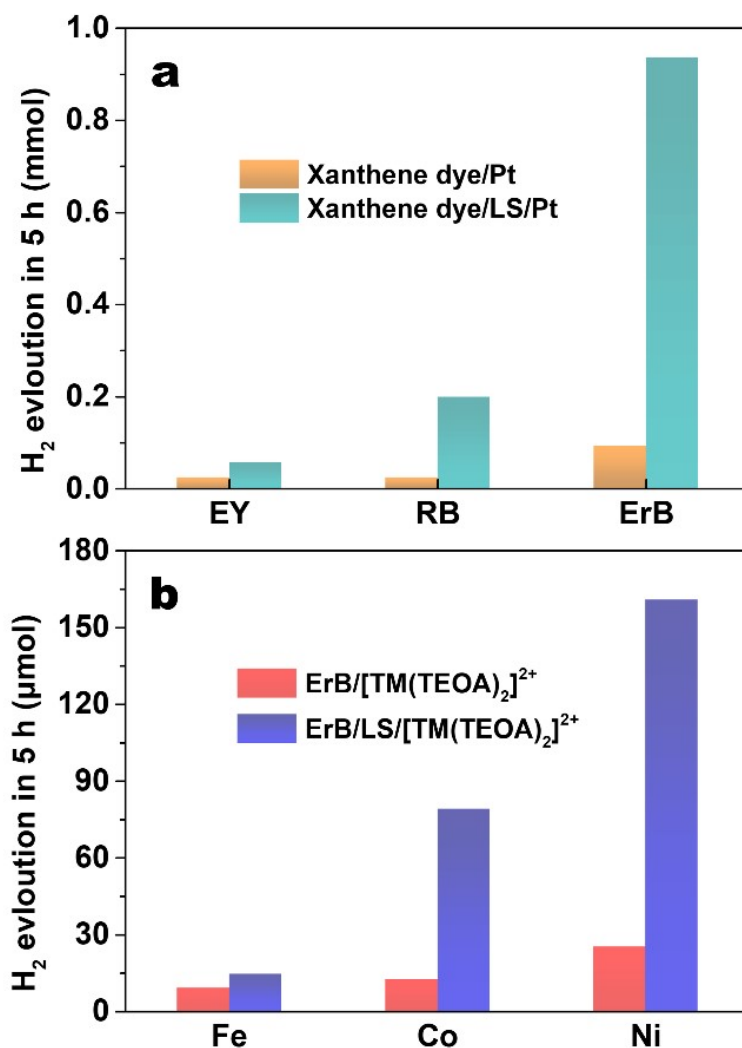


Fig. S8 (a) Photocatalytic H₂ evolution from the systems sensitized with different xanthene dyes (dye: 0.5 mM; Pt: 15 μM). (b) Photocatalytic H₂ evolution from the systems with different [TM(TEOA)₂]²⁺ complexes (ErB: 0.5 mM; TM: 15 μM). Light source: 30-W white LED lamp, λ_≥420 nm; TEOA: 10 vol%, 100 mL, pH 8; LS: 1.0 mg mL⁻¹.

References

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