

Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO₂ as a Reversible Electron Acceptor in a TiO₂—Re catalyst System for CO₂ Photoreduction

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Supporting Information

Experimental:

1. Synthesis, characterization and attachment of Re catalyst attached to TiO₂ surface: Rhenium tricarbonyl bipyridine bromide [Re^I(bpy)(CO)₃Br] with two phosphonate groups at the 4 and 4' positions in the bipyridine ring were prepared (fig. S1A) and characterized as described in reference S1.

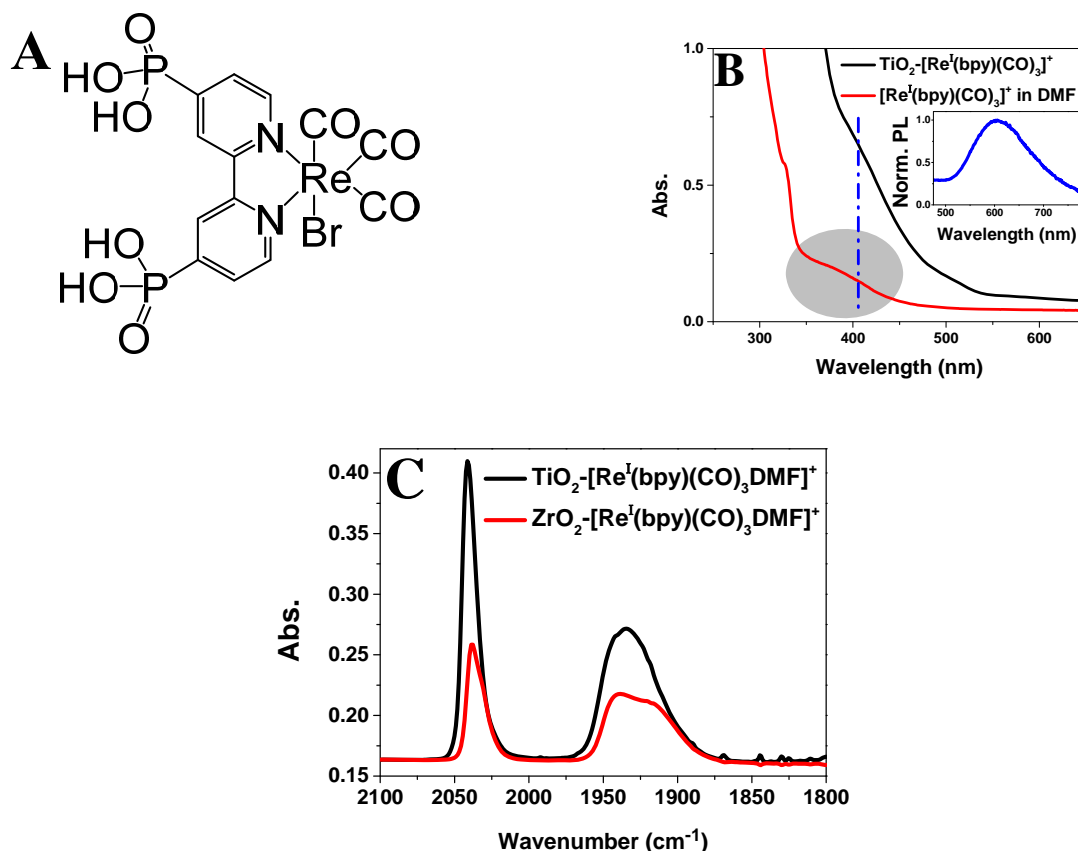


Figure S1: A) The chemical structure of [Re^I(bpy)(CO)₃Br]⁰ catalyst, B) Steady-state absorption of [Re^I(bpy)(CO)₃DMF]⁺ in DMF (solution) and attached to TiO₂ (film), inset: steady-state emission of [(bpy)Re^IBr]⁺ in DMF and C) Steady-state IR spectrum of TiO₂-[Re^I(bpy)(CO)₃DMF]⁺ film (black) and ZrO₂-[Re^I(bpy)(CO)₃DMF]⁺ film (red).

Herein we used steady-state absorption, emission and IR to characterize the catalyst and to confirm its attachment to the TiO₂ surface. 2 mg of [Re^I(bpy)(CO)₃Br]⁰ were dissolved in 10 ml DMF which was used afterwards to sensitize the TiO₂ surface. Figure S1B shows the steady-state absorption of [Re^I(bpy)(CO)₃]⁺ in DMF (solution, red curve) and attached to TiO₂ (TiO₂-[Re^I(bpy)(CO)₃DMF]⁺ film, black curve). For the samples, solution and film, the absorption spectrum maintains the shape of the ¹MLCT band at λ = 380 nm, which confirms the successful attachment of the catalyst into the surface of TiO₂. The inset of figure S1B, presents the steady-state emission of ³MLCT at 600 nm for [Re^I(bpy)(CO)₃DMF]⁺ solution. The TiO₂ films were prepared by doctor-blading technique on CaF₂ glasses followed by annealing at 450°C for one hour. Afterwards, the obtained TiO₂ films were suitable for the sensitization step. To copy the protocol used for the previous spectroscopy experiments, we followed the same procedure of making the films where the sensitization takes place in dark for 20 hours and for the illumination process we used a suitable filter to cut the light below 420 nm.

2. Electron injection from excited $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3\text{DMF}]^+$ to TiO_2 :

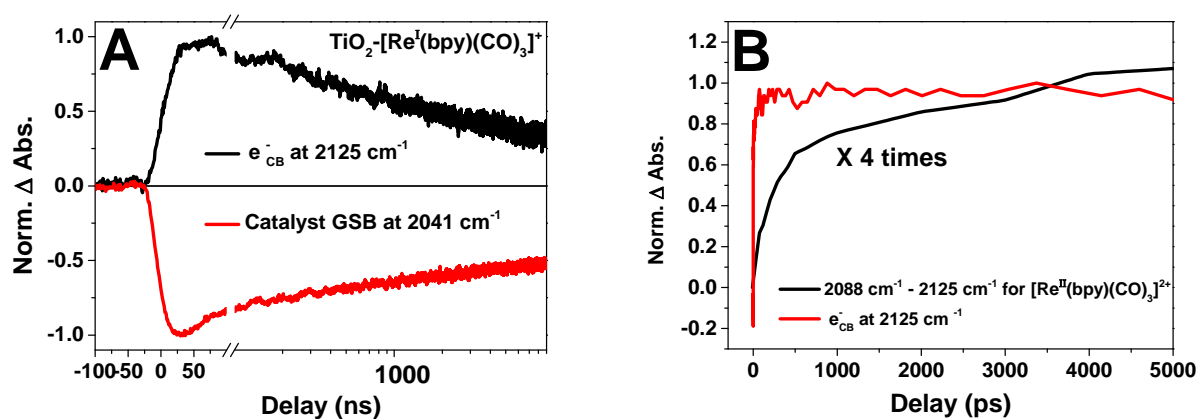


Figure S2: A) ns-TRIR for TiO_2 - $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3]^+$ sample at 2125 cm^{-1} (electron absorption) and at 2041 cm^{-1} for both catalyst GSB which dominates and the electron absorption, B) Traces of fs-TRIR for TiO_2 - $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3]^+$ sample at 2125 cm^{-1} (electron absorption) and at 2088 cm^{-1} (oxidized catalyst, $[\text{Re}^{\text{II}}(\text{bpy})(\text{CO})_3]^{2+}$).

3. The roles of TEOA in the photo-catalytic process:

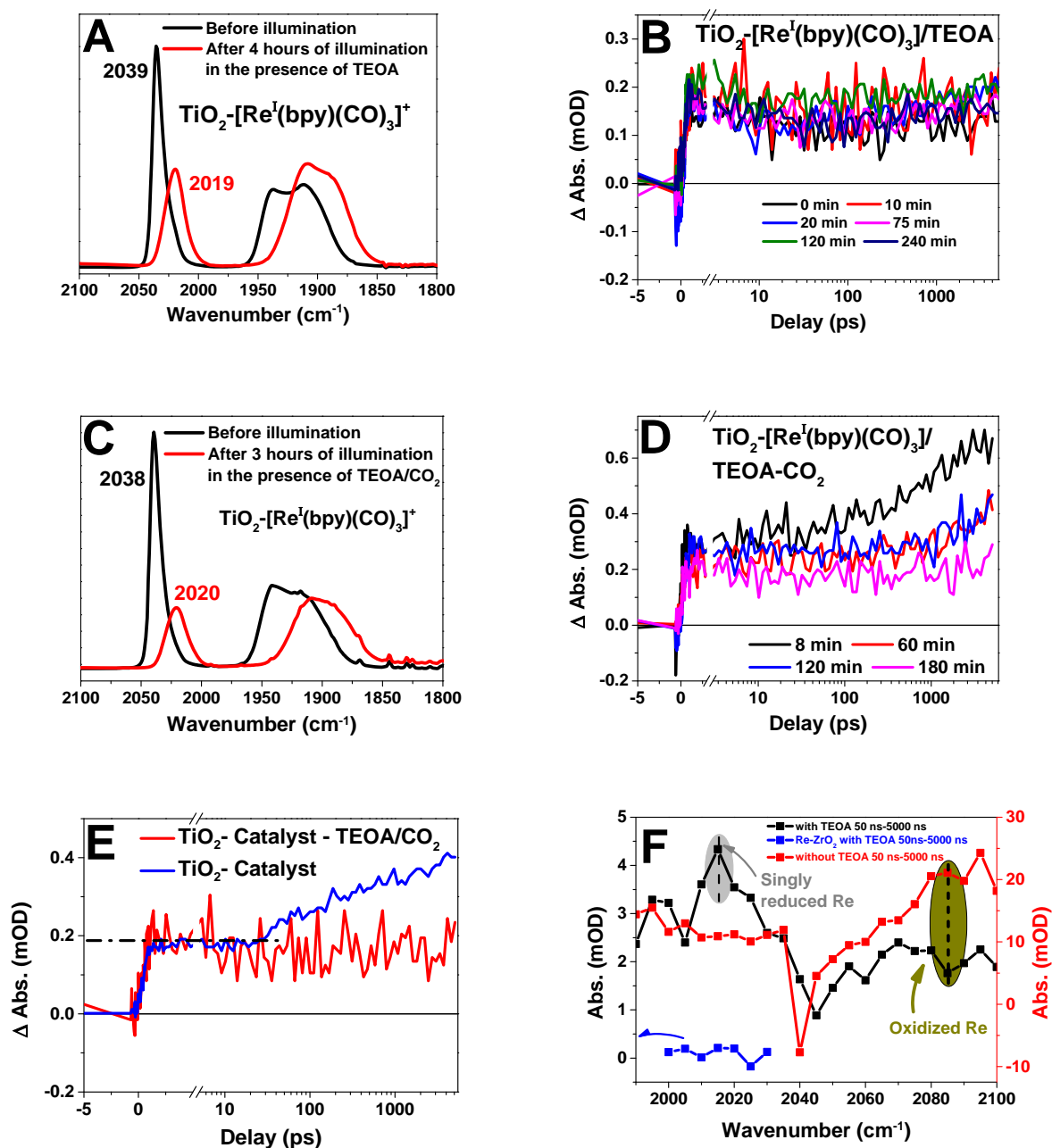


Figure S3: A) Steady-state IR for TiO_2 -[$\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3$] $^+$ in the presence of TEOA in air before and after 4 hours of illumination, B) Traces of fs-TRIR for TiO_2 -[$\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3$] $^+$ in the presence of TEOA at 2125 cm^{-1} (electron injection) at different illumination time, C) steady-state IR for TiO_2 -[$\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3$] $^+$ in the presence of TEOA/ CO_2 before and after 3 hours of illumination, D) Traces of fs-TRIR for TiO_2 -[$\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3$] $^+$ in the presence of TEOA/ CO_2 sample at 2125 cm^{-1} (electron injection) at different illumination time, E) electron injection amplitude of [$\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3$] $^+$ to the CB of TiO_2 without (blue) and with (red) TEOA/ CO_2 , and F) spectra subtraction (at 50 ns-5000 ns) showing the singly reduced Re formation in presence of TEOA/ CO_2 , the blue arrow is referring to the absorption axis of the same subtraction for the ZrO_2 -catalyst in the same condition. Based on the similarity of the red spectra in panels A and C, and supported by data in ref. S2 we believe that most of the Re complex have coordinated TEOA/ CO_2 .

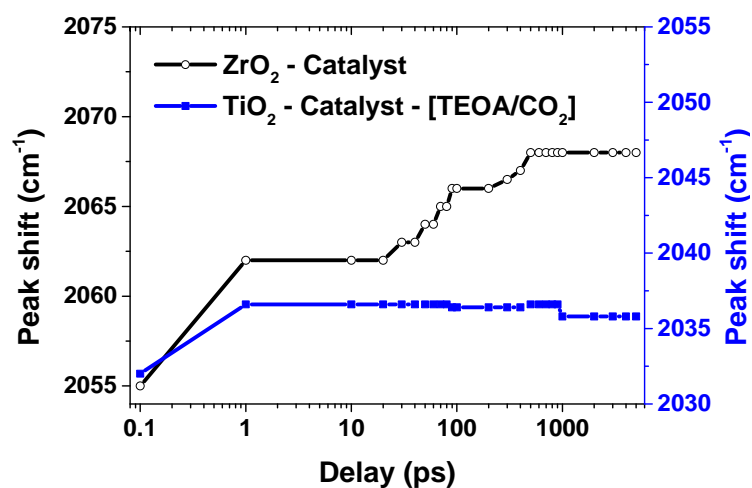


Figure S4: the excited state peak shift as a function of time delay for ZrO₂— Catalyst (black line) and for TiO₂—Catalyst-TEOA/CO₂ (blue line).

References

- (S1) Windle, C. D.; Pastor, E.; Reynal, A.; Whitwood, A. C.; Vaynzof, Y.; Durrant, J. R.; Perutz, R. N.; Reisner, E. *Chem. Eur. J.* **2015**, *21*, 3746.
 (S2) Morimoto, T.; Nakajima, T.; Sawa, S.; Nakanishi, R.; Imori, D.; Ishitani, O. *J. Am. Chem. Soc.* **2013**, *135*, 16825.