Direct time-resolved study of the interfacial reaction of metal-based catalysts in the CO_2 conversion

EMIRUM 2025

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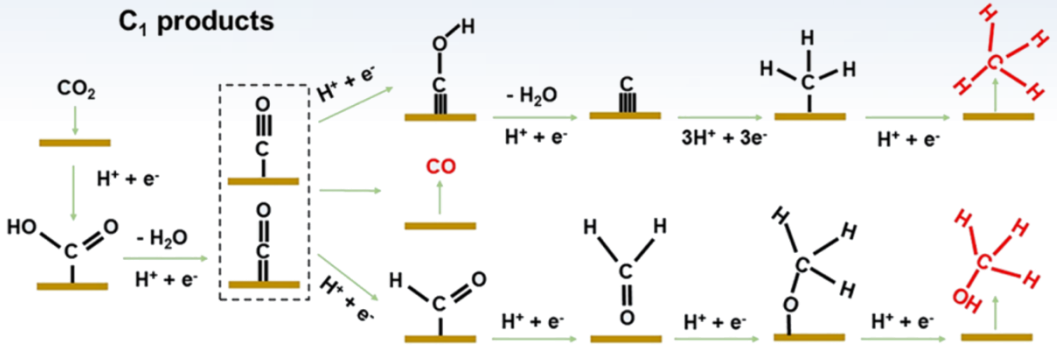
09/12/2025

Bordeaux

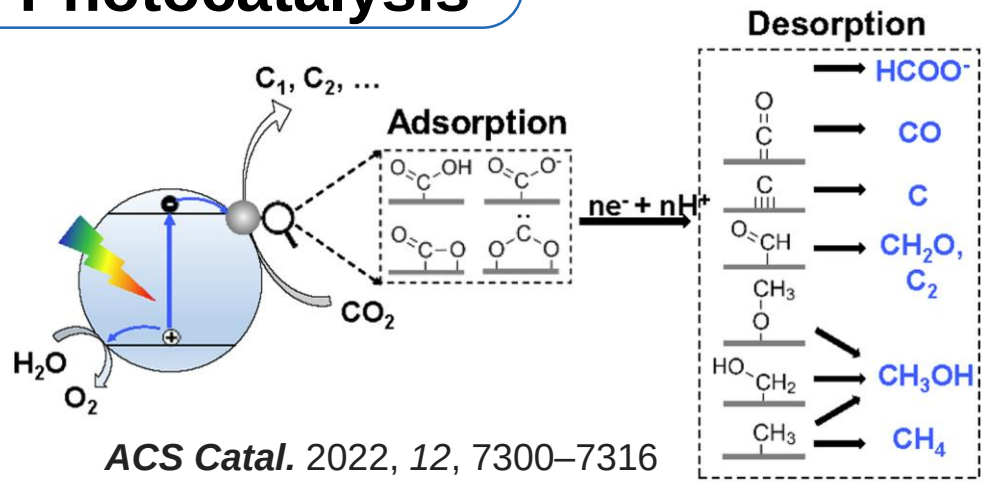
Heterogeneous Catalytic Carbon Dioxide Reduction

Electrocatalysis



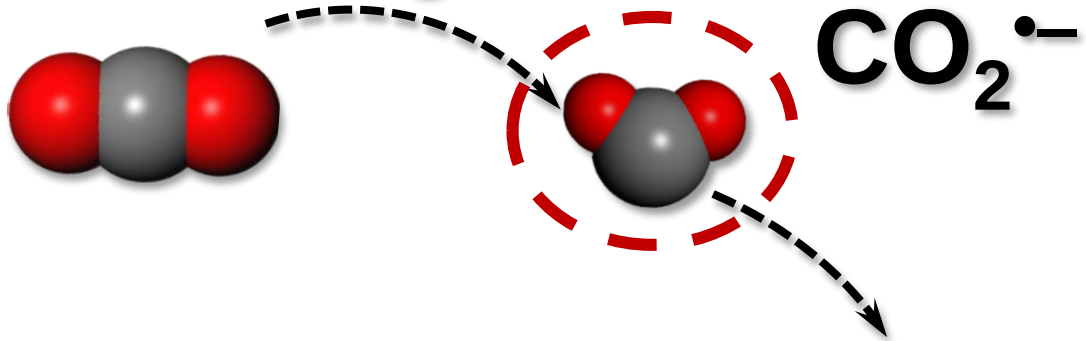
ACS **Nano** 2023, *17*, 18688−18705

Photocatalysis



ACS Catal. 2022, *12*, 7300–7316

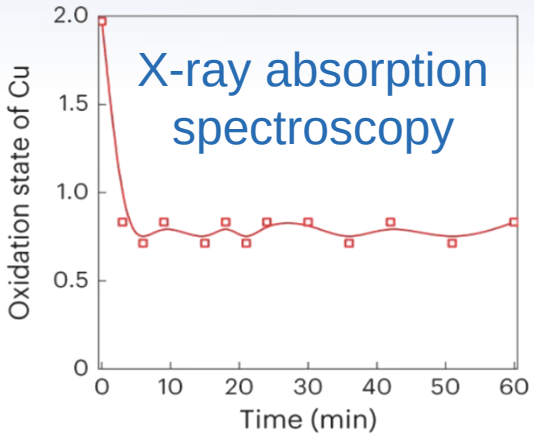
Photo-induced
Electro-induced
Radiation-induced
……

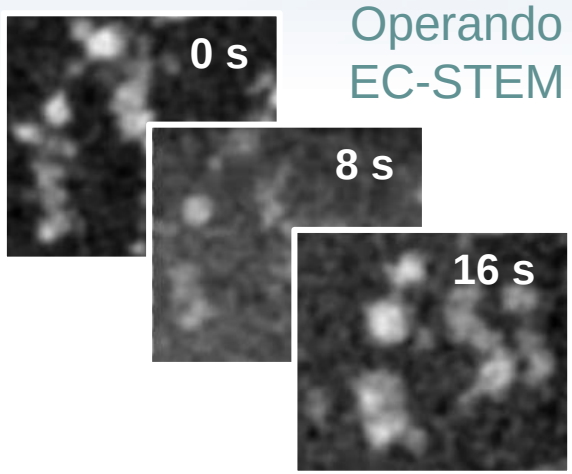


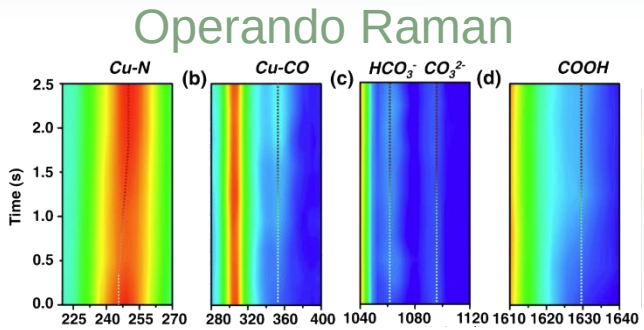
Products analysis √
Steady-state mechanism √

Elementary reaction?
Transient species?
Interfacial kinetics?

Multi-timescale interface reaction kinetics of intermediates







Nat. Catal. 2022, *5,* 1081-1088

Nature 2023, *614*, 262-269

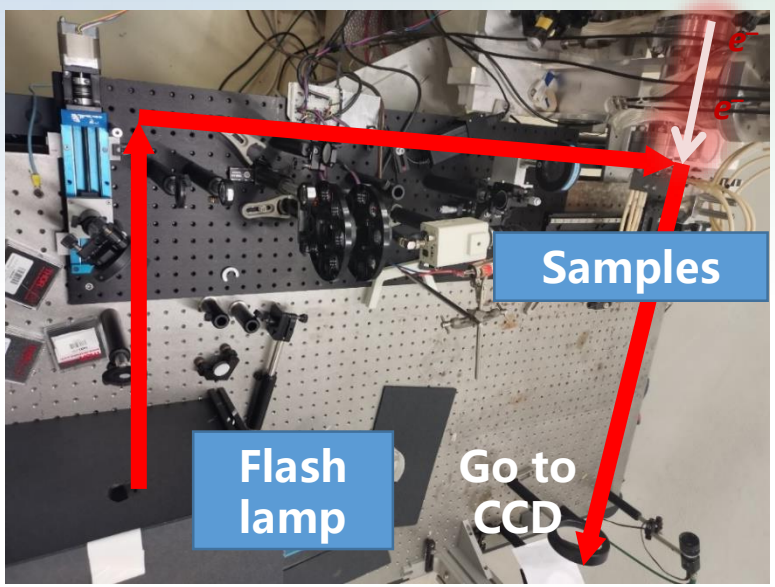
Nat. Commun. 2022, *13*, 6029

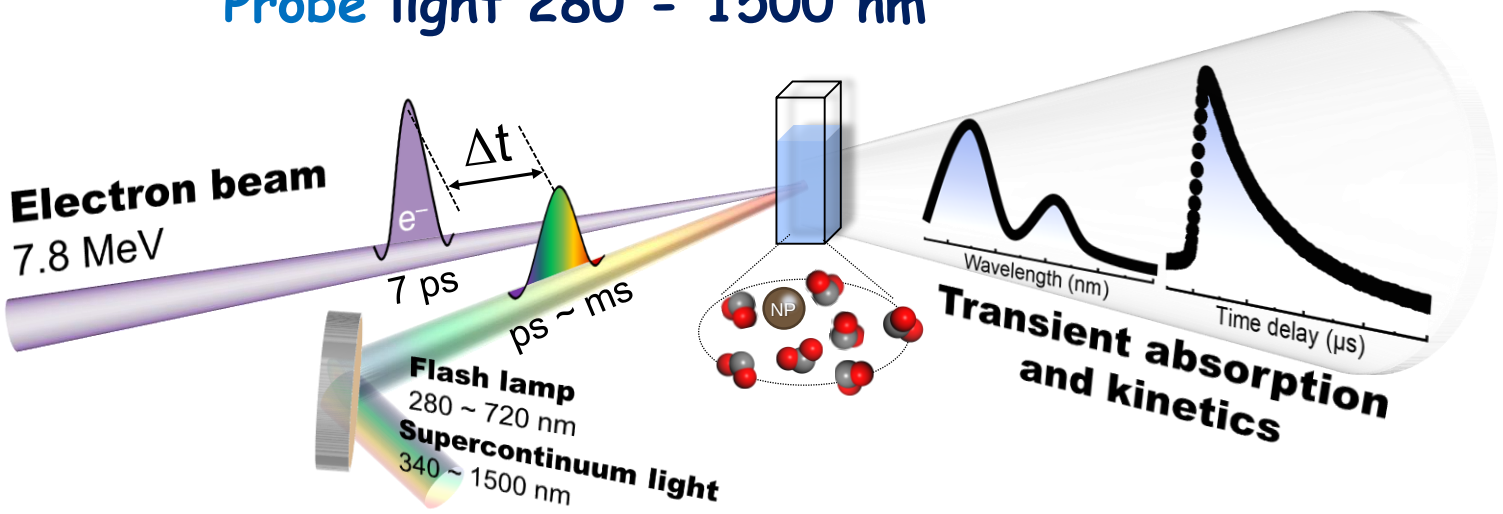
Minutes **Seconds** **Sub-seconds** **Micro- to nano-seconds**

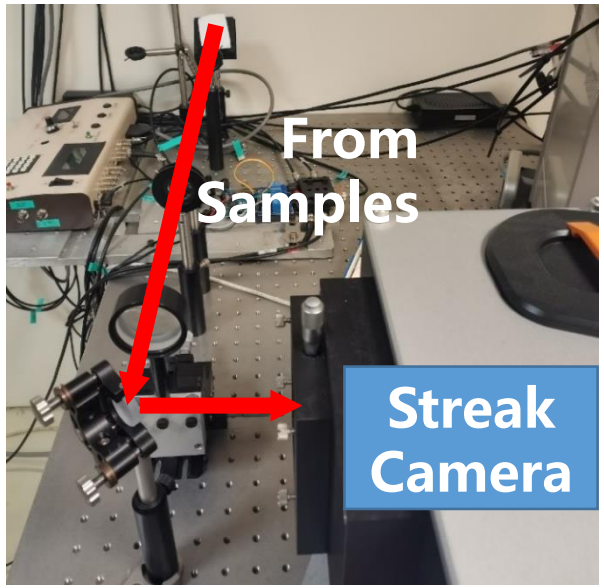
Time-resolution

Picosecond Pulse Radiolysis – ELYSE, Pulse – Probe spectroscopy

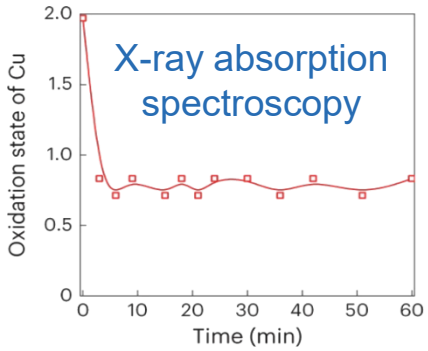
Pulse duration 4 – 15 ps
Energy 6 – 8 MeV
Charge 1 – 7 nC
Frequency 5 – 20 Hz
Probe light 280 – 1500 nm



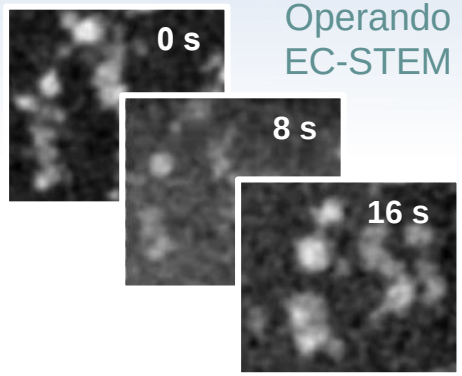




Multi-timescale interface reaction kinetics of intermediates



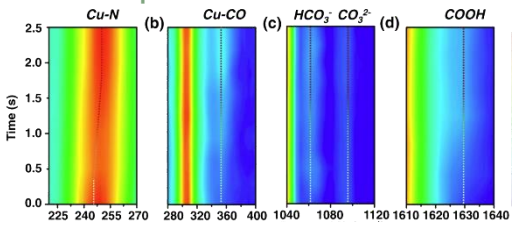
Nat. Catal. 2022, *5,* 1081-1088



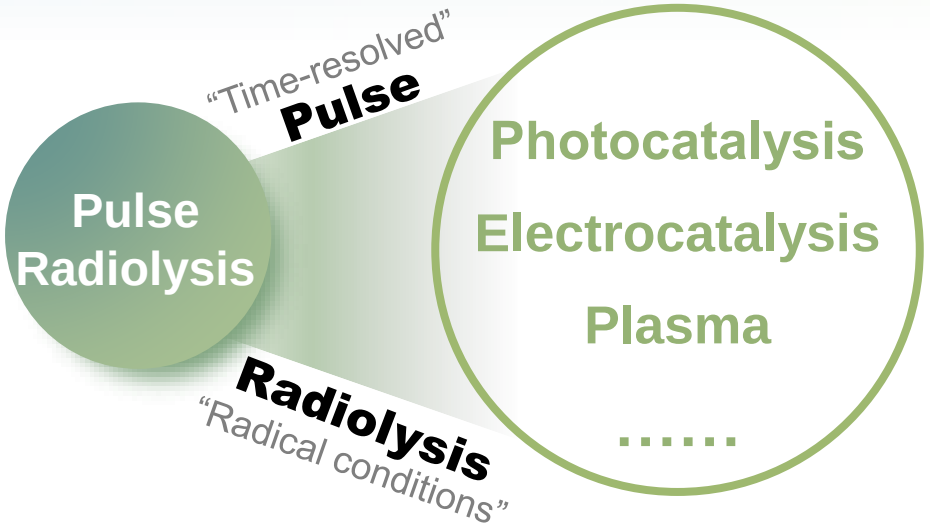
Operando EC-STEM

Nature 2023, *614*, 262-269

Operando Raman



Nat. Commun. 2022, *13*, 6029



Minutes to Sub-seconds — **Micro- to nano-seconds**

Time-resolution

Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

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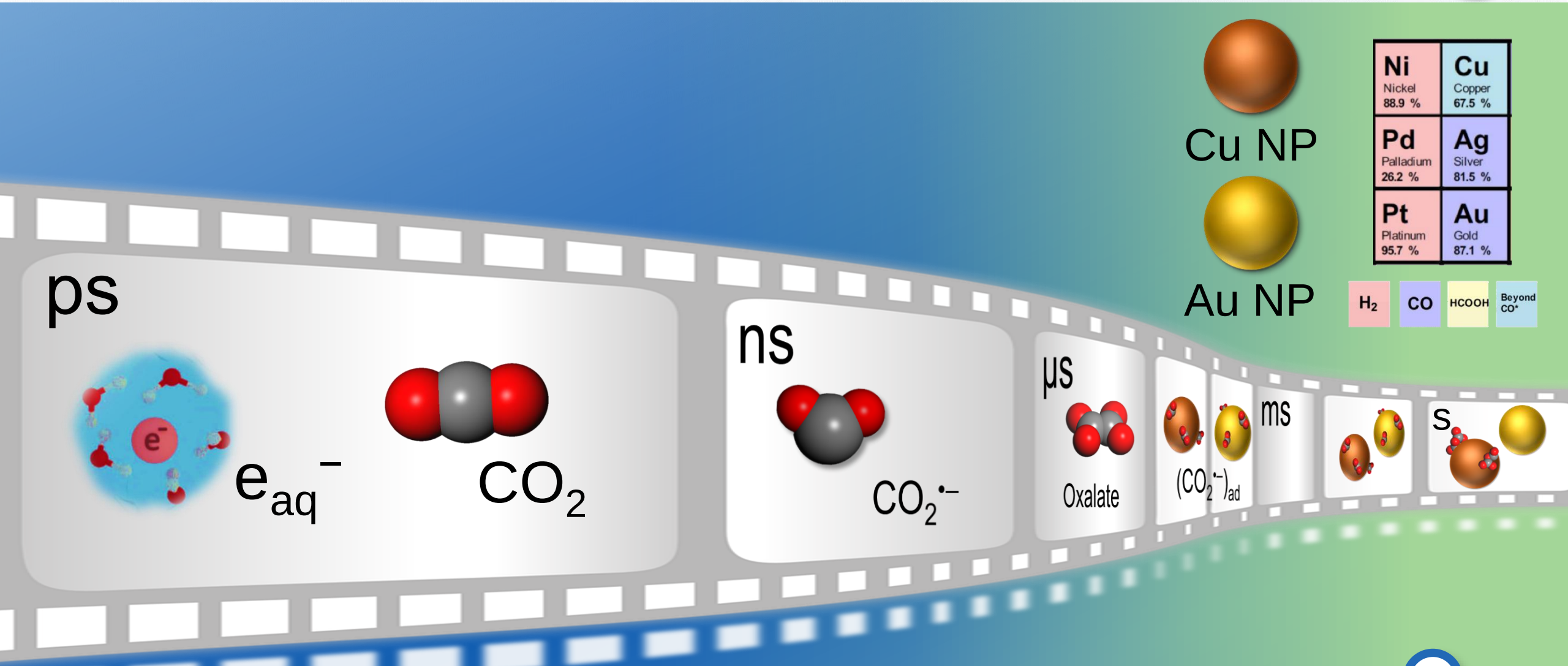
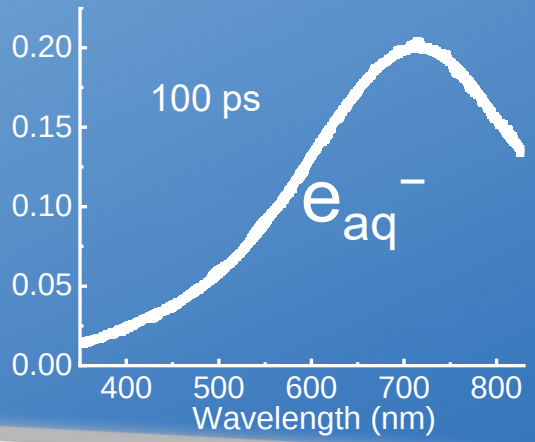
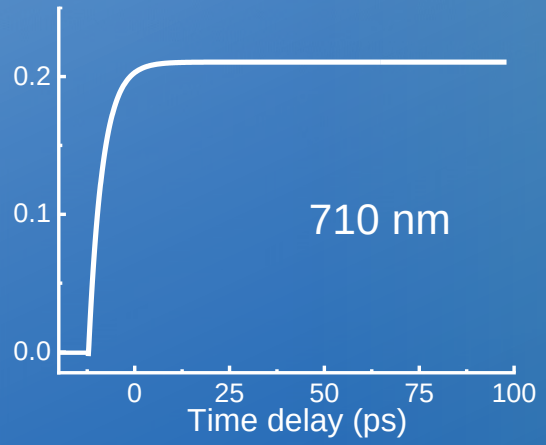


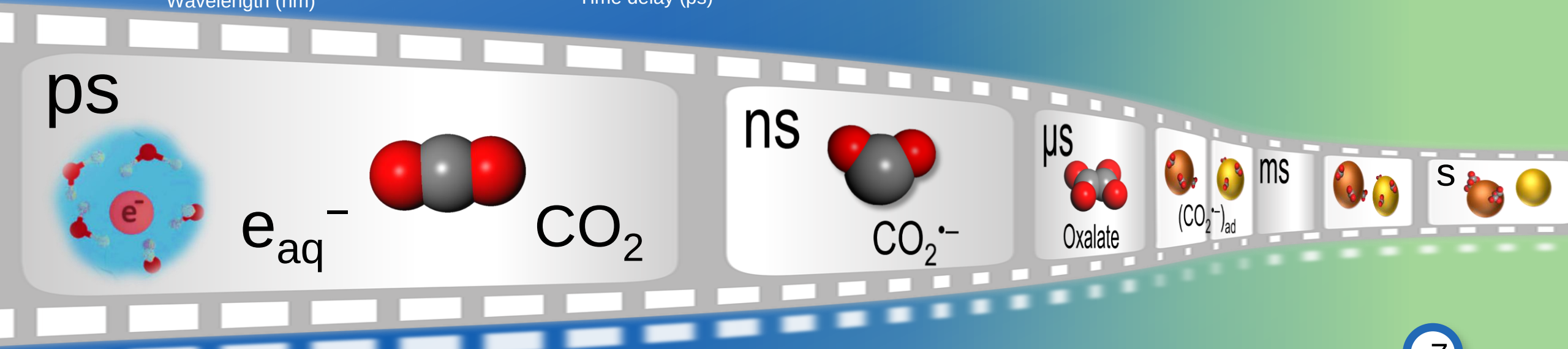
Nat. Commun., 2023, 14, 7116

Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

➢ **The formation of e_{aq}^-**







Nat. Commun., 2023, 14, 7116

Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

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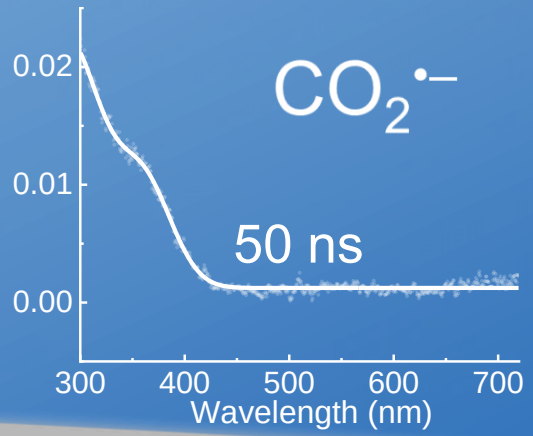
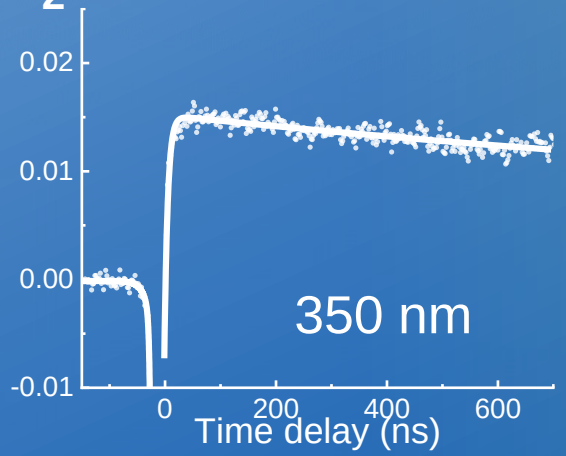
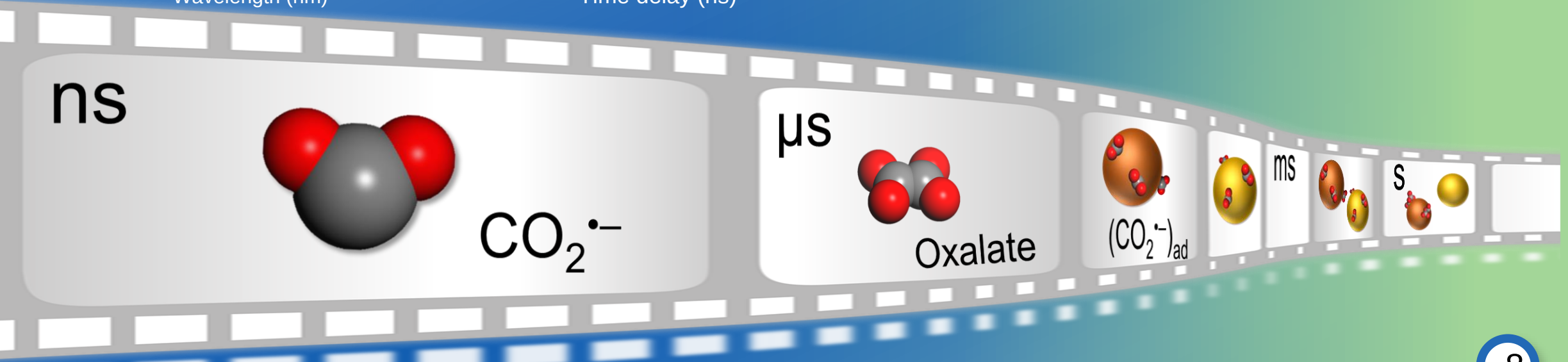
➢ The formation of $CO_2^{\bullet-}$





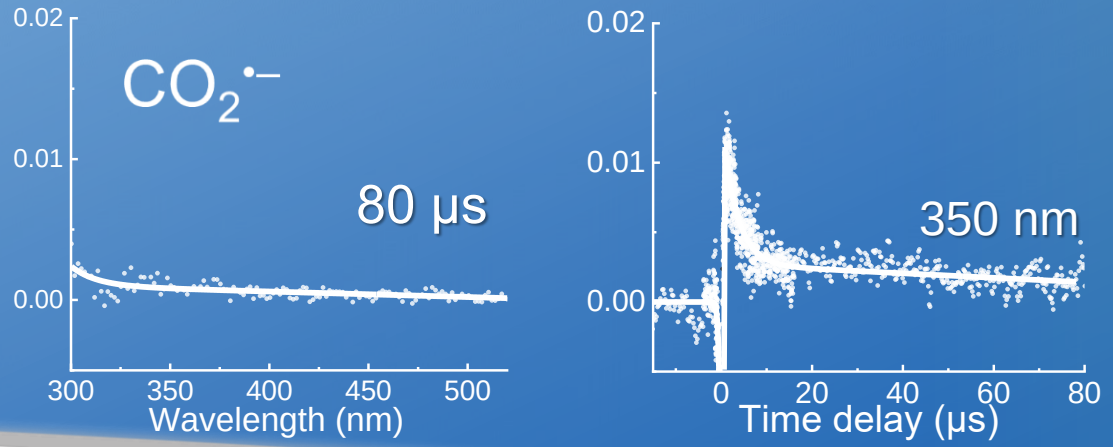
$$e_{aq}^- + CO_2 \rightarrow CO_2^{\bullet-}$$



Nat. Commun., 2023, 14, 7116

Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

➢ $CO_2^{\bullet-}$ recombination to form oxalate



$$CO_2^{\bullet-} + CO_2^{\bullet-} \rightarrow \text{Oxalate}$$

Nat. Commun., 2023, 14, 7116

Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

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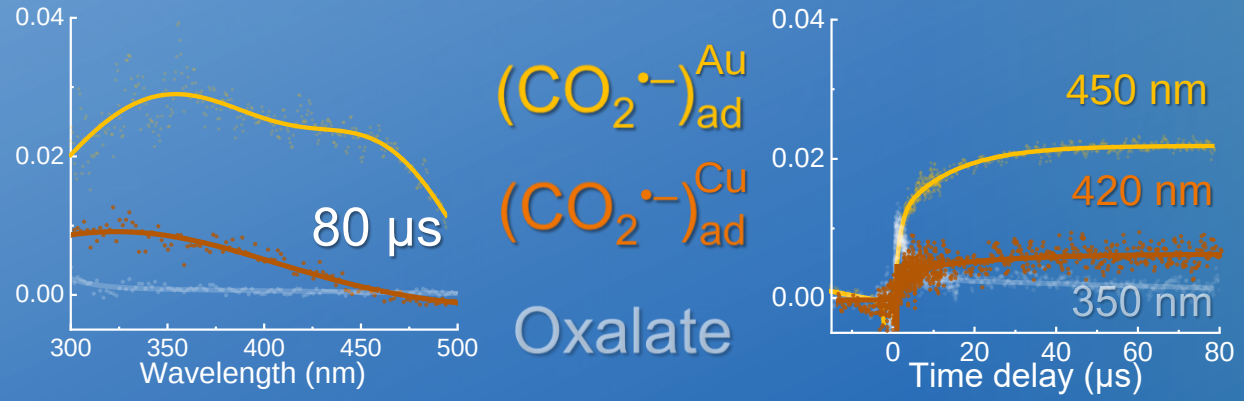
➢ The interfacial stabilization of $CO_2^{\bullet-}$ radicals

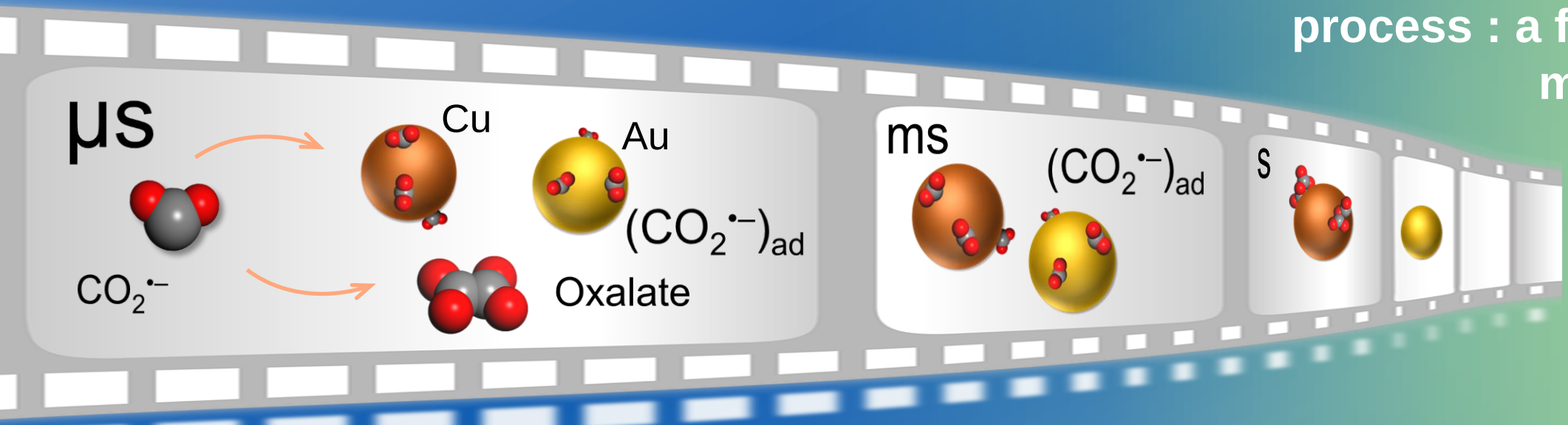


$$CO_2^{\bullet-} + Au \rightarrow (CO_2^{\bullet-})_{ad}^{Au}$$

$$CO_2^{\bullet-} + Cu \rightarrow (CO_2^{\bullet-})_{ad}^{Cu}$$

$$CO_2^{\bullet-} + CO_2^{\bullet-} \rightarrow Oxalate$$

Time-scale of surface-bound process : a few to tens of microseconds



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Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

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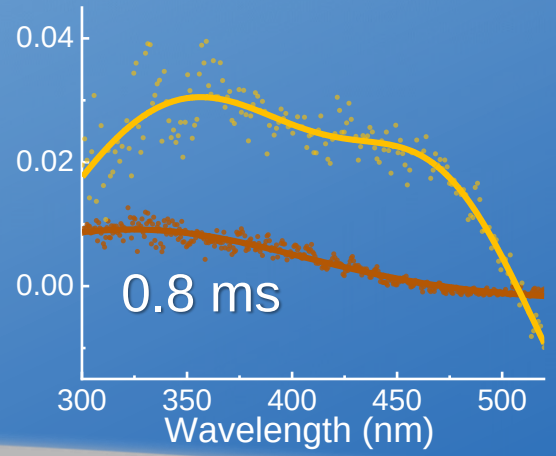
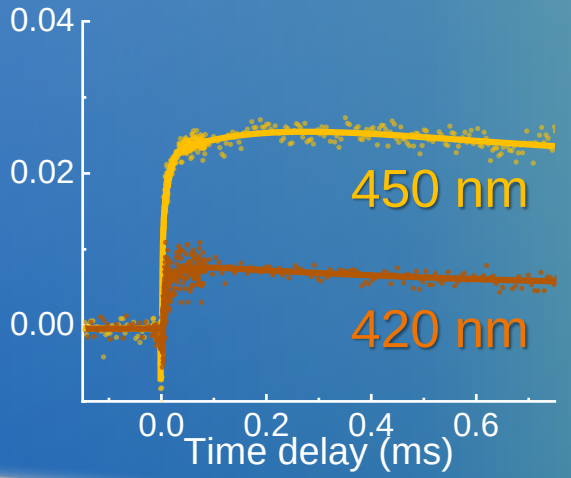
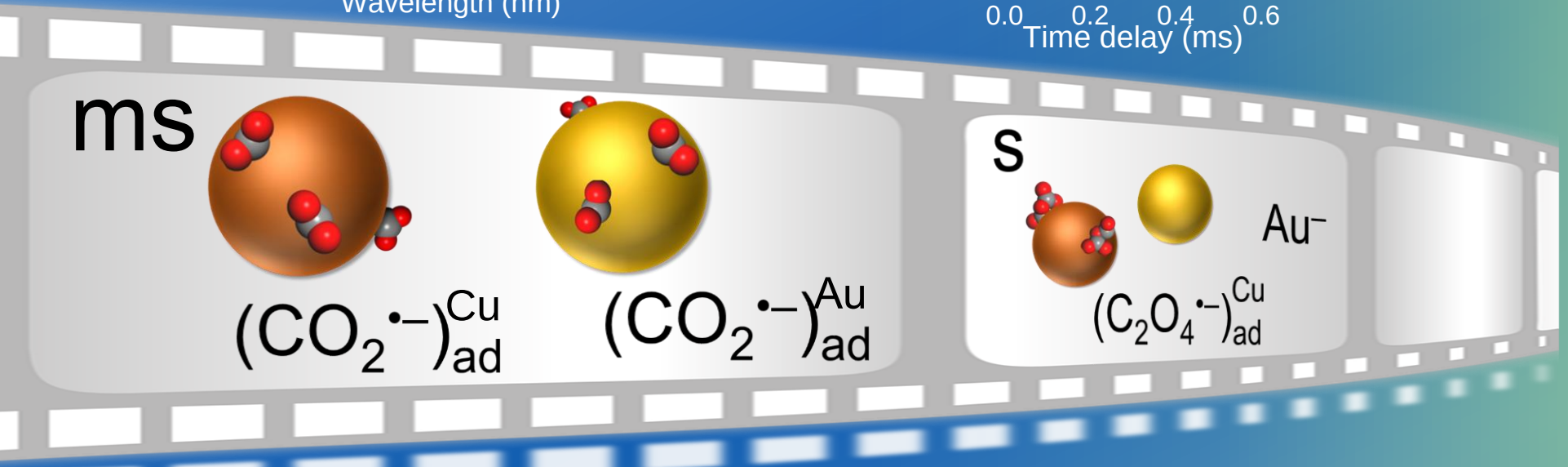
➢ The stabilization dynamics of $CO_2^{\bullet-}$ radicals



$(CO_2^{\bullet-})_{ad}^{Au}$

$(CO_2^{\bullet-})_{ad}^{Cu}$

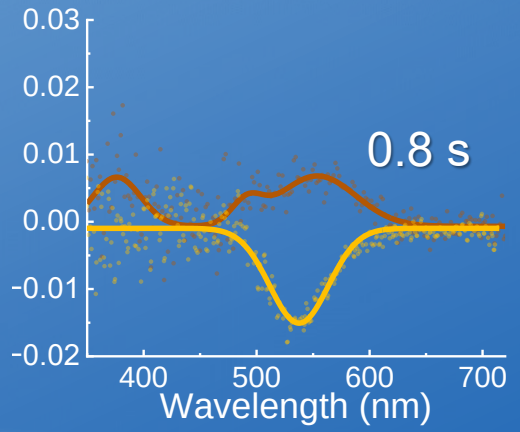




Nat. Commun., 2023, 14, 7116

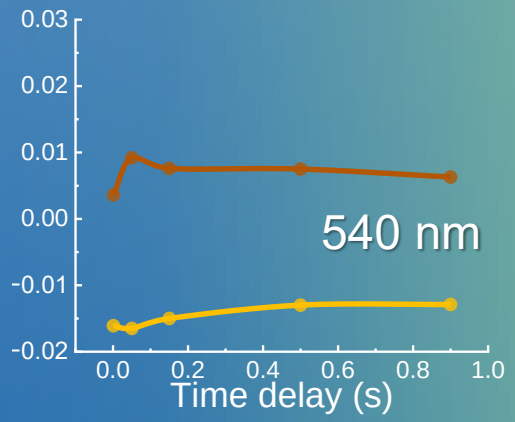
Direct time-resolved observation of surface-bound $CO_2^{\bullet-}$ radicals on metallic nanocatalysts

➢ The interfacial transition of $CO_2^{\bullet-}$ radicals

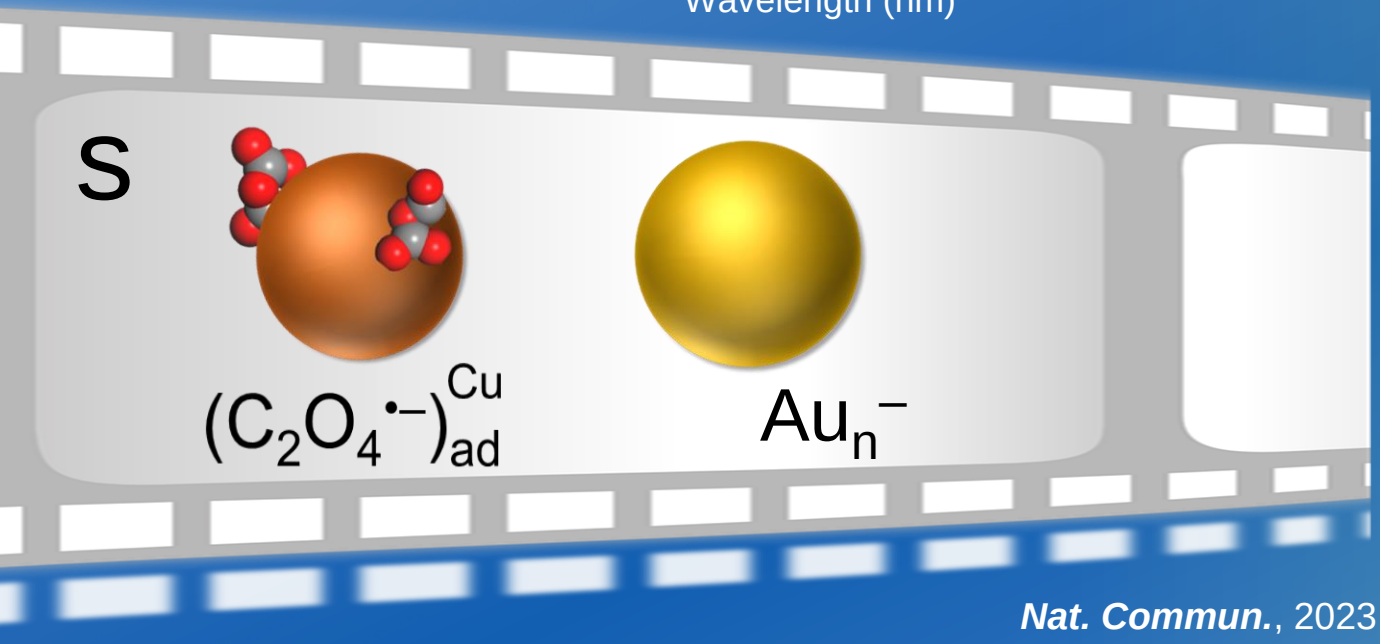


$(CO_2^{\bullet-})_{ad}^{Cu}$

$(CO_2^{\bullet-})_{ad}^{Au}$



Time-scale of interfacial reaction : seconds



$$(CO_2^{\bullet-})_{ad}^{Au} \rightarrow Au_n^- + CO_2$$

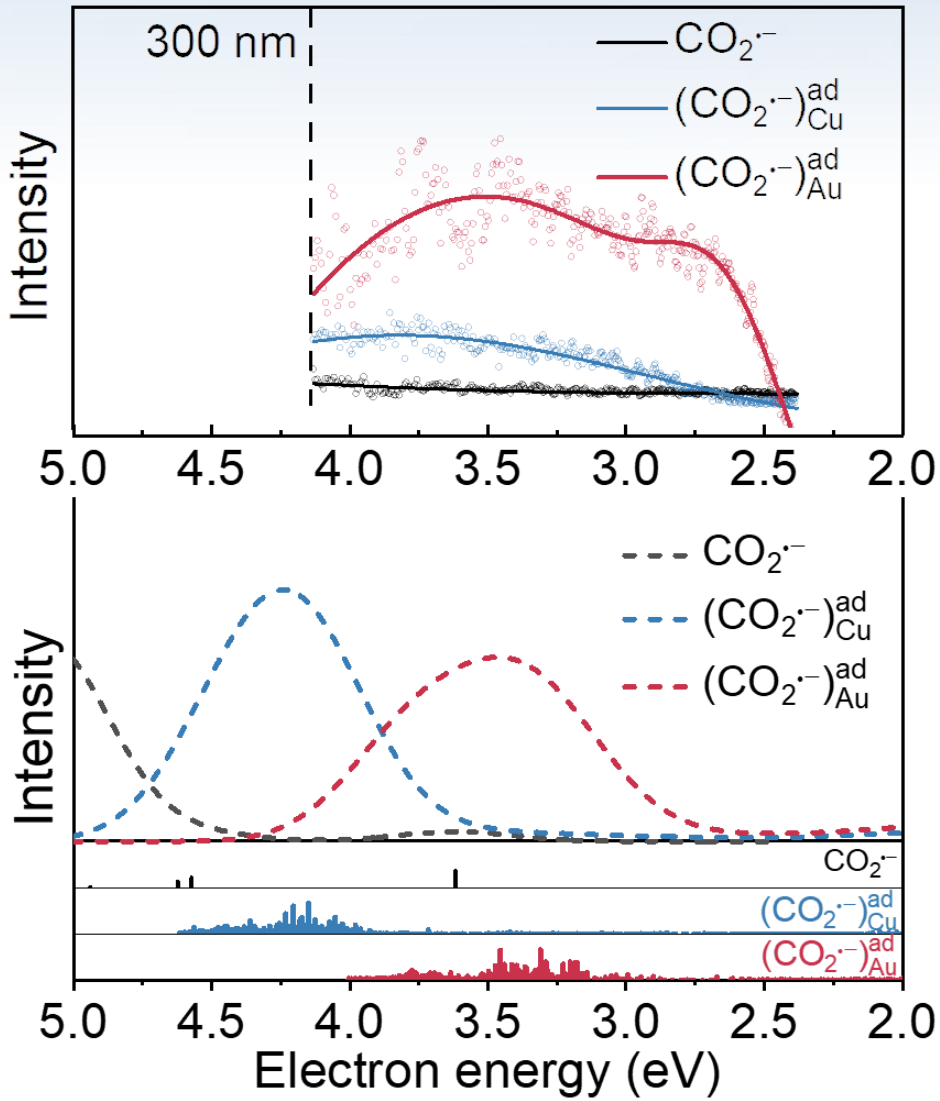
$$2(CO_2^{\bullet-})_{ad}^{Cu} \rightarrow (C_2O_4^{\bullet-})_{ad}^{Cu}$$

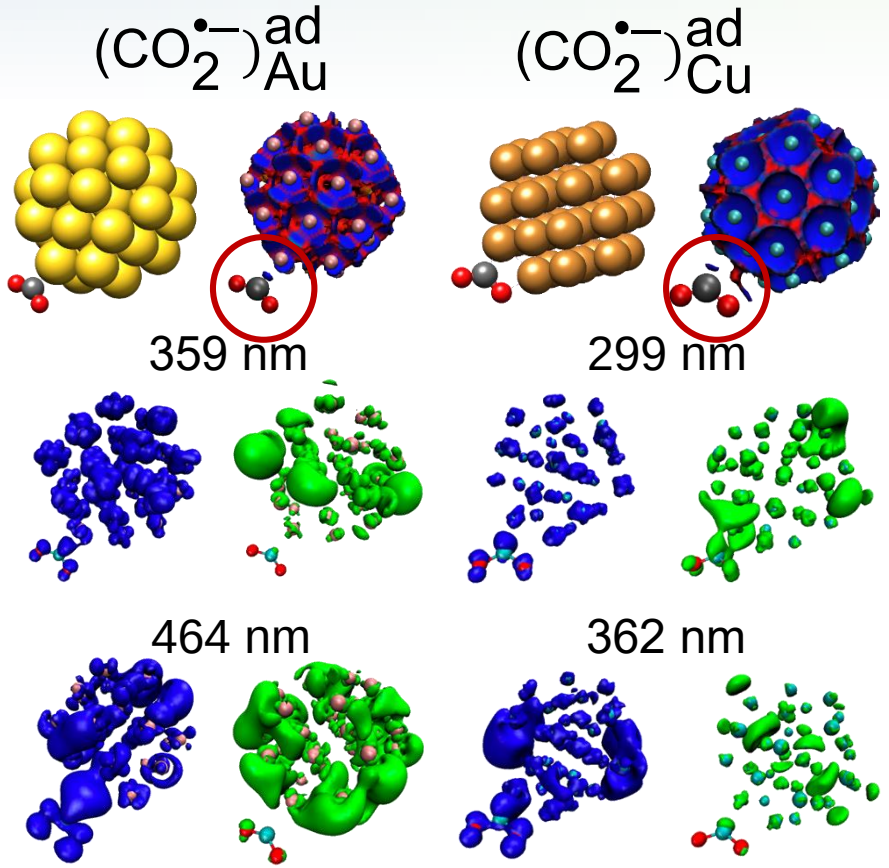
Nat. Commun., 2023, 14, 7116

Theoretical calculation

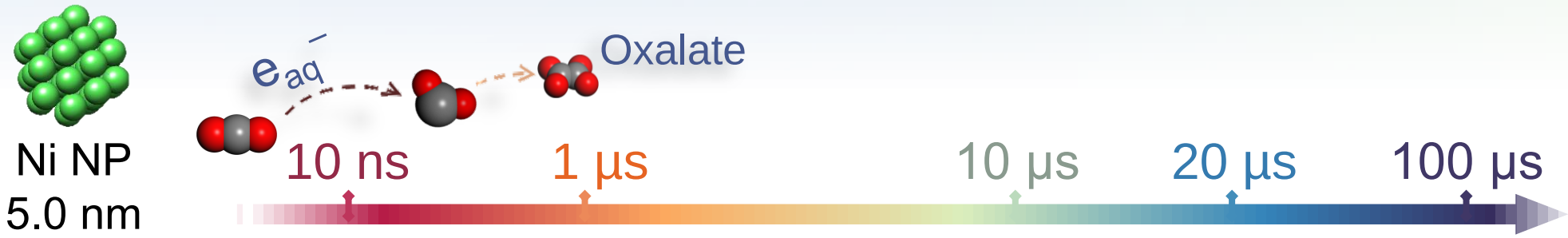
Exp.

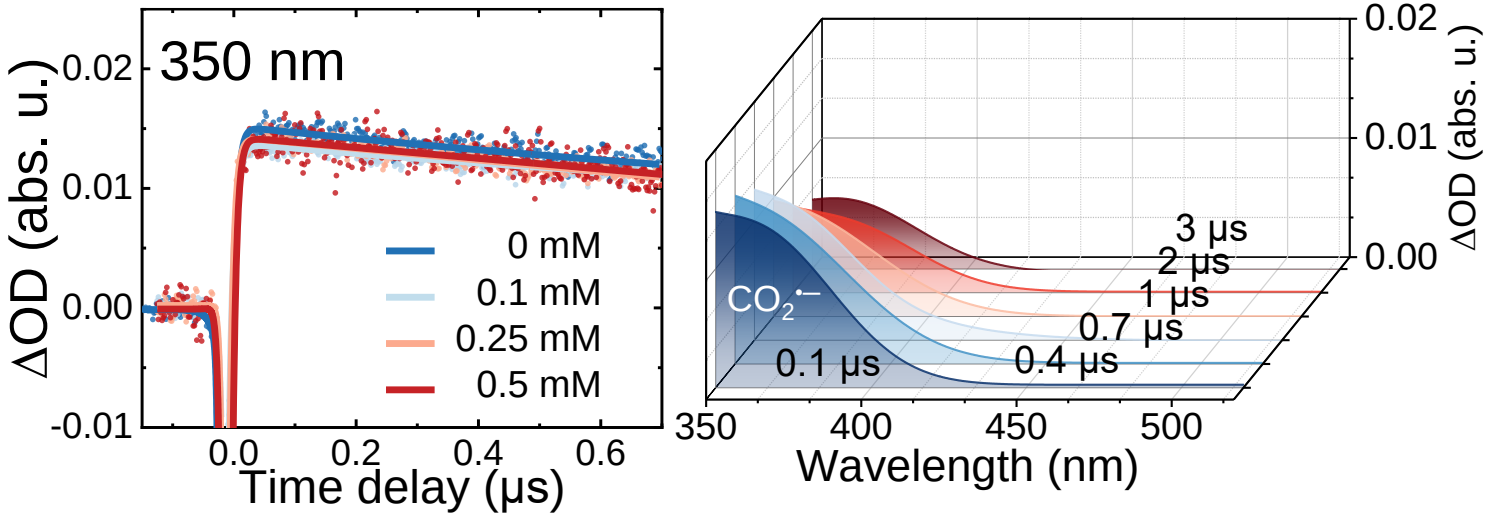
Cal.

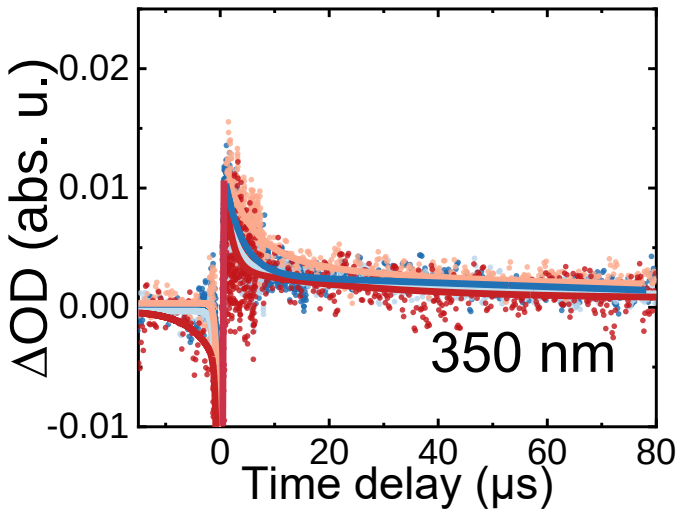




Ni without stabilization dynamics of $CO_2^{\bullet-}$ radicals

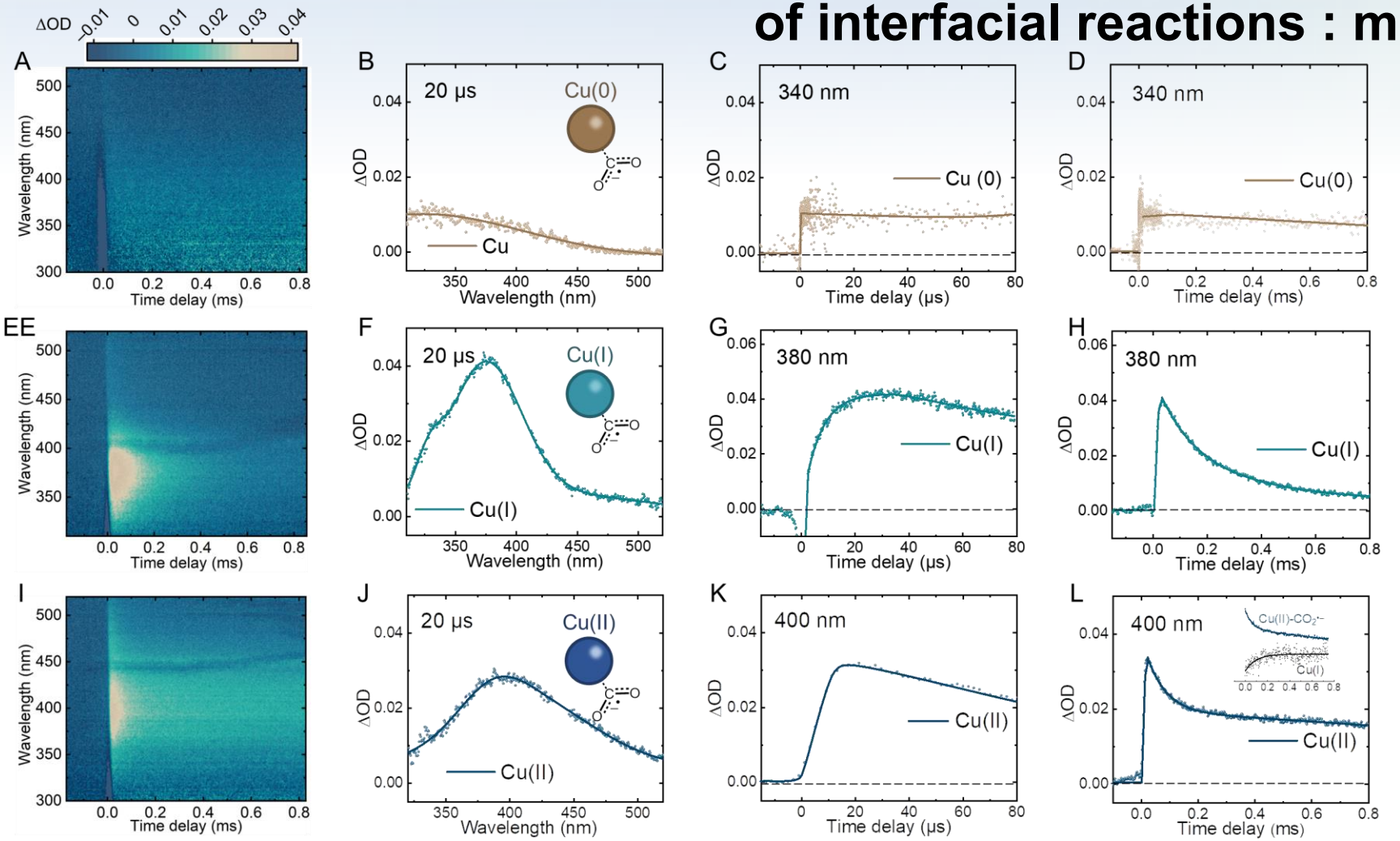






Oxidation state effect

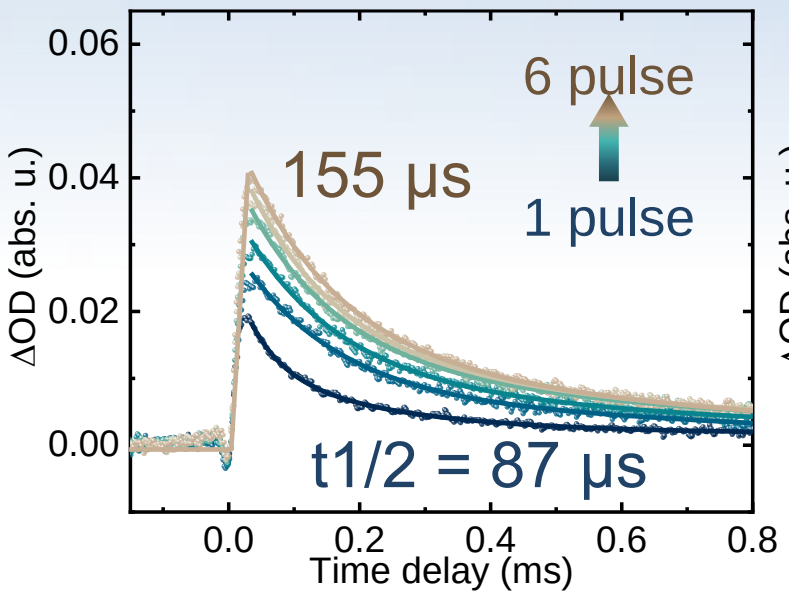
Time-scale of surface-bound process: microseconds of interfacial reactions : milliseconds

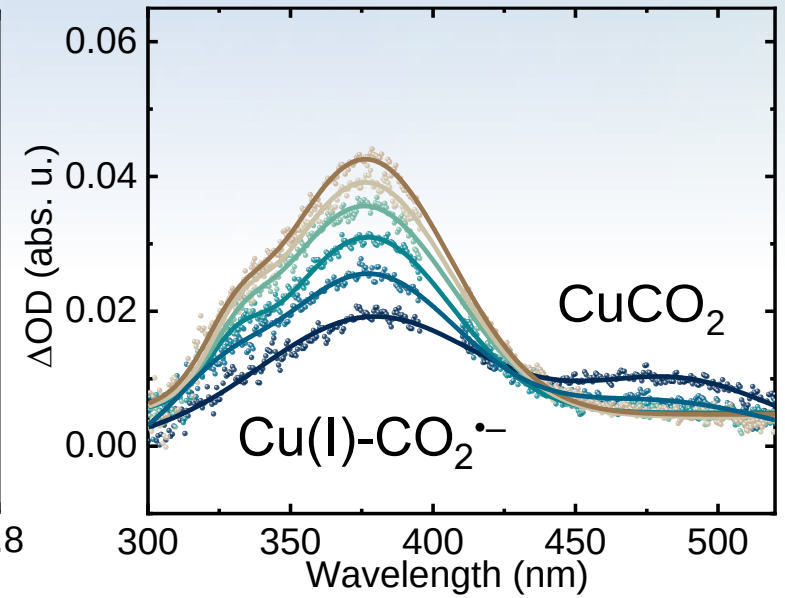


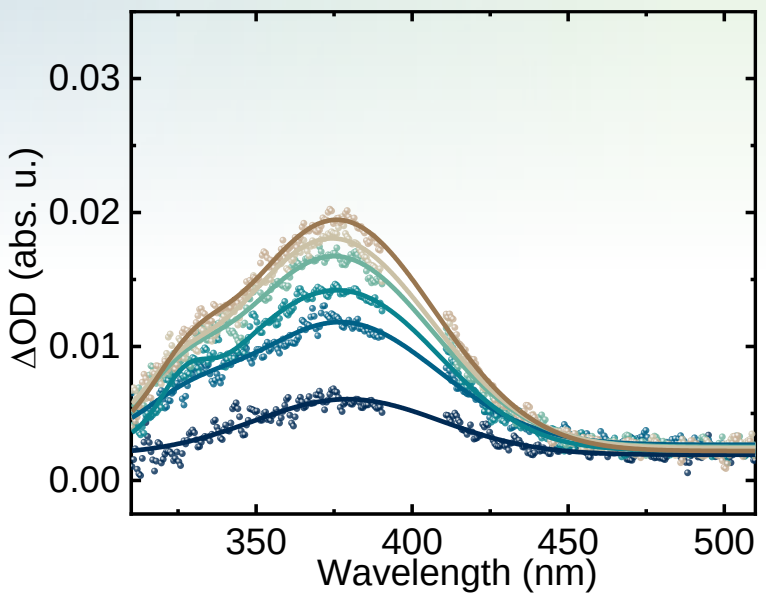
$(CO_2^{\bullet-})^{ad}$-Cu(0)	320 nm
$(CO_2^{\bullet-})^{ad}$-Cu(I)	370 nm
$(CO_2^{\bullet-})^{ad}$-Cu(II)	400 nm
$(CO_2^{\bullet-})^{ad}$-Cu(0)	Slow coupling
$(CO_2^{\bullet-})^{ad}$-Cu(I)	Fast coupling
$(CO_2^{\bullet-})^{ad}$-Cu(II)	Electron transfer

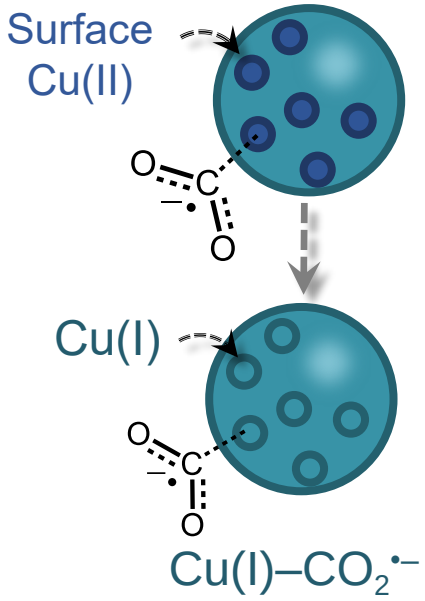
J. Am. Chem. Soc., 2024, 146, 30164–30173.

Oxidation state effect









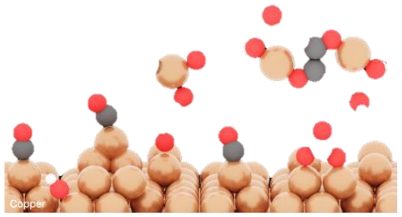
$Cu(I)/Cu(II) + CO_2^{\bullet-}$

$Cu(I)–CO_2^{\bullet-}$

Cu(0)

coupling reaction
($CO_2^{\bullet-}$ to C_{2+})

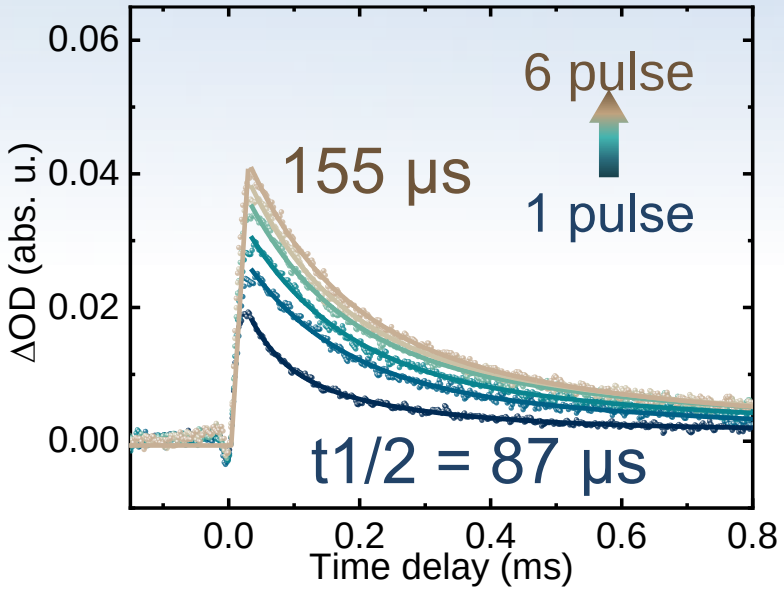
Cu^I/Cu_{atom} = –2.6 eV



Cu^I/Cu_{metal} = –0.36 eV

J. Am. Chem. Soc., 2024, 146, 30164–30173.

Rate constant calculations

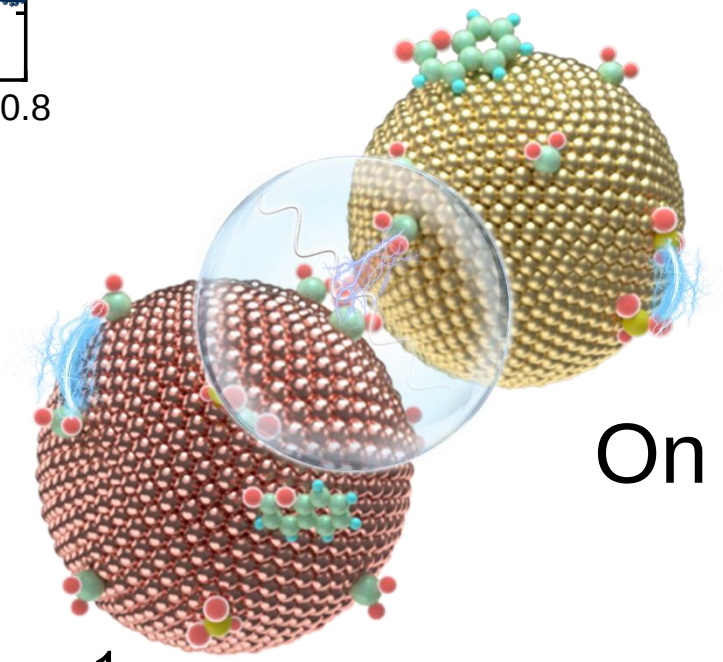


$Cu(I)/Cu(II) + CO_2^{\bullet-}$

$\downarrow$

$Cu(I)–CO_2^{\bullet-}$ ⇢ coupling reaction ($CO_2^{\bullet-}$ to C_{2+})

$$k = \frac{1}{t_{1/2} c_0}$$



On the same NP :

$C_0 = 2.7 \times 10^{-5}$ M

$k \approx 2.4 \times 10^{8}$ M^{-1} s^{-1}

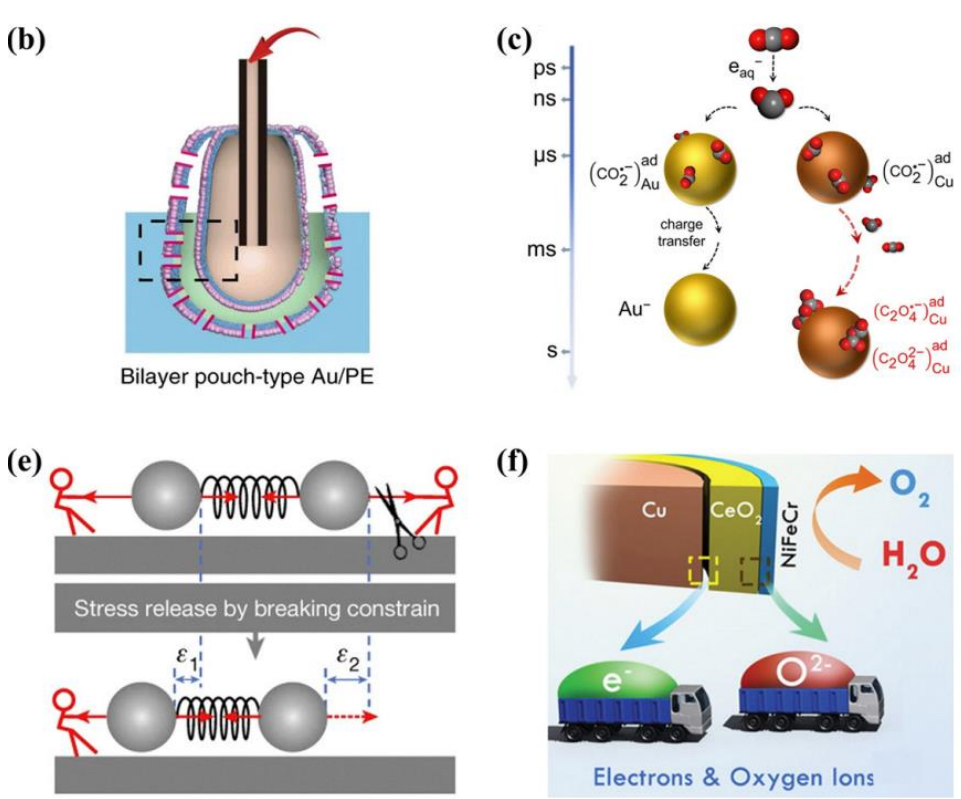
On different 5 nm NP(0.5 mM):

$C_0 \approx 3 \times 10^{-7}$ M

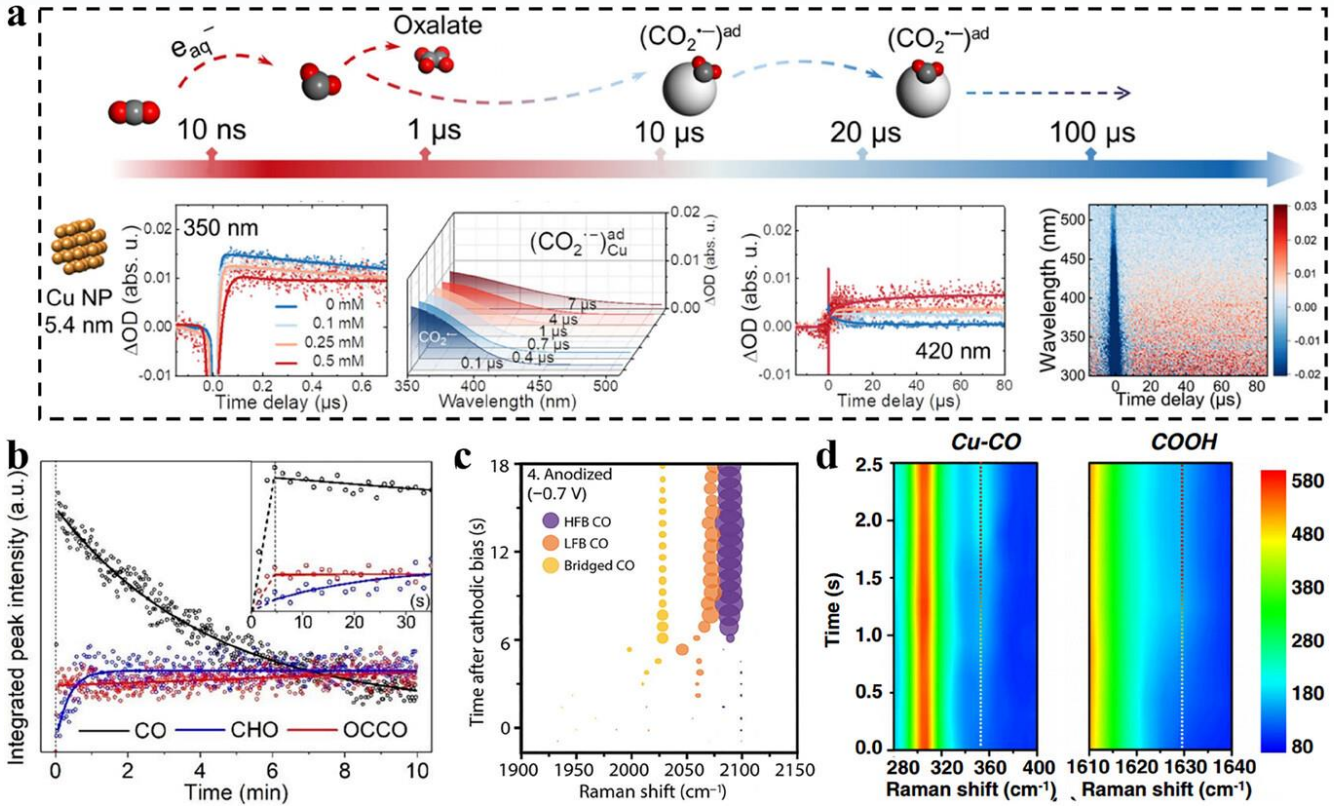
$k \approx 2.2 \times 10^{10}$ M^{-1} s^{-1}

Cited by …

Chem. Soc. Rev., **2025**, ASAP



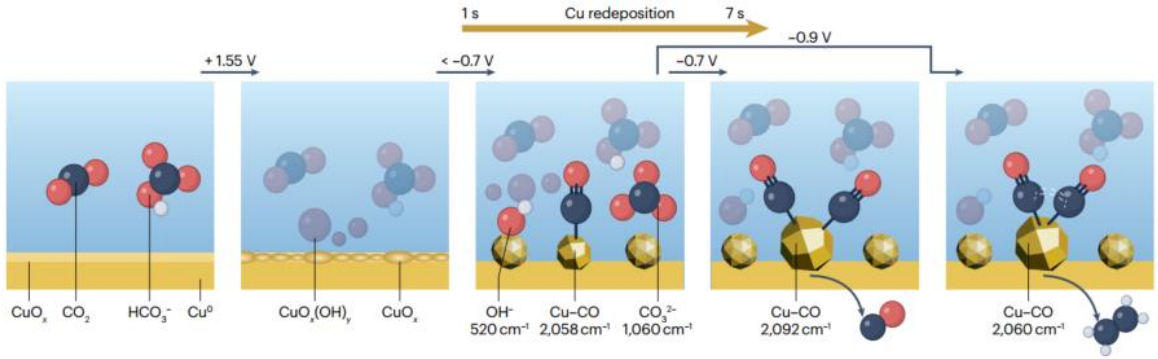
Small, **2025**, 21, 2411628.



Interfacial Radical Dynamics by Pulse Radiolysis

For electrocatalysis :

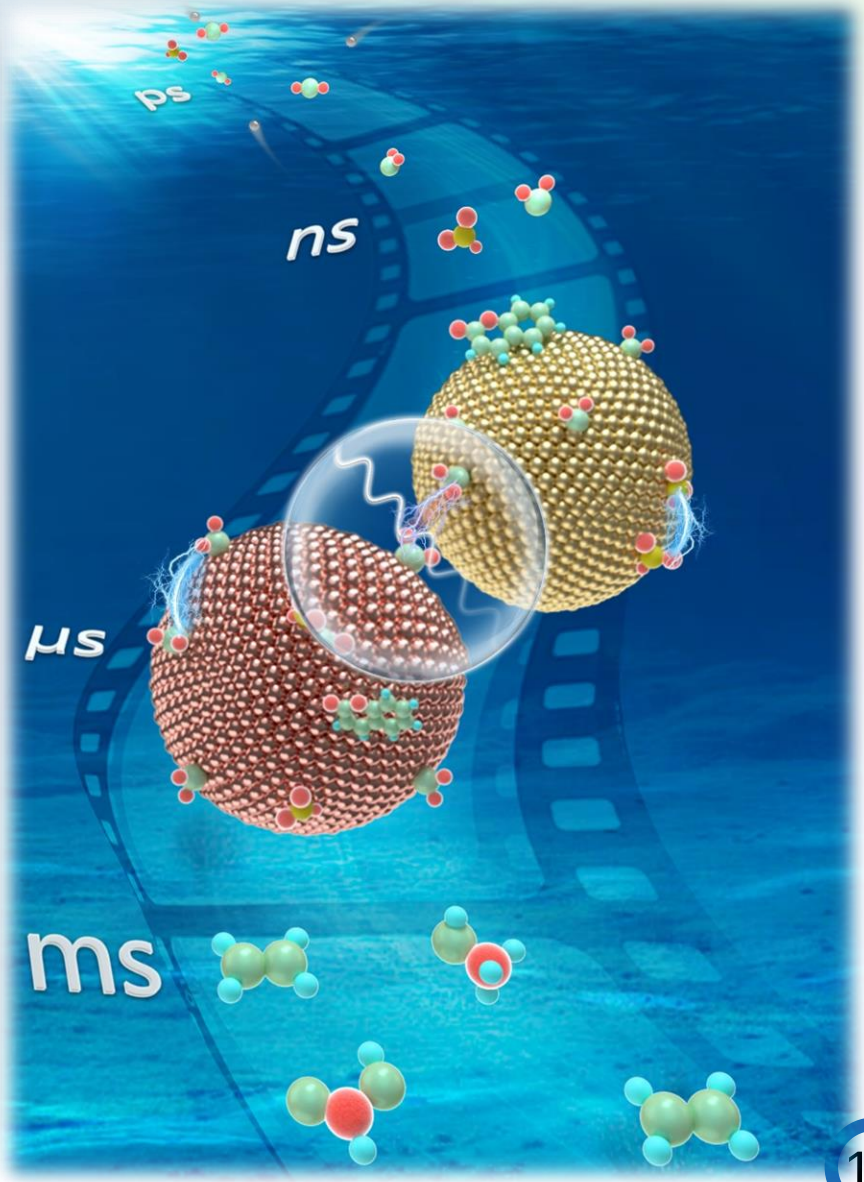
- Applied potential conditions



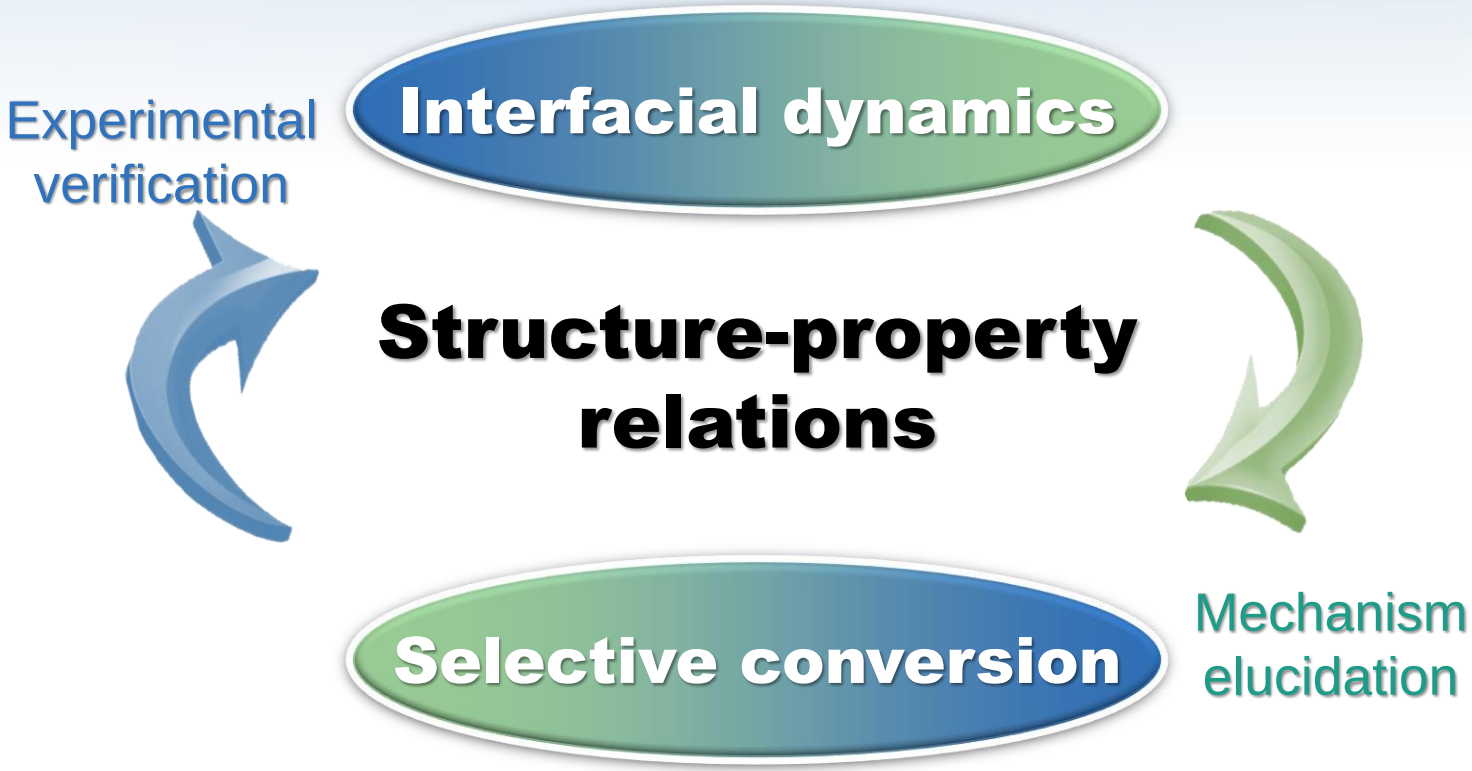
- Redox potential of surface-bound intermediates
- Competitive reaction and rate constants

For photocatalysis :

- Electron transfer kinetics (k_{et})
- Interfacial kinetics on different materials (……)



Time-resolved Interfacial Radical Dynamics by Pulse Radiolysis



Key intermediates of **CO_2 reduction**						
CO	+	e_{aq}^-	→	**$^{\bullet}CO^-$**		
HCHO	+	$^{\bullet}H(^{\bullet}OH)$	→	**$^{\bullet}CHO$**	+	$H_2(H_2O)$
CO	+	$^{\bullet}H$	→	**$^{\bullet}CHO$**		
CO	+	$^{\bullet}OH$	→	**$^{\bullet}COOH$**	+	
HCOOH	+	$^{\bullet}H(^{\bullet}OH)$	→	**$^{\bullet}COOH$**	+	$H_2(H_2O)$
Key intermediates of **nitrate reduction**						
HNO_3	+	$^{\bullet}OH$	→	**$^{\bullet}NO_3$**	+	H_2O
NO_2^-	+	$^{\bullet}OH$	→	**$^{\bullet}NO_2$**	+	OH^-
NH_3	+	$^{\bullet}OH$	→	**$^{\bullet}NH_2$**	+	H_2O

Small molecule conversion

(CO, N_2, NO_3^- ……)

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