

Direct time-resolved study of the interfacial reaction of metal-based catalysts in the CO₂ conversion

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Bordeaux



The diagram illustrates the electrochemical reduction of CO₂ to various C₁ products. The process begins with CO₂ adsorption on a surface, followed by protonation and electron transfer (H⁺ + e⁻) to form a surface-bound species. This intermediate can follow several pathways:

- Formic acid pathway:** The intermediate is protonated and reduced (H⁺ + e⁻) to form formic acid (HCOOH), which then desorbs.
- Carbon monoxide pathway:** The intermediate is protonated and reduced (H⁺ + e⁻) to form carbon monoxide (CO), which then desorbs.
- Formate pathway:** The intermediate is protonated and reduced (H⁺ + e⁻) to form formate (HCOO⁻), which then desorbs.
- Methanol pathway:** The intermediate is protonated and reduced (H⁺ + e⁻) to form methanol (CH₃OH), which then desorbs.
- Methane pathway:** The intermediate is protonated and reduced (H⁺ + e⁻) to form methane (CH₄), which then desorbs.

The diagram shows the intermediates and the final products, with the reaction steps labeled by the number of protons and electrons transferred (H⁺ + e⁻).

Photo-induced
Electro-induced
Radiation-induced



The diagram illustrates the activation of carbon dioxide (CO_2) through three pathways: Photo-induced, Electro-induced, and Radiation-induced. On the left, a CO_2 molecule is shown as a grey sphere (carbon) between two red spheres (oxygen). A dashed black arrow labeled e^- points from the CO_2 molecule to a central $\text{CO}_2^{\bullet -}$ radical anion. This radical anion is depicted with a grey carbon sphere and two red oxygen spheres, enclosed by a dashed red circle. A second dashed black arrow points away from the radical anion towards the right. To the right of the radical anion, the chemical formula $\text{CO}_2^{\bullet -}$ is written.

Products analysis ✓
Steady-state mechanism ✓

Photocatalytic CO₂ Reduction

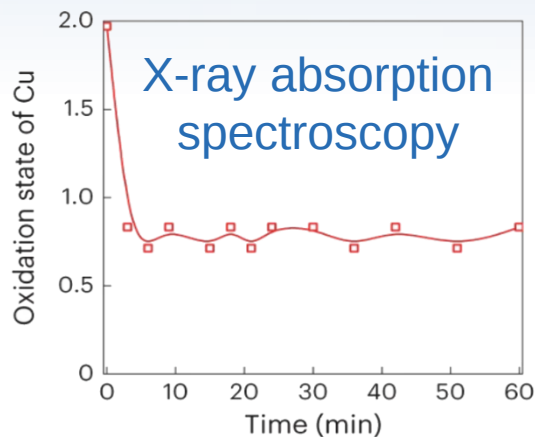
The diagram illustrates the photocatalytic reduction of CO₂ on a semiconductor surface. Light irradiation generates electron-hole pairs. Electrons (e⁻) drive the reduction of CO₂, while holes (h⁺) drive the oxidation of H₂O to O₂. The CO₂ reduction pathway involves adsorption of CO₂ on the surface, followed by a series of proton-coupled electron transfer steps (ne⁻ + nH⁺) to form various intermediates and products:

- Adsorption: CO₂ + * → *CO₂
- Intermediate 1: O=C-OH
- Intermediate 2: O=C-O⁻
- Intermediate 3: O=C-O
- Intermediate 4: O=C-O-O
- Desorption products:
 - HCOO⁻
 - CO
 - C
 - CH₂O, C₂
 - CH₃
 - CH₃OH
 - CH₄

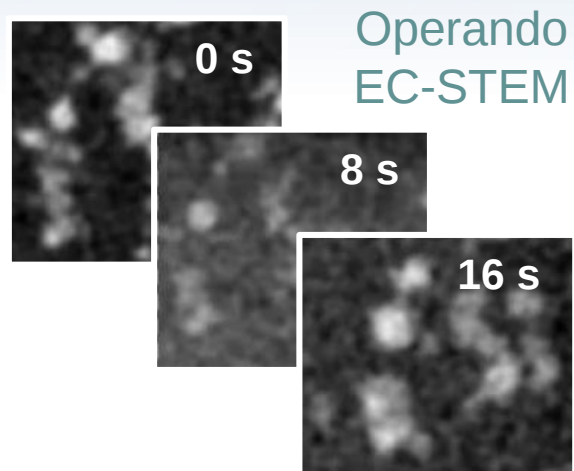
ACS Catal. 2022, 12, 7300–7316

Elementary reaction?
Transient species?
Interfacial kinetics?

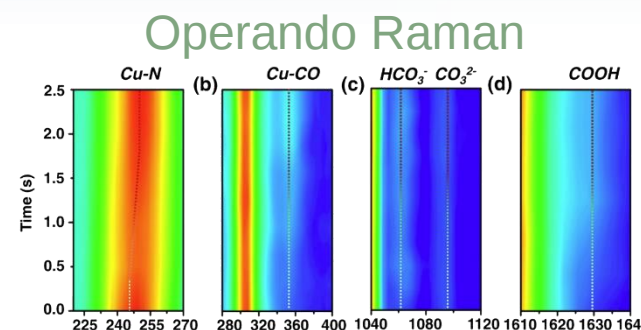
Multi-timescale interface reaction kinetics of intermediates



Nat. Catal. 2022, 5, 1081-1088



Nature 2023, 614, 262-269



Nat. Commun. 2022, 13, 6029



Minutes

Seconds

Sub-seconds

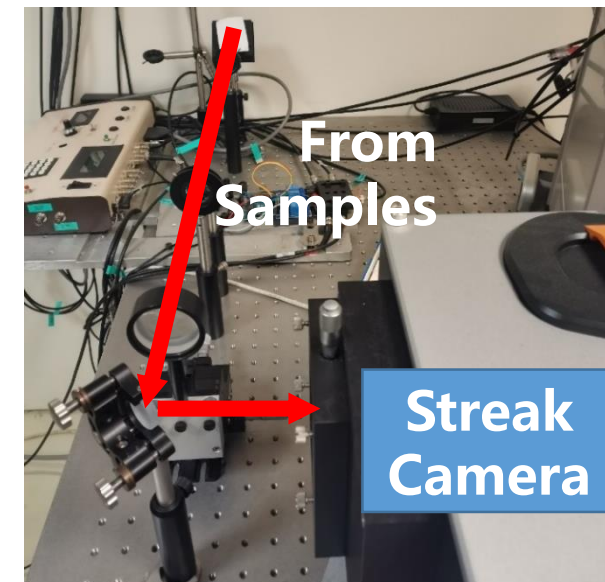
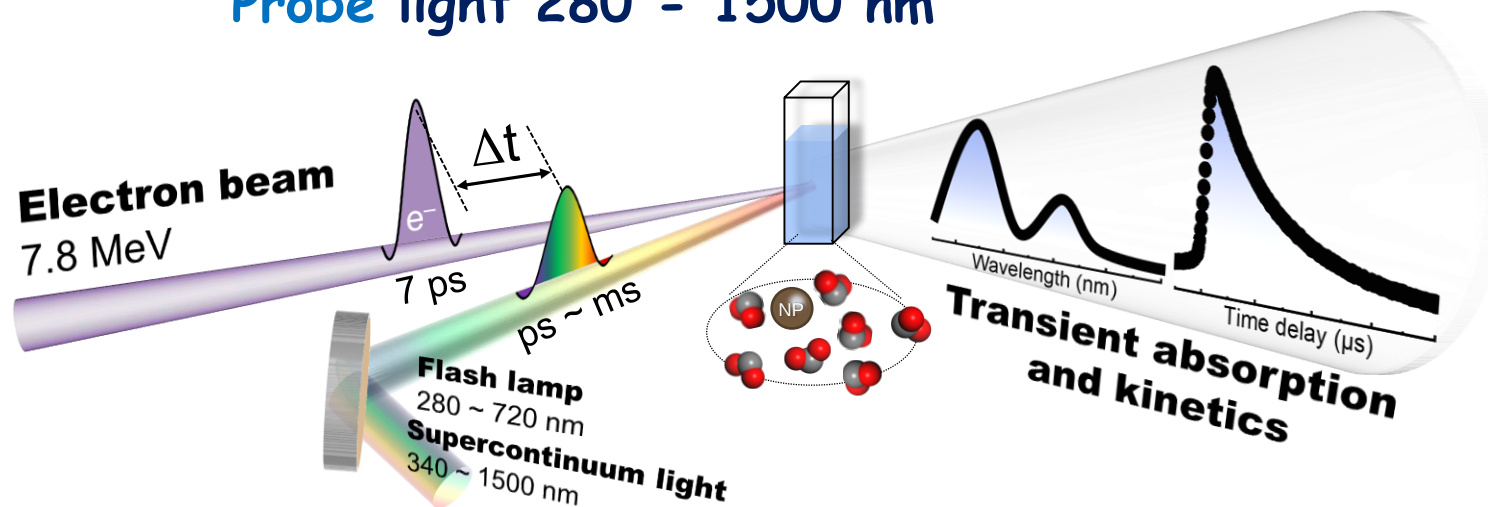
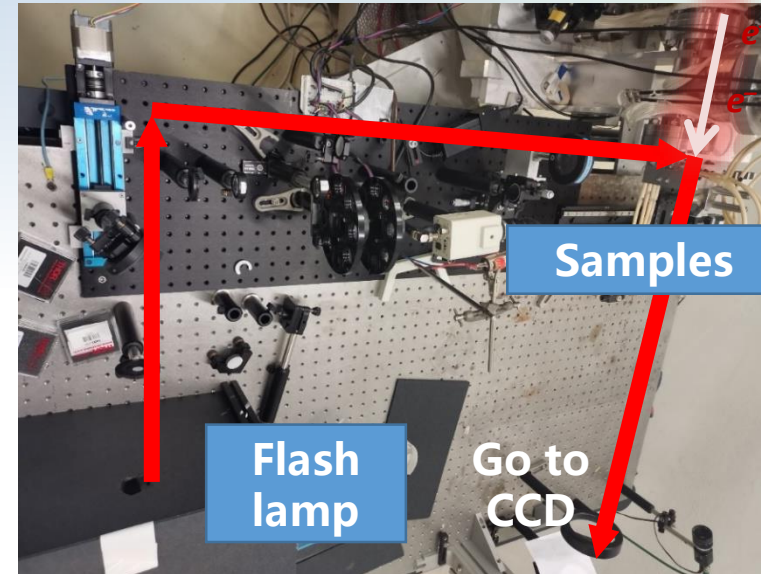
Micro- to nano-seconds

Time-resolution

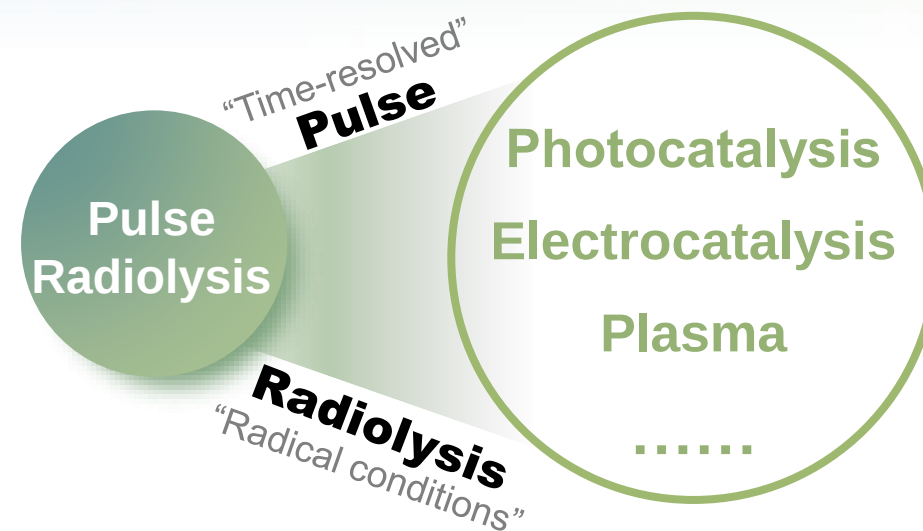
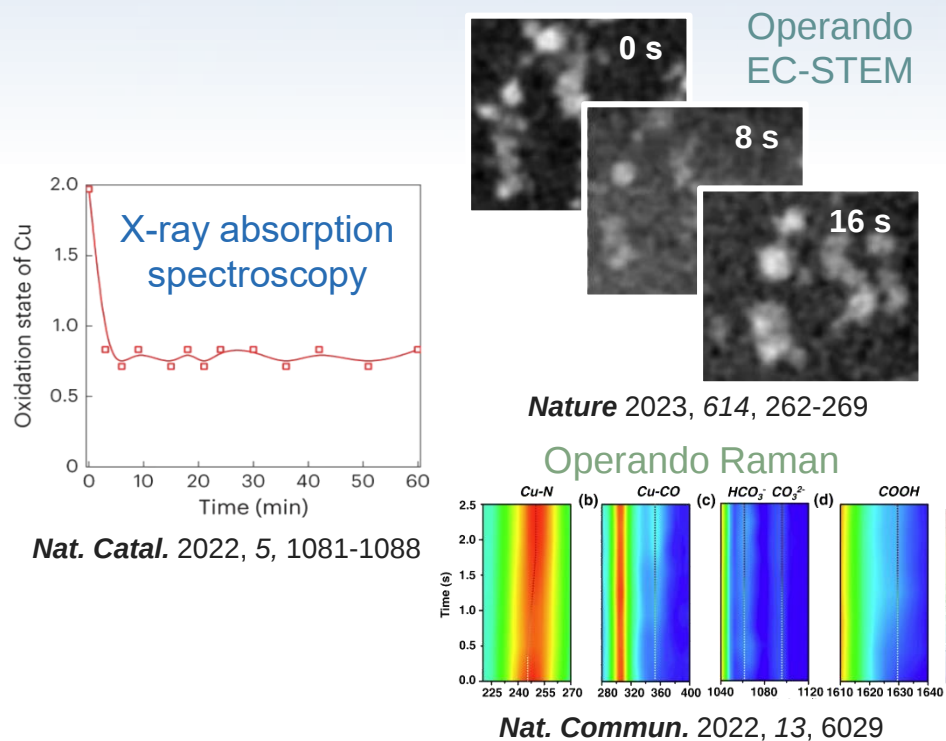
Picosecond Pulse Radiolysis - ELYSE, Pulse - Probe spectroscopy



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

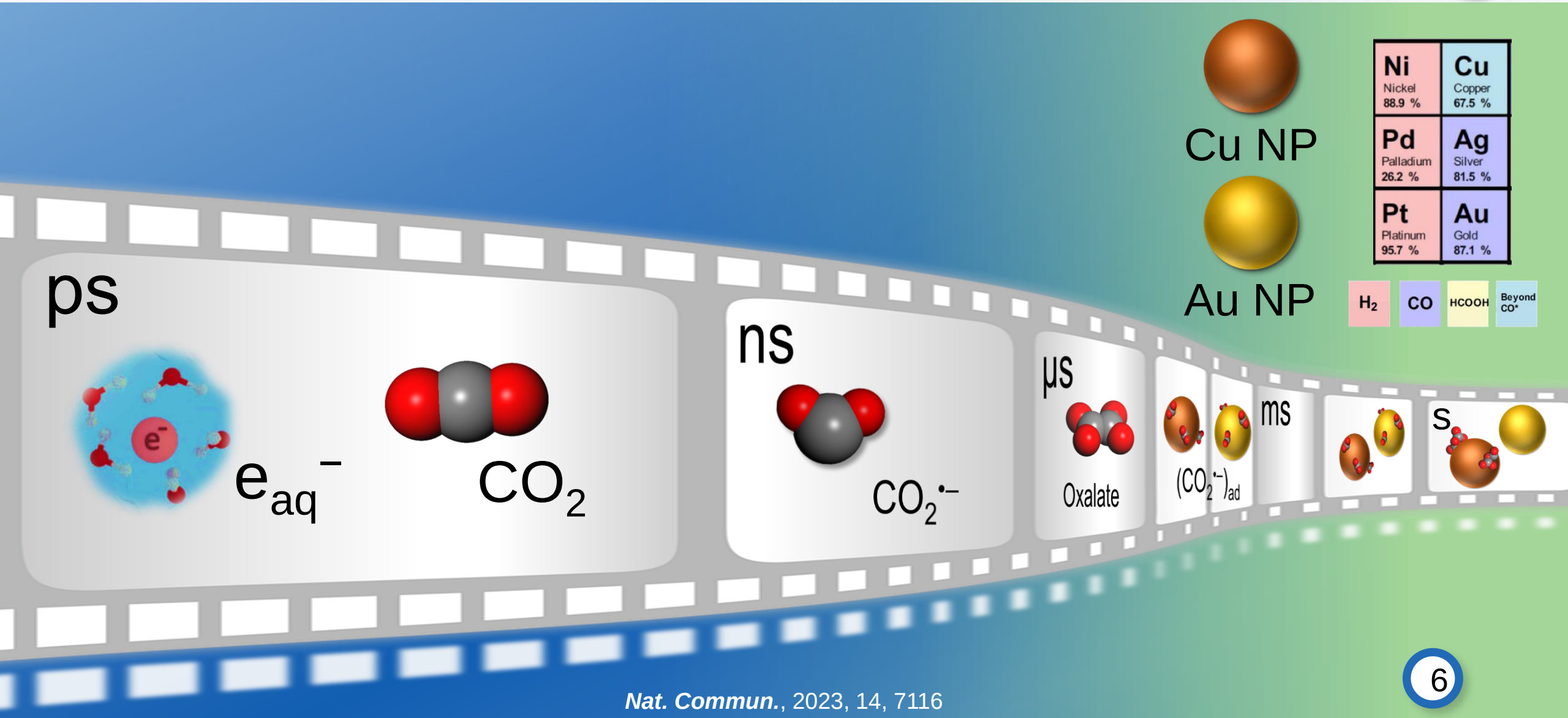


Minutes to Sub-seconds

Micro- to nano-seconds

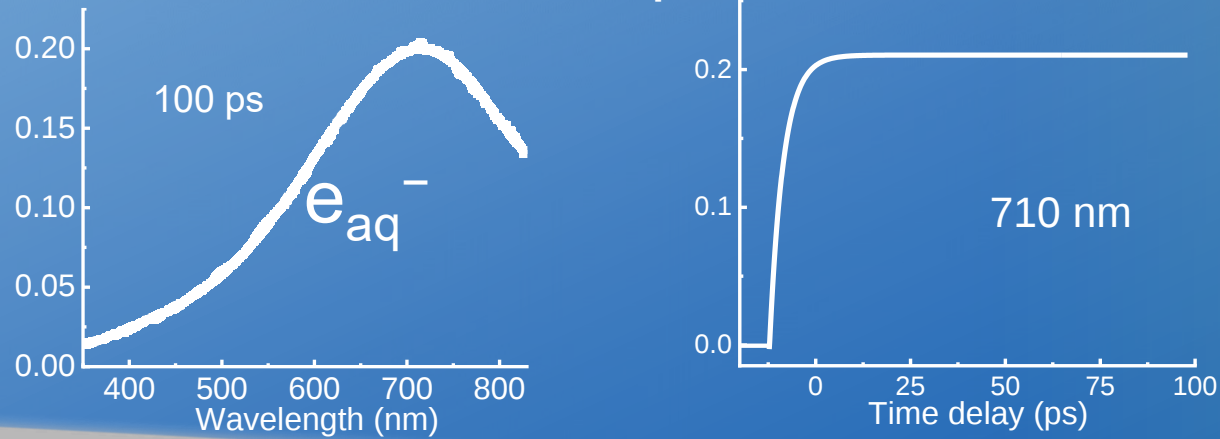
Time-resolution

Direct time-resolved observation of surface-bound $\text{CO}_2^{\bullet-}$ radicals on metallic nanocatalysts

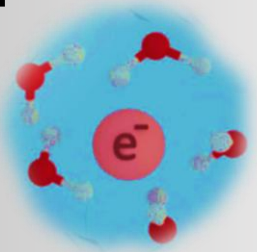


Direct time-resolved observation of surface-bound $\text{CO}_2^{\cdot-}$ radicals on metallic nanocatalysts

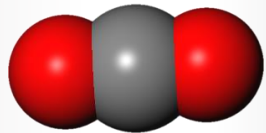
➤ The formation of e_{aq}^-



ps

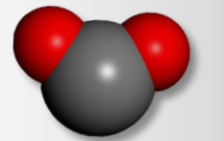


e_{aq}^-



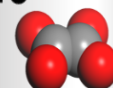
CO_2

ns

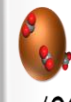


$\text{CO}_2^{\cdot-}$

μs

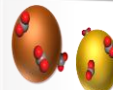


Oxalate

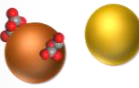


$(\text{CO}_2^{\cdot-})_{\text{ad}}$

ms

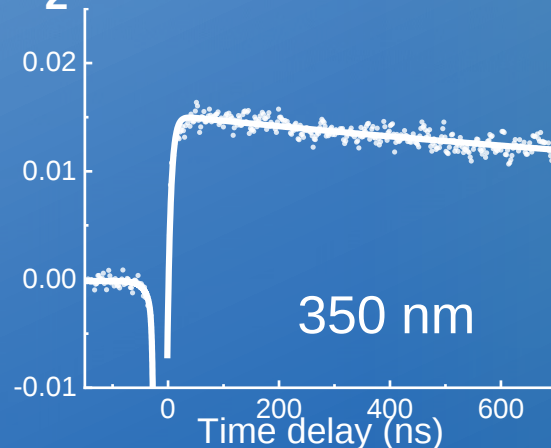
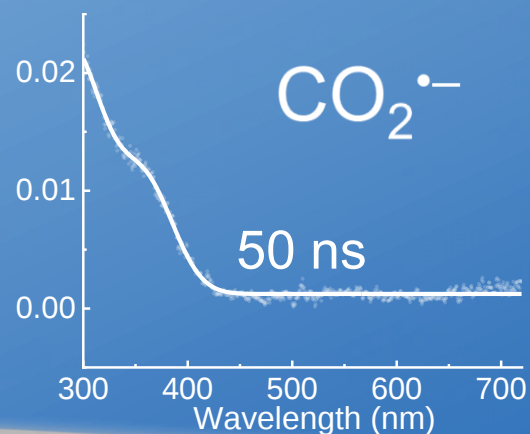


s

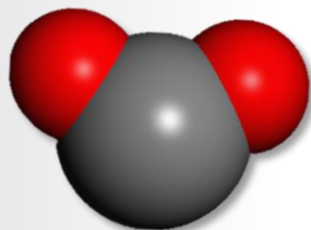


Direct time-resolved observation of surface-bound $\text{CO}_2^{\bullet-}$ radicals on metallic nanocatalysts

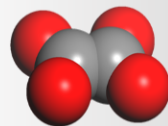
➤ The formation of $\text{CO}_2^{\bullet-}$



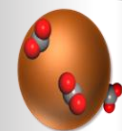
ns



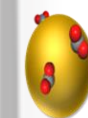
μs



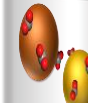
Oxalate



$(\text{CO}_2^{\bullet-})_{\text{ad}}$



ms

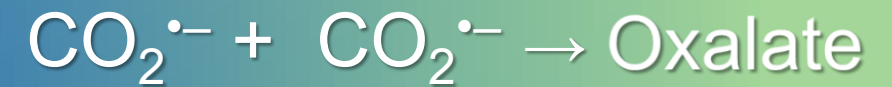
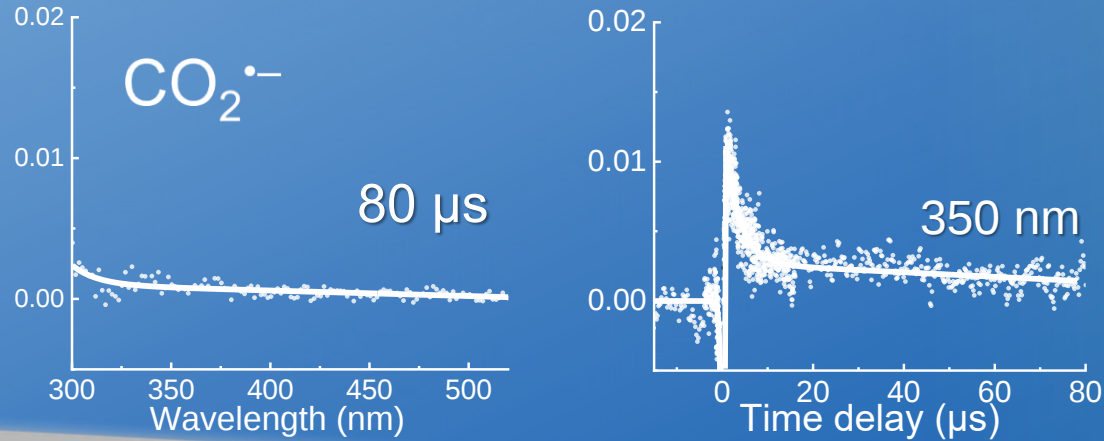


s



Direct time-resolved observation of surface-bound $\text{CO}_2^{\cdot-}$ radicals on metallic nanocatalysts

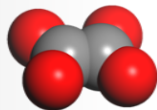
➤ $\text{CO}_2^{\cdot-}$ recombination to form oxalate



μs



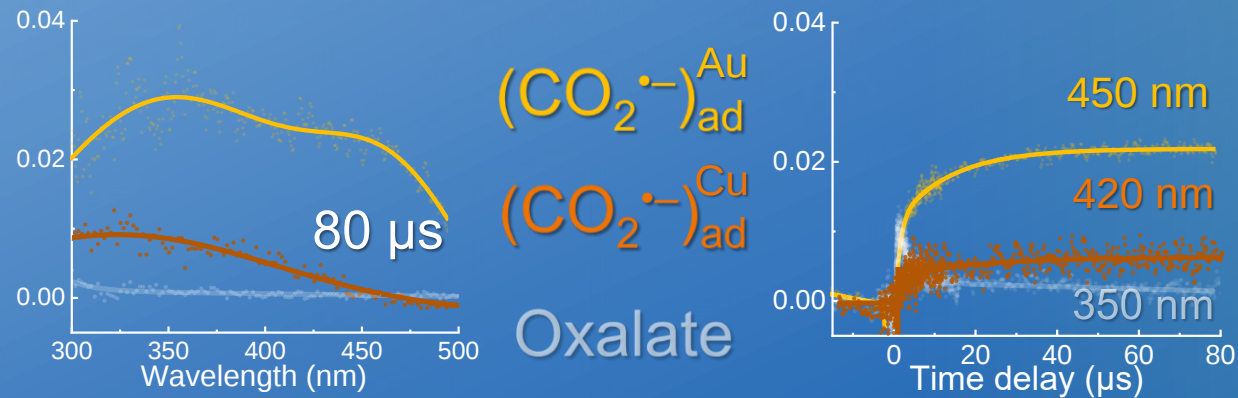
$\text{CO}_2^{\cdot-}$



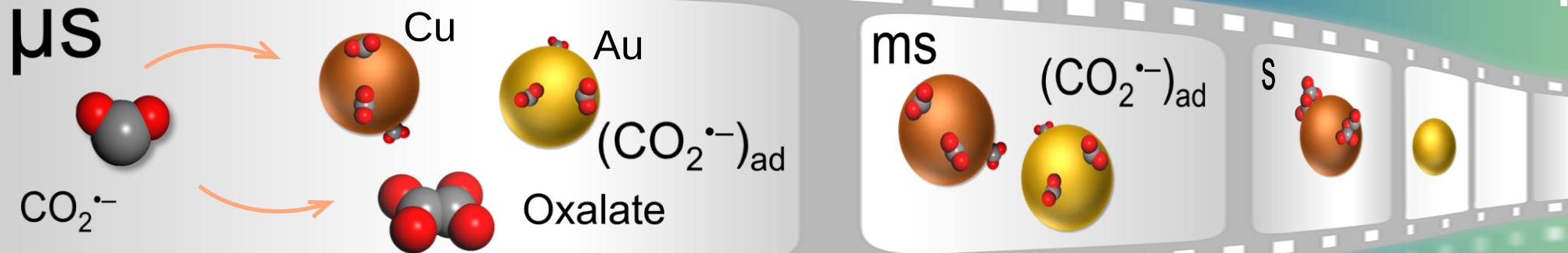
Oxalate

Direct time-resolved observation of surface-bound $\text{CO}_2^{\bullet-}$ radicals on metallic nanocatalysts

➤ The interfacial stabilization of $\text{CO}_2^{\bullet-}$ radicals

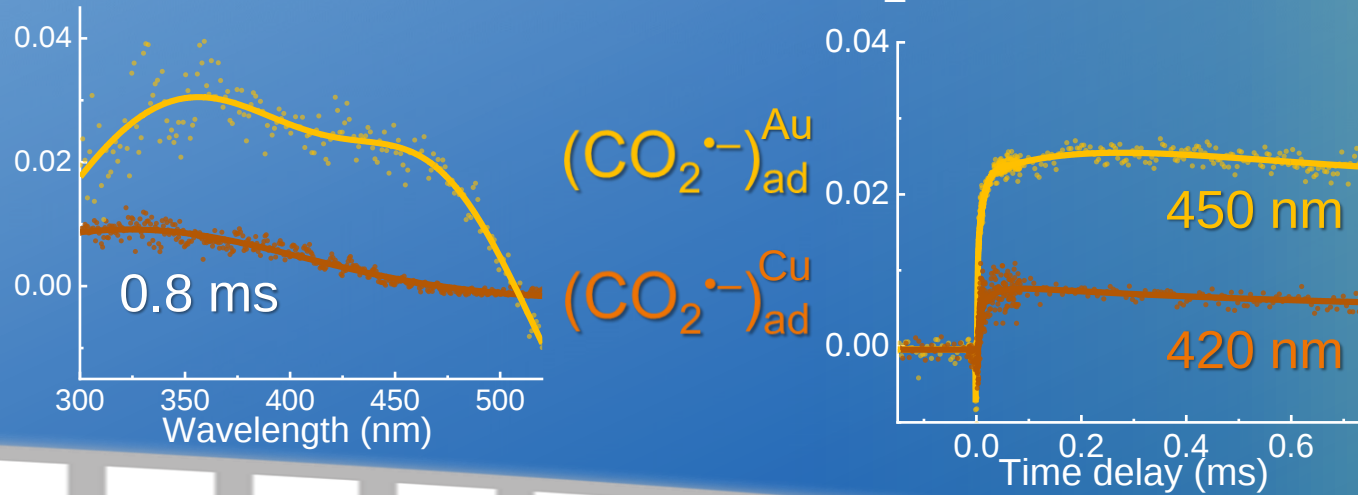


Time-scale of surface-bound process : a few to tens of microseconds

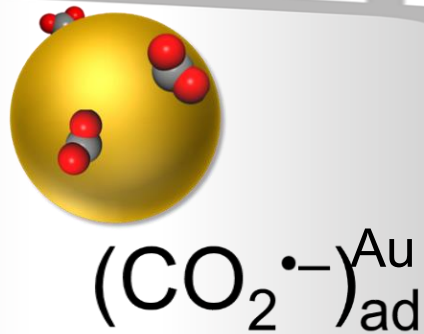
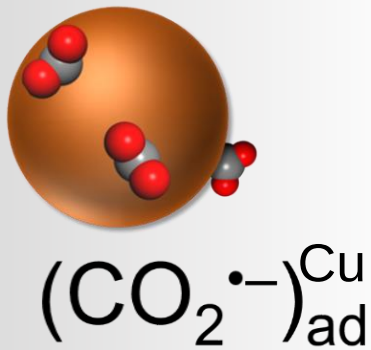


Direct time-resolved observation of surface-bound $\text{CO}_2^{\bullet-}$ radicals on metallic nanocatalysts

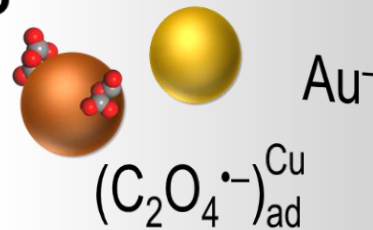
➤ The stabilization dynamics of $\text{CO}_2^{\bullet-}$ radicals



ms

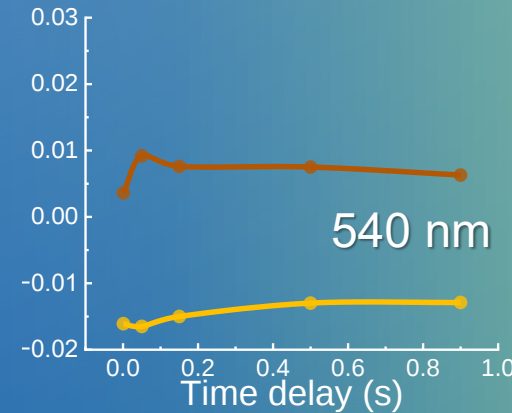
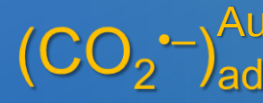
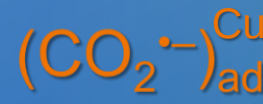
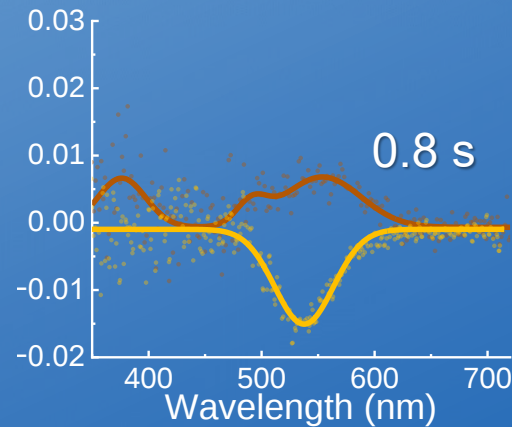


S



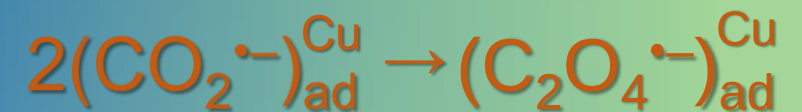
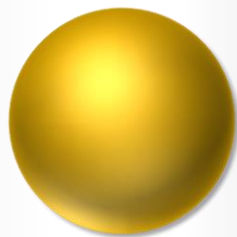
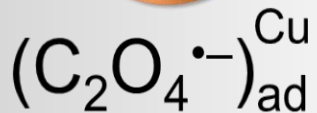
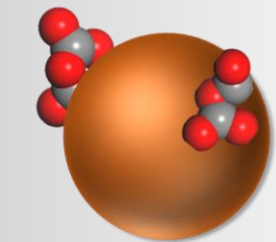
Direct time-resolved observation of surface-bound $\text{CO}_2^{\bullet-}$ radicals on metallic nanocatalysts

➤ The interfacial transition of $\text{CO}_2^{\bullet-}$ radicals



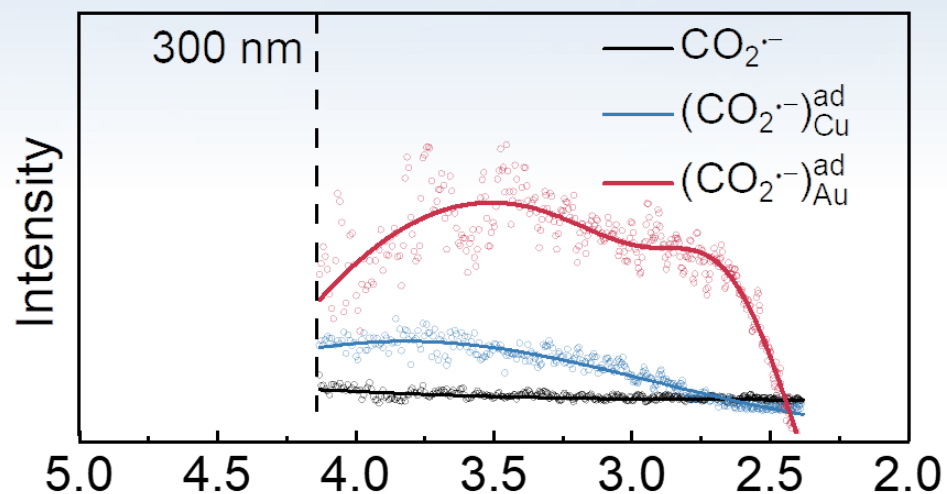
Time-scale of
interfacial reaction :
seconds

S

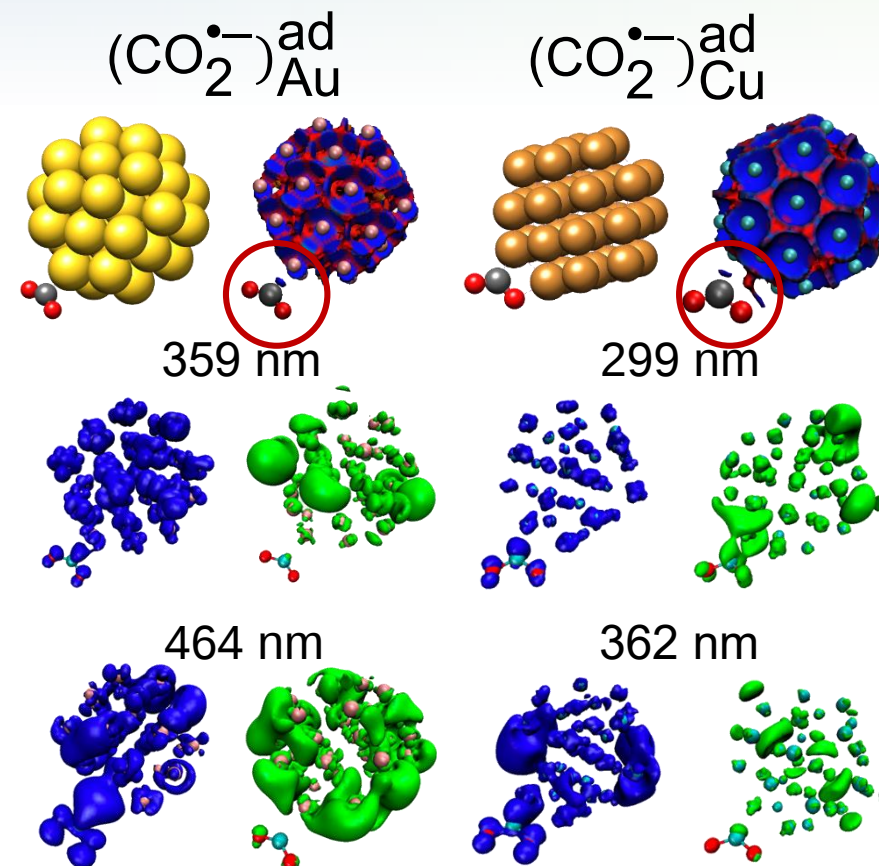
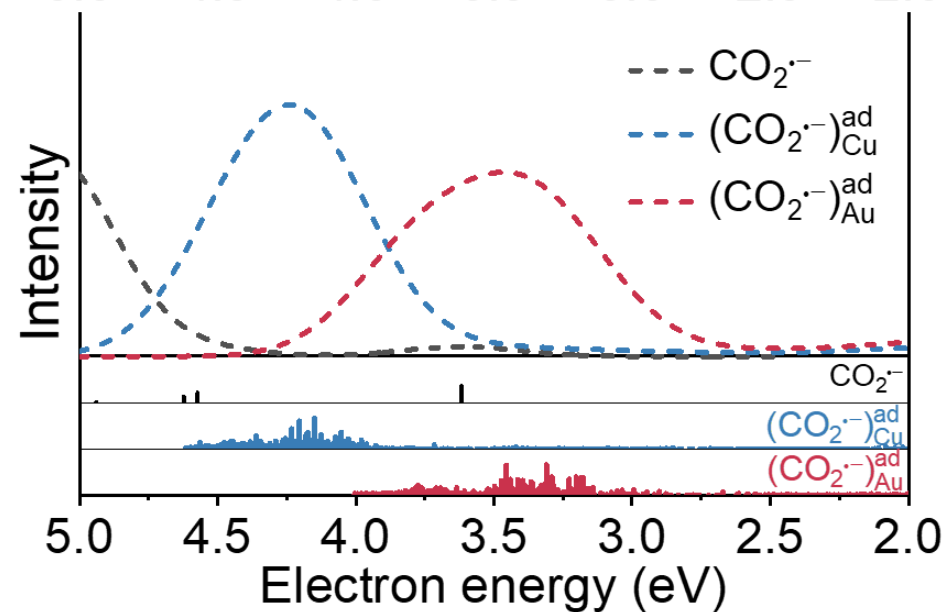


Theoretical calculation

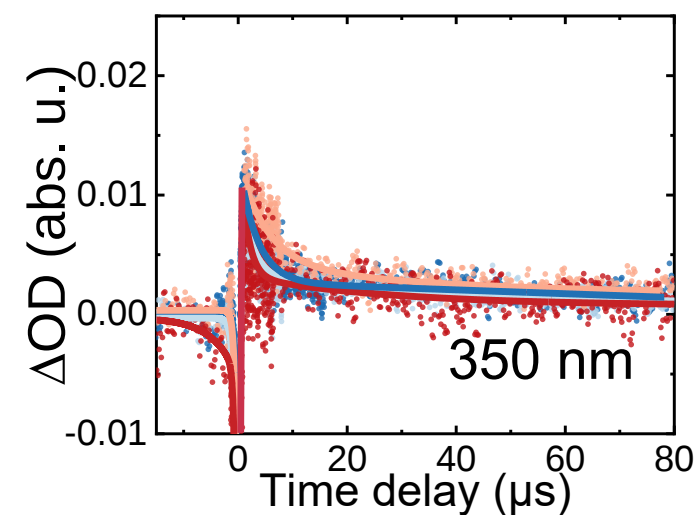
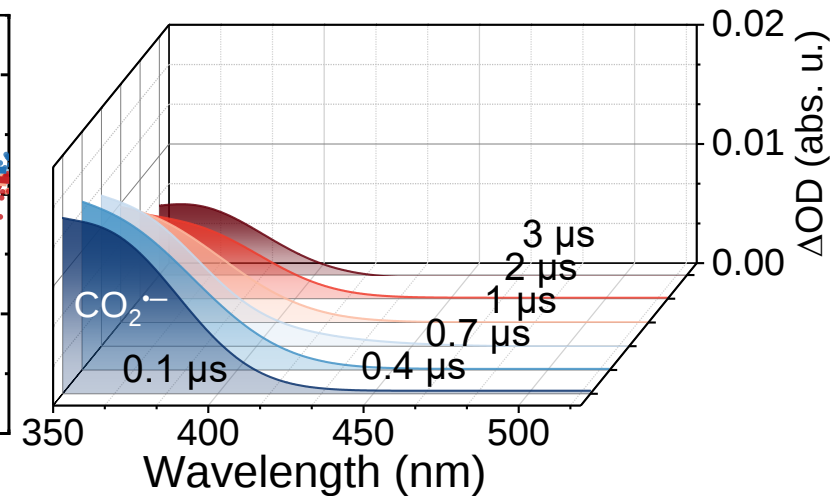
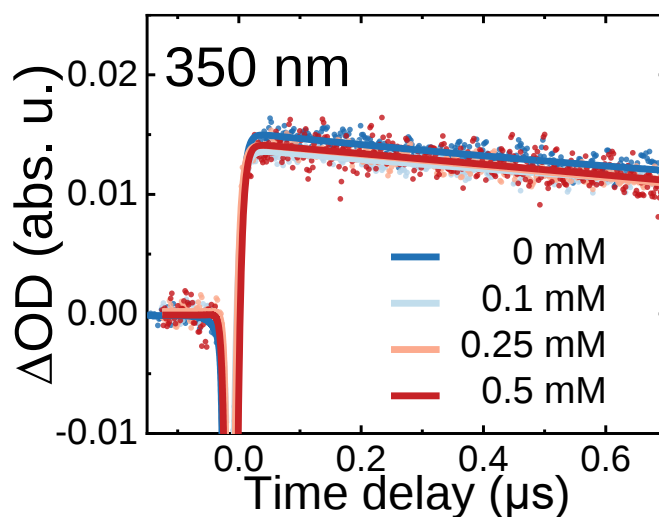
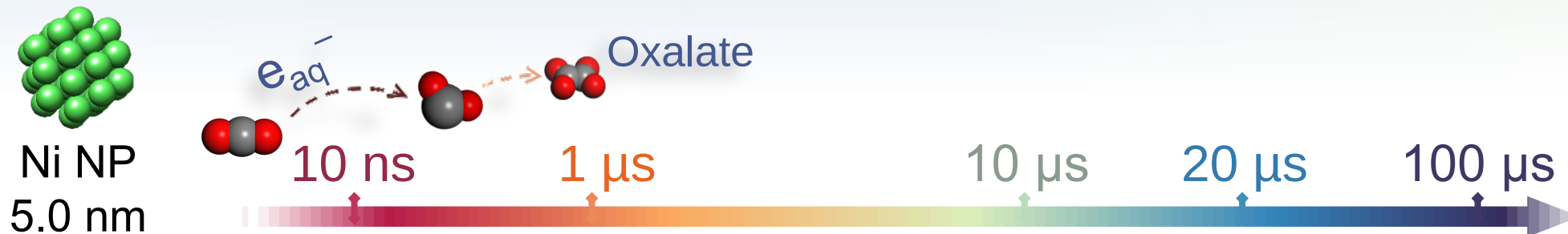
Exp.



Cal.

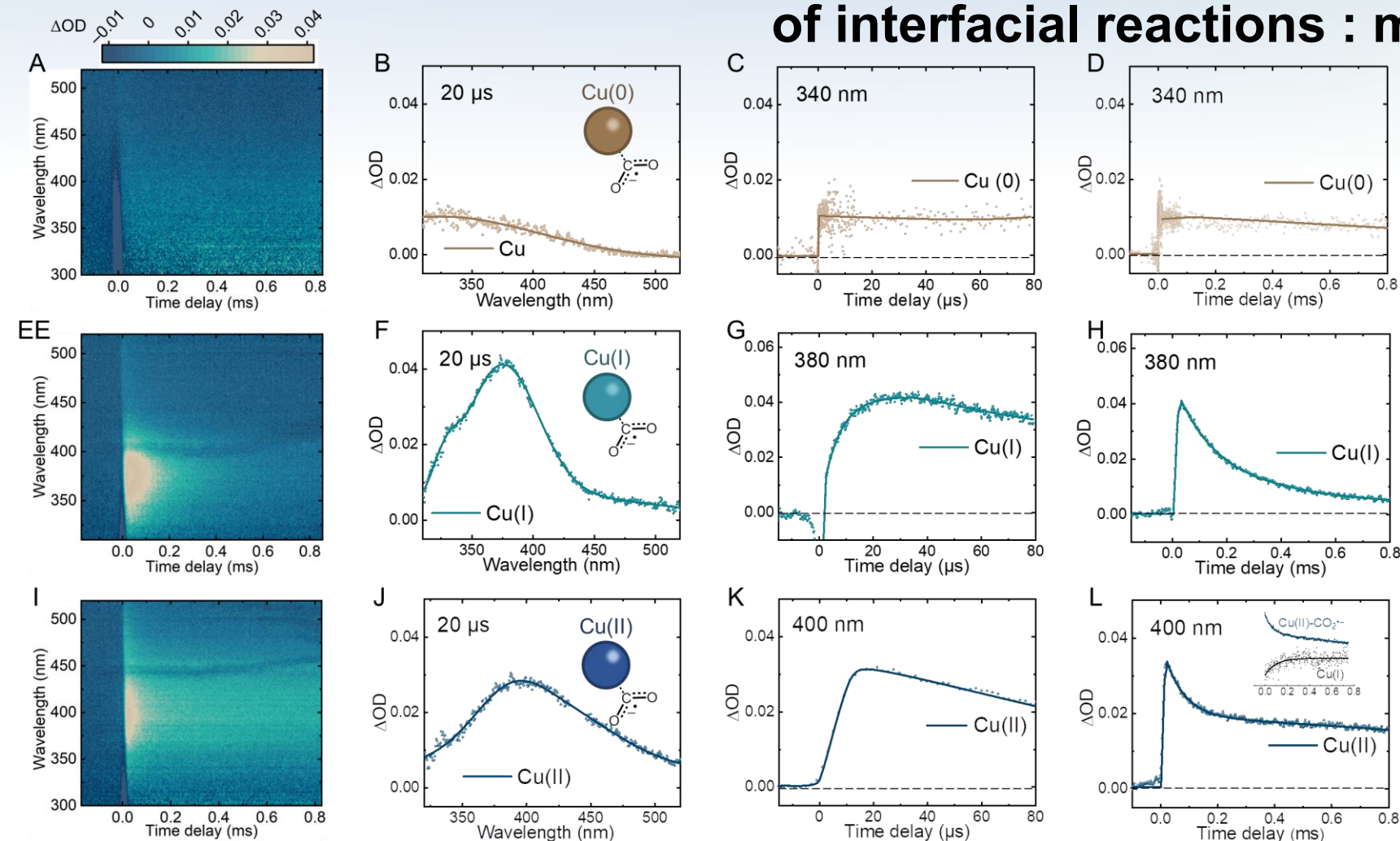


Ni without stabilization dynamics of $\text{CO}_2^{\bullet-}$ radicals



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

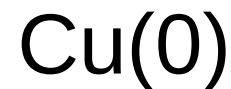
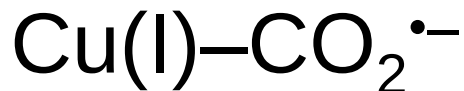
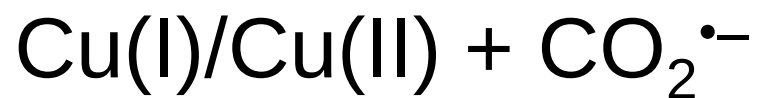
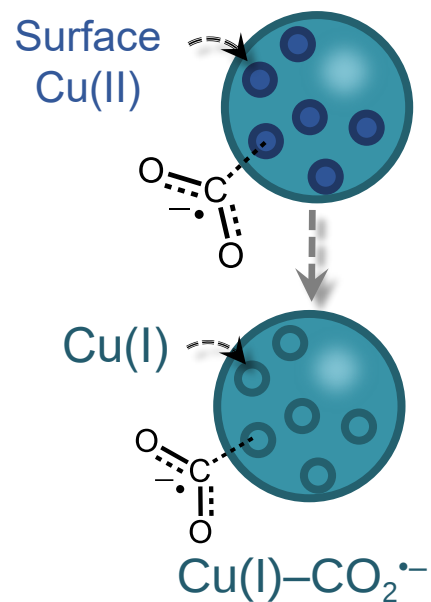
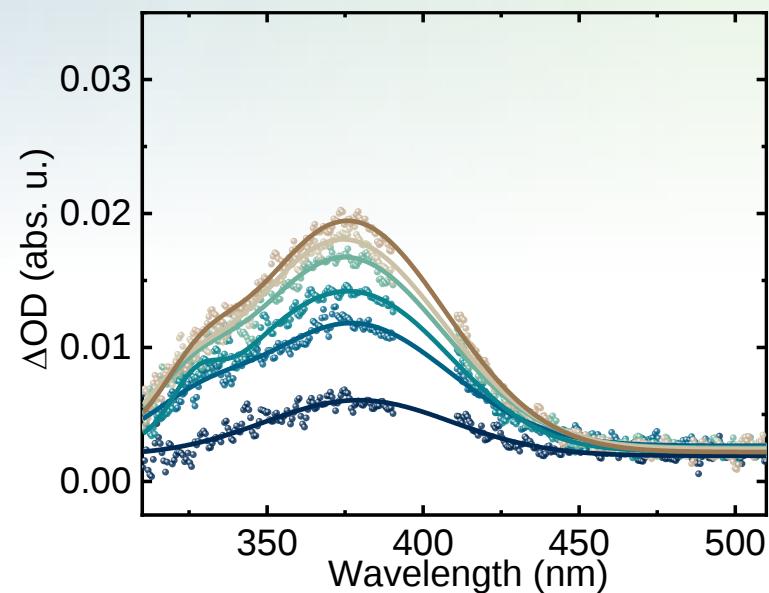
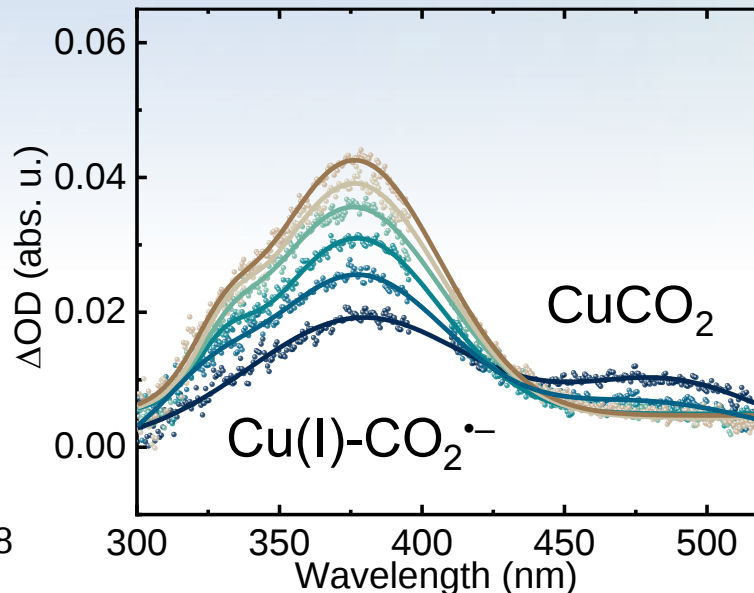
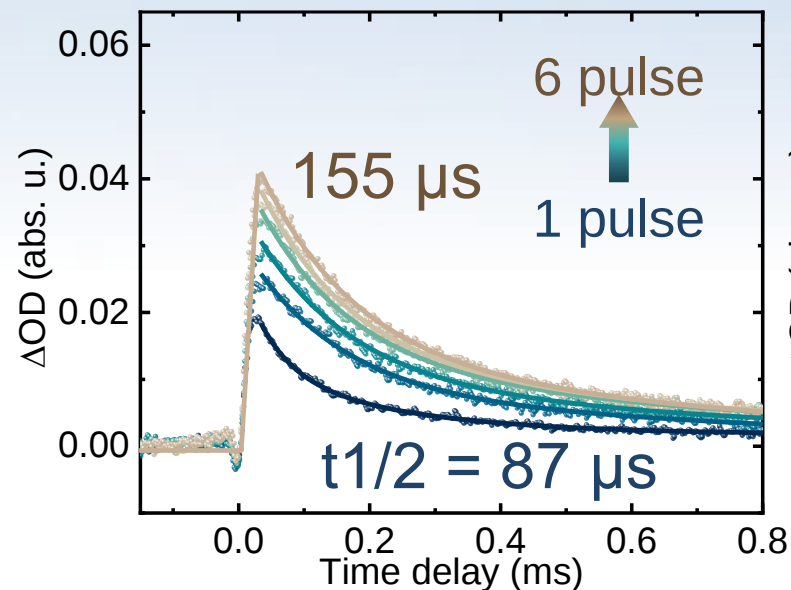
$(CO_2^{\bullet-})^{ad}-Cu(I)$

Fast
coupling

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

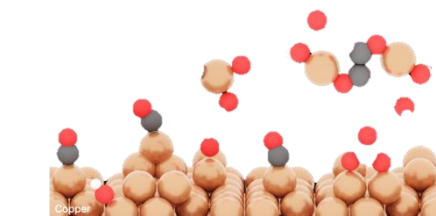
Electron
transfer

Oxidation state effect



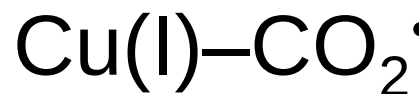
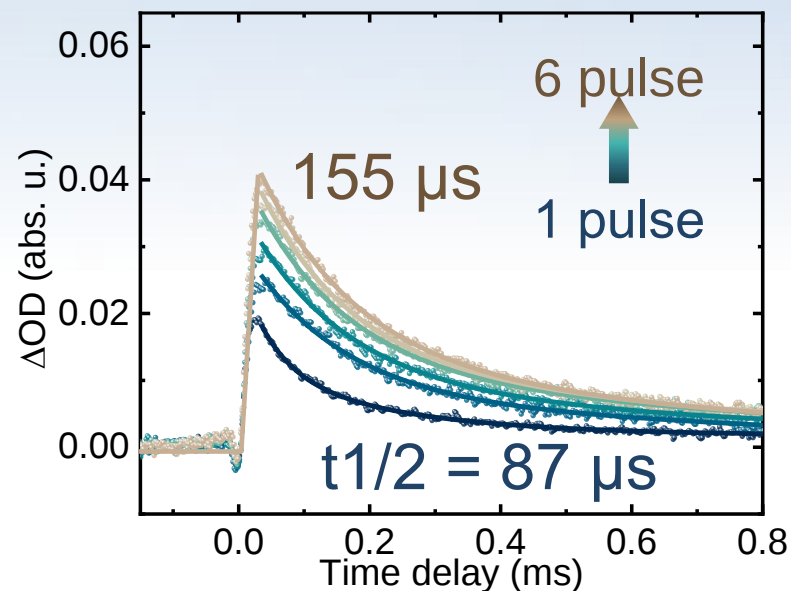
coupling reaction
($\text{CO}_2^{\bullet-}$ to C_{2+})

$$\text{Cu}^{\text{I}}/\text{Cu}_{\text{atom}} = -2.6 \text{ eV}$$



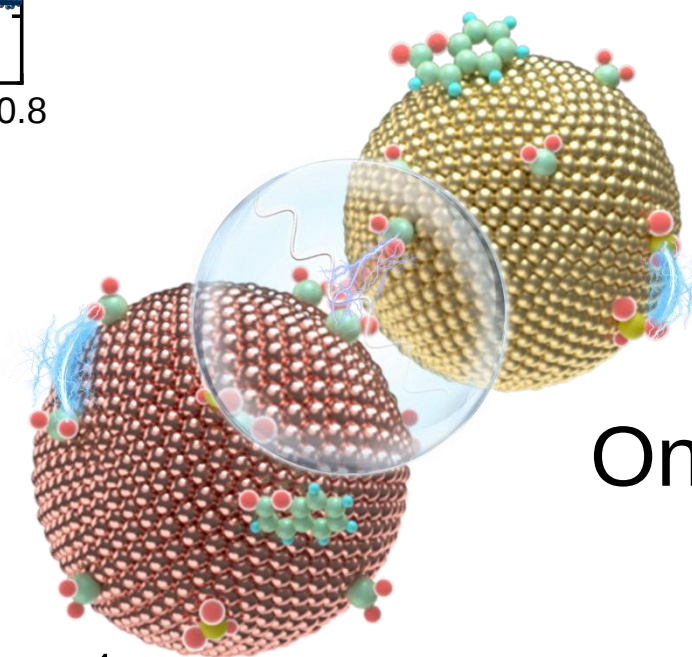
$$\text{Cu}^{\text{I}}/\text{Cu}_{\text{metal}} = -0.36 \text{ eV}$$

Rate constant calculations



coupling reaction
($\text{CO}_2^{\bullet-}$ to C_{2+})

$$k = \frac{1}{t_{1/2} C_0}$$



On the same NP :

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

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

On different 5 nm NP(0.5 mM):

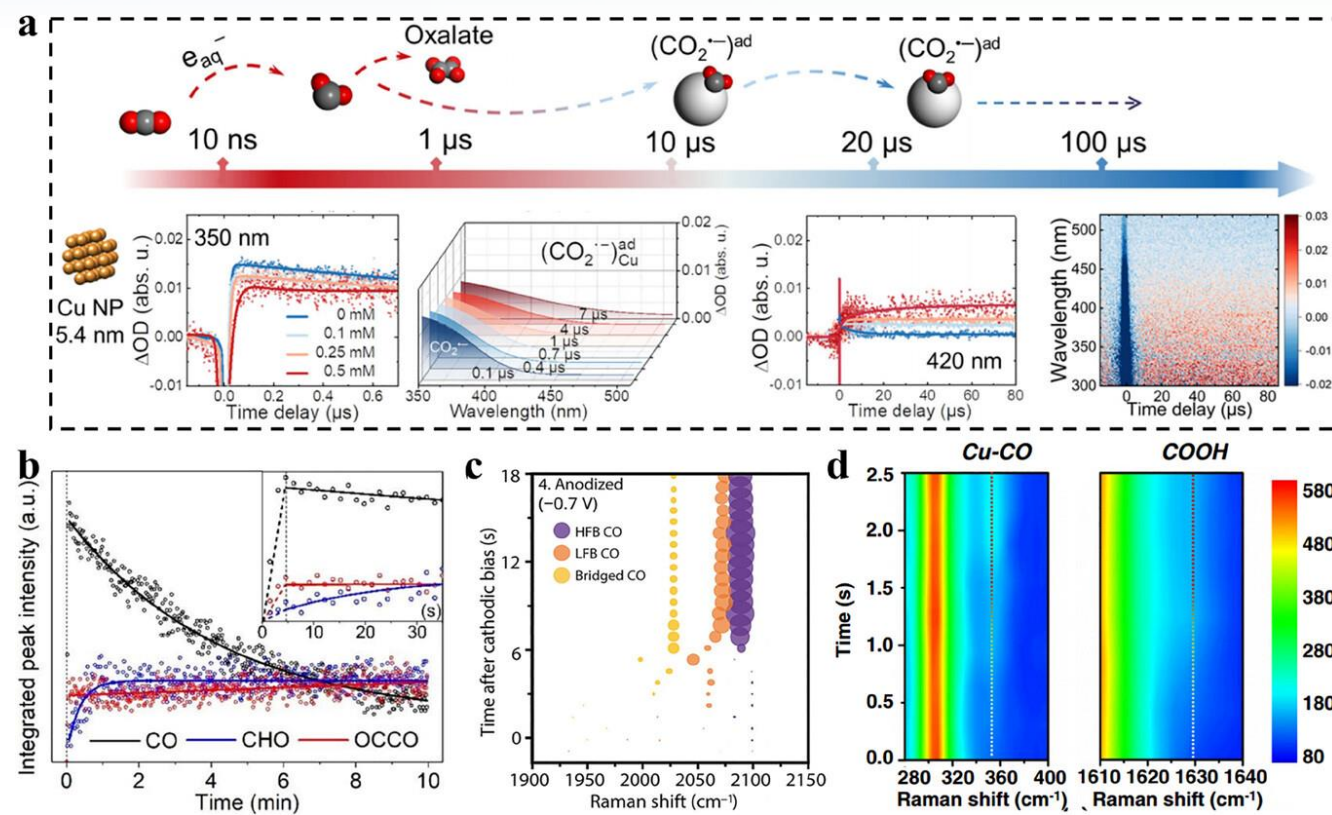
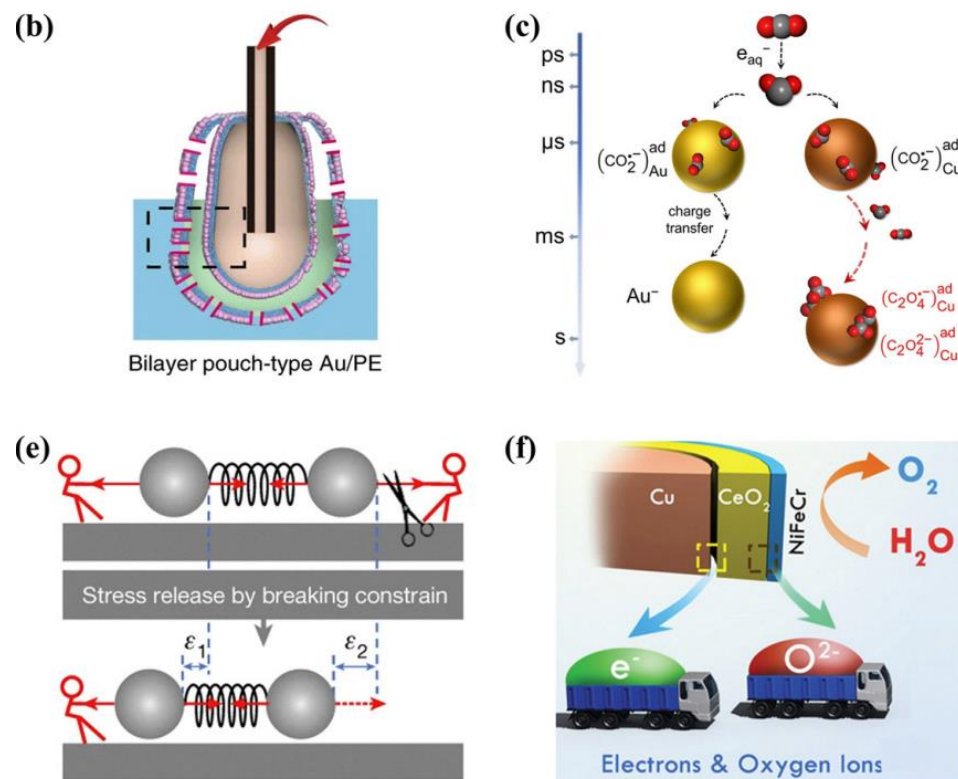
$$C_0 \approx 3 \times 10^{-7} \text{ M}$$

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

Cited by ...

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

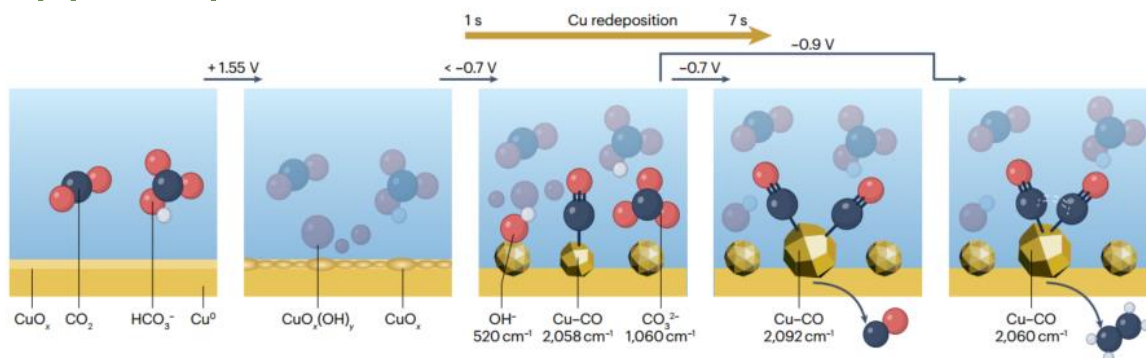
Small, **2025**, 21, 2411628.



Interfacial Radical Dynamics by Pulse Radiolysis

For electrocatalysis :

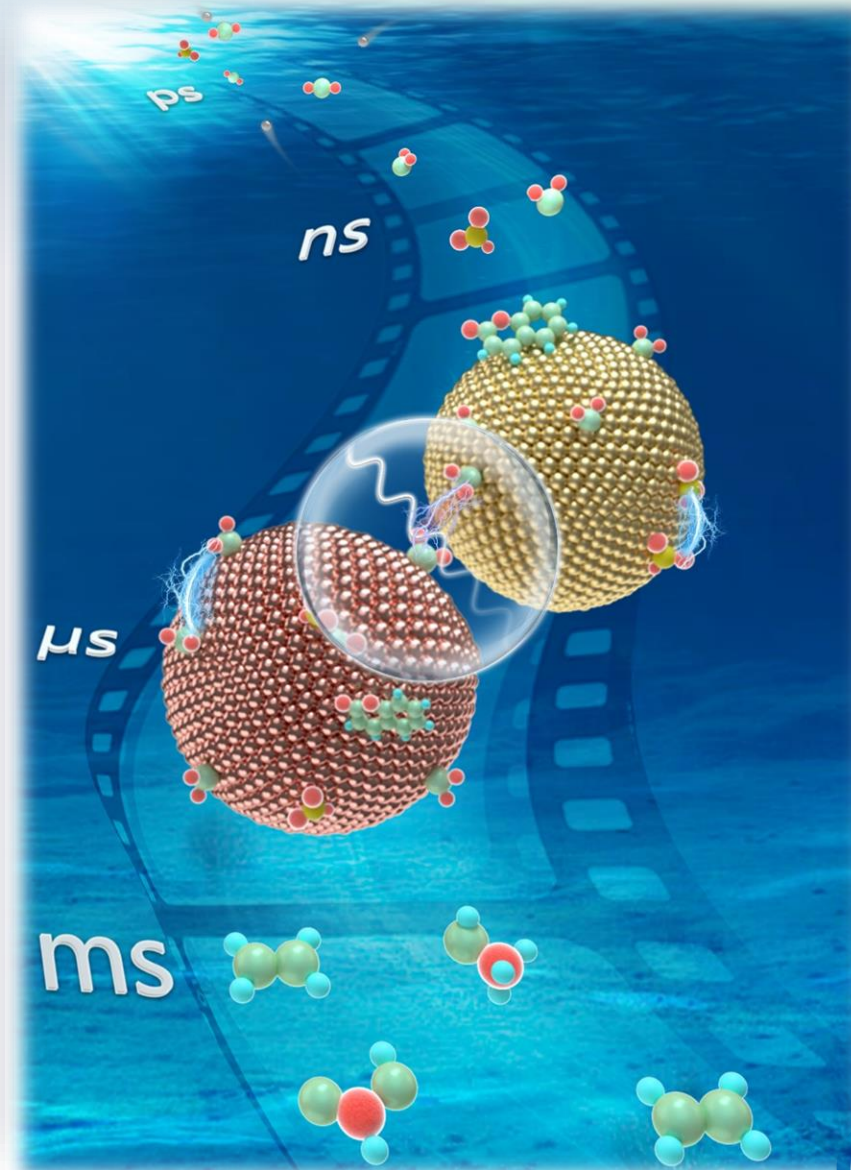
- Applied potential conditions



- 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

Experimental
verification

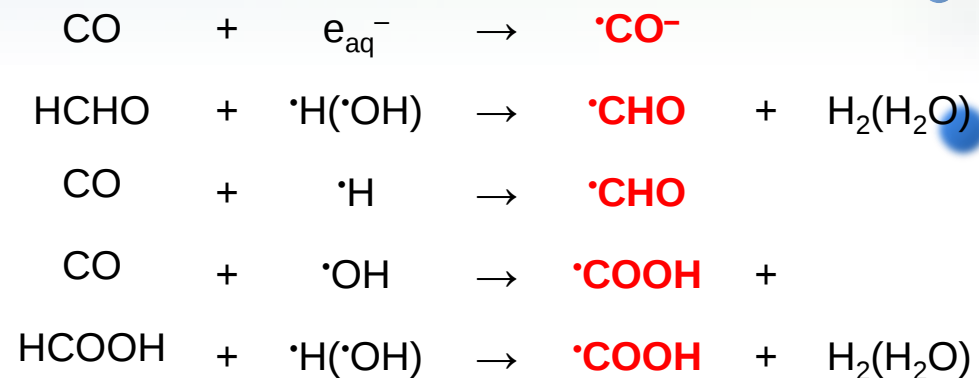
Interfacial dynamics

**Structure-property
relations**

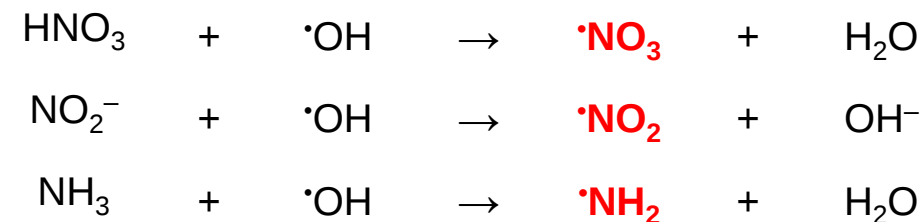
Selective conversion

Mechanism
elucidation

Key intermediates of CO₂ reduction



Key intermediates of nitrate reduction



Small molecule conversion
(CO, N₂, NO₃⁻)

Acknowledgement

Prof. Mehran Mostafavi

Dr. Carine Clavaguéra

Dr. Sergey A. DENISOV

Dr. Jean-Philippe

Dr. Daniel Adjei



Thanks



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