

Gold-Atom-Mediated Charge Transfer in Plasmonic Picocavity- Enabled CO₂ Dissociation

Xiaoting Ren

Shaanxi Normal University

Tingting Wang

Shaanxi Normal University

Huiru Xue

Shaanxi Normal University

Maoshan Hou

Shaanxi Normal University

Huan Chen

Shaanxi Normal University

Jinping Li

Shaanxi Normal University

Zhengkun Fu

Shaanxi Normal University

Lei Yan

yanlei@snnu.edu.cn

Shaanxi Normal University

Zhenglong Zhang

Shaanxi Normal University

Research Article

Keywords: Plasmonic picocavity, CO₂ dissociation, Charge-transfer bridge, TDDFT

Posted Date: October 15th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11056028/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Gold-Atom-Mediated Charge Transfer in Plasmonic Picocavity-Enabled CO₂ Dissociation

Xiaoting Ren, Tingting Wang, Huiru Xue, Maoshan Hou, Huan Chen, Jinping Li, Zhengkun Fu,

Lei Yan,* Zhenglong Zhang*

School of physics and information technology, Shaanxi Normal University, Shaanxi, Xi'an 710119, China.

*Corresponding author. Email: yanlei@snnu.edu.cn; zlzhang@snnu.edu.cn

Abstract: Plasmonic picocavities enable extreme light confinement at the atomic scale, making them highly promising for solar photochemical reactions. Here, ultrafast dynamics of CO₂ dissociation in a plasmonic picocavity is explored using time-dependent density functional theory (TDDFT). Atomic-scale structure in the picocavity has a strong influence on plasmon-driven reaction, and introducing a gold adatom significantly lowers the dissociation threshold. We identify that the reaction is dominated by direct charge transfer (DCT) rather than local field enhancement (FE). The gold adatom in the picocavity not only acts as a direct electron donor but also establishes a critical charge-transfer bridge across the gap, strongly enhancing transient population of CO₂ antibonding (AB) orbitals and thereby facilitating the reaction. Time-resolved analysis further reveals sequential charge-transfer channels between the nanoparticles (NPs), adatom, and CO₂, clarifying how atomic-scale junction structure controls the reaction dynamics. These findings uncover a single-atom-regulated plasmonic catalytic mechanism and provide microscopic insight into ultrafast photocatalytic processes in picocavities.

Keywords: Plasmonic picocavity · CO₂ dissociation · Charge-transfer bridge · TDDFT

Plasmonic photocatalysis has emerged as an effective strategy for harvesting visible light and converting it into chemical energy, attracting increasing attention in the field of solar-driven chemical transformations [1-3]. Owing to the ability to induce strong light-matter interactions at the subwavelength scale, plasmonic systems have been extensively explored for a broad range of photocatalytic reactions, including water

splitting [4,5], nitrogen reduction [6], CO₂ conversion [7,8] and H₂/O₂ dissociation [9-11]. Specially, plasmon-mediated CO₂ dissociation has attracted particular attention due to its potential significance for carbon-neutral energy conversion and mitigation of greenhouse gas emissions [12,13]. However, the activation of CO₂ remains intrinsically challenging due to its linear geometry and the high activation energy required for C=O bond cleavage, leading to low energy utilization efficiency and restricted control over reaction pathways [14,15].

Plasmonic picocavities recently proposed offer a promising route to address these challenges. By compressing metallic gaps to sub-nanometer or even atomic dimensions, picocavities could sustain extremely localized plasmonic modes with electromagnetic responses that are highly sensitive to atomic-scale structural variations [16-18], enabling applications such as single-molecule spectroscopy and ultrasensitive optical detection [19-21]. Such picocavities are typically formed by atomic protrusions or adatoms within metallic nanogaps, generating optical cavities with ultrasmall mode volumes and extraordinarily strong FE. These features provides a unique platform for probing light-matter interactions and hot-carrier processes at the atomic scale. Despite these advances, the role of picocavities in plasmonic photocatalysis, particularly in governing reaction dynamics and pathway control, remains unclear. In this sense, we construct a picocavity to investigate how atomic-scale structures regulate electron dynamics and charge-transfer processes in plasmon-mediated CO₂ dissociation.

Here, we investigate CO₂ dissociation in a plasmonic picocavity irradiated by femtosecond laser pulses using real-time TDDFT [22,23]. A comparative analysis reveals that the presence of the gold adatom in the picocavity is the critical for initiating CO₂ dissociation, whereas the adatom-free system remains non-reactive. Analysis of the local FE and electron transitions into CO₂ AB state shows that DCT dominates the reaction in the plasmonic picocavity. Specifically, multiple metal components contribute to charge injection through spatially distinct charge-transfer channels with a clear temporal sequence. These findings provide a deep understanding of the decisive role of

atomic-scale structures in plasmonic picocavity-induced molecular reaction.

First-principles calculations are performed with a real-space and real-time TDDFT code, OCTOPUS [24]. The interaction between atomic core and valence electrons is described by Troullier–Martins pseudopotentials [25] in the local density approximation (LDA) [26]. The simulation zone is defined by assigning a sphere around each atom with a radius of 15 Å and a spacing of 0.3 Å between grid points. Coupled electron–ion dynamics are treated within the Ehrenfest approximation [27]. In electron dynamic simulations, Kohn–Sham (KS) eigenstates are propagated with a time-dependent Hamiltonian. The system is evolved for 31000 steps with a time step of 0.0026 fs. A delta function for electromagnetic pulse is also used in order to obtain optical absorption spectrum [28,29].

The geometry of plasmonic picocavity consisting of two Au NPs and a gold atom adsorbed on one Au NP is shown in Fig. 1(a). We use a jellium sphere with electron density $r_s = 4.5$ a.u. to simulate the Au NPs with the diameter = 1 nm. This approximation is commonly used in the literature as it captures the most important properties of metallic NPs [30,31]. A CO₂ molecule is placed in the gap with the carbon atom 3.28 Å away from the gold atom and the lower Au NP. In detail, the surface-to-surface gap spacing between the upper and lower Au NPs is tested. When the gap spacing is 7 Å or less, chemisorption between the gold atom and the CO₂ molecule occurs, directly inducing CO₂ dissociation. Whereas at the gap spacing of 9–10 Å, the plasmonic coupling between the NPs is significantly weakened, making it difficult to drive the reaction. Based on molecular stability and coupling strength, we chose the gap spacing of 8 Å in our study.

We first explore the absorption spectra of the configuration to determine plasmonic resonant energy in Fig. 1(b). The dominant peak at 2.32 eV red shifts 0.01 eV and the linewidth is broaden, compared with adatom-free system. Induced charge distributions of the adatom-free system at dominant peak in Fig. S1 reveals dipolar oscillations of plasmonic response. Laser pulse in a Gaussian wave packet in Fig. 1(c) is explored to

the system and expressed as

$$E(t) = E_{\max} \exp\left[-\frac{(t-t_0)^2}{2\tau^2}\right] \cos(\omega t - \omega t_0) \quad (1)$$

where τ is set to 3.3 fs and the energy $\hbar\omega = 2.32$ eV. Laser field reaches the maximum intensity $E_{\max} = 2.15$ V/Å at $t_0 = 10$ fs.

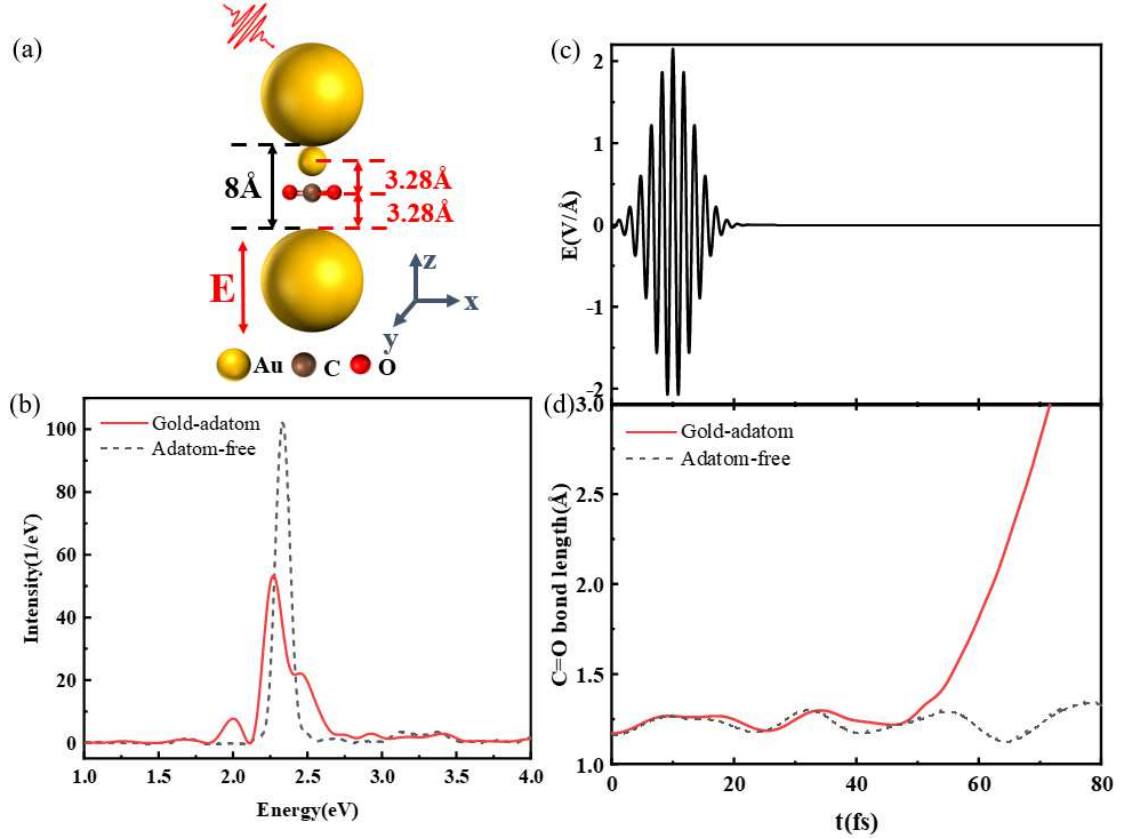


Fig. 1 (a) Schematic diagram of a CO₂ molecule and plasmonic picocavity consisting of two coupled Au nanoparticles (diameter = 1nm) and a gold adatom with the laser field polarized along the z direction. (b) Optical absorption spectra of the gold-adatom system and adatom-free system. (c) Time evolved laser field ($\hbar\omega = 2.32$ eV), with $E_{\max} = 2.15$ V/Å at the time $t_0 = 10$ fs. (d) Time evolution of the C=O bond length of CO₂ for the gold-adatom system and adatom-free system

Dynamic response of CO₂ in the picocavity under the laser pulse is investigated in Fig. 1(d). The C=O bonds begin to oscillate following the laser excitation, and an oscillatory distortion of the bond length occurs at $t = 10$ fs, as the laser field reaches its peak intensity. At $t = 15$ fs, the bond length is re-stretched instead of decreasing, while

after the laser pulse vanishes at $t = 20$ fs, the oscillation gradually returns to a regular pattern. At $t = 30$ fs, the two C=O bonds exhibit asymmetric distortion in Fig. S2(a) and (b), leading to asymmetric and asynchronous dissociation due to the Jahn–Teller effect [32,33]. For $t > 50$ fs, the C=O bonds elongate significantly, reaching the dissociation criterion of $2.0 \text{ \AA}$ at 62.4 fs and 68.9 fs, respectively [34,35]. As a result, CO_2 dissociates into one carbon atom and two oxygen atoms and the motion of all atoms occurs mainly in the xz plane (Fig. S3). In contrast, the CO_2 molecule in the adatom-free system under the same laser illumination never splits throughout the dynamics. We further examine the adatom-free system under a stronger field (Fig. S2 (c), (d)) and find that CO_2 dissociation occurs above a threshold of $E_{\text{max}} = 5 \text{ V/\AA}$. To exclude the distance effect, we also consider a configuration in which the CO_2 molecule is located $3.28 \text{ \AA}$ away from both Au NPs in the adatom-free- symmetry system and find that dissociation occurs only at $E_{\text{max}} = 3 \text{ V/\AA}$ (Fig. S2(e), (f)). Therefore, introducing a gold adatom in a plasmonic picocavity significantly lowers the dissociation threshold.

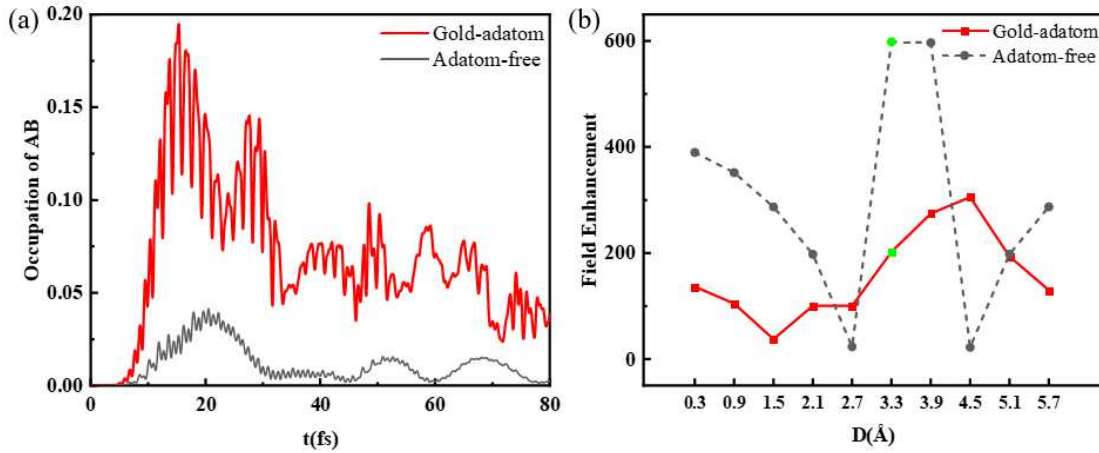


Fig. 2 (a) Time-evolved occupation of the CO_2 antibonding state for the gold-adatom system and adatom-free system under the laser with $E_{\text{max}} = 0.05 \text{ V/\AA}$. (b) Field enhancement factor along the laser polarization direction in the gap region. D denotes the sampling positions, starting $0.3 \text{ \AA}$ above the upper surface of the lower Au NP. Green point denotes the position of CO_2 molecule

To further elucidate the critical role of atomic-scale gold structure in plasmonic picocavity-driving CO_2 dissociation, we analyze the time-dependent occupation of AB state in CO_2 and local FE in the gap in Fig. 2. AB state of CO_2 molecule corresponds to

π^* orbital, which exhibits distinct hybridization with the lower NP (Fig. 3(b)). Under the laser excitation, the occupation of the AB state exhibits an overall oscillatory evolution. The occupation increases rapidly from initial time and reaches a maximum of 0.19 at $t = 15$ fs. This maximum coincides with the re-stretching of the C=O bond at $t = 15$ fs, indicating that the nucleus motion in the CO₂ is modulated by the evolution of electronic excitation. After $t = 20$ fs with the pulse vanishing, the occupation continues to oscillate but gradually decays.

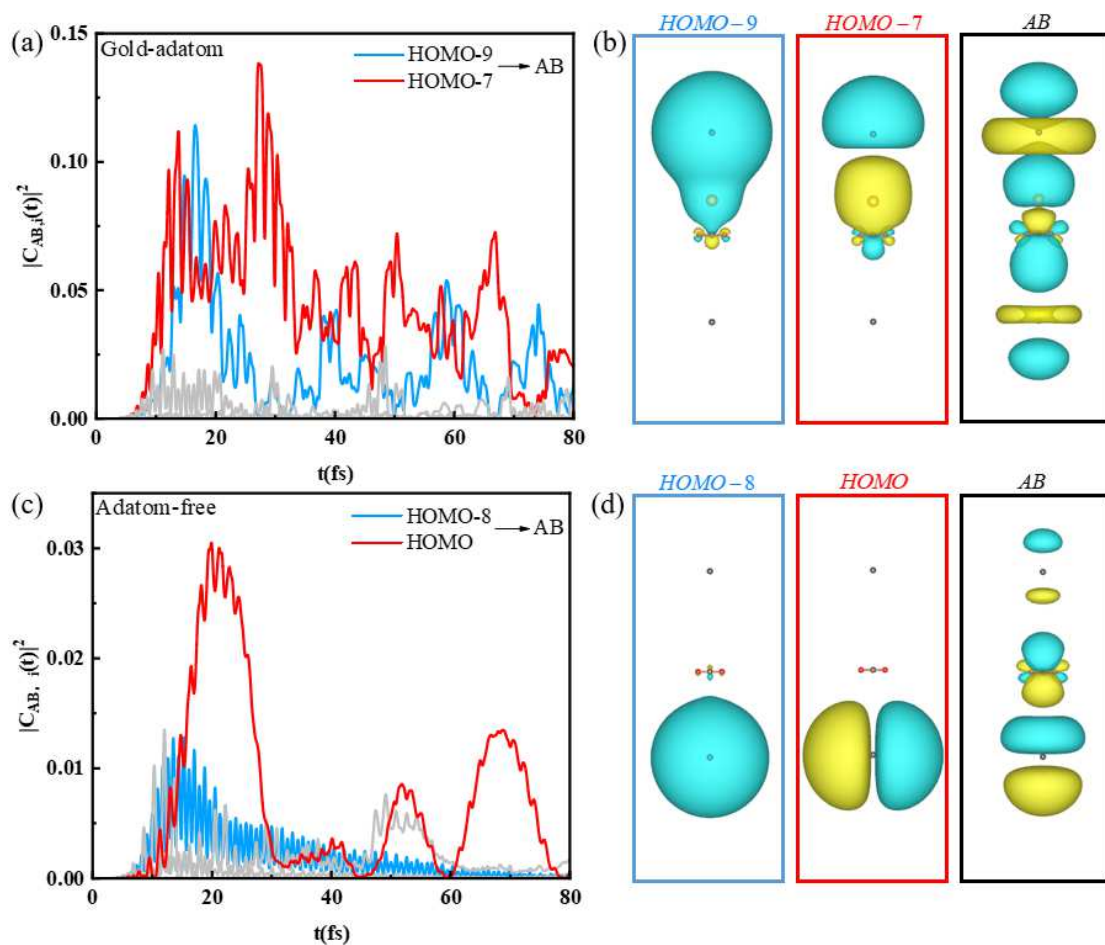


Fig. 3 Time-evolved transition coefficients $|C_{AB,i}(t)|^2$ from all occupied states to the AB state under the laser with $E_{\max} = 0.05$ V/Å in (a) the gold-atom system and (c) the adatom-free system. Two dominant contributing orbitals are highlighted, and all other transitions shown in gray lines. Corresponding wave functions for (b) the gold-atom system and (d) the adatom-free system. Isosurface value of wave functions is set to 0.008 Å^{-3}

In contrast, in the adatom-free system, the AB state is out of phase with the Au NP

surface p states in Fig. 3(d), which weakens their electronic coupling. Throughout the photoexcitation process, the AB state occupation in the gold-adatom system remains significantly higher than that in the adatom-free system. This indicates that the presence of atomic-scale gold structures enables plasmon-induced electrons injection into the AB orbitals of CO₂ molecule more efficiently, thereby weakening the C=O bond stability and driving the molecular dissociation.

We quantitatively assess the role of plasmon-induced FE in CO₂ dissociation by analyzing the spatial distribution of the FE within the picocavity gap in Fig. 2(b). Here, the local FE factor is defined as:

$$FE(x) = \frac{V_{\text{eff}}(x + \delta x) - V_{\text{eff}}(x)}{e\delta x E_{\text{ext}}} \quad (2)$$

where x denotes the spatial position, δx is the grid spacing along the polarization direction, V_{eff} is the effective potential, and E_{ext} is the external field strength. The FE was sampled at ten positions along the z direction starting 0.3 Å above the upper surface of the lower Au NP with an interval of 0.6 Å. Overall, the local FE in the gap region is weaker than that in the adatom-free system. In particular, the FE at the position of the CO₂ molecule reaches 598 in the adatom-free system, but decreases to 202 in the gold-adatom system. These results indicate that CO₂ dissociation in the gold-adatom system is primarily governed by plasmon-induced charge transfer rather than local FE.

To illustrate the dynamics of plasmonic response, we display the transition coefficients $|C_{\text{AB},i}(t)|^2$, defined as the time-dependent occupied KS orbital $|i(t)\rangle$ projected onto the initial AB state with laser intensity $E_{\text{max}} = 0.05$ V/Å in Fig. 3. Two dominant contributing orbitals and their corresponding wave-function distributions are highlighted. In the gold-adatom system, the dominant contributions to the AB state of CO₂ molecule arise from HOMO-9 and HOMO-7 (Fig. 3(a)). Transition coefficients keep oscillation following the laser pulse, and the contribution from HOMO-9 reaches maximum value of 0.11 at $t = 16$ fs. After the laser pulse vanishes, the transition coefficient from HOMO-9 continues to oscillate but gradually decays, while that for HOMO-7 increases to maximum of 0.14 at $t = 27$ fs. This indicates that HOMO-7 continues to play

an important role in the electron-injection process for dissociation dynamics after laser annihilating.

The charge density of HOMO-9 and HOMO-7 is mainly distributed on the upper Au NP and the gold atom with a minor part on the CO₂ molecule, and that of the AB state is distributed on the Au NPs and the CO₂ molecule as shown in Fig. 3(b). This indicates that DCT from the upper Au NP and the gold atom to the CO₂ molecule and intramolecular charge transfer (ICT) within CO₂ coexist. By comparison, in the adatom-free system, the dominant transitions to the AB state originate from HOMO and HOMO-8 (Fig. 3(c)). The wave functions of both orbitals are localized on the lower Au NP, while the AB state is primarily distributed on the lower Au NP and the CO₂ molecule with minor contributions from the upper Au NP in Fig. 3(d). Therefore electrons are mainly transferred from the lower Au NP to CO₂ in the adatom-free system. In fact, some orbitals such as HOMO-8 and HOMO-3 (Fig. S4(a)) with charge density distributed on the lower Au NP are also present in the gold-adatom system, indicating that charge transfer from the lower Au NP to CO₂ also occurs, although its contribution is smaller than that from the upper Au NP.

To further distinguish quantitatively the contributions of DCT and ICT to the AB state of CO₂ molecule, we define the contribution of ICT and DCT respectively as

$$\eta_{\text{ICT}} = \frac{\sum_i |C_{\text{AB},i}(t)|^2 P_i^{\text{CO}_2} P_{\text{AB}}^{\text{CO}_2}}{\sum_i |C_{\text{AB},i}(t)|^2 (P_i^{\text{CO}_2} + P_i^{\text{metal}}) P_{\text{AB}}^{\text{CO}_2}} \quad (3)$$

$$\eta_{\text{DCT}} = \frac{\sum_i |C_{\text{AB},i}(t)|^2 P_i^{\text{metal}} P_{\text{AB}}^{\text{CO}_2}}{\sum_i |C_{\text{AB},i}(t)|^2 (P_i^{\text{CO}_2} + P_i^{\text{metal}}) P_{\text{AB}}^{\text{CO}_2}} \quad (4)$$

where $P_i^{\text{CO}_2}$, P_i^{metal} and $P_{\text{AB}}^{\text{CO}_2}$ are as the ratio of the component local density of states (LDOS) to the total density of states (TDOS), evaluated at the corresponding occupied orbital i and the AB state, respectively. All contributions are normalized in the denominator [36,37]. The time is chosen at $t = 15$ fs, when the occupation of AB reaches its maximum in Fig. 2(a). DCT contribution is $\eta_{\text{DCT}} = 96.4\%$ and ICT within CO₂ is η_{ICT}

= 3.6%. These results indicate that DCT from the Au NPs and the gold atom to the CO₂ dominates the reaction, while ICT contributes only a minor fraction due to the intrinsic chemical inertness of CO₂.

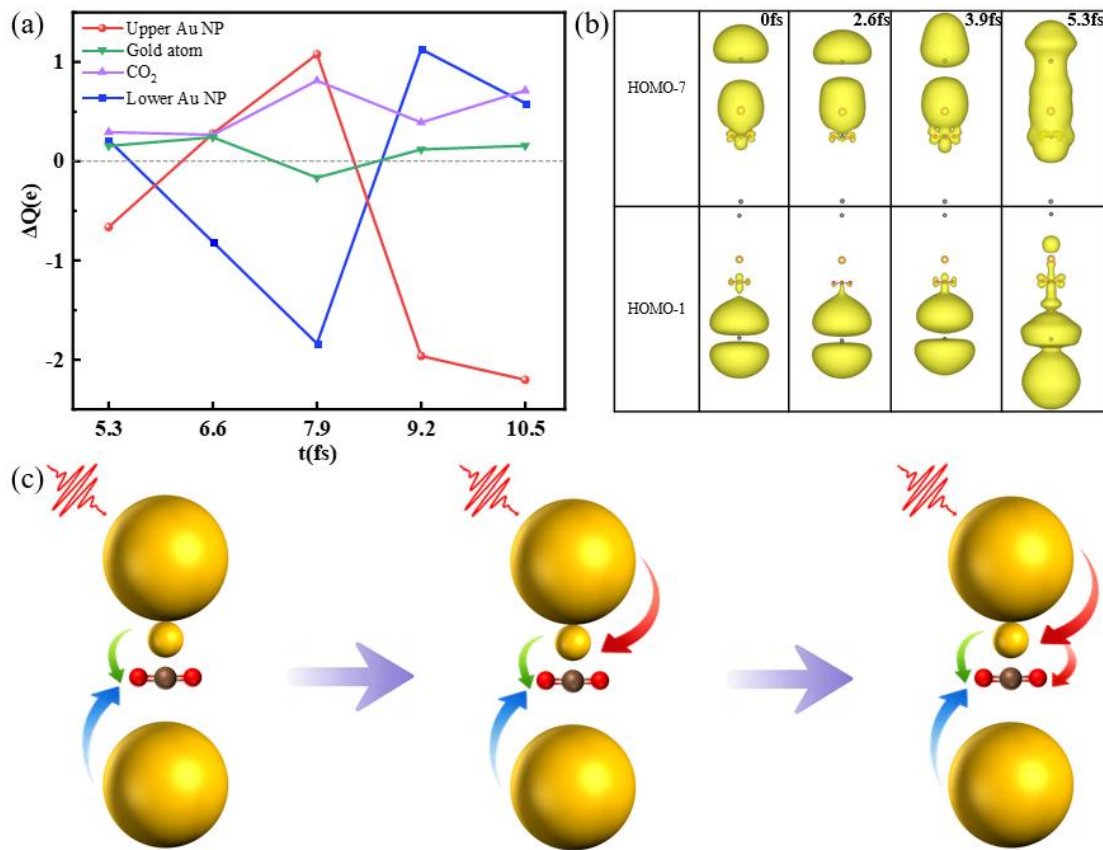


Fig. 4 (a) Charge variation in different regions of the gold-atom system under the laser with $E_{\max} = 2.15$ V/Å. (b) Time evolution of charge density at the HOMO-1 and HOMO-7 orbitals in the gold-atom system. Isosurface value is set to 0.004 Å^{-3} . (c) Schematic illustration of the charge transfer sequence from the Au NPs and the gold atom to the CO₂ molecule

To reveal the charge-transfer dynamics between different metallic components and CO₂, we examine the total charge variation of the system (Fig. 4(a)). From $t = 5.3$ fs to 7.9 fs, the charges of the lower Au NP and the gold atom decrease, and those of the upper Au NP and CO₂ increase. Similar behavior is observed in the charge density evolution of occupied orbital (Fig. 4(b)). The HOMO-7 orbital shows charge depletion on the gold atom accompanied by charge accumulation on CO₂, while the HOMO-1 orbital exhibits charge depletion on the lower Au NP and charge accumulation on CO₂

during the timespan $t = 2.6\text{--}3.9$ fs. Hence there exists charge transfer from the gold atom and the lower Au NP to CO₂ molecule.

The charges of the upper Au NP further decrease, whereas those of the gold atom and the lower Au NP increase from the time $t = 7.9$ fs to 9.2 fs. Consistently, the HOMO-7 orbital at $t = 3.9$ fs exhibits charge depletion on the upper Au NP together with charge accumulation around the gold atom compared with the case at $t = 5.3$ fs. This implies that charge transfer from the upper Au NP to the gold atom appear. During the time range $t = 9.2\text{--}10.5$ fs, the charges of both the upper and lower Au NPs further decrease, while the charge of the gold atom changes only slightly and that of CO₂ increases. Correspondingly, the HOMO-7 orbital shows charge accumulation around CO₂ at $t = 5.3$ fs with the accumulated charge mainly originating from the upper Au NP in contrast with the density at $t = 3.9$ fs. Therefore, charge from the upper Au NP to CO₂ molecule with the participation of the gold atom.

The charge-transfer processes described above are not unique to HOMO-7 and HOMO-1. Analysis of the other occupied orbitals reveals similar charge-transfer behaviors (Fig. S4(a)). To further quantify the contributions of different metallic components to the DCT, the same method based on Equation (4) is applied to the orbitals in Fig. S4(b). The result yields 12.6% from the gold atom and 83.9% from the Au NPs contributes to AB state of CO₂ at $t = 15$ fs. The evolution of the charge-transfer pathways is further illustrated by the charge density difference in Fig. S4(c). During the time range $t = 9.2\text{--}14.4$ fs, a continuous charge-transfer channel forms between the upper Au NP and the gold atom. This channel further extends to CO₂ from $t = 23.6$ fs to 30.2 fs, indicating efficient electron injection into the molecule. In contrast, no continuous charge transfer across the gap is observed in the adatom-free system.

Based on the above analysis, three spatially distinct charge-transfer channels with a clear temporal sequence are identified in Fig. 4(c): charge transfer first occurs from the gold atom and the lower Au NP to CO₂, followed by transfer from the upper Au NP mediated by the gold atom. In this process, the gold atom serves as both a direct electron donor and a charge-transfer bridge. Combined with the transition analysis discussed

above, the dominant contributions to the CO₂ antibonding states originate from HOMO-9 and HOMO-7 in Fig. 3(b). The charge-transfer behavior associated with both orbitals mainly originates from the gold atom and the upper Au NP mediated by the gold atom, which are dominant charge-transfer channels.

In conclusion, we employ real-time TDDFT to clarify the microscopic mechanism of plasmon-driven CO₂ dissociation in a picocavity. We demonstrate that the presence of a gold adatom significantly lowers the dissociation threshold by establishing a charge-transfer bridge, even though the adatom-free system exhibits stronger local FE. Quantitative analysis reveals that DCT from the Au NPs and the gold atom to AB orbital of CO₂ dominates the process with a 96.4% contribution. This originates from the strong electronic coupling between the gold atom and molecular orbitals, which significantly enhances the transient occupancy of CO₂ AB state. Our results reveal three spatially charge-transfer channels with clear temporal characteristics, highlighting the dual role of the gold atom as both a direct electron donor and a crucial charge-transfer bridge. These findings provide a feasible strategy for controlling plasmonic chemical reactivity through atomic-scale modulation of charge-transfer processes in picocavities. Furthermore, this study offers critical theoretical insights for the rational design of plasmonic catalysts and the development of next-generation ultrafast optoelectronic devices based on picocavity structures.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 12304426) and the Fundamental Science Foundation of Shaanxi (No. 23JSQ007) to Huan Chen; the National Key Research and Development Program of China (No. 2024YFA1409900), the National Natural Science Foundation of China (No. 12574442), and the Scientific Research Program Funded by Education Department of Shaanxi Provincial Government (No. 24JP040) to Zhengkun Fu; the Natural Science Foundation of Shaanxi Province (No. 2025JC-YBQN-062) to Lei Yan; and the National Key Research and Development Program of China (No. 2021YFA1201500), the National Natural Science Foundation of China (Nos. U22A6005 and 12474389), the Natural Science Foundation of

Shaanxi Province (No. 2024JC-JCQN-07), the Fundamental Science Foundation of Shaanxi (No. 22JSZ010), and the Fundamental Research Funds for the Central Universities (Nos. GK202201012 and GK202308001) to Zhenglong Zhang.

References

1. Wan X, Li Y, Chen Y, Ma J, Liu Y-A, Zhao E-D, Gu Y, Zhao Y, Cui Y, Li R, Liu D, Long R, Liew KM, Xiong Y (2024) A nonmetallic plasmonic catalyst for photothermal CO₂ flow conversion with high activity, selectivity and durability. *Nat Commun* 15:1273. <https://doi.org/10.1038/s41467-024-45516-4>
2. Liu S, Wu Z, Zhu Z, Feng K, Zhou Y, Hu X, Huang X, Zhang B, Dong X, Ma Y, Nie K, Shen J, Wang Z, He J, Wang J, Ji Y, Yan B, Zhang Q, Genest A, Zhang X, Li C, Wu B, An X, Rupprechter G, He L (2025) Quantifying the distinct role of plasmon enhancement mechanisms in prototypical antenna-reactor photocatalysts. *Nat Commun* 16:2245. <https://doi.org/10.1038/s41467-025-57569-0>
3. Gan Y, Kalantari Osgouei A, Ahrens A, Wang B, Zhou J, Zhan J-Z, Zeng D, Nie S, Zhao X, Chen G, Nordlander P, Zhou L (2025) 2D Plasmonic Photocatalyst Enables Highly Efficient Hot-Electron-Mediated Surface Reactions under Red Light Irradiation. *ACS Nano* 19:17006–17013. <https://doi.org/10.1021/acsnano.5c03598>
4. Yan L, Wang F, Meng S (2016) Quantum Mode Selectivity of Plasmon-Induced Water Splitting on Gold Nanoparticles. *ACS Nano* 10:5452–5458. <https://doi.org/10.1021/acsnano.6b01840>
5. You P, Chen D, Liu X, Zhang C, Selloni A, Meng S (2024) Correlated electron–nuclear dynamics of photoinduced water dissociation on rutile TiO₂. *Nat Mater* 23:1100–1106. <https://doi.org/10.1038/s41563-024-01900-5>
6. Yang Y, Jia H, Su S, Zhang Y, Zhao M, Li J, Ruan Q, Zhang C (2023) A Pd-based plasmonic photocatalyst for nitrogen fixation through an antenna–reactor mechanism. *Chem Sci* 14:10953–10961. <https://doi.org/10.1039/D3SC02862C>
7. Zhang Y, Yan L, Guan M, Chen D, Xu Z, Guo H, Hu S, Zhang S, Liu X, Guo Z, Li S, Meng S (2022) Indirect to Direct Charge Transfer Transition in Plasmon-Enabled CO₂ Photoreduction. *Adv Sci* 9:2102978. <https://doi.org/10.1002/advs.202102978>
8. Jin P, Guo P, Luo N, Zhang H, Ni C, Chen R, Liu W, Li R, Xiao J, Wang G, Zhang F, Fornasiero P, Wang F Photochemical H₂ dissociation for nearly quantitative CO₂ reduction to ethylene
9. Li H, Shang H, Jiang F, Zhu X, Ruan Q, Zhang L, Wang J (2021) Plasmonic O₂ dissociation and spillover expedite selective oxidation of primary C–H bonds. *Chem Sci* 12:15308–15317. <https://doi.org/10.1039/D1SC04632B>
10. Guo A, Lu Y, Song Y, Cao Y, Du R, Li J, Fu Z, Yan L, Zhang Z (2023) Plasmon-Mediated Hydrogen Dissociation with Symmetry Tunability. *J Phys Chem Lett* 14:5748–5753. <https://doi.org/10.1021/acs.jpcclett.3c01146>
11. Yuhui Song(宋玉慧) YL (2024) Microscopic mechanism of plasmon-mediated photocatalytic H₂ splitting on Ag-Au alloy chain. *Chin Phys B* 33:33101–033101. <https://doi.org/10.1088/1674-1056/ad123d>
12. Verma R, Belgamwar R, Polshettiwar V (2021) Plasmonic Photocatalysis for CO₂ Conversion

- to Chemicals and Fuels. ACS Mater Lett 3:574–598. <https://doi.org/10.1021/acsmaterialslett.1c00081>
13. Xue J, Chen Z, Zhang Y, Zhao J (2024) A review on plasmonic enhancement of activity and selectivity in electrocatalytic CO₂ reduction. Front Energy 18:399–417. <https://doi.org/10.1007/s11708-024-0950-8>
 14. Albero J, Peng Y, García H (2020) Photocatalytic CO₂ Reduction to C₂+ Products. ACS Catal 10:5734–5749. <https://doi.org/10.1021/acscatal.0c00478>
 15. Wang Y, Chen E, Tang J (2022) Insight on Reaction Pathways of Photocatalytic CO₂ Conversion. ACS Catal 12:7300–7316. <https://doi.org/10.1021/acscatal.2c01012>
 16. Benz F, Schmidt MK, Dreismann A, Chikkaraddy R, Zhang Y, Demetriadou A, Carnegie C, Ohadi H, De Nijs B, Esteban R, Aizpurua J, Baumberg JJ (2016) Single-molecule optomechanics in “picocavities.” Science 354:726–729. <https://doi.org/10.1126/science.aah5243>
 17. Griffiths J, De Nijs B, Chikkaraddy R, Baumberg JJ (2021) Locating Single-Atom Optical Picocavities Using Wavelength-Multiplexed Raman Scattering. ACS Photonics 8:2868–2875. <https://doi.org/10.1021/acsp Photonics.1c01100>
 18. Liu S, Bonafe FP, Appel H, Rubio A, Wolf M, Kumagai T (2023) Inelastic Light Scattering in the Vicinity of a Single-Atom Quantum Point Contact in a Plasmonic Picocavity. ACS Nano 17:10172–10180. <https://doi.org/10.1021/acsnano.3c00261>
 19. Jakob LA, Deacon WM, Zhang Y, De Nijs B, Pavlenko E, Hu S, Carnegie C, Neuman T, Esteban R, Aizpurua J, Baumberg JJ (2023) Giant optomechanical spring effect in plasmonic nano- and picocavities probed by surface-enhanced Raman scattering. Nat Commun 14:3291. <https://doi.org/10.1038/s41467-023-38124-1>
 20. Chikkaraddy R, Arul R, Jakob LA, Baumberg JJ (2023) Single-molecule mid-infrared spectroscopy and detection through vibrationally assisted luminescence. Nat Photonics 17:865–871. <https://doi.org/10.1038/s41566-023-01263-4>
 21. Shiotari A, Liu S, Trenins G, Sugimoto T, Wolf M, Rossi M, Kumagai T (2025) Picocavity-Enhanced Raman Spectroscopy of Physisorbed H₂ and D₂ Molecules. Phys Rev Lett 134:206901. <https://doi.org/10.1103/PhysRevLett.134.206901>
 22. Runge E, Gross EKV (1984) Density-Functional Theory for Time-Dependent Systems. Phys Rev Lett 52:997. <https://doi.org/10.1103/PhysRevLett.52.997>
 23. Ramakrishna K, Cangi A, Dornheim T, Baczewski A, Vorberger J (2021) First-principles modeling of plasmons in aluminum under ambient and extreme conditions. Phys Rev B 103:125118. <https://doi.org/10.1103/PhysRevB.103.125118>
 24. Castro A, Appel H, Oliveira M, Rozzi CA, Andrade X, Lorenzen F, Marques MAL, Gross EKV, Rubio A (2006) *octopus*: a tool for the application of time-dependent density functional theory. Phys Status Solidi B 243:2465–2488. <https://doi.org/10.1002/pssb.200642067>
 25. Troullier N, Martins JL (1991) Efficient pseudopotentials for plane-wave calculations. Phys Rev B 43:1993–2006. <https://doi.org/10.1103/PhysRevB.43.1993>
 26. Ceperley DM, Alder BJ (1980) Ground State of the Electron Gas by a Stochastic Method. Phys Rev Lett 45:566–569. <https://doi.org/10.1103/PhysRevLett.45.566>
 27. Alonso JL, Andrade X, Echenique P, Falceto F, Prada-Gracia D, Rubio A (2008) Efficient Formalism for Large-Scale *Ab Initio* Molecular Dynamics based on Time-Dependent Density Functional Theory. Phys Rev Lett 101:096403. <https://doi.org/10.1103/PhysRevLett.101.096403>

sRevLett.101.096403

28. Castro A, Marques MAL, Rubio A (2004) Propagators for the time-dependent Kohn–Sham equations. *J Chem Phys* 121:3425–3433. <https://doi.org/10.1063/1.1774980>
29. Yan J, Yuan Z, Gao S (2007) End and Central Plasmon Resonances in Linear Atomic Chains. *Phys Rev Lett* 98:216602. <https://doi.org/10.1103/PhysRevLett.98.216602>
30. Zheng J, Zhang C, Dickson RM (2004) Highly Fluorescent, Water-Soluble, Size-Tunable Gold Quantum Dots. *Phys Rev Lett* 93:077402. <https://doi.org/10.1103/PhysRevLett.93.077402>
31. Manjavacas A, Liu JG, Kulkarni V, Nordlander P (2014) Plasmon-Induced Hot Carriers in Metallic Nanoparticles. *ACS Nano* 8:7630–7638. <https://doi.org/10.1021/nn502445f>
32. Bersuker IB (2001) Modern Aspects of the Jahn–Teller Effect Theory and Applications To Molecular Problems. *Chem Rev* 101:1067–1114. <https://doi.org/10.1021/cr0004411>
33. Bersuker IB (2013) Pseudo-Jahn–Teller Effect—A Two-State Paradigm in Formation, Deformation, and Transformation of Molecular Systems and Solids. *Chem Rev* 113:1351–1390. <https://doi.org/10.1021/cr300279n>
34. Öström H, Öberg H, Xin H, LaRue J, Beye M, Dell’Angela M, Gladh J, Ng ML, Sellberg JA, Kaya S, Mercurio G, Nordlund D, Hantschmann M, Hieke F, Kühn D, Schlotter WF, Dakovski GL, Turner JJ, Minitti MP, Mitra A, Moeller SP, Föhlisch A, Wolf M, Wurth W, Persson M, Nørskov JK, Abild-Pedersen F, Ogasawara H, Pettersson LGM, Nilsson A (2015) Probing the transition state region in catalytic CO oxidation on Ru. *Science* 347:978–982. <https://doi.org/10.1126/science.1261747>
35. Zhang X-G, Zhang L, Feng S, Qin H, Wu D-Y, Zhao Y (2021) Light Driven Mechanism of Carbon Dioxide Reduction Reaction to Carbon Monoxide on Gold Nanoparticles: A Theoretical Prediction. *J Phys Chem Lett* 12:1125–1130. <https://doi.org/10.1021/acs.jpcclett.0c03694>
36. Rossi TP, Erhart P, Kuisma M (2020) Hot-Carrier Generation in Plasmonic Nanoparticles: The Importance of Atomic Structure. *ACS Nano* 14:9963–9971. <https://doi.org/10.1021/acsnano.0c03004>
37. Kumar PV, Rossi TP, M-Dafcik D, Reichmuth D, Kuisma M, Erhart P, Puska MJ, Norris DJ (2019) Plasmon-Induced Direct Hot-Carrier Transfer at Metal-Acceptor Interfaces. *ACS Nano* 13 (3): 3188–3195. <https://doi.org/10.1021/acsnano.8b08703>

Statements and Declarations

Funding

This work was supported by the National Key Research and Development Program of China (Nos. 2024YFA1409900 and 2021YFA1201500), the National Natural Science Foundation of China (Nos. U22A6005, 12574442, 12474389, and 12304426), the Natural Science Foundation of Shaanxi Province (Nos. 2024JC-JCQN-07 and 2025JC-YBQN-062), the Fundamental Science Foundation of Shaanxi (Nos. 22JSZ010 and 23JSQ007), the Scientific Research Program Funded by Education

Department of Shaanxi Provincial Government (No. 24JP040), and the Fundamental Research Funds for the Central Universities (Nos. GK202201012 and GK202308001).

Competing Interests

The authors declare no competing interests.

Author Contributions

Xiaoting Ren performed the research calculations, analyzed the data, prepared the figures, and wrote the original draft. Tingting Wang analyzed the data and provided guidance on the calculations. Huiru Xue and Maoshan Hou contributed to data analysis. Huan Chen and Zhengkun Fu acquired funding. Jinping Li revised the manuscript. Lei Yan designed the research, acquired funding, supervised the project, and revised the manuscript. Zhenglong Zhang acquired funding and supervised the project. All authors reviewed and approved the final manuscript.

Data Availability

All data generated or analysed during this study are included in this published article and its Supporting Information.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.pdf](#)