Supplementary Information

Synergistic Plasmonic-Semiconductor Heterointerfaces Enabling Efficient CO_2 Hydrogenation to Methanol under Visible-Light Irradiation

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Fig. S1 Schematic synthesis procedure of the Ag-Si/MgO/ZnO nanocomposite.

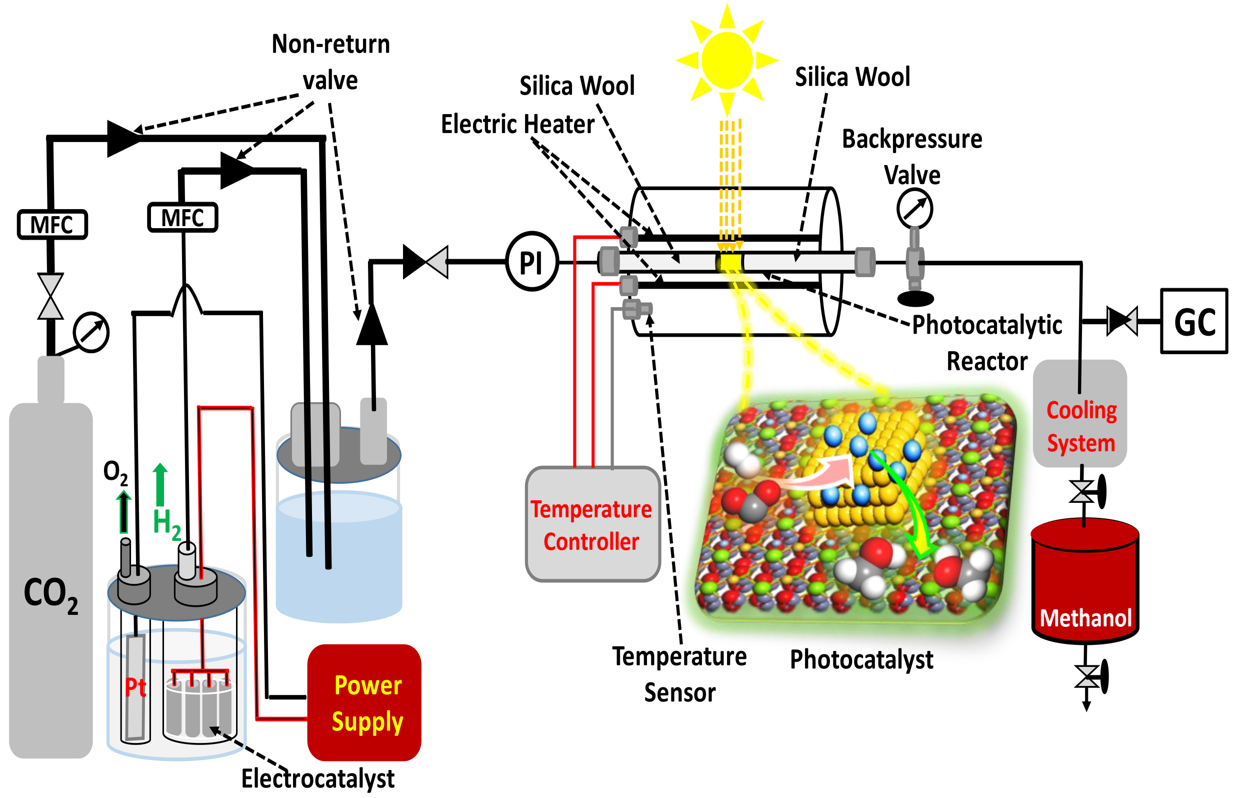


Fig. S2 Schematic diagram of experimental setup for photocatalytic CO_2 hydrogenation to CH_3OH under visible light.

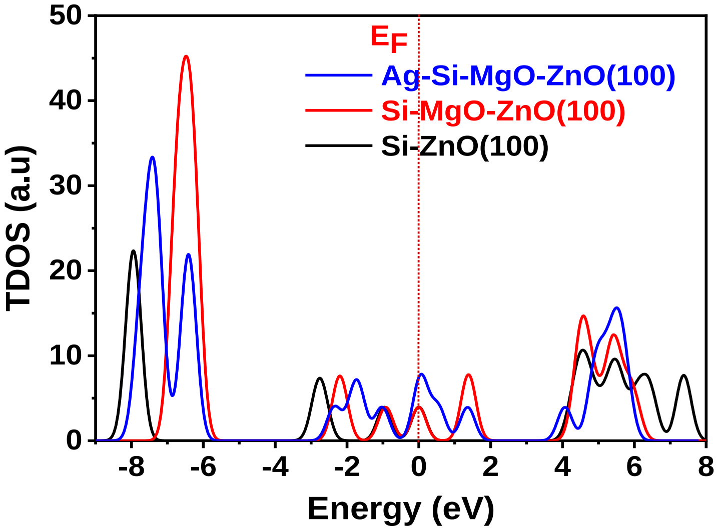
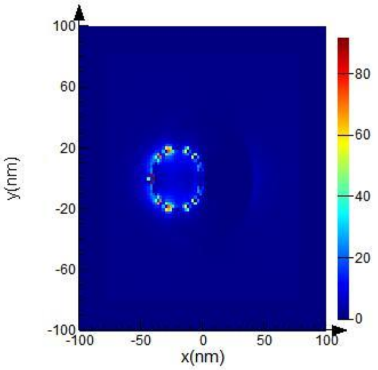


Fig. S3 DFT calculations of CO_2 reduction. The total density of states for Ag-Si/MgO/ZnO, Si/MgO/ZnO, and Si/ZnO.

Finite-difference time-domain (FDTD) simulations were performed to visualize the wavelength-dependent electric field distribution ($|E|^2$) around Ag–Si nanoparticle (NP) assemblies supported on MgO/ZnO in the visible range (400–800 nm). The electric field intensity in all maps (Fig. S4A–F) was plotted on a logarithmic scale so that both highly enhanced plasmonic hot spots and weaker background fields could be simultaneously resolved. In Fig. S4A–C (λ = 400, 450, and 485 nm), pronounced $|E|^2$ localization was observed within the ~2 nm gaps between adjacent NPs and at the NP–oxide interfaces, indicating the excitation of strongly coupled gap-mode plasmons characteristic of closely spaced silver aggregates. Comparable nanogap-induced field enhancements were previously reported by Gill et al.,[1] who demonstrated that sub-5 nm interparticle separations yield large electromagnetic amplification suitable for surface-enhanced spectroscopies.[1] At $\lambda \approx$ 533 nm (Fig. S4D), the electric fields became moderately delocalized along the NP perimeters, suggesting a transition regime in which interparticle coupling remained significant but the system began to deviate from its strongest plasmonic resonance. In Fig. S4E (λ = 640 nm), the most intense and spatially confined hot spots were obtained, together with the highest overall $|E|^2$, implying that the Ag–Si/MgO/ZnO configuration was optimally tuned to its localized surface plasmon resonance at this wavelength. By contrast, Fig. S4F (λ = 800 nm) exhibited weaker and more spatially extended fields, consistent with diminished plasmonic coupling and increased radiative damping as the excitation wavelength moved further away from resonance. The corresponding spectral response (Fig. S4G) showed a clear maximum in $|E|^2$ at ~640 nm, corroborating the near-field maps and confirming that strong, wavelength-selective electromagnetic amplification could be engineered through precise control of NP spacing and the MgO/ZnO dielectric environment.

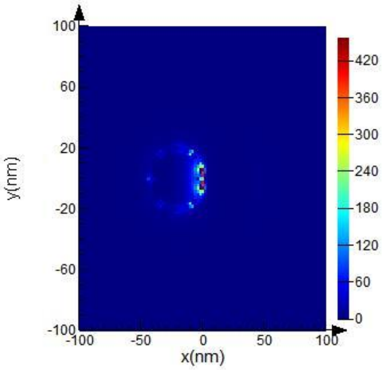
The simulated field-enhancement patterns were found to correlate well with the experimental photocatalytic performance. The wavelength at which the strongest $|E|^2$ enhancement was predicted (≈640 nm) coincided with the region where the highest photocatalytic activity and methanol formation rates were experimentally observed. This correlation suggests that the intense nanogap and interfacial hot spots promoted enhanced light harvesting, increased generation of hot carriers in Ag, and more efficient charge transfer across the Ag–Si and NP–oxide interfaces. Consequently, the strong near-field amplification at resonance was inferred to facilitate improved activation of CO_2 and reaction intermediates on the catalyst surface, thereby contributing directly to the superior visible-light-driven photocatalytic performance.

(A)



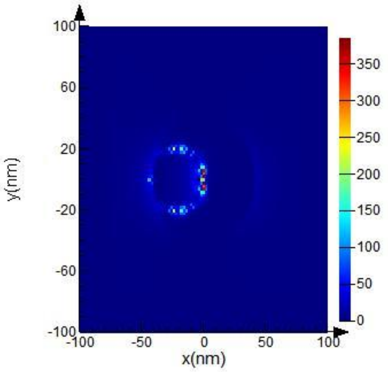
λ=400 nm

(B)



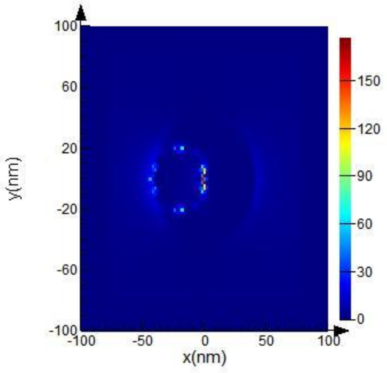
λ=450 nm

(C)



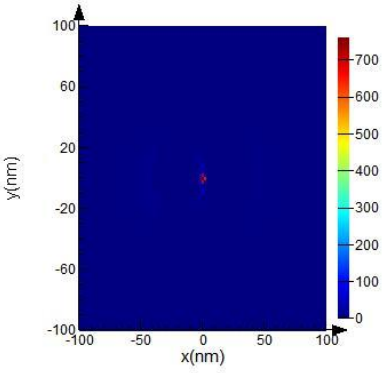
λ=485 nm

(D)



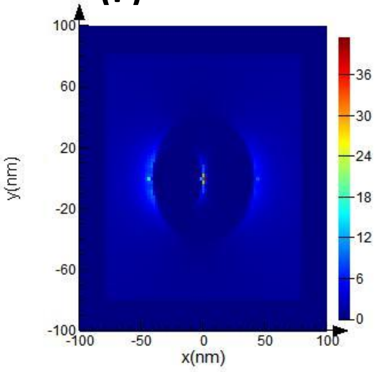
λ=533.33 nm

(E)



λ=640 nm

(F)



λ=800 nm

(G)

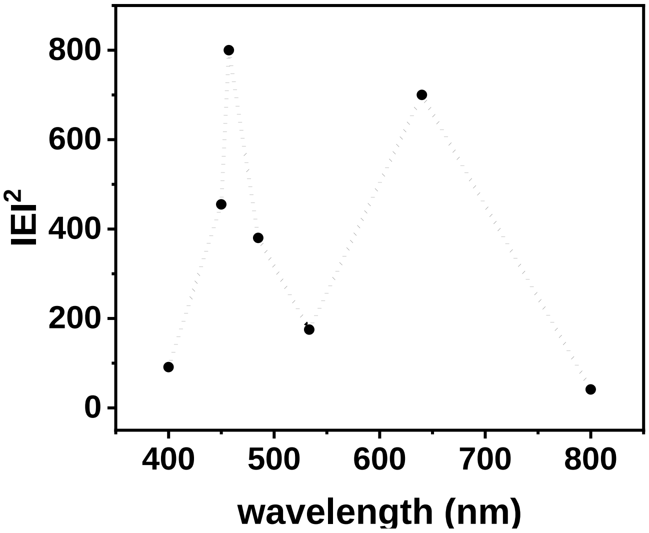


Fig. S4(A-F) Finite-difference time-domain (FDTD) simulation of electric field distribution $|E|^2$ around the surface of Ag-Si nanoparticles (NPs) assemblies on MgO/ZnO, separated by a distance of 2 nm, excited by visible light at different wavelengths (400 nm-800nm). The electric field intensity was visualized on a logarithmic scale. (G) Analyzing electric field distribution, $|\mathrm{E}|^2$, around the surface of the Ag-Si/MgO/ZnO as a function of wavelength in visible range (400 nm-800 nm) using FDTD simulation.

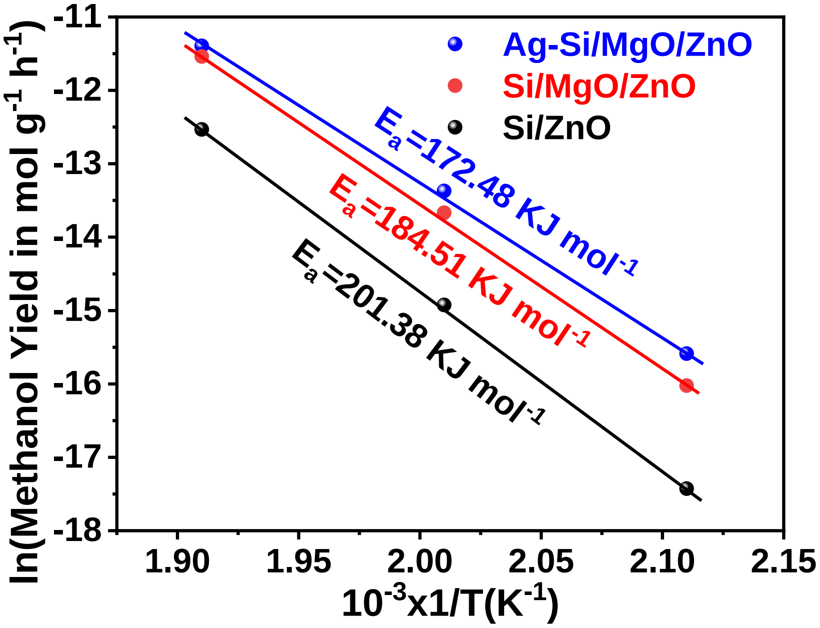


Fig. S5 Apparent activation energy (E_a) evaluated using Arrhenius plots based on hydrogenation of CO_2 into methanol under dark condition (under purely thermal condition).

Equations:

The change of total energy for all reactions was determined by the following Eq. S1:

$$\Delta E = E_{catalyst+adsorbate} - (E_{catalyst} - E_{adsorbate}) \qquad (S1)$$

Where $E_{catalyst+adsorbate}$, $E_{catalyst}$, and $E_{adsorbate}$ represent optimized total energies of the catalyst with a single absorbate, catalyst, and single absorbate, respectively performed with the Material Studio.

Zero point energy of an absorbate was calculated by the following Eq. S2:

$$ZPE = \frac{1}{2}(h\upsilon) \qquad (S2)$$

Where h and υ denote the plank's constant and harmonics frequency.

The change of zero-point energy for all reactions (Table-1) was calculated by the following Eq. S3:

$$\Delta ZPE = \text{ZPE of product} - \text{ZPE of reactant} \qquad (S3)$$

The change of entropy at T=298.15 K for all reactions (Table-1) was calculated by the following Eq. S4:

$$T\Delta S = \text{TS of product} - \text{TS of reactant} \qquad (S4)$$

Reference:

1 R. Gill, L. Tian, W.R. Somerville, E.C. Le Ru, H. van Amerongen and V. Subramaniam, J. Phys. Chem. C, 2012, 116(31), 16687-16693.