Supplementary Information

Electronic interaction between transition metal single-atoms and anatase TiO₂ boosts CO₂ photoreduction with H₂O

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Materials

All reagents were used as received without further purification. Titanium(IV) n-butoxide (TBOT) was purchased from Strem Chemicals. Tetraethyl orthosilicate (TEOS), cobalt (II) chloride trihydrate (CoCl₂·3H₂O), nickel (II) chloride hexahydrate (NiCl₂·6H₂O), copper (II) chloride dihydrate (CuCl₂·2H₂O), rhodium (II) chloride hydrate (RhCl₃·xH₂O), and polyvinylpyrrolidone (PVP) (Mw = 55,000) were purchased from Sigma Aldrich. Acetonitrile, anhydrous ethyl alcohol (purity = 99.9%), sodium hydroxide (NaOH) and ammonia solution (28–30 wt%) were purchased from Samchun Chemical.

Synthesis of M_1/TiO_2 (M = Cu, Co, Ni, Rh)

Pristine TiO₂ and M_1/TiO_2 were synthesized by the thermodynamic redistribution approach based on the previous report.^[1] First, core SiO₂ nanoparticle was prepared through basic solgel reaction. First, 0.86 ml of TEOS was added into an aqueous ethanol solution (4.3 ml of H₂O, 23 ml of ethyl alcohol and 0.6ml of aqueous ammonia). After 6 h reaction, SiO₂ particles were collected by centrifugation, washed with ethanol 2 times and redispersed in 40 ml anhydrous ethanol. Then, acetonitrile (14 ml) and ammonia (0.4 ml, 28–30 wt%) were added to the solution containing SiO₂ nanoparticle. Second solution containing 0.8 ml of TBOT, 6 ml of ethyl alcohol and 2 ml of acetonitrile was prepared. The TBOT solution was then rapidly poured into SiO₂ nanoparticle solution and stirred for 3h for TiO₂ coating. The product was centrifuged and washed with ethanol and water, and finally dispersed in 40 ml of H₂O. A calculated amount of metal chloride (CoCl₂·3H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O and RhCl₃·xH₂O) was added into the above 40 ml colloidal solution of SiO₂@TiO₂ nanoparticles. The resulting product was centrifuged and washed with water after 3h stirring at room temperature, and dispersed in 40 ml of water. 0.4g of PVP was added to the above nanoparticle solution and stirred overnight to allow adsorption of PVP on the nanoparticle surface. After PVP adsorption, the product was separated by centrifugation, and redispersed in a solution of ethanol (46 ml) and H₂O (8.6 ml) by sonication for 10 min. Then. 1.2 ml of 28-30 wt% aqueous ammonia and 1.6 ml of TEOS were added to the above solution. After 4 h, the resulting products were washed, centrifuged and dried in convection oven at 80 °C overnight. The resulting powder were calcined in ambient air condition at 950 °C for 2h. SiO₂ templates were etched in 0.5 M NaOH solution at 90 °C for 6h. The final M₁/TiO₂ products were obtained after drying in an oven at 80 °C overnight. Pristine TiO₂ is prepared by the same method except the metal precursor adsorption process.

Synthesis of Cu_{NP}/TiO_2 with different Cu concentration

Cu nanoparticles were photochemically deposited onto pristine TiO_2 samples. 100 mg of pristine TiO_2 was mixed in different volumes of $CuSO_4 \cdot 5H_2O$ (Alfa Aesar, 99 %) solution (1 mg/ml). Then, 5 ml of CH₃OH and DI water were added the solution to make a final volume of 25 ml and stirred for 1h under dark condition. The suspension was illuminated with a 300 W Xe lamp (Newport) for 2h under stirring. The samples were washed with DI water centrifuged and finally dried under vacuum at 90 °C for 12 h.

Characterization

TEM imaging was conducted on a JEOL EM-2010 microscope operated at 200 kV. EDS measurements were performed in STEM mode equipped with a single drift detector (X-MaxN, Oxford Instruments). STEM images, and EELS spectra were acquired on a spherical aberration-corrected scanning transmission electron microscope (JEM ARM-200F, JEOL) at

the National Center for Inter-University Research Facilities at Seoul National University. X-ray diffraction patterns were acquired using a D/MAX-2500 Rigaku powder X-ray diffractometer (Cu Kα radiation).

X-ray absorption spectroscopy measurements

XAFS were acquired at the 8C nano-probe XAFS beamline (BL8C) of Pohang Light Source II. The incident beam was monochromatized by a Si(111) crystal and detuned 30% to minimize the higher harmonics. An energy calibration was conducted before the measurement using reference foil. XAFS spectra were collected in both transmission and fluorescence modes. The obtained spectra were processed using Demeter software. EXAFS spectra were fitted in a Fourier-transform range of 3-11 Å⁻¹ with a Hanning window applied between 1 and 2.5 Å.

Photochemical experiments

The photocatalytic CO_2 reduction was carried out in a homemade stainless steel batch reactor (15.4 cm³) with a quartz window on the top of reactor. In a typical test, a 40 mg sample was placed on a holder at the bottom of the reactor. The reactor was thoroughly evacuated by a vacuum pump and filled with moist CO_2 gas (1000 ppm in He) through a deionized H₂O bubbler for 30 min. Subsequently, the reactor was illuminated by a 100 W Xenon lamp (Oriel, LCS-100) with a 1.5 AM filter for 1 h. The reaction products were analyzed by a gas chromatograph (Shimadzu, GC-2014) with a flame ionization detector (FID, Restek Rt Q-bond column, ID = 0.53 mm, length = 30 m) using helium as carrier gas. Photocatalyst stability was measured by repeated testing with regenerated catalyst, which was vacuum annealed at 100 °C for 2 h after 1 h illumination.

Time-resolved photoluminescence (TRPL) measurements

The TRPL measurements were performed by using a home-built confocal micro-PL set-up. Samples were excited by a pico-second pulsed diode laser (PicoQuant, LDH-P-FA-355) with the wavelength of 355 nm (FWHM \approx 60 ps) and a repetition rate of 40 MHz. The laser beam was focused by a 40x (NA=0.6) objective (Nikon). The PL decay signal was detected by a hybrid photomultiplier detector (PicoQuant, PMA hybrid series) and a time-correlated single photon counting system (PicoQuant).

Carbon isotope and control experiments

Isotopic ¹³CO₂ and control experiments were performed to verify the origin carbon source. ¹³CO₂ (¹³C 99%), diluted to ¹³CO₂ concentration of 500 ppm by pure helium gas (99% He), was purchased from Sigma Aldrich. Moist ¹³CO₂ was used as reactant and the evolved ¹³CH₄ was analyzed by gas chromatography-mass spectrometer (Shimadzu, GC-MS QP2010 ULTRA (Restek Rt Q-bond column, ID = 0.32 mm, length = 30 m). The control experiment was performed under He/H₂O atmosphere instead of CO₂/H₂O.

Computational details

Density functional calculations were performed by using Vienna *ab initio* Software Package (VASP) 5.4.1,^[2,3] and Perdew-Burke-Ernzerhof (PBE) functional^[4] was chosen for a density functional with Grimme's D3 method^[5] for van der Waals correction. Pseudopotentials were chosen as those generated by projector-augmented wave (PAW) method^[6] with the kinetic energy cutoff set to be 450 eV. Structures were optimized until the last two steps have 10^{-4} eV differences, respectively. The slab structure was constructed from anatase TiO₂ structure with into a 2×1 supercell of 3-layer (101) surface structure which consists of 24 Ti atoms and 48 O atoms, and the atoms at the bottom half were fixed during the optimization. DFT simulation of slab models employed the Monkhorst-Pack (3 × 4 × 1)*k* grid. Molecular species were optimized

in a 30 Å-thick vacuum box. The vibrational free energy of lattice was calculated to determine the zero-point energy and entropic contribution to the free energy based on finite difference method of phonon calculation at gamma point. Charge density and molecular orbital density were plotted by VESTA 3.4.7.^[7] For an accurate density of states (DOS), hybrid density functional HSE06^[8] single point calculations were performed until the energy difference of the last two steps being 10⁻⁵ eV.

The chemical potential of a proton-electron pair was defined by considering water as a proton source for oxygen vacancy reaction such that $\mu(H^+ + e^-) = 1/2 [\mu(H_2O) - \mu(O)]$ and $\mu(O) = 1/2 \mu(O_2)$. On the other hand, during the photoexcitation process of CO₂ reduction, an electron is photoexcited to the conduction band minimum (CBM) that is located at e^- (CB) = $-0.25 V_{SHE}^{[9]} = -0.25 V_{SHE} + 0.0592 \text{ pH } V_{RHE}$, where SHE and RHE stand for standard and reversible hydrogen electrodes, respectively. Then, the chemical potential of the photogenerated electron coupled with a proton can be defined by $\mu(H^+, \text{ pH } 0) + 0.0592 \text{ pH} + \mu(e^-, 0V_{RHE}) - e(0.25 + 0.0592 \text{ pH}) = \mu(H^+, \text{ pH } 0) + \mu(e^-, 0V_{RHE}) - 0.25e$, where e is an elementary charge, and $\mu(H^+, \text{ pH } 0) + \mu(e^-, 0V_{RHE})$ is determined by $1/2 \mu(H_2)$ based on the computational hydrogen electrode model^[10].



Figure S1. Photoexcitation of Cu_1/TiO_2 with an oxygen vacancy (Cu_1/TiO_{2-x}) . a) Structure and isosurface of the spin magnetic moment of Cu_1/TiO_{2-x} at rest state (left) and after photoexcitation and protonation for charge balance (right). The atoms are colored in red for oxygen, light blue for titanium and blue for copper. An isosurface is colored in yellow and cyan depending on the sign of magnetic moment. Dynamic changes of b) the density of states (DOS) calculated using HSE06 functional and c) the spin magnetic moment change of copper (green) during the localization of photoexcited electron.



Figure S2. a) Photocatalytic CO_2 reduction mechanism at TiO_2 , and b) the DFT thermodynamics of CO_2 reduction at TiO_2 (blue).



Figure S3. Gibbs energy comparison of site preference for hydrogenation at structure 4 (top) of Cu_1/TiO_{2-x} in Figure 2, resulting in the hydrogenation at carbon site (bottom, left), copper site (bottom, middle) and terminal oxygen site (bottom, right).



Figure S4. Representative TEM image of a) SiO_2 , b) $SiO_2@Cu_1/TiO_2$ and c) $SiO_2@Cu_1/TiO_2@SiO_2$.



Figure S5. Representative TEM image of a) Cu_1/TiO_2 (0.21), b) Cu_1/TiO_2 (0.70) and c) Cu_1/TiO_2 (1.42).



Figure S6. Representative SEM image of as synthesized Cu_1/TiO_2 .

Figure S7. XRD patterns of Cu_1/TiO_2 (0.21), Cu_1/TiO_2 (0.70) and Cu_1/TiO_2 (1.42).

Figure S8. Ti 2p XPS spectra of pristine TiO_2 , and Cu_1/TiO_2 (1.42).

Figure S9. High angle annular dark field (HAADF) a) low-resolution and b) high-resolution Cs-corrected STEM image of Cu_1/TiO_2 (0.70). c) Bright-field STEM image of Cu_1/TiO_2 (0.70).

Figure S10. Electron energy loss spectroscopy (EELS) characterization of Cu_1/TiO_2 (0.70). Images and spectroscopic data represent areas with (site 1 and 2) and without (site 3) Cu atoms.

Figure S11. k^2 weighted extended X-ray absorption fine structure (EXAFS) characterization of Cu₁/TiO₂ (0.21), Cu₁/TiO₂ (0.70) and Cu₁/TiO₂ (1.42). Collected k space data and the best fitting results are presented. The circles represent experimental data, and the solid lines represent the fitting curve.

Figure S12. Cu K edge EXAFS spectra of reference samples (CuO, Cu₂O and Cu foil).

Figure S13. Cu K edge WT-EXAFS spectra of reference samples (CuO, Cu₂O and Cu foil).

Figure S14. Cu K edge WT-EXAFS spectra of Cu_1/TiO_2 samples with different Cu concentration.

Figure S15. Schematics of photocatalytic CO_2 reduction setup used for photoreduction experiments.

Figure S16. Time resolved photoluminescence spectra of pure TiO_2 and Cu_1/TiO_2 (0.21).

Figure S17. Photocatalytic CO_2 reduction to CH_4 performance comparison of Cu_1/TiO_2 (0.21) and Cu_{NP}/TiO_2 photocatalysts.

Figure S18. Photocatalytic CO₂ reduction performance of Cu₁/TiO₂ (0.21) with (1000 ppm) and without CO₂.

Figure S19. Isotopic ${}^{13}CH_4$ generation with ${}^{13}CO_2$ photoreduction on Cu_1/TiO_2 (0.21).

Figure S20. a) and b) Low resolution STEM and c) high-resolution Cs-corrected STEM images of Cu_1/TiO_2 (0.21) after 5 cycles of CO_2 photoreduction.

Figure S21. Representative EDS-STEM images of Cu_1/TiO_2 (0.21) after 5 cycles of CO_2 photoreduction.

Figure S22. Representative EELS spectra of Cu_1/TiO_2 (0.21) at different sites after 5 cycles of CO_2 photoreduction.

Figure S23. a) The molecular orbital scheme for electronic interaction between Cu *d* states and CO₂ in Cu₁/TiO_{2-x} and the molecular orbital density of the Cu *d* states at the active site of b) Cu₁/TiO_{2-x} and c) Cu₂/TiO_{2-x} (isovalue = 0.01 e/Å³).

Figure S24. Comparison of the molecular orbital density of the Cu dz^2 states of a) CO₂-adsorbed Cu₂/TiO_{2-x} (isovalue = 0.01 e/Å³) in Figure S23.

Samples	Cu contents (at%)	Cu contents (wt%)
Cu ₁ /TiO ₂ (0.21)	0.21	0.17
Cu ₁ /TiO ₂ (0.70)	0.70	0.57
Cu ₁ /TiO ₂ (1.42)	1.42	1.15

Table S1 | ICP-OES analysis result of Cu_1/TiO_2 catalysts

Sample	Path	Ν	R (Å)	σ ² (Å ²)	R-factor (%)
Cu ₁ /TiO ₂ (0.21)	Cu-O	4.8 ± 0.3	1.95 ± 0.01	0.005 ± 0.001	0.3
Cu ₁ /TiO ₂ (0.70)	Cu-O	4.6 ± 0.3	1.95 ± 0.01	0.005 ± 0.001	0.3
Cu ₁ /TiO ₂ (1.42)	Cu-O	4.6 ± 0.4	1.95 ± 0.01	0.004 ± 0.001	0.5

Table S2 | Summary of EXAFS fitting of Cu_1/TiO_2 catalysts

Sample	t1 (ns)	A1 (counts)	t2 (ns)	A2 (counts)	Average lifetime (ns)
Cu ₁ /TiO ₂ (0.21)	1.030	445.2	0.138	5409	0.477
Pure TiO ₂	1.602	201.1	0.113	4245	0.711

Table S3 | Summary of TRPL measurements on $Cu_1/TiO_2\left(0.21\right)$ and pure TiO_2

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