Supporting Information

Phase-selective Disordered Anatase/ordered Rutile Interface System for Visible-Light-driven Metal-free CO₂ Reduction

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Material characterizations: X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Versa Probe II system (Ulvac-PHI) by using a monochromatic Al K α source. The base pressure was below 3×10^{-10} Torr. The instrument work function was calibrated based on ISO 15472:2001 using Au, Ag, and Cu pure films. The X-ray beam diameter was set to 50 μ m, and a charge neutralizaer was used to minimize an undesirable charging effect. The binding energy for all spectra was calibrated by referring the C 1s peak from ubiquitous hydrocarbon contamination to 284.8 eV. The XPS peak component fitting (Casa XPS software) was performed by using a Shirley background subtraction and mixed Gaussian-Lorentzian. The fitting parameters

were set to reduce the residual standard deviation (STD) of the measured and fitted XPS spectra. Ultraviolet photoelectron spectroscopy (UPS) (ESCALAB250, Thermo) was performed with He-I radiation. Powder XRD pattern was acquired using a D8-Advance instrument (Germany) with Cu-Ka radiation. Raman spectroscopy measurements were recorded using a Renishaw RM 1000-Invia micro-Raman system with an excitation energy of 2.41 eV (514 nm). To investigate the energy bandgap properties and diffuse reflectance spectra, the UV-3600 and UV-VIS-NIR spectrophotometers (Shimadzu Corp.) were used. Aberration-corrected TEM (JEM-ARM200CF, JEOL) equipped with a cold-field emission source operating at an accelerating voltage of 200 kV was used to acquire the BF and HRTEM images. For low-loss EELS mapping, HAADF imaging mode was used with an angle range of 70-175 mrad. The EELS data were acquired using a Gatan Quantum spectrometer (ER965) attached to the microscope. The EELS spectrum imaging (SI) data were acquired with the dual EELS acquisition mode to obtain the full energy loss information over both low-loss and high-loss ranges with energy dispersion of 0.25 eV/ch and probe dwell times of 2.00 s/pix for core-loss and 0.05 s/pix for low-loss signal, respectively. Principal component analysis (PCA, implemented in MSA software, HREM research ltd.) on the core-loss spectra was applied to reduce random noise and then a power-law dependency of the background noise floor was removed before signal extraction of the core-loss Ti L and O K edges over the sample. For low-loss EELS mapping, multiple linear least squares (MLLS) fitting method was used with the local spectra separately obtained from the regions of surface and inside of the particle as reference spectra. The FFT images were processed using Gatan Microscopy Suite: Digial MicrographTM and were indexed using CrysTBox - diffractGUI. The Brunauer-Emmett-Teller (BET) theory was used to determine the specific surface area and the Horvath-Kawazoe (HK) method was used for subnanopore analysis via a BELSORP-max. Gas chromatography-mass spectrometry (GC-MS) were

carried out with column-Agilent DB-WAX, Temp. 250 °C and oven temp. 35 °C. Electron spin resonance (ESR; X-band CW-EPR, QM09, RT, 2.97 mW, 9.64 GHz microwave frequency, 100 KHz modulation frequency, modulation amplitude: 1G, powder: 5 G, 10G ESR spectral data) measurements were obtained from the Korea Basic Science Institute in Seoul, Korea. The CO₂-Tepmperature Programmed Desorption (TPD) (AutoChem II), Pre: He/120 °C/1hr, Ads: CO₂/40 °C/1hr, Measured Flow Rate: 50.12 cm³ STP/min were measured by Korea Research Institute of Chemical Technology in Deajeon, Koera

Apparent quantum yield (AQY) is calculated by given equation :

$$AQY (\%) = \frac{Number of reacted electrons}{Number of incident photons} \times 100 (1)$$

Number of reacted electrons calculated by

Number of reacted electrons =
$$(8 \times [CH_4] + 2 \times [CO]) \times N_A$$
 (2)

The [CH₄] and [CO] represents generation rate of each products and the reaction electrons of CH₄ and CO from CO₂ reduction reaction required 8 and 2, respectively. NA is the Avogadro's number which is 6.022 x 1023 mol⁻¹. In case of A_d/R_o sample, [CH₄] was 0.016 µmol/h and [CO] was 0.018 µmol/h under 430±5 nm bandpass filtered solar light.

Thus,

Number of reacted electrons = $(8 \times 0.016 + 2 \times 0.018) \times 10^{-6} \times 6.022 \times 10^{23}$

$$= 9.8761 \times 10^{16} h^{-1}$$
 (3)

Number of incident photons calculated by

Number of incident photons =
$$\frac{\text{Incident light energy}}{\text{The average photon energy}}$$
 (4)

The incident light energy was deduced from well-known AM1.5G spectra between 425 to 435 nm wavelength range (11.3758 $W/m^2 = 4.0953 J/cm^2 h$). And our reaction carried with 4 cm² light source.

Therefore,

Incident light energy =
$$4.0953 \times 4 = 16.3812 \text{ J} h^{-1}$$
 (5)

Avarage photon energy was,

Avarage photon energy =
$$\frac{hc}{\lambda}$$
 (6)

Where h is Planck's constant (h = $6.626 \times 10-34 \text{ J s}$), c is speed of light (2.998 x 108 m/s) and λ was 430 nm centered light applied.

Therefore,

Avarage photon energy =
$$\frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{430 \times 10^{-9}} = 4.6197 \times 10^{-19} J$$
 (7)

Thus,

Number of incident photons =
$$\frac{16.3812}{4.6197 \times 10^{-19}} = 3.5459 \times 10^{19} h^{-1}$$
 (8)

Finally, the AQY calculated as,

$$AQY = \frac{9.8761 \times 10^{16}}{3.5459 \times 10^{19}} \times 100 = 0.2785 \%$$
(9)

The experiments were carried out under 430 ± 5 nm bandpass filter for AM1.5G solar simulator with 2 x 2 cm2 light area on the photocatalyst sample at 150 °C.



Figure S1. AM1.5G global standard spectrum [manuscript reference 67-69].



Figure S2. XPS spectra of Na-EDA treated P25 TiO₂ before (a) and after (b) and K-EDA treated P25 before (b) and after (d).



Figure S3. Schematic images of the top view TiO_2 lattice sizes and alkali metal sizes (red: O, white: Ti). Our simple calculations based on sizes of alkali metals *(i.e.* the diameter of Li (0.27 nm), Na (0.31 nm), and K (0.39 nm)) suggest that Li-EDA can attack the rutile crystalline phase (0.296 nm x 0.296 nm, top view of the 2D surface) while Na and K-EDA can attack the crystalline anatase phase (0.286 nm x0.379 nm, top view of the 2D surface).



Figure S4. Digital images of Na/K metal-EDA treated TiO₂ samples.



Figure S5. Effect of metal (Na) and various alkyl amine treatments on the characteristics of the P25 samples. (a) Treatment with Na-1,3-diaminopropane and Na-hexamethylenediamine resulted in a gray color with decreased XRD peak intensity for the anatase phase. (b) However, no alkyl monoamines changed the XRD peaks of the anatase phase, and however colors changed to gray color. Treatment with Na-1,2-diamine ethane completely disordered only the anatase phase, while Na-1,4 diaminobutane only partially reduced the anatase phase, resulting in a blue color, which was confirmed by a decrease in XRD peaks. Most XRD peaks of Na-alkyl monoamine-treated TiO₂ NPs did not completely disappear due to the low solubility in alkyl monoamines. As a result, the number of released electrons was insufficient to change the anatase TiO₂ phase.



Figure S6. XRD curve of various TiO₂ samples from K-alkyl (a) diamine and (b) monoamine solution. The rest of the alkyl diamines and alkyl monoamines in the case of K metal did not change the anatase phase since K had low solubility even in alkyl diamines.

		Sodiu	m	Potasiu	100
		Color (image)	Disordered phase	Color (image)	Disordered phase
Ethylenediamine	H ₂ N NH ₂		Anatase		Anatase
1,3- Diaminopropane	H ₂ N NH ₂		Anatase	- Agrica	No
1,4- Diaminobutane	H ₂ NNH ₂		Anatase	35	No
Hexamethylene diamine	H ₂ N~~NH ₂	*	Anatase		Anatase
Methylamine	-NH ₂		No	Sé	No
Propylamine	∼_ _{NH₂}	100	No		Anatase
Esopropylamine	NH ₂		No	*	No
Diisopropylamine	~ ^k ~	atin	No	-	No

Figure S7. Digital images of various TiO_2 samples prepared from Na and K-amine solutions.



Figure S8. XRD patterns and Raman spectra of various TiO₂ samples. (a, d) Before and after reaction measurement of K-EDA-treated anatase, (b, e) K-EDA-treated rutile, and (c, f) K-EDA-treated P25.



Sample	BET[m ² g ⁻¹]	Total Pore	Mean pore size[nm]
		volume[cm ³ /g]	
P25	10.85	0.0808	21.845
A _d /R _o	61.83	0.3377	29.804

Figure S9. BET analysis of P25 and A_d/R_o TiO₂.



Figure S10. HR-TEM images of anatase, rutile, and P25 TiO₂. (a, b) Diffractograms for anatase and rutile TiO₂ nanoparticles are obtained from the insets marked with yellow dotted squares, which are identified as [010] and [314] diffraction patterns, respectively, showing them to be a single crystalline structure. (c) Diffractogram of P25 TiO₂ nanoparticles shows a mixture of anatase and rutile, as is evident in the ring pattern (left: raw FFT, right: rotationally averaged FFT). From peak analysis of the ring pattern, the sample shows mainly the anatase phase with a minor portion of the rutile phase.



Figure S11. Ti $L_{2,3}$ and O K energy-loss near-edge spectrum (ELNES) of pristine P25 TiO₂. The ELNES profiles of Ti L and O K edges show that the surface and interior parts of the particle are chemically and electronically identical to each other.

A_d/R_o : Core-loss EELS mapping



Figure S12. Core-loss EELS mapping images of A_d/R_o TiO₂. The result of core-loss EELS mapping for the A_d/R_o sample indicates that the sample is composed of Ti (green) and O (red) chemical species without difference between the surface and interior parts of the particle.



Figure S13. Band gap transformed from the Kubelka-Munk function. A reduction of A_d gives 2.69 eV. In the case of one phase reduction, TiO₂ (A_d/R_o) also shows 2.62 eV. These values are lower than the band gap of pristine TiO₂ (>3.0 eV) and can absorb visible light.



Figure S14. UPS spectra of A_d , R_o and A_d/R_o TiO₂. (a, b,c) high binding cut-off energy of A_d , R_o and A_d/R_o . (d, e, f) low binding energy of A_d , R_o and A_d/R_o (UPS valence band).



Figure S15. XPS spectra of all TiO₂ samples for calculation of the valence band. All VB values of A_d , R_o and A_d/R_o TiO₂, were obtained. The edge positions that correspond to the VB values were calculated by crossing the expanded slope line of the XPS curve on the x-axis to represent the binding energy (eV).



Figure S16. Band position change of A_d in mixed TiO₂ samples.



Figure S17. Band gap analysis of 3, 5 days Na-EDA treated A_d in mixed TiO₂. (a) DRS spectroscopy of 3, 5 days Na-EDA treated TiO₂ samples. (b) XRD patterns of 3, 5 days Na –EDA treated TiO₂ samples. (c, d) XPS spectra of 3, 5 days Na-EDA treated TiO₂ samples for calculation of the valence band. (d, f) Band gap transformed from the Kubelka-Munk function of 3, 5 days Na-EDA treated TiO₂ samples.



Figure S18. Blank experiments of A_d/R_o TiO₂ under various conditions. (a) Under photo irradiation with N₂ (b) Without photo irradiation with CO₂ (c) With photo irradiation with CO₂ without catalyst



Figure S19. GC raw data for gas analysis. The noise is from the valve change of GC.



Figure S20. Stability test of A_d/R_o TiO₂.



Figure 21. XPS data of A_d/R_o TiO₂ before and after photocatalytic experiment.

Table S1. Apparent quantum yield (AQY) of Pristine P25, A_d/R_o TiO₂ and previous literatures under visible light.

	Literature 1	Literature 2	Literature 3	P25 TiO ₂	$A_d/R_o TiO_2$
AQY (%)	0.010	0.060	0.063	Non detect	0.273

	P25	W-P25	Ru-P25	Ag-P25	Pt-P25	3d Ad/Ro	5d Ad/Ro	7d Ad/Ro
СО	0.534	2.782	2.679	2.011	1.538	1.197	1.472	3.026
CH ₄	0	0.430	0.260	0.580	0.680	0.758	1.598	3.983

Table S2. CO₂ reduction performance of various TiO₂ samples. (unit: μ mol/g)

Table S3. Comparison of CO production yields for photocaltaytic CO₂ reduction using metal free TiO₂ materials

Photocatalyst	Light source	Conditions	Products	Refs.
A _d /R _o TiO ₂	>425 nm, visible	Gas phase, 20 mg catalyst, 150 °C	CH ₄ , 3.983 µmol g ⁻¹ h ⁻¹	This work
Anatase	Solar simulator	Gas phase, 100 mg catalyst	CH4, 1.35 µmol g ⁻¹ h ⁻¹	1
TiO _{2-x} nanocrystals, mainly rutile	Solar simulator, 400 nm cut-off	Gas phase, 30 mg catalyst	CH ₄ , 0.225 μmol g ⁻¹ h ⁻¹ CO, 0.188 μmol g ⁻¹ h ⁻¹	2
Defective anatase- (001)/(101)	100 W Ha		CO, 10.8 μmol g ⁻¹ h ⁻¹ No CH4	
Defective anatase-(101)	vapor lamp, 400-700 nm	Gas phase, 40 mg catalyst, 150 °C	CO, 7.5 μmol g ⁻¹ h ⁻¹ No CH4	3
Defective anatase-(001)			CO, 8.5 μmol g ⁻¹ h ⁻¹ No CH ₄	
Ag/brookite- (210)/ (001) cubes	300 W Xe lamp, solar	Gas phase, 0.15 g catalyst	CO, 858.7 ppm g ⁻¹ h ⁻¹	4

			CH ₄ , 76.7 ppm g ⁻¹ h ⁻¹	
RuO ₂ /hollow anatase-(101) mesocrystals	300 W Xe lamp	Gas phase, 50 mg catalyst, 60 kPa	CH4, 1.72 μmol g ⁻¹ h ⁻¹	5
Anatase-(001)			CH4, 0.9 μmol g ⁻¹ h ⁻¹	
Anatase-(010)	300 W Hg	Gas phase, 0.1 g catalyst	CH ₄ , 1.7 μmol g ⁻¹ h ⁻¹	6
Pt/anatase-(001)	lamp, solar		CH ₄ , 2.6 μmol g ⁻¹ h ⁻¹	
Pt/anatase-(010)			CH ₄ , 0.8 μmol g ⁻¹ h ⁻¹	
N-TiO ₂ - (001)/graphene	15 W energy – saving daylight lamp	Gas phase, 1 g catalyst, ambient temperature (25 ± 5 °C)	CH ₄ , 0.37 μmol g ⁻¹ h ⁻¹	7
MoS ₃ /anatase- (001)	500 W xenon- mercury lamp, solar	Liquid phase (0.02 M EDTA aqueous solution), 0.15 g catalyst	CO, 0.53 µmol g ⁻¹ h ⁻¹ H ₂ , 361.1 µmol g ⁻¹ h ⁻¹ CH ₄ , 0.03 µmol g ⁻¹ h ⁻¹	8

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