Supporting Information (SI)

Interfacial charge transfer at black carbon-mineral dust hybrids boosts atmospheric photooxidation

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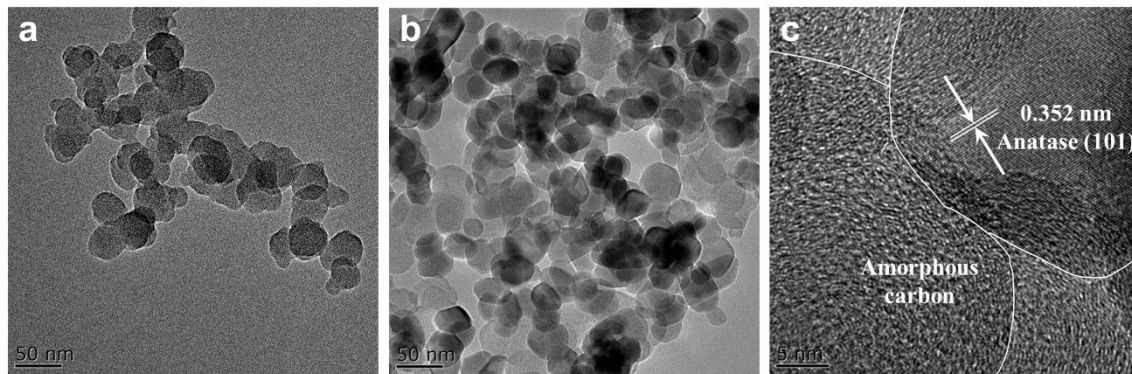Corresponding author: Jiejing Kong (kongjj3@gdut.edu.cn)

Figure S1. TEM (HRTEM) image of (a) BC and (b,c) BC/TiO$_2$.

The static contact angle analysis of water droplets on TiO_2 and BC/TiO_2 surfaces reveals distinct differences in hydrophobicity. As shown in **Figure S1a**, the water droplet on the pure TiO_2 surface exhibits a contact angle of 25.6°, indicating strong hydrophilicity due to the low contact angle and pronounced liquid spreading. Conversely, upon incorporating 10% BC into TiO_2 (**Figure S1b**), the contact angle increases to 36.8°, marking an approximate 50% enhancement compared to TiO_2. This suggests that BC/TiO_2 surface exhibits improved hydrophobicity. This observed behavior can be attributed to two key factors: the intrinsic hydrophobic nature of BC and its high specific surface area, which collectively reduce the surface energy of TiO_2, thereby enhancing the hydrophobic properties.
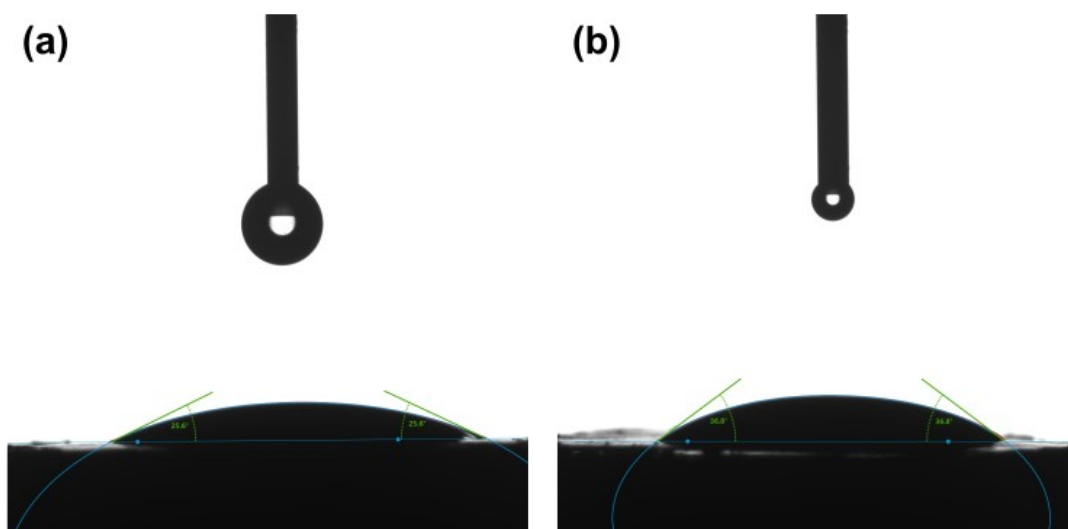

Figure S2. Static contact angles of water droplets on (a) TiO_2 and (b) BC/TiO_2 surfaces.

The shift in the XPS valence band maximum (VBM) of the BC/TiO$_2$, from 2.60 eV for pristine TiO$_2$ to 3.75 eV, indicates a downward displacement of the valence band edge relative to the Fermi level (**Figure S3**). This phenomenon is attributed to interfacial charge redistribution, driven by the formation of Ti–O–C bonds between TiO$_2$ and oxygen-functionalized BC. The electron-withdrawing effect of oxygen atoms (electronegativity = 3.44) within these bonds reduces electron density in the valence band of TiO$_2$, thereby lowering its energy position. This downshift in VBM carries two critical implications:

(1) The lowered valence band edge strengthens the thermodynamic driving force for photogenerated holes, improving their ability to oxidize adsorbed species (e.g., converting H$_2$O/OH$^-$ into •OH).

(2) The realignment of energy levels promotes electron transfer from TiO$_2$ to the conductive BC via Ti–O–C pathways, effectively suppressing charge recombination. This synergizes with the previously observed surge in adsorbed oxygen species, collectively boosting reactive oxygen species generation (e.g., •O$_2^-$, •OH).
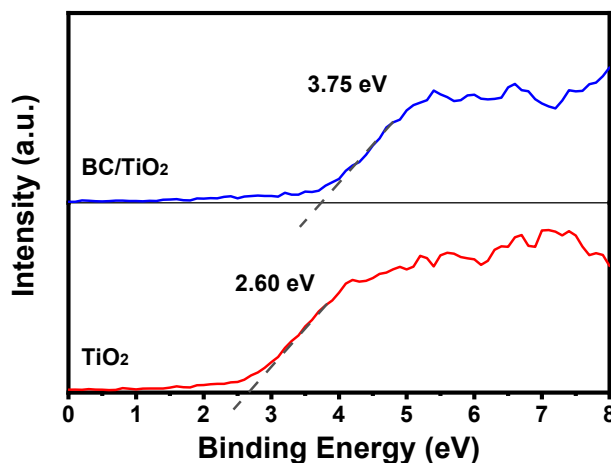

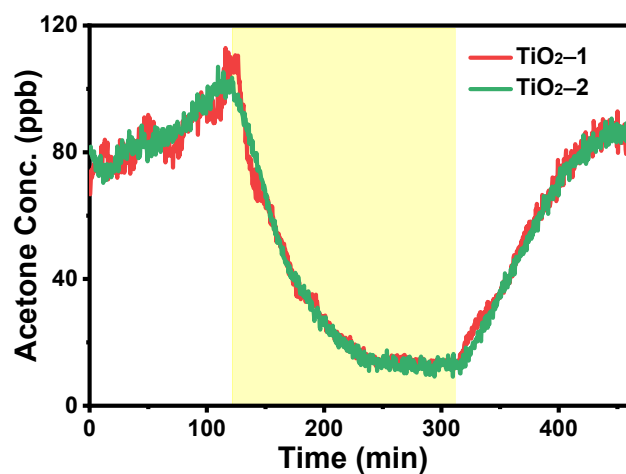**Figure S3.** XPS valence band spectra of the mineral particles

Figure S4. Time-dependent concentration profiles of gaseous acetone over TiO_2 from independent replicate experiments conducted in a flow tube experiment, the yellow window highlights the intervals under UV light (λ_{max} = 365 nm, 2.0 mW cm^{-2}) .

The minimal decrease (~1 ppb) upon illumination and weak recovery after darkening indicate no significant photocatalytic activity of BC alone.
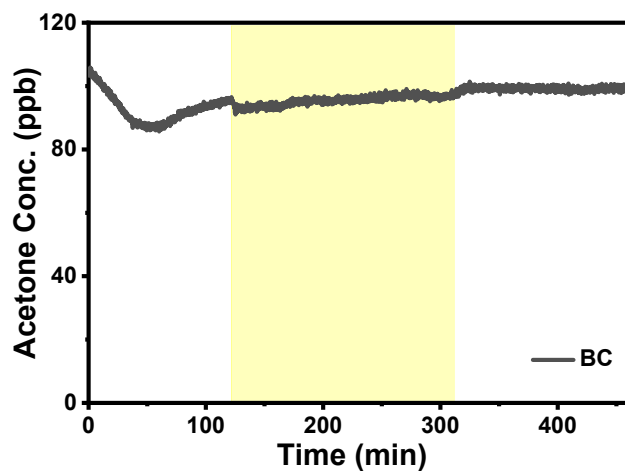

Figure S5. Time-dependent acetone concentration profile in the presence of BC only under UV light irradiation (λ_{max} = 365 nm, 2.0 mW cm^{-2}).
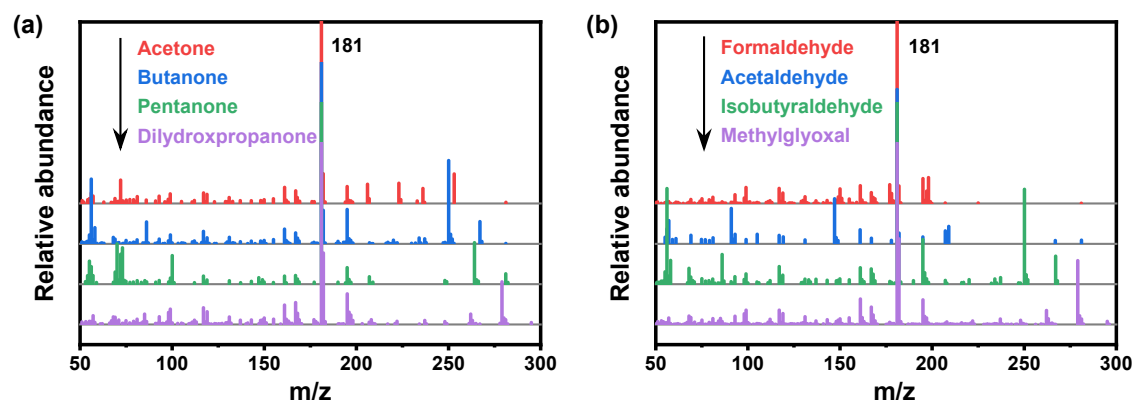
Figure S6. Major products accumulated on TiO$_2$ surface

Table S1. Relative composition of O 1s species from XPS spectral deconvolution for the mineral particles.

Dust	O 1s	Test 1 (%)	Test 2 (%)	Test 3 (%)	Mean ± SD (%)
TiO$_2$	O$_{latt.}$ (530.8 eV)	52.5	53.8	52.7	53.0 ± 0.7
	O$_{ads.}$ (530.5 eV)	18.2	16.9	17.7	17.6 ± 0.7
	O$_{H2O}$ (531.4 eV)	29.3	30.1	28.8	29.4 ± 0.7
BC/TiO$_2$	O$_{latt.}$ (529.9 eV)	37.9	35.2	37.0	36.7 ± 1.4
	O$_{ads.}$ (531.3 eV)	46.3	44.8	45.7	45.6 ± 0.8
	O$_{H2O}$ (532.7 eV)	18.5	17.0	17.6	17.7 ± 0.8

Note: Values are presented as mean ± standard deviation (SD) from n = 3 independent measurements

To assess the statistical significance of the differences in oxygen species distribution between TiO$_2$ and BC/TiO$_2$ samples, a one-way analysis of variance (ANOVA) was performed on the O 1s XPS data presented in **Table S1**. Each sample group consisted of three independent measurements (n = 3). The ANOVA results revealed extremely significant differences ($p < 0.001$) for all three oxygen species.

To evaluate the statistical significance of the differences in oxygen species distribution between TiO$_2$ and BC/TiO$_2$ samples, a one-way analysis of variance (ANOVA) was conducted on the O 1s XPS data from **Table S1**, with three independent

measurements per group (n = 3). The ANOVA compared the mean values of each oxygen species ($O_{latt.}$, $O_{ads.}$, and O_{H2O}) between the two sample types.

The ANOVA procedure involved calculating the following for each oxygen species:

(1) The between-group variance ($MS_{between}$), based on the squared deviations of group means from the overall mean.

(2) The within-group variance (MS_{within}), derived from the variability of individual measurements around their respective group means.

(3) The F-statistic, computed as the ratio $MS_{between}$ / MS_{within}.

The results showed extremely significant differences for all oxygen species (p < 0.001). Specifically:

For $O_{latt.}$: F = 334.9, p = 3.8 × 10^{-6}

For $O_{ads.}$: F = 2485.3, p = 4.8 × 10^{-7}

For O_{H2O}: F = 410.7, p = 2.9 × 10^{-6}

These results confirm that BC incorporation significantly alters the surface oxygen chemistry of TiO_2. The pronounced increase in $O_{ads.}$ and decrease in both $O_{latt.}$ and O_{H2O} in BC/TiO₂ are statistically robust. These changes align with the formation of Ti–O–C bonds and electron redistribution, which enhance surface reactivity and promote ROS generation, as discussed in the main text. The high statistical significance (p < 0.001) underscores the reliability of these trends.

Table S2. Contact angle measurements of TiO_2 and BC/TiO_2 Samples

Sample	Contact Angle Measurements (°)					Mean (°)	SD[a] (°)
	Test 1	Test 2	Test 3	Test 4	Test 5		
TiO_2	24.8	25.6	26.0	25.5	25.9	25.6	0.47
BC/TiO_2	35.6	37.5	37.0	37.2	36.7	36.8	0.73

[a] Standard Deviation

The mean values were used to calculate the ~44% increase in hydrophobicity. The standard deviation represents the variability in the measurements.

To rigorously evaluate the significance of this difference, an unpaired two-sample t-test assuming equal variances was performed. The calculations are summarized below:

(1) Pooled variance:

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} = \frac{4 \times (0.47)^2 + 4 \times (0.73)^2}{8} = 0.3769$$

(2) Standard error of the difference:

$$SE = s_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} = \sqrt{0.3769} \times \sqrt{0.4} \approx 0.388$$

(3) t-statistic:

$$t = \frac{\bar{X}_2 - \bar{X}_1}{SE} = \frac{36.8 - 25.6}{0.388} \approx 28.87$$

(4) Degrees of freedom:

$$df = n_1 + n_2 - 2 = 8$$

The resulting t-value is 28.87, which corresponds to a p-value much less than 0.001. This confirms that the observed enhancement in hydrophobicity upon BC incorporation is statistically highly significant.