

Supporting information

Zn⁺-O⁻ dual-spin surface states formation by modification of ZnO nanoparticles with diboron compounds

Yang Cao,[†] Yongguang Tu,[‡] Peng Zhou,[§] Jianning Zhang,[†] Yuchen Deng,[‡] Biao Kong,[#] Xu Zhang,[⊥] Shaojun Guo,^{†,§} Rui Zhu,[‡] Ding Ma,^{†,‡} Yang Yang[¶] and Fanyang Mo^{*,†,∇}

[†]Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, China

[‡]State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing, 100871, China

[§]Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, 100871, China

[‡]College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

[#]Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Department of Chemistry Laboratory of Advanced Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai, 200433, China

[⊥]Department of Physics and astronomy, California State University Northridge, California 91330, United States

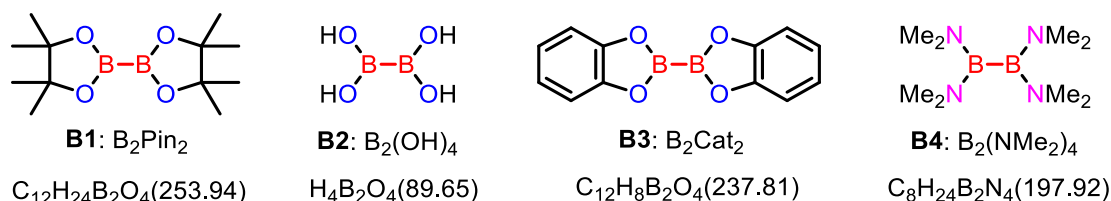
[¶]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

[∇]Jiangsu Donghai Silicon Industry S&T Innovation Center, Donghai County, Jiangsu 222300, China

*Corresponding Author Email: fmo@pku.edu.cn.

Measurement:

Solid-state ^{11}B NMR data were collected by a JEOL JNM-ECZ600R NMR spectroscopy under 14.1 T. The sample were stored in a 3.2 mm probe (the volume of the solid sample was 50 μL) and the experiment were performed when the probe at a spinning rate of 20 kHz at room temperature. The XRD (X-ray diffraction) spectra were performed on a Rigaku RINT 2000 spectrometer at room temperature with a sweeping rate at $8^\circ/\text{min}$ in the region of $20\sim 80^\circ$. The X-ray spectrometry were performed on a Thermo Scientific Escalab 250Xi spectrometer. ATR-FTIR spectra were collect on a Thermo Nicolet iS 50 spectrometer equipped with a MCT detector with high resolution and a Specas Gateway ATR 6 reflection horizontal ATR accessory with 6 reflection ZnSe crystal with an active area of 70 mm x 10 mm. The *in-situ* ATR-FTIR spectrum were collect for every 12 second at room temperature lasting for 60 min. Electron paramagnetic resonance were collect on a Bruker EMX plus under continuous wave model corresponding to X band at low temperature equipped with a liquid Helium cooling system. Solid-state UV-VIS NIR spectroscopy were collected on a UV-3600 plus Shimzdu UV-VIS-NIR spectroscopy with a 20 grating and the baseline of the spectroscopy were calibrated and deduct by a standard BaSO_4 sample. X-ray photoelectron spectroscopy were collect on a Thermo Fisher EscaLab 250Xi spectroscopy. The binding energy of Zn 2p, O 1s were calibrated with a C 1s spectra centered at 284.8 eV. Liquid ^1H NMR data were collected on an Advance III Bruker 400 MHz NMR spectroscopy with 16 pulse accumulations. The sample were dissolved in CDCl_3 with a 0.03% v/v TMS for calibration of 0 ppm. Transmittance electron micrograph were taken on a Titan Themis (Thermo Scientific) in HRTEM mode as well as in HADDF mode from at a accelerate voltage of 80 kV.



Scheme S1. The chemical structure diagram and the chemical formula for the diboron (4) compound used in this manuscript.

ATR-FTIR experimental details:

The ATR-FTIR spectroscopy were performed on a Thermo Nicolet iS 50 equipped a MCT detector and a Specas Gateway ATR 6 reflection ATR accessory with 6 reflection ZnSe crystal (70 mm x 10 mm). IR spectra in $4000\sim 650\text{ cm}^{-1}$ were recorded for every 12 second. 50 mg ZnO nanoparticle were dispersed in 1 mL dry methanol and then the mixture were treat by ultrasound for 5 min. Then the dispersion were dip-coated on the surface of ZnSe crystal. The background were collected when the methanol were evaporated. Then **B4** liquid were dip onto ZnO layer. The corresponding ATR-FTIR spectra were collect for every 12 second and lasting for 60 min.

XAS experimental details:

The XAS measurements of the ZnO and diboron modified ZnO sample were operated in transmittance mode at the XAS beamline of BL14W of Shanghai Synchrotron Source (3.5 GeV). The energy range of the beamline were 4 to 15 keV. The collect data were fitted using the ATHENA software package. The test sample were prepared by mixing of 50 mg LiF and 9 mg **B**-ZnO and then press to a tablet. A Si (311) monochromator were used to collect the data and

the energy were calibrated by using a Zn metal foil. We collect the Zn K line data around 9662 eV.

The O K line were collected on the BL08U1 of Shanghai Synchrotron Source. Oxygen K-edges sXANE spectra were collected in total electron yield (TEY) mode at beamline 08U1A of Shanghai Synchrotron Radiation Center. The spectra were calibrated with a clean gold mesh which give a simultaneous photocurrent based on the photon flux.

Computational details:

Atomic structure of B molecule alone was firstly optimized by Gaussian 09 software using a DFT method at the 6-31G* level. The simulations of **B1-B4** molecule adsorption on the ZnO surface of ZnO nanoparticle were carried out by using the Vienna Ab-initio Simulation Package (VASP). The ZnO {110} surface were simulated by a repeating (4 × 4) slab of hexagonal containing four ZnO layers. The geometry optimizations of these models were performed at the gamma point. A vacuum spacer of 15 Å were used to avoid interaction between surface adsorbates and the slab. The energy cutoff of the plane-wave basis was set to 350 eV and the energy convergence was set to 1.0×10^{-4} eV. The Perdew-Burke-Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the exchange-correlation function.¹⁻² PAW pseudo-potential were used to describe the interaction between the valance electrons and the ionic core. The on-site Coulomb repulsion parameter U for Zn 3d orbital is set to be 7.5 eV, which yield the correct band gap of bulk ZnO according to the literature.³

A Monkhorst-Pack $2 \times 2 \times 1$ K-point grid were set for the partial density of states (PDOS) calculations. The charge density difference plots and Bader charge of atoms were calculated to describe the charge transfer between the B molecule and the ZnO surface.

The adsorption/binding energy E_{ad} for adsorption of O₂ molecule to the ZnO surface with B molecule were calculated according to the equation below:

$$E_{ad} = E_{O_2-ZnO-B} - E_{O_2} - E_{ZnO-B}$$

Where $E_{O_2-ZnO-B}$ and E_{ZnO-B} are the total energies for the ZnO-B surface with and without O₂ adsorption, respectively. E_{O_2} is the total energy of an O₂ molecule in the gas phase.

Photodetector device fabrication:

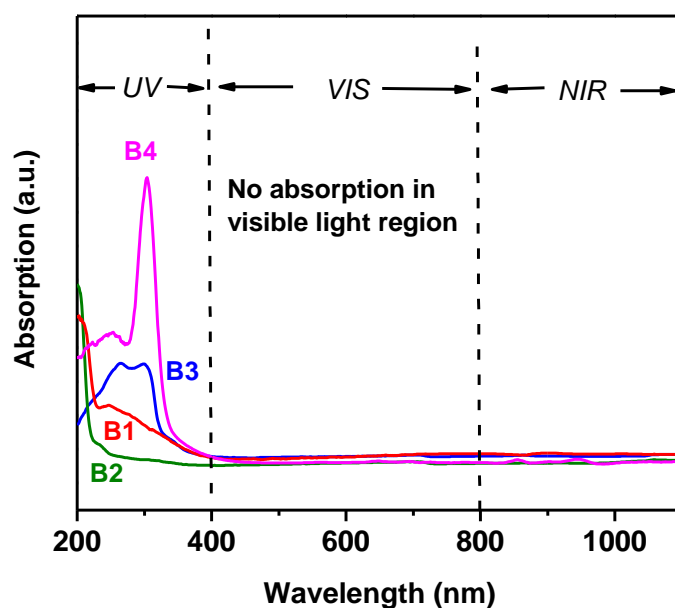


Figure S1 The UV-VIS absorption spectra of **B1~B4** molecules.

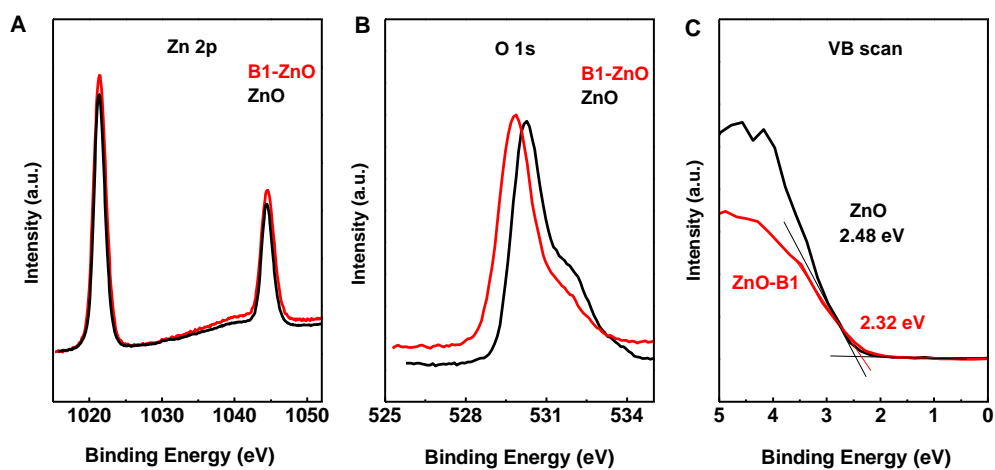


Figure S2 (A) Zn 2p (B) O 1s and (C) 0~5 eV VB scan XPS spectra of the **B1-ZnO** and ZnO as control.



Figure S3 The photograph of the ZnO nanoparticle without any treatment and the fresh prepared B-ZnO sample. (from left to right: ZnO nanoparticles, **B1-ZnO**, **B2-ZnO**, **B3-ZnO**, **B4-ZnO**)

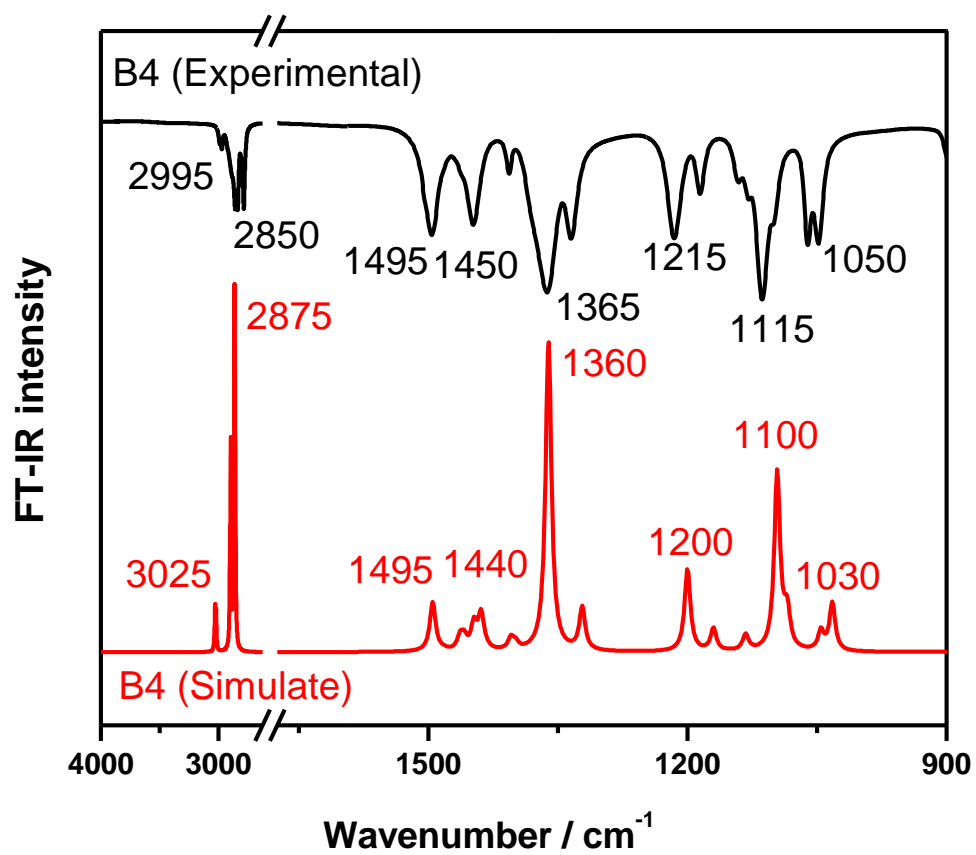


Figure S4 FT-IR spectra of **B4** molecule and **B4** molecule calculated by Gaussian 09 software. (the vibration frequency was corrected by a factor of 0.9614)

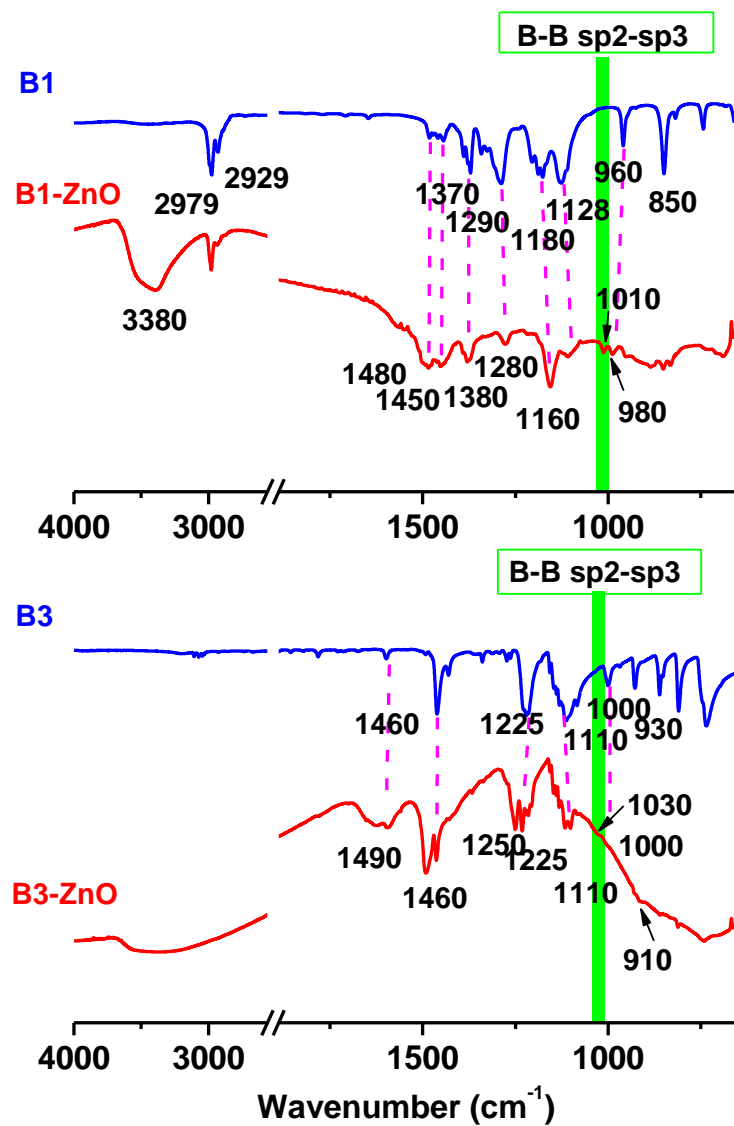


Figure S5 FT-IR spectra of **B1-ZnO** and **B3-ZnO**. And the green rectangle shows the asymmetry B-B vibration induced by adsorption on the surface of ZnO nanoparticle. (The green rectangle shows the dissymmetric sp2-sp3 B-B vibration at the adsorption site)

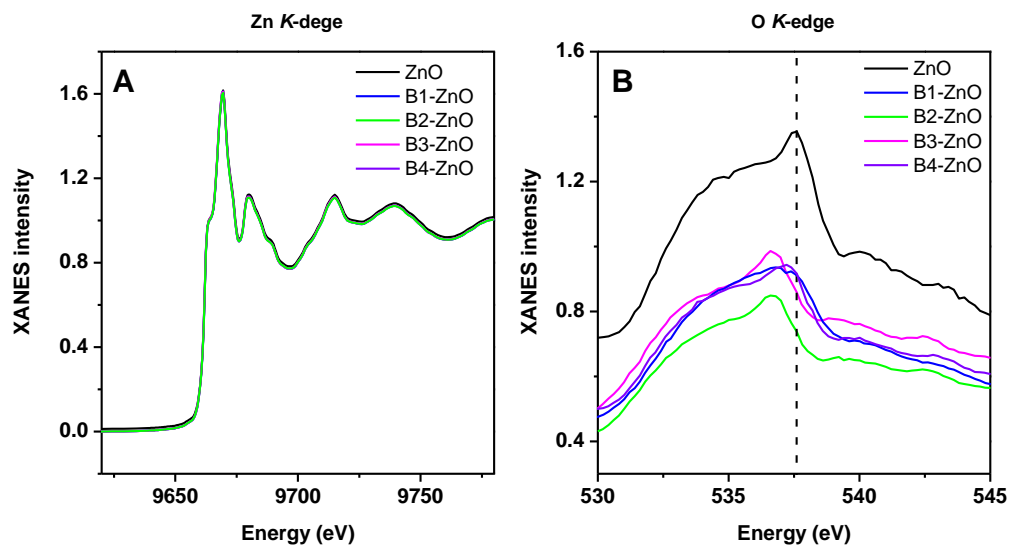


Figure S6 (A) Zn K-edge (B) O K-edge spectra of ZnO and B-ZnO.

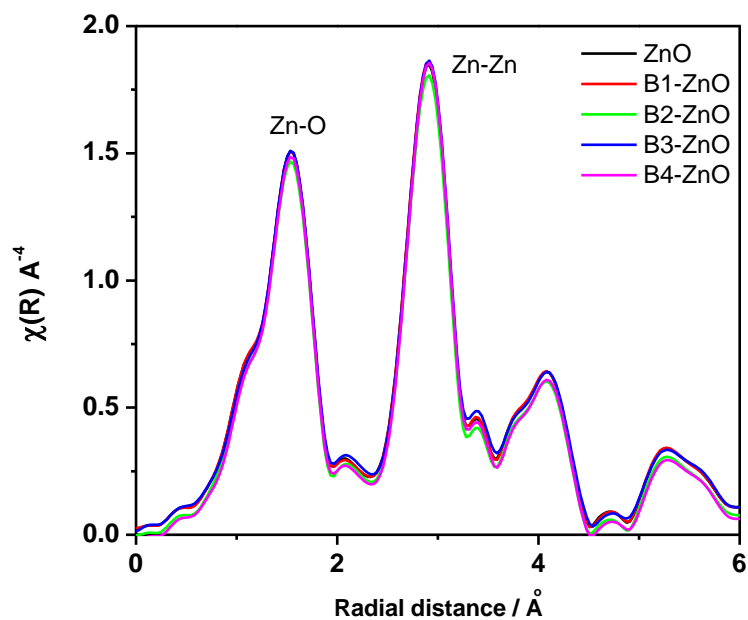


Figure S7 Extend XANES of ZnO and B-ZnO.

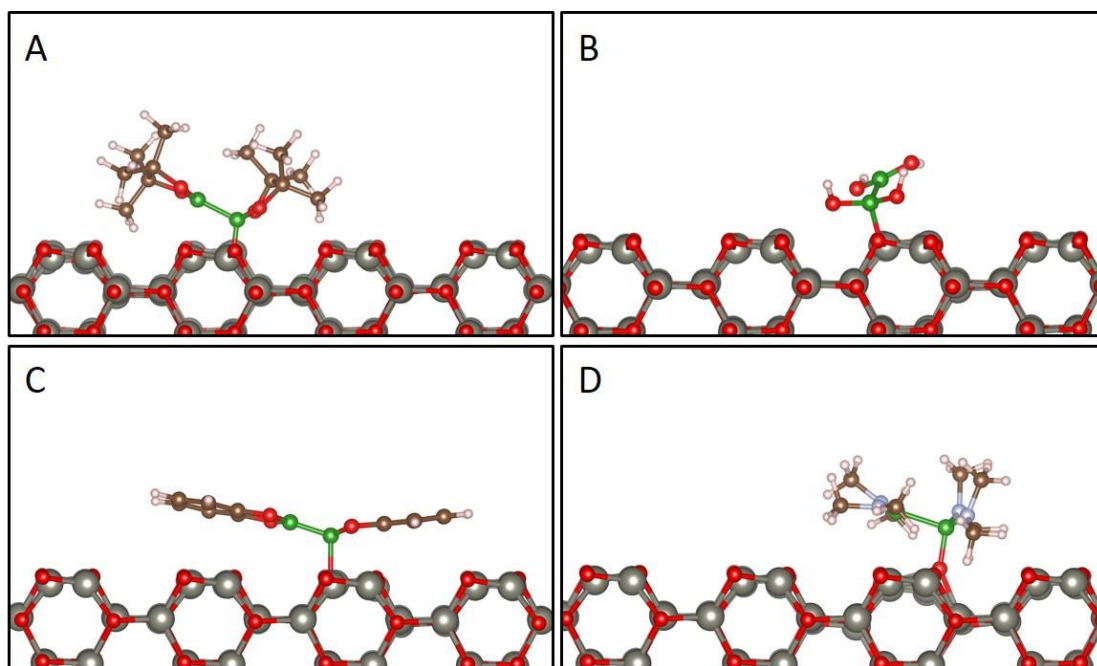


Figure S8 Optimized atomic geometry of (A) **B1** (B) **B2** (C) **B3** (D) **B4** molecule adsorption on the ZnO {110} plane.

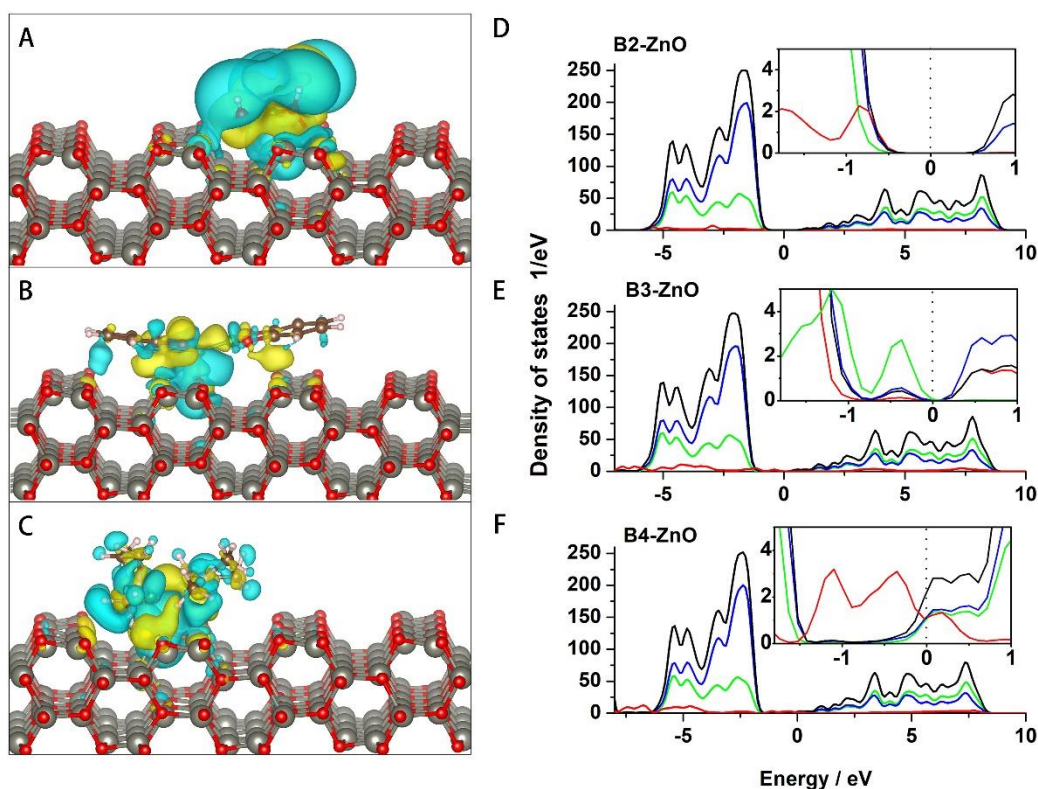


Figure S9 Charge density difference mappings for the (A) **B2** (B) **B3** (C) **B4** adsorption on the ZnO {110} surface. The isosurfaces of the electron density difference plots are all $0.001 \text{ e} \text{ \AA}^{-3}$. The yellow and light blue surfaces represent electron depletion and accumulation. The Silvery gray, red, earth yellow, green and pink spheres stands for the Zn, O, C, B and H atoms, respectively. The projected density of state (PDOS) plots of (D) **B2** (E) **B3** (F) **B4** molecule adsorption on ZnO {110} plane and (D) pristine ZnO {110} surface calculated by GGA+U. ($U=7.5$, the insert was magnification of the PDOS around the Fermi level)

Table S1. The adsorption energy of an O_2 molecule to the ZnO surface with B molecule.

	$E(\text{ZnO-B})$	$E(\text{O}_2)$	$E(\text{ZnO-B-O}_2)$	E_{ad}
B1 - ZnO	-1305.98924060	-9.44011081	-1314.81295253	0.61639888
B2 - ZnO	-1126.80937497	-9.44011081	-1135.55084946	0.69863632
B3 - ZnO	-1246.27395274	-9.44011081	-1255.16395559	0.55010796
B4 - ZnO	-1271.77328205	-9.44011081	-1281.37378562	-0.16039276

1. Perdew, J. P.; Wang, Y., Accurate and simple analytic representation of the electron-gas correlation energy. *Physical Review B* **1992**, 45 (23), 13244-13249.
2. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, 77 (18), 3865-3868.
3. Tang, Q.-L.; Zou, W.-T.; Huang, R.-K.; Wang, Q.; Duan, X.-X., Effect of the components' interface on the synthesis of methanol over Cu/ZnO from CO_2/H_2 : a microkinetic analysis based on DFT + U calculations. *Physical Chemistry Chemical Physics* **2015**, 17 (11), 7317-7333.