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Zn⁺–O[–] Dual-Spin Surface State Formation by Modification of ZnO Nanoparticles with Diboron Compounds

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Supporting Information

ABSTRACT: ZnO semiconductor oxides are versatile functional materials that are used in photoelectronics, catalysis, sensing, etc. The Zn^+-O^- surface electronic states of semiconductor oxides were formed on the ZnO surface by Zn 4s and O 2p orbital coupling with the diboron compound's B 2p orbitals. The formation of spin-coupled surface states was based on the spin-orbit interaction on the interface, which has not been reported before. This shows that the semiconductor oxide's spin surface states can be modulated by regulating surface orbital energy. The Zn⁺-O⁻ surface electronic states were confirmed by electron spin resonance results, which may help in expanding the fundamental research on spintronics modulation and quantum transport.



INTRODUCTION

ZnO are key semiconductor oxide materials for widespread applications in optoelectronic devices,^{1,2} piezoelectronic devices,³ catalysis,⁴ sensing,⁵ etc. Surface engineering of zinc oxide has been studied for decades.⁶ Surface disorder treatment^{7,8} and defect engineering⁹ are basically surface state engineering methods. The organic molecule modification method has also been developed to modulate the surface states and the charge transfer method to adjust electronic structures and band structures.^{6,10} According to a previous study, the orbitals on the surface of the nanoparticles are distinct from that of bulk and should be sensitive to surface modification, which can induce unique surface states.¹¹ Surface spin orbitronics is an important issue and is mostly studied in transition metal surfaces, topological insulators, and twodimensional materials,¹² but there exists no similar reference in semiconductor oxide systems. Zn⁺(3d¹⁰4s¹) systems possess a special electronic structure that has been reported and studied in ZnO-related chemistry.¹³ Monovalent zinc ions have been prepared under extremely harsh physical conditions, such as γ irradiation,¹⁴ electron impact ionization,¹⁵ glow discharge, and laser vaporization.¹⁷ In 2004, the Carmona group reported a landmark discovery of the dimetallic sandwich compound

decamethyldizincocene ($Zn_2(\eta 5-C_5Me_5)_2$), containing a central subvalent Zn-Zn bond with both Zn atoms formally in the +1 oxidation state.¹⁸ Chen's group recently reported the first example of mononuclear univalent Zn⁺ in solid materials of zeolite.^{19,20}

Organodiboron compounds represent a group of stable and highly versatile reagents that are extremely useful in organic synthesis.²¹ Despite their widespread use in synthetic chemistry, these diboron(4) species have not been used to modify inorganic materials. We find that surface modification of ZnO nanoparticles with diboron compounds can induce surface $Zn^+ - O^-$ dual spin states. Based on the experimental characterization as well as the reference that modulate the magnetic spin of SrRuO₃ by tuning the oxygen coordination environment,²² we surmise that the spin surface states originated from surface orbital hybridization accompanied by electron redistribution induced by modulation of the oxygen coordination environment. To the best of our knowledge, there is no similar report on forming these dual spin states. A

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Figure 1. (a) Structure of wurtzite ZnO. (b) Adsorption model of the organic diboron compound on the ZnO surface. (c) Surface orbital energy modulation induced by diboron compound modification. (d) Schematic diagram of spin states induced in ZnO by the diboron molecule.

conceptually new method for the facile generation of abundant surface Zn^+-O^- surface states on ZnO nanoparticles was developed under mild conditions (<80 °C) by means of diboron(4) reagents. In this process, the intimate interaction of the diboron(4) reagent's B center with the surface bridging O_{2c} of ZnO facilitates the adsorption of the organodiboron reagents onto the ZnO nanoparticles, which leads to spontaneous electron transfer, resulting in Zn^+-O^- dual-spin surface states (Figure 1b-d). Notably, this process exhibits a facile method to modulate ZnO's surface states by introducing dual-spin electrons coupled to surface orbitals.

According to the literature, coordination changes in surface oxygen sites can induce electron behaviors like magnetism.² We posited that electrophilic organic adsorbates with an appropriate reduction potential might favorably interact with the surface O_{2c} sites. Importantly, this binding changed the coordination behavior of surface O_{2c} and affected the surface states. We were particularly interested in the use of organic diboron(4) reagents due to their unique Lewis acidity and reducing ability (vide supra). Previous work in the area of synthetic organic chemistry showed that upon binding to a Lewis basic oxygen atom, these organic diboron(4) species could function as single electron reducing agents, thus allowing various important transformations.²³⁻²⁹ Based on these reasons, we envisioned that the coordination of such diboron(4) compounds with the surface oxygen atom in metal oxide materials may lead to the formation of surface diboron-oxygen Lewis pairs, which may induce single electron transfer from the ipso-O_{2c} site to the adjacent Zn site. Furthermore, the interaction of diboron(4) species with the oxygen atom may stabilize the resulting low valent Zn-high valent O pair (Figure 1b-d).

EXPERIMENTAL DETAILS

B1-ZnO-N₂ sample: In a glovebox, 10, 20, or 50 mg of B1 (B_2 Pin₂, the molecular structure is depicted in Figure 2a) was dissolved in 2

mL of dried CH₃OH (Energy Chemical Co. Ltd., China). Then, 0.5 g of ZnO nanoparticles (30 nm, Shanghai Macklin Biochemical Co. Ltd) were dispersed in B1 solution and the mixture was stirred at room temperature (~30 °C) overnight. After evaporation of the solvent under vacuum at room temperature for 2 h, a blue powder of the B1-ZnO–N₂ sample was obtained. This sample was sensitive to air and should be stored in an inert atmosphere.

B1-ZnO sample: In a glovebox, the above B1-ZnO–N₂ sample was heated at 80 $^{\circ}$ C under vacuum for 3 h. The redundant B1 molecules were removed under vacuum via volatilization. After heat treatment, the sample becomes insensitive to air.

Other B-ZnO samples were prepared with the sample procedure by using the corresponding diboron compounds.

RESULTS AND DISCUSSION

The diboron(4) compound could be uniformly dispersed onto the ZnO nanoparticles in a diboron(4)-soluble solvent, such as methanol or ether. Blue samples were obtained after solvent evaporation and heating at 80 $^\circ$ C under vacuum for 3 h. These blue samples are tagged as B-ZnO. They can be stored outside of a glovebox for at least 6 months while retaining the blue color. This color change only occurs with diboron(4)compounds. Monoboron compounds, such as methyl borate, are unable to sensitize ZnO with no color change when mixed with ZnO. We investigated the structures and properties of these diboron(4)-sensitized ZnO nanoparticles with UVvisible spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy, transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and boron nuclear magnetic resonance (¹¹B NMR). The UV-visible absorption spectra (Figures 2b and S1) of B-ZnO show that the sample with the diboron compound modification exhibits enhanced visible light absorption (wavelength >400 nm). The blue color and the visible light absorption of the B-ZnO samples imply the formation of the reduced state of zinc(I).³⁰



Figure 2. (a) Four commercially available diboron(4) compounds used in this study: B_2Pin_2 (bis(pinacolato)diboron), $B_2(OH)_4$ (tetrahydroxydiborane), B_2Cat_2 (bis(catecholato)diboron), and $B_2(NMe_2)_4$ (tetrakis(dimethylamino)diboron). (b) UV-visible spectral absorbance of the white ZnO and B-ZnO samples. (c) High-resolution transmission electron microscopy photo of the B1-ZnO sample (The red dotted curve shows the interface of the surface molecule, whereas the white arrow shows the organic molecule layer). (d) High-angle annular dark-field (HADDF) image of the B1-ZnO sample. (e) Carbon mapping image in the HADDF mode. (f) Zn mapping image of the B1-ZnO sample. (g) C mapping image of the B1-ZnO sample. (h) O mapping image of the B1-ZnO sample. (i) X-ray diffraction (XRD) spectra of pristine ZnO and four B-ZnO samples. (j) In situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectrum of B4 on ZnO over 60 min at room temperature with a B4 molecule for comparison (in red).

We then performed TEM characterization to explore the surface structure of the material. A thin organic molecule layer (ca. 0.5-2 nm) on the surface of the material can be seen in the TEM picture (Figure 2c). The corresponding C phase mapping in the HADDF mode (Figure 2e) and the corresponding Zn, C, and O elemental mapping (Figure 2fh) show that C phase mapping distributes over a larger area than Zn and O phase mapping, which means a carboncontaining layer on the surface of ZnO nanoparticles (Figure 2d). Powder X-ray diffraction analysis (Figure 2i) showed that the commercial ZnO and diboron-compound-modified ZnO samples can be indexed to wurtzite lattice nanoparticles. There were no new peaks after modification, which indicates no changes in the crystal structure upon adsorption. The X-ray photoelectron spectroscopy showed that the O 1s and Zn 2p binding energies of B1-ZnO are lower than those of the

pristine ZnO sample. The valence band of B1-ZnO also shifted to a lower energy, which means that the valence band electron was much closer to the Fermi level energy, and the electron may be more likely to jump to the conduction band (Figure S2).

ZnO shows increased visible light absorption based on the surface interaction with the diboron compound. To gain a better understanding of the adsorption process, in situ FTIR analysis was used to track the surface bonding behavior. Figure 2j shows the in situ ATR-FTIR spectra along a 60 min course of the B4 molecule interaction with ZnO nanoparticles. The magnification of vibration at 1600–900 cm⁻¹ shows the fingerprint of the B4 molecule when interacting with ZnO. For comparison, IR signals of the free B4 molecule were found to agree well with simulations using the Gaussian09 software (Figure S4). The calculated results suggest a B–B bond



Figure 3. (a–d) EPR spectra of four B-ZnO samples at 2 K. The inset in (b) shows the magnification of the green rectangular areas with g values of 2.2-1.99. (e–h) Solid-state boron nuclear magnetic resonance spectra of B1–B4 and four B-ZnO samples. (i) Zn K-edge and (j) O K-edge TEY spectra of B1-ZnO and ZnO.

stretching vibration peak at ca. 1000 cm⁻¹, where the intensity is zero. This conforms to the fact that B4 is a C_2 symmetric molecule. The symmetry may be lost when B4 was adsorbed on ZnO, resulting in the appearance of the corresponding B–B bond vibration signal. Indeed, new vibrations at around 1268 and 1028 cm⁻¹ appear, which can be indexed to the B–B bond vibration. The B-B bond vibration was silent in the free B4 molecule, which suggests that B4 interacts with the ZnO nanoparticle through the B-B moiety. ATR-FTIR spectra of other B-ZnO samples all show an extra absorption band around 1020 cm⁻¹ compared to the free diboron molecule, which was indexed to the asymmetric sp²-sp³ B-B bond vibration (Figure S5). On the other hand, most typical pure diboron(4) compound absorption peaks have very small changes in the wavenumber in the modified samples, which means that the main chemical structure of the molecule remains unchanged.

Then, the surface electronic states and the diboron molecule's structure were characterized by electron spin resonance, NMR, and X-ray absorption fine structure (XAFS) (Figure 3). The electron paramagnetic resonance (EPR) spectrum of the B1-ZnO sample showed a strong singlet line centered on a g value of 1.960 at 2 K (Figure 3a). Some g > 2.0 signals were also observed, which could be indexed to the radical state of the organic molecule. The observed g values were characteristic of a paramagnetic Zn⁺ center as exemplified in a few reports such as ZnO synthesized by evaporation (g = 1.96),³¹ heat treated ZnO (g = 1.955),³² defect-rich ultrathin ZnAl-LDH (g = 1.99),³³ and Zn⁺-doped ZSM-5 obtained by molecular sieving (g = 1.99).³⁴

Furthermore, the solid-state boron nuclear magnetic resonance (¹¹B NMR) can be used to elucidate the binding details of the diboron(4) adsorbed on ZnO (Figure 3e-h). The peaks around 20-40 ppm for the free diboron(4) compounds were assigned to the two identical symmetric boron atoms in the pure B1-B4 molecule (B1: 24.3, B2: 22.2, B3: 23.0, and B4: 36.5 ppm). In the adsorption samples, the bonding on the boron atom will cause the molecule to lose its symmetry resulting in two distinct chemical environments

around the two boron atoms. Thus, a chemical shift was observed at 4.4 ppm for B1-ZnO in ¹¹B NMR, which was presumably responsible for the complexation mode (B2: 1.63, B3: 7.5, and B4: 1.6 ppm). This new peak appeared in the very upfield region compared to that for the free B1, indicating a change in the coordination on the boron atom. Mechanistically, tetracoordinating boron has a higher electron density than the tricoordinating species due to its formal negative charge, which results in a chemical shift upfield in the NMR spectrum.³⁵ Moreover, Marder and co-workers reported a Nheterocyclic carbene-B1 adduct with a 0.34 ppm chemical shift, which they assigned to the tetracoordinating boron.³⁶ The peak close to 0 ppm in the present case should be attributed to one of the boron atoms in the diboron(4) molecule coordinating with the bridged oxygen or the hydroxyl group on the ZnO surface.

X-ray absorption fine structure (XAFS) spectra were used to investigate the surface complexation. The X-ray absorption near-edge structure (XANES) spectra of the Zn K-edge (Figure 3i) showed that B-ZnO and ZnO have little difference, indicating that the diboron(4) compounds only interacted with the surface ZnO layer. The introduction of the diboron compound did not influence the bulk properties of the ZnO substrate, which was in accordance with the Fourier-transformed (FT) k^2 -weighted extended X-ray absorption fine structure spectra in Figure S6. The XANES spectra of the O Kedge were measured in the FEY mode, which provided information about the surface O atoms.³⁷ We compared ZnO with B4-ZnO to exclude the influence of the O atoms in the diboron compounds. The absorption around 537.6 eV could be ascribed to the hybridization of the Zn 4p and O 2p orbitals. 38,39 The negative shift $(-0.4\ eV)$ of the absorption peak to 537.2 eV showed that the surface O atom shifted to a lower valance state (Figure 3j), due to the formation of a B–O coordination bond that led to the formation of a lower valence state of the Zn⁺ species.

Density functional theory calculations were further used to study the adsorption of the diboron molecule on the ZnO nanoparticle surface. This study focuses on the ZnO {110}



Figure 4. (a) Optimized geometric structures and (b) charge density difference mappings for the B1 adsorption on the ZnO {110} surface. The isosurfaces of the electron density difference plots are all 0.001 e Å⁻³. The yellow and light blue surfaces represent electron depletion and accumulation. The silvery gray, red, earth yellow, green, and pink spheres are the Zn, O, C, B and H atoms, respectively. The projected density of states (PDOS) plots of (c) B1 molecule adsorption on the ZnO {110} plane and (d) pristine ZnO {110} surface calculated by GGA + U(U = 7.5 eV). The inset shows the magnification of the PDOS around the Fermi level.

surface, which is nonpolar and contributes up to 80% of the ZnO total surface area.⁴⁰ The optimized geometry of the B1 adsorption on the ZnO surface is shown in Figure 4a. The B1 molecule was tightly bound with the surface O_{2c} atom through the B-O coordination bond. The charge density difference plots in Figure 4b showed the charge redistribution around the adsorption site of the ZnO {110} surface mainly on the p orbital of O atoms and s orbital of surface Zn atoms, and it also exhibited electron redistribution in the organic molecule. This charge redistribution could result in the formation of a Zn⁺-O⁻ pair. Next, the projected density of states (PDOS) of the ZnO surface with the adsorption of the B1 molecule is shown in Figure 4c. As a comparison, the PDOS of the pristine ZnO {110} surface is shown in Figure 4d. Some intermediate states just below the Fermi level appeared upon the adsorption of the B1 molecule. What is more, O 2p states in the B1-ZnO model showed a density of states of 199 eV^{-1} at -1.4 eV, whereas in pristine ZnO, the relative density was 204 eV^{-1} at -1.9 eV, Zn 4s states at 1 eV was 1.3 eV^{-1} in the model of the pristine ZnO {110} surface, and it was 1.4 eV^{-1} at around 0.66 eV in the B1-ZnO model. It could be concluded that O 2p states were reduced but Zn 4s states were increased in the B1-ZnO model, and the band gap was shrinked. The circumstance showed that the surface adsorption of the B1 molecule induces electron redistribution so that some states were moved from O 2p to Zn 4s, which is consistent with the formation of the $Zn^+ - O^-$ pair. The adsorption of B2, B3, and B4 molecules on the ZnO {110} surface was also analyzed (Figure S8). The PDOS plots (Figure S9) showed the presence of electron-filled Zn 4s states within the band gap, suggesting that the adsorption of the diboron molecule could lead to the formation of the Zn⁺ species on the ZnO surface. The stability of the newly formed Zn⁺-O⁻ pair was examined by calculating the adsorption energy of an O_2 molecule on the adjacent sites of the $Zn^+ - O^$ pair. The adsorption energy is generally positive (Table S1), indicating that it is energetically unstable for the O₂ molecule to get close to the Zn⁺-O⁻ center. This result demonstrated that the organic complexation could prevent further oxidation of the Zn⁺ species by the O₂ molecule, thus stabilizing the formed $Zn^+ - O^-$ pair in the air atmosphere.

CONCLUSIONS

 Zn^+-O^- dual-spin surface states were formed by a surface modification method. The diboron compound successfully induced surface charge redistribution by adjusting the surface orbital energy. Based on changing the coordination environment of O_{2c} and the unique structure of the diboron compound itself, new spinning surface states constituting Zn 4s, O 2p, and organic molecules' orbitals were formed, and the spin—orbit coupling was induced by the surface states to form dual-spin Zn⁺-O⁻ states.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.9b01955.

ATR-FTIR, XAS experiment; computational details; UV–vis absorption, XPS, FT-IR, K-edge spectra; ZnO nanoparticle; XANES of ZnO and B-ZnO; optimized atomic geometry of (A) B1 (B) B2 (C) B3 (D) B4; adsorption energy of an O_2 (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Özgür, U.; Hofstetter, D.; Morkoc, H. ZnO devices and applications: a review of current status and future prospects. *Proc. IEEE* **2010**, *98*, 1255–1268.

(2) Djurišić, A.; Ng, A.; Chen, X. ZnO nanostructures for optoelectronics: material properties and device applications. *Prog. Quantum Electron.* **2010**, *34*, 191–259.

(3) Wang, X.; Song, J.; Wang, Z. L. Nanowire and nanobelt arrays of zinc oxide from synthesis to properties and to novel devices. *J. Mater. Chem.* **2007**, *17*, 711–720.

(4) Kumar, B. V.; Naik, H. S. B.; Girija, D.; Kumar, B. V. ZnO nanoparticle as catalyst for efficient green one-pot synthesis of coumarins through Knoevenagel condensation. *J. Chem. Sci.* 2011, 123, 615–621.

(5) Wang, L.; Kang, Y.; Liu, X.; Zhang, S.; Huang, W.; Wang, S. ZnO nanorod gas sensor for ethanol detection. *Sens. Actuators, B* **2012**, *162*, 237–243.

(6) Hewlett, R. M.; McLachlan, M. A. Surface Structure Modification of ZnO and the Impact on Electronic Properties. *Adv. Mater.* **2016**, *28*, 3893–3921.

(7) Chen, X.; Liu, L.; Peter, Y. Y.; Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystals. *Science* **2011**, *331*, 746–750.

(8) Lin, L.; Huang, J.; Li, X.; Abass, M. A.; Zhang, S. Effective surface disorder engineering of metal oxide nanocrystals for improved photocatalysis. *Appl. Catal.*, B **2017**, 203, 615–624.

(9) Schmidt-Mende, L.; MacManus-Driscoll, J. L. ZnO-nanostructures, defects, and devices. *Mater. Today* **2007**, *10*, 40–48.

(10) Zhang, G.; Kim, G.; Choi, W. Visible light driven photocatalysis mediated via ligand-to-metal charge transfer (LMCT): an alternative approach to solar activation of titania. *Energy Environ. Sci.* 2014, 7, 954–966.

(11) Freund, H. J. Metal oxide surfaces: electronic structure and molecular adsorption. *Phys. Status Solidi B* **1995**, *192*, 407–440.

(12) Huang, Z.; Zhang, Y.; He, Y.; Song, H.; Yin, C.; Wu, K. A chemist's overview of surface electron spins. *Chem. Soc. Rev.* 2017, 46, 1955–1976.

(13) Chen, G.; Zhao, Y.; Shang, L.; Waterhouse, G. I. N.; Kang, X.; Wu, L.-Z.; Tung, C.-H.; Zhang, T. Recent Advances in the Synthesis, Characterization and Application of Zn⁺-containing Heterogeneous Catalysts. *Adv. Sci.* **2016**, *3*, No. 1500424.

(14) Isoya, J.-I.; Fujiwara, S. ESR of Hot Ions: Zn (I), Cd (I), and Hg (I) in γ -Irradiated Potassium Tetracyano Zincate (II), Cadmate (II), and Mercurate (II). *Bull. Chem. Soc. Jpn.* **1972**, 45, 2182–2188. (15) Rogers, W. T.; Stefani, G.; Camilloni, R.; Dunn, G. H.; Msezane, A. Z.; Henry, R. J. W. Electron-impact ionization of Zn⁺ and Ga⁺. *Phys. Rev. A* **1982**, 25, 737–748.

(16) Weis, P.; Kemper, P. R.; Bowers, M. T. Mn^+ (H₂) n and Zn^+ (H₂)_n Clusters: Influence of 3d and 4s Orbitals on Metal–Ligand Bonding. *J. Phys. Chem. A* **1997**, *101*, 2809–2816.

(17) Duncan, M. A. Invited review article: laser vaporization cluster sources. *Rev. Sci. Instrum.* **2012**, *83*, No. 041101.

(18) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. Decamethyldizincocene, a Stable Compound of Zn(I) with a Zn-Zn Bond. *Science* **2004**, 305, 1136–1138.

(19) Tian, Y.; Li, G.-D.; Chen, J.-S. Chemical formation of mononuclear univalent zinc in a microporous crystalline silicoaluminophosphate. *J. Am. Chem. Soc.* **2003**, *125*, 6622–6623.

(20) Li, L.; Li, G. D.; Yan, C.; Mu, X. Y.; Pan, X. L.; Zou, X. X.; Wang, K. X.; Chen, J. S. Efficient Sunlight-Driven Dehydrogenative Coupling of Methane to Ethane over a Zn⁺-Modified Zeolite. *Angew. Chem., Int. Ed.* **2011**, *50*, 8299–8303.

(21) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091–9161.

(22) Kan, D.; Aso, R.; Sato, R.; Haruta, M.; Kurata, H.; Shimakawa, Y. Tuning magnetic anisotropy by interfacially engineering the oxygen coordination environment in a transition metal oxide. *Nat. Mater.* **2016**, *15*, 432–437.

(23) Mo, F.; Jiang, Y.; Qiu, D.; Zhang, Y.; Wang, J. Direct Conversion of Arylamines to Pinacol Boronates: A Metal-Free Borylation Process. *Angew. Chem., Int. Ed.* **2010**, *49*, 1846–1849.

(24) Pietsch, S.; Neeve, E. C.; Apperley, D. C.; Bertermann, R.; Mo, F.; Qiu, D.; Cheung, M. S.; Dang, L.; Wang, J.; Radius, U.; Lin, Z.; Kleeberg, C.; Marder, T. B. Synthesis, Structure, and Reactivity of Anionic sp2-sp3 Diboron Compounds: Readily Accessible Boryl Nucleophiles. *Chem. - Eur. J.* 2015, *21*, 7082–7098.

(25) Wang, G.; Zhang, H.; Zhao, J.; Li, W.; Cao, J.; Zhu, C.; Li, S. Homolytic Cleavage of a B–B Bond by the Cooperative Catalysis of Two Lewis Bases: Computational Design and Experimental Verification. *Angew. Chem., Int. Ed.* **2016**, *55*, 5985–5989.

(26) Mo, F.; Qiu, D.; Zhang, Y.; Wang, J. Renaissance of Sandmeyer-Type Reactions: Conversion of Aromatic C–N Bonds into C–X Bonds (X = B, Sn, P, or CF_3). Acc. Chem. Res. **2018**, 51, 496–506.

(27) Liu, Q.; Hong, J.; Sun, B.; Bai, G.; Li, F.; Liu, G.; Yang, Y.; Mo, F. Transition-Metal-Free Borylation of Alkyl Iodides via a Radical Mechanism. *Org. Lett.* **2019**, DOI: 10.1021/acs.orglett.9b01951.

(28) Wang, G.; Cao, J.; Gao, L.; Chen, W.; Huang, W.; Cheng, X.; Li, S. Metal-Free Synthesis of C-4 Substituted Pyridine Derivatives Using Pyridine-boryl Radicals via a Radical Addition/Coupling Mechanism: A Combined Computational and Experimental Study. J. Am. Chem. Soc. 2017, 139, 3904–3910.

(29) Zhang, L.; Jiao, L. Super electron donors derived from diboron. *Chem. Sci.* **2018**, *9*, 2711–2722.

(30) Schrauben, J. N.; Hayoun, R.; Valdez, C. N.; Braten, M.; Fridley, L.; Mayer, J. M. Titanium and Zinc Oxide Nanoparticles Are Proton-Coupled Electron Transfer Agents. *Science* **2012**, *336*, 1298– 1301.

(31) Li, D.; Leung, Y. H.; Djurišić, A. B.; Liu, Z. T.; Xie, M. H.; Shi, S. L.; Xu, S. J.; Chan, W. K. Different origins of visible luminescence in ZnO nanostructures fabricated by the chemical and evaporation methods. *Appl. Phys. Lett.* **2004**, *85*, 1601–1603.

(32) Morazzoni, F.; Scotti, R.; Di Nola, P.; Milani, C.; Narducci, D. Electron paramagnetic resonance study of the interaction of the ZnO surface with air and air–reducing gas mixtures. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1691–1694.

(33) Zhao, Y.; Chen, G.; Bian, T.; Zhou, C.; Waterhouse, G. I.; Wu, L. Z.; Tung, C. H.; Smith, L. J.; O'Hare, D.; Zhang, T. Defect-Rich Ultrathin ZnAl-Layered Double Hydroxide Nanosheets for Efficient Photoreduction of CO_2 to CO with Water. *Adv. Mater.* **2015**, *27*, 7824–7831.

(34) Li, L.; Li, G. D.; Yan, C.; Mu, X. Y.; Pan, X. L.; Zou, X. X.; Wang, K. X.; Chen, J. S. Efficient Sunlight-Driven Dehydrogenative Coupling of Methane to Ethane over a Zn⁺-Modified Zeolite. *Angew. Chem.* **2011**, *123*, 8449–8453.

(35) Nöth, H.; Wrackmeyer, B. ¹¹B NMR of Tetracoordinate Boron. In Nuclear Magnetic Resonance Spectroscopy of Boron Compounds; Nöth, H.; Wrackmeyer, B., Eds.; Springer: Berlin, Heidelberg, 1978; pp 74–101.

(36) Kleeberg, C.; Crawford, A. G.; Batsanov, A. S.; Hodgkinson, P.; Apperley, D. C.; Cheung, M. S.; Lin, Z.; Marder, T. B. Spectroscopic and Structural Characterization of the CyNHC Adduct of B_2pin_2 in Solution and in the Solid State. J. Org. Chem. 2012, 77, 785–789. (37) Kobayashi, H.; Emura, S.; Arachi, Y.; Tatsumi, K. Investigation of inorganic compounds on the surface of cathode materials using Li and O K-edge XANES. *J. Power Sources* **2007**, *174*, 774–778.

(38) de Groot, F. M. F.; Grioni, M.; Fuggle, J. C.; Ghijsen, J.; Sawatzky, G. A.; Petersen, H. Oxygen 1s x-ray-absorption edges of transition-metal oxides. *Phys. Rev. B* **1989**, *40*, 5715–5723.

(39) Dong, C. L.; Persson, C.; Vayssieres, L.; Augustsson, A.; Schmitt, T.; Mattesini, M.; Ahuja, R.; Chang, C. L.; Guo, J. H. Electronic structure of nanostructured ZnO from x-ray absorption and emission spectroscopy and the local density approximation. *Phys. Rev.* B 2004, 70, No. 195325.

(40) Vo, C. T.; Huynh, L. K.; Hung, J. Y.; Jiang, J.-C. Methanol adsorption and decomposition on ZnO(1010) surface: A density functional theory study. *Appl. Surf. Sci.* 2013, 280, 219–224.