

Plasmonic Enhanced Reactive Oxygen Species Activation on Low-Work-Function Tungsten Nitride for Direct Near-Infrared Driven Photocatalysis

Weicheng Huang, Yan Gao, Jinxin Wang, Pengcheng Ding, Mei Yan, Fengmin Wu, Jian Liu, Danqing Liu,* Chongshen Guo,* Bin Yang,* and Wenwu Cao

Realizing near-infrared (NIR) driven photocatalytic reaction is one of the promising strategies to promote the solar energy utilization and photocatalytic efficiencies. However, effective reactive oxygen species (ROS) activation under NIR irradiation remains to be great challenge for nearly all previously reported photocatalysts. Herein, the cubic-phase tungsten nitride (WN) with strong plasmonic NIR absorption and low-work function (≈3.59 eV) is proved to be able to mediate direct ROS activation by both of experimental observation and theoretical simulation. The cubic WN nanocubes (NCs) are synthesized via the hydrothermal-ammonia nitridation process and its NIR-driven photocatalytic properties, including photocatalytic degradation, hydroxylation, and de-esterification, are reported for the first time in this work. The 3D finite element simulation results demonstrate the size dependent and wavelength tuned plasmonic NIR absorption of the WN NCs. The NIR-driven photocatalytic mechanism of WN NCs is proposed based on density functional theory (DFT) calculated electronic structure and facet dependent O₂ (or H₂O) molecular activation, radicals scavenging test, spin trapped electron paramagnetic resonance measurements, and ultraviolet photoelectronic spectrum (UPS). Overall, the results in this work pave a way for the application of low-workfunction materials as highly reactive NIR photocatalyst.

1. Introduction

Employing photocatalyst to convert the solar energy into the available chemical energy or achieve environmental purification has been widely investigated since the rising concerns on energy crisis and environmental pollution.^[1] Until now, most of reported photocatalysts are ultraviolet–visible responsive,^[2] failing in

W. Huang, J. Wang, P. Ding, Prof. J. Liu, Prof. B. Yang, Prof. W. Cao School of Instrumentation Science and Engineering Harbin Institute of Technology Harbin 150080, P. R. China E-mail: binyang@hit.edu.cn
Y. Gao, Dr. M. Yan, Prof. C. Guo School of Chemistry and Chemical Engineering Harbin Institute of Technology Harbin 150080, P. R. China E-mail: chongshenguo@hit.edu.cn
The ORCID identification number(s) for the author(s) of this article

can be found under https://doi.org/10.1002/smll.202004557.



utilizing NIR light that takes up to about 50% of solar spectrum. One of the reasons is that the low energetic NIR photons only can be utilized to generate free carriers by narrow bandgap semiconductors, up-conversion luminescent material or some localized surface plasmon resonance (LSPR) enhanced noble metal nanomaterials.^[3] These materials always suffer from single-wavelength response, poor chemical stability and potentials mismatching. In many cases, the chemical potentials of hole-electrons are not suitable to support the generation of ROS (\cdot OH, \cdot O₂⁻ and 1 O₂) through individual transition for previous materials.^[4] What is more, the NIR-driven photocatalytic mechanism remains to be ambiguous due to the absence of theoretical investigation on the mechanism of NIR absorbance and surface/interface ROS generation kinetics. Therefore, exploiting highefficiency NIR-reactive photocatalyst and comprehensive understanding NIR-driven photocatalytic mechanism are urgent.^[5]

Compared with traditional semiconductive photocatalysts, metallic photocatalysts

with higher carrier density, excellent conductivity, and low-work function open the door for the aimed NIR-responsive photocatalysis. Until now, many theoretical calculations and experimental results have revealed that low-work-function catalysts, such as $Ti_3C_2T_X$ MXene ($\Phi = 3.4$ eV), halogen-doped monolayer g- C_3N_4 ($\Phi = 3.3-4.15$ eV), LaCu_{0.67}S_{1.33} ($\Phi = 3.5$ eV) and MgO ($\Phi = 3.7$ eV), can server as good electron donor and facilitate

Prof. F. Wu
Department of Physics
School of Science
Harbin University of Science and Technology
Harbin 150080, China
Dr. D. Liu
School of Chemical and Environmental Engineering
Harbin University of Science and Technology
Harbin 150040, China
E-mail: danqingliu76@163.com
Prof. W. Cao
Department of Mathematics and Materials Research Institute
The Pennsylvania State University
Pennsylvania, PA 16802, USA



the escaping of the electron from the surface of material, and thus promote ROS activation potentially.^[6] Meanwhile, some metallic candidates such as Co111Te2, MoO2, CuS nanosheet, and MoN have been successfully applied for the Vis/NIR-driven photocatalytic CO₂ reduction, water splitting or organic compound degradation.^[7] Small or zero bandgap, quasi-continuous occupation electronic state and high carrier density of metallic materials are benefit for the NIR-induced consecutive plasmonic interband/intraband electronic transition, which can pump the free carriers to suitable energy state and initiate photocatalytic process.^[8] Meanwhile, under the light irradiation, the photoexcited hot electrons are more readily to escape from surface of materials for the low-work-function metallic photocatalysts, being in favor of efficient electrons transfer between photocatalyst and the lowest unoccupied molecular orbitals of absorbed molecules (O₂ and H₂O). Resultantly, the ROS can be activated with low energy barrier and it makes the utilization of low energetic NIR light in the photocatalytic reaction to be possible.

The metallic WN with high free electron density and good conductivity is quite similar to these metallic photocatalysts, and thus the strong plasmonic enhanced NIR absorption and direct NIR-driven photocatalytic performance are highly expected.^[9] However, to the best of our knowledge, application of WN as NIR-driven photocatalyst has not caught much attentions yet. Previously, Wang et al. operate an overall-waterspitting photocatalysis with black WN under 765 nm, which enlighten us to employ real NIR light above 800 nm for the

photocatalyis application^[10] In this work, the theoretical calculation of DFT and finite element analysis (FEA) are carried out to investigate the electronic structure and optical property of the cubic phase (WN-cub) firstly. Then, the NIR-driven photocatalytic performance of cubic phase WN is systematically studied. Finally, a possible plasmonic enhanced ROS activation and NIR-driven photocatalytic mechanism of low-work-function WN NCs are proposed based on the DFT calculation of crystal facet dependent ROS activation and ROS detection results.

2. Results and Discussion

In this work, we predicted that the WN species would be a promising candidate as directly NIR-driven photocatalyst. We first carry out the first-principle calculations of DFT to predict the electronic structure and optical properties of cubic WN. (Details of the calculation are available in the Supporting Information) The relaxed lattice parameters are a = b = c = 4.347 Å for WN-cub, which are in good accordance with previous results.^[11] In the **Figure 1a** and Table S1 (Supporting Information), the enthalpy of WN-cub is calculated –2204.6 eV, indicating that it is thermodynamically stable phase as expected. The sliced EDD map with quadruple symmetry (Figure 1b) correspond to the (1 1 0) crystal facet of WN-cub.^[12] According to the Mulliken charge analysis (Table S1, Supporting Information) and the EDD map, it is easily to find that WN-cub shows strong charge transfer between W and N atoms



Figure 1. DFT calculated electronic structure and optical properties of WN-cub. a) The optimized 3D structure. b) Electron density difference (EDD) distribution sliced along (1 1 0) facets, wherein red and blue color represent charge accumulation and depletion respectively. c) Total density of state (DOS) and the corresponding projected DOS for W and N atoms. d,e) Calculated dielectric function and optical absorption spectra of WN from visible to NIR region.

(0.72 e⁻ for WN-cub). The calculated total DOS and band structure (Figure S1, Supporting Information) both demonstrate the metallic behavior of WN-cub as the continuously electronic occupation states across the fermi level.[13] According to previous studies, the DOS and band structure can be divided into $B_{.1}$, CB and B_1 band, where $B_{.1}$ band is occupied by the strong hybridized W 5d and N 2p states, CB band is the conduction band and partially occupied by W 5d states, and B1 band is the empty band above the Fermi level (Figure 1c).^[10,14] What is more, the work function of WN-cub is about 3.47 eV (Figure S2, Supporting Information), being much lower than most of previously reported photocatalysts.^[6a,c] Therefore, the lower work function of WN-cub foreseeing its superiority potential on electron donation and ROS activation.^[15] Finally, the dielectric function and optical absorption coefficient are calculated (Figure 1d,e). The real part of the dielectric function presents a negative value window between 600 and 2100 nm for WN-cub, and the image part dielectric function of WN-cub shows a peak at 1500 nm, revealing the significant NIR-plasmonic behavior the metallic WN.^[16]

According to above DFT calculation results, the metallic cubic WN possesses low-work function and strong plasmonic assisted NIR absorption, endowing it with more favorable electronic property as promising NIR-driven photocatalyst. Therefore, the cubic phase WN and its NIR-driven photocatalytic performance are systematically investigated in this work later. WN NCs are fabricated via a three-step procedure, as shown in **Figure 2a**. The green WO₃•H₂O NCs are first synthesized by a hydrothermal method, wherein the tartaric acid and Na₂WO₄ solution are used as raw materials.^[17] Followed by annealing of WO₃•H₂O NCs, the yellow WO₃ NCs are formed. Finally, the black WN NCs are obtained via high temperature nitridation of WO₃ NCs under NH₃ atmosphere (see Supporting Information for the details).^[18] According to X-ray diffraction analysis in

Figure 2b-d, all the peaks are well-matched with the standard PDF card and verify the successful synthesis of WO₃•H₂O NCs, WO₃ NCs, WN NCs step by step. The scanning electron microscopy (SEM) (Figure 3a-c) and transmission electron microscopy (TEM) (Figure 3d-f) are employed to reveal the morphological features of the samples. The WO₃•H₂O NCs are seen with sharp edges, and statistical particle size from SEM image is about 166.0 nm (Figure S3, Supporting Information). The subsequent thermal process makes all the edges become blunt and the particles size increases to 225.3 nm eventually (Figure S4, Supporting Information). To further investigate the crystallographic structure of the samples, the high resolution TEM and select area electronic diffraction (SAED) are performed. The clear crystal fringes in Figure 3g,i,k are measured as 0.378, 0.334, and 0.234 nm, which could be well indexed as the (200), (021), and (111) crystal facet of the orthorhombic WO3•H2O, monoclinic WO3 and cubic WN, respectively. What is more, the corresponding SAED (Figure 3h,j,l) with symmetrical and theoretical self-consistent diffraction pattern also shows the high crystallinity of the samples. Thus, we could confirm that the cubic WN NCs are successfully synthesized with suitable size, phase, and crystallinity.

To further investigate the chemical nature of WN NCs, the X-ray photoelectronic spectra (XPS) are conducted. The full range survey in Figure 3m shows the clear elemental peaks of W (4s, 4p, 4d, and 4f), N1s, O1s, and C1s orbits, and no other impurity elements are evidently observed. The dominant peak in the high resolution XPS spectra of N 1s (Figure S5, Supporting Information) locates at 397.4 eV, which can be assigned to the W–N bonding of WN. N–O peaks at 399.8 may originate from the superficially adsorbed H₂O. What is more, the high-resolution core-level of W_{4f} in the range of 32.3 to 39.3 eV (Figure 3n) can be fitted into the quadruple peaks, among which the doublet peaks at low binding energy region (35.8 and 33.3 eV) are corresponding to the W–N chemical



Figure 2. a) Schematic illustration of synthetic process of the WN NCs. XRD pattern and 3D crystal structure of b) orthorhombic $WO_3 \cdot H_2O$, c) monoclinic WO_3 and d) cubic WN.







Figure 3. Morphology and crystal structure analysis on the samples. SEM, TEM, HRTEM, and SAED of orthorhombic a,d,g,h) WO₃•H₂O NCs; b,e,i,j) monoclinic WO₃ NCs; and c,f,k,l) cubic WN NCs NCs. m) Full XPS and n) high resolution deconvoluted W 4f XPS.

bond (W^{3+} 4f^{5/2} and W^{3+} 4f^{7/2}),^[19] while the shoulder peaks at the high binding energy range (38.0 eV and 35.0 eV) may come from the trace superficially adsorbed H₂O or oxygen (Figure S6, Supporting Information).

Then, the optical properties and the NIR-driven photocatalytic performance of the WN NCs are evaluated. **Figure 4**a shows the optical absorbance of the WN NCs. The black powder of WN NCs (inset of Figure 4a) shows strong photoabsorption over the full tested spectra range, especially in the visible–NIR region, being in accordance with our previous DFT prediction. To further verify the plasmonic nature of the metallic WN, the 3D FEA is performed to simulate the local electric field distribution and the absorption cross-section $\sigma_{\text{absorbance}}$ (see Supporting Information).^[7d] According to the statistical particle size from SEM image (Figure S4, Supporting Information), the 3D FEA model is built by taking particle size of 100–350 nm into consideration. As revealed by computation results in Figure 4b–e, the irradiated WN may generate localized surface plasmon resonance (LSPR) hot spots and the homogeneity of the hot spots could be significantly improved with wavelength increment. What is more, the peaks of the localized electric field enhancement $|E/E_0|$ (Figure 4f) and the absorption cross-section



Figure 4. Optical property and NIR-driven photocatalytic investigation of WN NCs. a) UV–Vis–NIR diffuse reflection spectrum (the inset photograph shows the black powder of WN NCs); FEA simulation of WN NCs: b–e) The *xz*-plan $|E/E_0|$ distribution for single particle (particle size D = 225 nm) under $\lambda = 800$, 1200, 1600, and 2000 nm monochromatic light irradiation; f) the calculated particle size dependent of $|E/E_0|$ distribution and g) the absorption cross-sections. h) The NIR light excited transition photocurrent at 1 V versus Ag/AgCl in 0.1 M Na₂SO₄ electrolyte; WN NCs used as NIR-driven photocatalyst for photocatalytic i) degradation of MB, j) hydroxylation of TPA, and k) de-esterification of H₂DCFDA.



(Figure 4g) red-shift obviously to NIR region as particle size increasing. Hence, the broadband photoabsorption of WN NCs in Figure 4a could be interpreted as the collective LSPR effect from different sized WN NCs. Upon NIR irradiation, the enhancement of the localized electromagnetic (EM) field coupling may happen at the interfaces of WN NCs, and then form "hot spots" to promote the generation of the energetic hot electrons (or holes).^[1] Thereafter, these plasmonic-excited hot electrons (holes) may further transfer to the material interface and participate in photochemical reactions. Given this, the NIR excited photoelectronic effect is then studied on WN NCs by photocurrent measurements. As shown in the Figure S7 (Supporting Information) and 4h, the photocurrent under NIR light is higher than that in dark condition in the full test region and the transient photocurrent signals exhibit evident lighttuned behavior with net photocurrent response of $\approx 2.5 \ \mu\text{A cm}^{-2}$ upon NIR irradiation, indicating that the NIR-excited hot electron-hole pairs could be effectively separated.^[14d] The strong LSPR photoabsorption and robust photocurrent response of WN NCs are beneficial for the generation of ROS during the photocatalytic process. Consequently, above results forecast the WN NCs as direct NIR-driven photocatalyst.

In this work, NIR-driven photocatalytic activity is first evaluated by photodegradation of methylene blue (MB) with a 200 W NIR lamp (see Supporting Information for experimental details). The photocatalytic behavior of C_t/C_0 with time is given in Figure 4i. About 48% of MB is degraded by WN NCs within 4 h in comparison with control group received NIR irradiation only, which is superior to previously reported NIR photocatalysts of up-conversion or polaron transfer.^[5] Besides, the NIR-driven photocatalytic hydroxylation and de-esterification performance of colorless aromatic compounds, such as terephthalic acid (TPA) and 2',7'-dichlorodihydrofluorescein diacetate (H₂DCFDA), are also taken into assessment. The nonluminous TPA and H₂DCFDA could be oxidized by ROS and form photoluminescent 2,5-dihydroxyterephthalic acid (DTPA) and 2',7'-dichlorofluorescein (DCF). The DTPA and DCF could be excited by 320 and 510 nm light and give luminescence at 425 and 520 nm, respectively.^[7d] As the results shown in Figure 4j,k, the photoluminescence intensity of DTPA and DCF increases with the NIR irradiation time, demonstrating the high photocatalytic activity of WN NCs in hydroxylation and de-esterification reaction as well. Such encouraging NIR-driven photocatalytic performances of WN NCs show promising applications in many ROS-mediated chemical reactions.

The previous results of DFT calculations, characterizations, FEA simulation and photocatalytic performance have revealed the excellent direct NIR-driven photocatalytic properties of the brand-new metallic WN NCs. However, the mechanism behind the experimental results has not yet been disclosed. It is well known that the generation of ROS is the prerequisite to initiate photocatalytic reactions, and the activation of O₂ and H₂O molecular is the prerequisite to generate ROS. Then, the absorption and activation of O₂ and H₂O molecular on the typical (100), (110), and (111) crystal facets of cubic WN (noted as WN-100, WN-110 and WN-111, Figure S8, Supporting Information) are studied by DFT calculation. The WN-100 shows the lowest surface energy (Table S2, Supporting Information), proving that the (100) crystal facet is the most thermostable.^[10] However, the WN-110 seems to be more preferable to absorb the O₂ and H₂O molecular as the adsorption energies of both H₂O and O₂ are smallest as compared with other crystal facets (Table S3 and Figures S9 and S10, Supporting Information). The charge transfer between the adsorbate (O₂ and H₂O molecular) and the WN slabs is investigated by the Bader charge Δq .^[20] As shown in **Figure 5**a–c, the total charge changes (Δq) of H₂O molecular in WN-100, WN-110, and WN-111 are -0.014 e⁻, -0.043 e⁻ and +0.0065 e⁻, respectively. The positive Δq (H₂O)



Figure 5. Theoretical calculation and experimental evidence for demonstrating facet dependent H_2O and O_2 molecule activation and the NIR-triggered ROS formation on WN. a–c) EDD distribution of different WN facet after H_2O adsorption. d) ESR spectra of WN NCs in the present of DMPO for •OH detection. e–g) EDD distribution of different WN facet after O_2 adsorption. h) ESR spectra of WN NCs in the present of TEMP for $^{1}O_2$ detection. Bader charge Δq presents the EDD of the H_2O or O_2 molecule, positive value indicates electrons transfer from WN surface to the absorption molecule, vice versa.



value in WN-111 forecasts the poor H2O activation ability in (111) surface. The oxidation process of H₂O to •OH requires the photocatalyst to facilitate the electron transfer from H₂O to the catalysts. Obviously, WN-110 shows most negative value and resultant best activation ability on H2O. Meanwhile, the total charge changes (Δq) of O₂ molecular in WN-100, WN-110 and WN-111 (Figure 5e-g) are determined as +0.61 e⁻, +0.91 e⁻, and +0.25 e⁻, respectively. By capturing electrons from the slab, the bonding length of O2 is prolonged (Table S3, Supporting Information), corresponding to catalytic activation of O2 molecular.^[21] Similarly, WN-110 also accounts for the best activation of O₂ ability as evidenced by highest total charge change and bonding length. From above results, we can conclude that the WN-110 slab presents the strongest electron transfer between O₂ (H₂O) molecular and WN, which is beneficial to the ROS generation and the subsequent surface catalytic reaction.

We then conduct photocatalytic degradation of MB in presence of ROS scavengers of EDTA-2Na and isopropanol (IPA) for quenching •OH and hole (h⁺), respectively. As the results shown in Figure 4i, the C_t/C_0 neither increases nor keeps steady when the ROS scavengers is added into the photocatalytic system, indicating the •OH and h⁺ have been generated and played important role during the photocatalytic process. Moreover, the ROS are directly probed by the DMPO and TEMP spin-trapping electron spin resonance (ESR) measurement. The typical 1:2:2:1 quadruple resonant peak (Figure 5d) and 1:1:1 triplex resonant peak (Figure 5h) in the range of 3480-3530 Gs could be evidently observed after 20 min NIR irradiation, demonstrating the formation of •OH and ¹O₂ under NIR excitation with WN NCs.^[4] To further understand the generation of ROS, we use the colorless nitrotetrazolium blue chloride (NBT) solution as model to evaluate the generation of superoxide.^[22] As shown in Figures S11 and S12 (Supporting Information), the concentration of NBT shows significant decrement within 2 h photocatalytic reaction and the NIR-driven photocatalytic NBT degradation rate could maintain about 7% after four cycle runs with no crystal phase transition and morphology changing on WN NCs (Figures S13 and S14, Supporting Information), indicating the excellent ROS generation and good stability of WN NCs as well.

The energy level matching between WN NCs mediated electron-hole pairs and redox potential of ROS generation $(O_2/\bullet O_2^-, OH^-/\bullet OH)$ is another important issue we should confirm. We believe that the ability of WN to reduce O_2 and oxidize H₂O for producing superoxide radical and hydroxyl radical simultaneously originates from the typical metallic like band structure. First, to further confirm the metallic property of the cubic WN NCs, we also test the electrical resistivity of WN NCs vis 4-terminal method. The resistivity of WN at room temperature (300 K) is about $2.5 \times 10^{-3} \Omega$ m, which is smaller than the previous reports, revealing the high electron conductivity and mobility in the WN nanoparticles as well. Then, the electronic structures of the as prepared WN NCs were characterized by UPS and XPS valance band spectra. The intercepts in the high (17–19 eV) and low (–5–3 eV) binding energy region are demined to be 17.61 and -0.65 eV. Accordingly, the work function of WN NCs can be calculated as 3.59 eV.

The sequential electronic state occupying across the Fermi level also indicates the metallic nature of WN (Figure 6a). The VB-XPS spectrum in Figure S15 (Supporting Information) shows two intense peaks in 0-4 and 4-12 eV, which are denoted to the CB and B_{.1} band, respectively. The measured work function and relative band position of CB and B.1 are quiet agreement with the DFT calculation results showed in Figure S2 (Supporting Information) (3.47 eV) and Figure 1c. Resultantly, the chemical potential of the $E_{\rm f}$ can be calculated as -0.91 eV (vs NHE), being lower than O_2/O_2^- of -0.046 eV. On the other hand, the chemical potential of B_{.1} band is about -4.2 eV relative to the Fermi level. So the B_{.1} band relative to NHE is about 3.33 eV, being higher than OH⁻/•OH of 1.99 eV. Consequently, •OH and $•O_2^-$ can be generated by NIR plasmonic excitation, which can further turn into other ROS, such as •HO₂ and ¹O₂. At this point, it can be confirmed that the LSPR-excited hot carriers (e^- and h^+) and ROS can be effectively generated under NIR light radiation, and WN-110 crystal facet gives the highest photocatalytic activity during surface chemical reaction (as the schematic diagram shown in Figure 6b) by combining all the theoretical and experimental results. The plausible mechanism (Figure 6c) and relevant chemical reactions related to the NIR-driven photocatalytic property of WN NCs can be summary as following:

$$WN + h\nu(NIR) \rightarrow WN^* + e^- + h^+$$
(1)

$$WN_{(110)}^* + O_2 + e^- \to WN_{(110)} + \bullet O_2^-$$
 (2)

$$WN_{(110)}^* + H_2O + h^+ \rightarrow WN_{(110)} + H_2O^+$$
 (3)

$$H_2O^+ \to H^+ + \bullet OH \tag{4}$$

$$\bullet O_2^- + H^+ + \to \bullet HO_2 \tag{5}$$

$$\bullet O_2^- + \bullet OH \to OH^- + {}^1O_2 \tag{6}$$

- (1) NIR light excites the collective LSPR effect in WN NCs and plenty of "hot electron-hole pairs" are generated by the plasmonic interband/intraband quasi-continuous transition (Equation 1).
- (2) The most reactive photocatalytic surface of WN 110 prefers to adsorb O_2 and H_2O molecular. Then, the activation of O_2 and H_2O molecular can be achieved by charge transfer between the molecular and WN (Equations 2 and 3).
- (3) The activated H_2O^+ turns into •OH on the WN 110 surface (Equation 4). The activated O_2 turns into $•O_2^-$, and subsequently reacts with H^+ to form $•HO_2$ on the WN surface (Equation 5). The $•O_2^-$ may further react with •OH to generate ${}^{1}O_2$ (Equation 6).
- (4) All the ROS generated by WN NCs participate in the NIRdriven photocatalytic reactions, including degradation of MB (or NBT), hydroxylation of TPA and de-esterification of H₂DCFDA.







Figure 6. NIR-driven photocatalytic mechanism investigation of WN NCs. a) UPS valance band spectra. b) Schematic diagram of the NIR-excited holes and electrons in WN NCs. c) Illustration of NIR-driven photocatalytic process.

3. Conclusion

In summary, we have confirmed that WN NCs can be utilized as NIR-driven photocatalyst through the combination of DFT calculation and many experimental evidences in this work. The full spectra absorption and good NIR photocurrent response originated from the LSPR effect of the metallic WN. The 3D FEA results demonstrated the size dependent and wavelength tuned plasmonic behavior as well. The DFT calculated facet dependent O_2 and H_2O molecular activation revealed that the most reactive catalytic facet was the (110) surface. The UPS results proved the metallic nature and the suitable chemical redox potential for generating ROS by WN NCs. Therefore, the successful direct NIR-driven photocatalytic degradation of MB, hydroxylation of TPA and de-esterification of H_2DCFDA were realized in this work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 51572056, 51572059 & 51602083), Heilongjiang Provincial Natural Science Foundation for Distinguished Young Scholar (Grant No. JC2017001), and Harbin Applied Technology Research and Development Project (2017RAXXJ003). W.H. extends his gratitude to Mr. Zhiqiang Yu, Mr. Xiaobin Hao, and Dr. Chengyue Sun for their strong support and enthusiastic help in 3D modeling and experimental implementation.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

DFT calculation, finite element analysis, nanocubes, NIR photocatalysts, tungsten nitride

Received: July 28, 2020 Revised: September 23, 2020 Published online:

- L. Zhou, D. F. Swearer, C. Zhang, H. Robatjazi, H. Zhao, L. Henderson, L. Dong, P. Christopher, E. A. Carter, P. Nordlander, N. J. Halas, *Science* 2018, *362*, 69.
- [2] a) K. Wenderich, G. Mul, Chem. Rev. 2016, 116, 14587; b) S. Shen, J. Chen, M. Wang, X. Sheng, X. Chen, X. Feng, S. S. Mao, Prog. Mater. Sci. 2018, 98, 299; c) L. Lin, Z. Yu, X. Wang, Angew. Chem., Int. Ed. 2019, 58, 6164.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [3] a) X. Wu, Y. Li, G. Zhang, H. Chen, J. Li, K. Wang, Y. Pan, Y. Zhao, Y. Sun, Y. Xie, J. Am. Chem. Soc. 2019, 141, 5267; b) Y. Sang, Z. Zhao, M. Zhao, P. Hao, Y. Leng, H. Liu, Adv. Mater. 2015, 27, 363; c) J. Li, X. Wu, W. Pan, G. Zhang, H. Chen, Angew. Chem., Int. Ed. 2018, 57, 491; d) J. Wu, Z. Zhang, B. Liu, Y. Fang, L. Wang, B. Dong, Sol. RRL 2018, 2, 1800039; e) Q. Zhang, X. Liu, L. Tan, Z. Cui, X. Yang, Z. Li, Y. Liang, S. Zhu, K. W. K. Yeung, X. Wang, Y. Zheng, S. Wu, Appl. Catal., B 2019, 258, 117980; f) W. Gao, B. Tian, W. Zhang, X. Zhang, Y. Wu, G. Lu, Appl. Catal., B 2019, 257, 117908; g) J. Li, J. Wang, G. Zhang, Y. Li, K. Wang, Appl. Catal., B 2018, 234, 167.
- [4] Y. Nosaka, A. Y. Nosaka, Chem. Rev. 2017, 117, 11302.
- [5] L. Wang, X. Xu, Q. Cheng, S. X. Dou, Y. Du, Small 2019, 1904107, https://doi.org/10.1002/smll.201904107.
- [6] a) B. Zhu, J. Zhang, C. Jiang, B. Cheng, J. Yu, Appl. Catal., B 2017, 207, 27; b) T. N. Ye, Y. Lu, J. Li, T. Nakao, H. Yang, T. Tada, M. Kitano, H. Hosono, J. Am. Chem. Soc. 2017, 139, 17089; c) T. Jaouen, B. Hildebrand, P. Aebi, G. Delhaye, S. Tricot, B. Lépine, G. Jézéquel, P. Schieffer, J. Phys. Chem. C 2017, 121, 4363; d) C. Peng, P. Wei, X. Li, Y. Liu, Y. Cao, H. Wang, H. Yu, F. Peng, L. Zhang, B. Zhang, K. Lv, Nano Energy 2018, 53, 97.
- [7] a) Y. Xu, J. Mo, G. Xie, D. Ding, S. Ding, X. Wang, C. Li, Chem. Commun. 2019, 55, 6862; b) Z. Hu, G. Liu, X. Chen, Z. Shen, J. C. Yu, Adv. Funct. Mater. 2016, 26, 4445; c) X. Li, L. Liang, Y. Sun, J. Xu, X. Jiao, X. Xu, H. Ju, Y. Pan, J. Zhu, Y. Xie, J. Am. Chem. Soc. 2019, 141, 423; d) W. Huang, H. Meng, Y. Gao, J. Wang, C. Yang, D. Liu, J. Liu, C. Guo, B. Yang, W. Cao, J. Mater. Chem. A 2019, 7, 18538; e) J. Ran, H. Wang, H. Jin, C. Ling, X. Zhang, H. Ju, L. Jing, J. Wang, R. Zheng, S. Qiao, J. Mater. Chem. A 2018, 6, 23278.
- [8] X. Zhang, X. Li, M. E. Reish, D. Zhang, N. Q. Su, Y. Gutierrez, F. Moreno, W. Yang, H. O. Everitt, J. Liu, *Nano Lett.* 2018, *18*, 1714.
- [9] H. Wang, E. J. Sandoz-Rosado, S. H. Tsang, J. Lin, M. Zhu, G. Mallick, Z. Liu, E. H. T. Teo, *Adv. Funct. Mater.* **2019**, *29*, 1902663.

- [10] Y. Wang, T. Nie, Y. Li, X. Wang, L. Zheng, A. Chen, X. Gong, H. Yang, Angew. Chem., Int. Ed. 2017, 56, 7430.
- [11] Y. Benhai, W. Chunlei, S. Xuanyu, S. Qiuju, C. Dong, J. Alloys Compd. 2009, 487, 556.
- [12] K. Balasubramanian, S. Khare, D. Gall, Phys. Rev. B 2016, 94, 174111.
- [13] M. Kavitha, G. Sudha Priyanga, R. Rajeswarapalanichamy, K. Iyakutti, J. Phys. Chem. Solids 2015, 77, 38.
- [14] a) X. Xu, C. Randorn, P. Efstathiou, J. T. S. Irvine, *Nat. Mater.* 2012, 11, 595; b) X. Jiao, K. Zheng, Z. Hu, Y. Sun, Y. Xie, *ACS Cent. Sci.* 2020, 6, 653; c) L. Liang, X. Li, J. Zhang, P. Ling, Y. Sun, C. Wang, Q. Zhang, Y. Pan, Q. Xu, J. Zhu, Y. Luo, Y. Xie, *Nano Energy* 2020, 69, 104421; d) S. Xu, S. Gong, H. Jiang, P. Shi, J. Fan, Q. Xu, Y. Min, *Appl. Catal., B* 2020, 267, 118661.
- [15] Z. Kou, T. Wang, H. Wu, L. Zheng, S. Mu, Z. Pan, Z. Lyu, W. Zang, S. J. Pennycook, J. Wang, *Small* **2019**, *15*, 1900248.
- [16] a) A. Habib, F. Florio, R. Sundararaman, J. Opt. 2018, 20, 064001;
 b) Y. P. Zhu, J. K. El-Demellawi, J. Yin, S. Lopatin, Y. Lei, Z. Liu, X. Miao, O. F. Mohammed, H. N. Alshareef, Adv. Mater. 2020, 32, 1908392.
- [17] X. Su, F. Xiao, Y. Li, J. Jian, Q. Sun, J. Wang, Mater. Lett. 2010, 64, 1232.
- [18] C. Zhang, S. Wang, Z. Chen, J. Fan, Z. Zhong, X. Zhang, Nanoscale 2019, 11, 2027.
- [19] H. Jin, H. Zhang, J. Chen, S. Mao, Z. Jiang, Y. Wang, J. Mater. Chem. A 2018, 6, 10967.
- [20] H. Liu, P. Chen, X. Yuan, Y. Zhang, H. Huang, L. Wang, F. Dong, *Chin. J. Catal.* **2019**, 40, 620.
- [21] X. Sun, X. Luo, X. Zhang, J. Xie, S. Jin, H. Wang, X. Zheng, X. Wu, Y. Xie, J. Am. Chem. Soc. 2019, 141, 3797.
- [22] a) N. Tian, H. Huang, Y. He, Y. Guo, T. Zhang, Y. Zhang, *Dalton Trans.* 2015, 44, 4297; b) Y. Zhao, Y. Wang, X. Liang, H. Shi, C. Wang, J. Fan, X. Hu, E. Liu, *Appl. Catal., B* 2019, 247, 57; c) J. Guo, Y. Liu, Y. Hao, Y. Li, X. Wang, R. Liu, F. Li, *Appl. Catal., B* 2018, 224, 841.