Isolated Iridium Sites on Potassium-Doped Carbon-nitride wrapped Tellurium Nanostructures for Enhanced Glycerol Photooxidation

Pawan Kumar, Abdelrahman Askar, Jiu Wang, Soumyabrata Roy, Srinivasu Kancharlapalli, Xiyang Wang, Varad Joshi, Hangtian Hu, Karthick Kannimuthu, Dhwanil Trivedi, Praveen Bollini, Yimin A. Wu, Pulickel M. Ajayan, Michael M. Adachi,* Jinguang Hu,* and Md Golam Kibria*

Many industrial processes such transesterification of fatty acid for biodiesel production, soap manufacturing and biosynthesis of ethanol generate glycerol as a major by-product that can be used to produce commodity chemicals. Photocatalytic transformation of glycerol is an enticing approach that can exclude the need of harsh oxidants and extraneous thermal energy. However, the product yield and selectivity remain poor due to low absorption and unsymmetrical site distribution on the catalyst surface. Herein, tellurium (Te) nanorods/nanosheets (TeNRs/NSs) wrapped potassium-doped carbon nitride (KCN) van der Waal (vdW) heterojunction (TeKCN) is designed to enhance charge separation and visible-NIR absorption. The iridium (Ir) single atom sites decoration on the TeKCN core-shell structure (TeKCNIr) promotes selective oxidation of glycerol to glyceraldehyde with a conversion of 45.6% and selectivity of 61.6% under AM1.5G irradiation. The catalytic selectivity can reach up to 88% under 450 nm monochromatic light. X-ray absorption spectroscopy (XAS) demonstrates the presence of undercoordinated IrN₂O₂ sites which improved catalytic selectivity for glycol oxidation. Band energies and computational calculations reveal faile charge transfer in the TeKCNIr heterostructure. EPR and scavenger tests discern that superoxide $(O_2^{\bullet-})$ and hydroxyl (•OH) radicals are prime components driving glycerol oxidation.

1. Introduction

To tackle the challenges of rising petroleum prices and CO2 concentration, governments around the globe are enacting "biofuel blending mandates" which necessitated the addition of 2-10% biofuel in petroleum fuel.^[1] Biodiesel production from the transesterification of fatty acid occupies a market size worth USD 32.09 billion and is expected to grow at the rate of 10.0% from 2022 to 2030.^[2] For each 10 Kg biodiesel production from the transesterification process, 1 Kg glycerol is produced as a major by-product which has limited utility in the cosmetic, food, tobacco and pharmaceutical industries.[3] Utilizing the carbon content of glycerol to upgrade to value-added chemicals is a valuable complement. Many chemocatalytic processes such as hydrogenolysis (1,2 propanediol, ethylene glycol), dehydration (acrolein, acetol), oxidation (dihydroxyacetone; DHA, glyceric acid, hydroxypyruvic acid, formic acid),

P. Kumar, J. Wang, H. Hu, K. Kannimuthu, D. Trivedi, J. Hu, M. G. Kibria Department of Chemical and Petroleum Engineering University of Calgary

2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada E-mail: jinguang.hu@ucalgary.ca; md.kibria@ucalgary.ca

A. Askar, M. M. Adachi School of Engineering Science Simon Fraser University Burnaby, BC V5A 1S6, Canada E-mail: mmadachi@sfu.ca

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202313793

© 2024 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/adfm.202313793

S. Roy, P. M. Ajayan Department of Materials Science and Nanoengineering **Rice University** Houston, TX 77005, USA S. Kancharlapalli Theoretical Chemistry Section **Chemistry Division** Bhabha Atomic Research Centre Trombay, Mumbai 400085, India S. Kancharlapalli Homi Bhabha National Institute Anushaktinagar, Mumbai 400094, India X. Wang, Y. A. Wu Department of Mechanical and Mechatronics Engineering Waterloo Institute for Nanotechnology Materials Interface Foundry University of Waterloo Waterloo, Ontario N2L 3G1, Canada

FUNCTIONAL MATERIALS www.afm-journal.de



amination (alanine) etc have been investigated to upgrade the glycerol.^[4] Among them, catalytic oxidation of glycerol is more conducive to scale-up due to the requirement of a simple oxidation process. Photocatalytic oxidation of glycerol can proceed in benign conditions and exclude the requirement of harsh chemicals and extraneous temperature.^[5] However, the oxidation of glycerol is a complex reaction pathway and can accumulate several oxidation products in the reaction mixture which reduces economic value and adds purification cost. Therefore, developing photocatalysts with improved chemoselectivity is essential to make the process profitable. 2D graphitic carbon nitride (CN; g- C_3N_4) with an N-linked heptazine (C_6N_7) network has emerged as a material of choice due to its desirable photophysical properties, chemoselectivity and tunable optical band gap.^[6] The optical absorption of CN can be further red-shifted to a longer wavelength region by cyanamide (N-C = N; CN_2) functionalization and alkali metal doping.^[7] Lotsch et al. demonstrated that post-annealing of melon with KSCN affords CN₂ functionalized carbon nitride which can significantly boost the hydrogen evolution.^[8] Later Yu et al. demonstrated that the presence of alkali (KOH) during thermal annealing cleaves C₆N₇ and introduces CN₂ nitrogen defect which downshifts the LUMO position to improve the visible light-driven hydrogen evolution.^[9] Despite the improved absorption, the catalytic performance of CN remains poor due to the severe charge recombination. Furthermore, due to the less positive valence band (VB) position of CN (+1.6 eV vs NHE), the hole migration in CN remains poor which compromises its oxidizing power.^[10] Fabrication of heterojunction between modified carbon nitride with low bandgap semiconductors has been envisioned to improve the charge separation kinetics. Recently discovered 2D tellurene (Te) possesses a low band gap (0.92 eV for monolayer; 0.33 eV for bulk) and p-type nature with a hole mobility of \approx 700 cm² V⁻¹ s⁻¹ (3 times higher than black phosphorous; black P) is an ideal candidate to make heterojunction with poor oxidizing n-type semiconductors.^[11] Qiu et al. designed a heterojunction between CdS and Te which can afford a better charge separation resulting in efficient oxidation of lactic acid to hydrogen.^[12] CN can form vdW heterojunction with Te which excludes the requirement of epitaxial matching and minimizes the carrier loss at semiconductor interfaces.^[13] The surface oxidation of Te also forms native tellurium dioxide (TeO₂₎ (2.29 eV) with high theoretical electron (1000 cm² V⁻¹ s⁻¹) and hole (9100 cm² V^{-1} s⁻¹) mobility which can further reinforce charge separation.^[14]

In addition to improved visible absorption and charge separation, the product selectivity is largely governed by the nature of catalytic centers. In bulk materials, the unsymmetrical exposed facets and multiple binding sites lead to non-selective reactions. Atomic scale distribution in single atom catalysts (SACs) can minimize non-uniform active sites while an undersaturated coordination site increases the rate of reaction.^[15] Due to their high stability and requirement of a diluted concentration SACs can

V. Joshi, P. Bollini

William A. Brookshire Department of Chemical and Biomolecular Engineering University of Houston Houston, TX 77204, USA significantly reduce the operation cost. Various SACs decorated on inorganic crystalline scaffolds have been used for selective photocatalytic glycerol conversion.^[16] Xiong et al. showed that Ni single atom grafted TiO₂ (Ni/TiO₂) can achieve a 60% selectivity for glycerol to glyceraldehyde conversion.^[17] However, the presence of nonuniform facets, vacancies and tedious synthetic process with a low single atom (SA) site population limits catalytic activity/selectivity of inorganic support grafted SACs.^[18] On the other hand, CN-based supports provide uniform C₆N₇ cavities and structural flexibility to accommodate the isolated sites effectivity for improved catalytic performance of the SACs.^[19] Careful selection of the SA site is also crucial to get the desired catalytic effect. Chen et al. demonstrated that low-coordinate IrO₂ nanoparticles (NPs) decorated on CN can significantly increase the oxygen evolution reaction.^[20]

Motivated by these findings, herein, we design K-doped/CN₂ functionalized CN (KCN) and Te-nanostructures based heterojunction followed by decoration of IrN_2O_2 isolated sites (TeKC-NIr) for glycerol oxidation. The TeKCNIr catalyst demonstrated superior H₂ evolution performance and glycerol oxidation to glyceraldehyde. After 24 h reaction under AM1.5G irradiation, TeKC-NIr demonstrated a glycerol conversion of 45.6% with a catalytic selectivity of 61.6%. Under optimized conditions and 450 nm visible light irradiation, an astonishing 88.6% selectivity for the glyceraldehyde was achieved. The well-distributed IrN_2O_2 catalytic sites as revealed by XAS were attributed to drive selective catalytic oxidation of glycerol.

2. Results and Discussions

2.1. Synthesis and Characterization

The synthesis of various catalytic components is depicted in Figure 1a and Figures S1,S2 (Supporting Information). The potassium-doped CN₂-functionalized carbon nitride (KCN) was synthesized by thermal annealing of dicyandiamide and potassium thiocyanate at 550 °C for 2 h (Figure 1a and section 2.1 in Supporting Information).^[21] While the mixture of elemental 1D Te nanorods (NRs) and 2D Te nanosheets (NSs) was prepared by the hydrothermal reduction of sodium tellurite (Na₂TeO₃) using hydrazine (NH₂NH₂) in the presence of polyvinylpyrrolidone (PVP) as a crystal face-blocking ligand (section 2.2 in SI).^[11b] The KCN-wrapped Te NRs/NSs (TeKCN) vdW nanostructures were prepared by taking advantage of electrostatic interaction between negatively charged KCN and positively charged PVP functionalized Te NRs/TeNSs (Figure 1b and section 2.3 in Supporting Information). Three samples containing 5, 10, and 15wt% Te (denoted as TeKCN5, TeKCN10 and TeKCN15) were prepared to evaluate the catalytic performance. Since TeKCN10 demonstrated the highest photocatalytic performance, it was used for single atom decoration and TeKCN will be generally referred to as TeKCN10 catalyst. The Ir single atom sites were deposited on TeKCN catalysts by hydrolysis decomposition of IrCl₃.xH₂O using a very diluted aqueous solution (Figure 1c and section 2.4 in Supporting Information).^[22] For comparison, IrSA pinned KCN (KCNIr) and CN (CNIr) were also synthesized (Figure S1a,b, sections 2.5 and 2.6 in Supporting Information). A control sample (TeKCNIrP) by mixing Te NRs/NSs and KCN in DMF solvent followed by the immediate addition of IrCl₃.xH₂O was also prepared





Figure 1. a) Synthesis scheme of K doped and CN₂-functionalized carbon nitride (KCN) b) Te NRs/NSs wrapping with KCN c) Decoration of Ir single atoms on TeKCN to fabricate TeKCNIr.

(Figure S1c, section 2.7 in Supporting Information). Pristine CN was prepared by polymerization condensation of dicyandiamide (Figure S2, section 2.8 in Supporting Information).^[23]

The fine chemical attributes of materials were determined using high-resolution transmission electron microscopy (HR-TEM) (Figure 2; Figures S3-S14, Supporting Information). The TEM image of CN displayed graphenic 2D sheets with an amorphous structure (Figure S3, Supporting Information). KCN also displayed a similar 2D structure, however, it showed slightly increased crystallinity as evident from the FFT and SAED pattern (Figure S4a-d, Supporting Information). The EDX elemental mapping of KCN displayed the presence of ample K distributed uniformly in the material (Figure S4e-k, Supporting Information). TEM images of TeNRs/KCN show a wrapped 1D nanorod structure with a dense Te core and light KCN shell (Figure S5a-c, Supporting Information). The thickness of the core was measured to be \approx 420 nm while the KCN shell was \approx 5–10 nm (Figure S5c, Supporting Information). Elemental mapping of TeKCN displayed a significant contribution of O signal in elemental mapping due to surface oxidation of Te into TeO₂ which was also confirmed from X-ray photoelectron spectroscopy (XPS) analysis (Figure S5e-l, Supporting Information). Furthermore, strong K and N signals overlapping with Te, and O signals verify the uniform coating of KCN in the materials (Figure S5e-l, Supporting Information). The images of TeKCN at high magnification show a continuous lattice fringe of 2.5 Å spacing as evident from FFT and iFFT suggesting a monocrystalline core embedded in the KCN structure (Figure S6, Supporting Information).

TeNSs/KCN also displayed a similar pattern with the uniform wrapping of KCN all over the surface (Figure S7, Supporting Information). After the decoration of Ir SA sites in TeKCNIr, the dark Te core and KCN shell morphology of TeKCN remains unchanged (Figure 2a,b). The 5–10 nm thick KCN shell was mostly amorphous, and observance of some lattice fringes was due to the stacking of CN sheets (Figure 2c,d) TeKCNIr composed of TeNSs showed flat Te sheets with the comparatively thin wrapping of KCN (Figure 2e,f). The filtering of different d-spacing signals using iFFT reveals the presence of three planes in the materials with a d-spacing of 1.9, 2.6 and 4.0 Å (Figure 2g).^[24] The selected area electron diffraction (SAED) shows a reciprocal plane and represents preserved Te crystallinity.^[25] The EDX elemental mapping displayed a uniform distribution of Te, O, K, C and N suggesting uniform wrapping, however, Ir was not visible due to lower concentration (Figure 2i-t). Electron energy loss spectra (EELS) of TeKCNIr exhibited energy loss peaks for C K-edge, N K-edge, O K-edge and Te M-edge. However, the energy loss peak for Ir cannot be detected due to the diluted concentration of Ir (Figure S8, Supporting Information). TEM image of KCN with IrSA sites (KCNIr) displayed graphenic sheets with a lattice spacing of 3.3 Å due to improved crystallinity while no Ir/Ir-oxide related features were observed suggesting the atomic distribution of Ir sites (Figure S9, Supporting Information). The AC-HAADF-STEM image clearly showed the presence of dense Ir sites pinned on sparse CN sites (Figure S10, Supporting Information). Control TeKCNIrP catalysts showed spherical Te nanoparticles embedded in KCN sheets due to the breakdown of Te nanostructures www.advancedsciencenews.com

CIENCE NEWS



Figure 2. HR-TEM images of TeKCNIr NRs a) at 100 nm scale bar showing dense Te-core or thin KCN shell. b) at 20 nm scale bar c,d) at 5 nm scale bar showing the presence of dense core and sparse amorphous KCN shell. HR-TEM images of TeKCNIr nanosheets e) at 0.2 μm scale f) at 5 nm scale showing dominant Te single crystal lattice and amorphous KCN at the edge. Inset showing FFT of image and g) enlarged part of image f showing overlapped iFFT and corresponding interplanar distance. h) SAED pattern of TeKCNIr showing periodic bright spots for monocrystalline Te. EDX elemental mapping of i–n) TeKCNIr NRs for K, Te, N, C, O and o–t) TeKCNIr NSs HAADF, Te, O, N, K, and Te/K composite.

(TeNRs/NSs) using high polarity DMF (Figure S11, Supporting Information).^[11b] However, the atomic distribution of the Ir sites were clearly visible in the AC-HAADF-STEM images (Figure S12, Supporting Information).

As expected, the diffuse reflectance UV-vis spectra of elemental Te show strong absorption in visible and near infra-red (NIR) regions extended up to 1000 nm due to an ultrasmall band gap (0.3 for bulk materials) (**Figure 3a**).^[12,26] CN displayed an intense band with band tailing extended up to 450 nm due to direct bandto-band transition from VB to CB (Figure 3a).^[27] On the other hand, the KCN displayed increased visible absorption due to K doping and extended conjugation mediated by CN₂ functional groups.^[28] It should be noted that KCN displayed improved NIR absorption as well due to the increased electron density of carbon nitride, in line with previous reports on alkali metal-doped carbon nitride.^[29] While the KCN-wrapped TeKCN shows intermediate absorption due to combinational UV–vis absorption of Te and KCN components.^[30] The IrSA decorated TeKCNIr catalysts do not show any significant change due to the less populated concentration of IrSA sites. The FTIR spectra of KCN and KCN-containing composites demonstrated the presence of CN_2 functional groups (2166 cm⁻¹) along with heptazine ring stretch and bending vibrations (Figure S13a, Supporting Information).^[9] Raman spectra of KCN show a signature band $\approx 1609 \text{ cm}^{-1}$ due to a combination of D and G bands originating from in-plane and out-of-plane vibration of sp² hybridized C-N functionalities (Figure S13b, Supporting Information).^[31] Elemental Te NRs/NSs show an intense band at 123 cm⁻¹ for A₁ mode along with a small

www.afm-journal.de



www.afm-journal.de



Figure 3. a) DR-UV-vis spectra, b) synchrotron-based WAXS spectra, inset 2D WAXS map of TeCNIr c) PL spectra at an excitation wavelength of 370 nm. Excitation-Emission Matrix Spectroscopy (EEMS) map of d) CN, e) KCN, f) Te and g) TeKCN showing C K, N K, K L, and Te L edges. NEXAFS spectra of materials in h) C K-edge i) N K-edge j) Te L-edge region. Color: CN (black), KCN (violet), KCNIr (green), Te (yellow), TeKCN (blue), TeKCNIr (red).

contribution of the E_2 band which remains preserved after wrapping KCN.^[32] Additional peaks at 354, 545, 985, and 1158 cm⁻¹ were also observed for TeKCN deciphering the presence of the TeO₂ phase in the materials.^[33] In contrast to CN, the XRD pattern of KCN shows intense peaks at 28.4°, 40.5°, 50.1°, 58.7°, 66.5°, and 74.1° for residual KSCN salt suggesting not all KSCN was decomposed during the annealing process (Figure S13c, Supporting Information).^[34] After integration of Te and Ir SA sites the XRD clearly demonstrates the presence of Te and TeO₂ peaks in the TeKCNIr catalyst (Figure S13d, Supporting Information).^[35] The presence of TeO₂ peak suggest surface oxi-

dation of Te nanostructures during synthesis steps. Synchrotronbased wide-angle X-ray scattering (WAXS) 2D map and azimuthally integrated intensity versus q plot of CN and KCNIr show an intense scattering ring originated from (002) plane with a small contribution of (100), (006), and (004) planes (Figure S14a,b, Supporting Information).^[36] After hybridization of Te with KCN (TeKCN) and Ir SA, a small diffraction ring and pattern were observed at 2.64 and 2.78 Å⁻¹ Q values suggesting integration of Te in composites (Figure 3b and Figure S14c).^[37] No peak associated with nanometric or sub-nanometric Ir-related species was observed substantiating the presence of Ir sites in atomic state. The charge carrier dynamics and emissive quenching in CN-based materials were determined using steady-state photoluminescence (ssPL) spectroscopy (Figure 3c). As expected, PL spectra of CN displayed an intense broad band centered at 463 nm due to direct band-to-band emission quenching of charge carriers in the 2D heptazine motif.^[38] A significant quenching was observed for KCN which was associated with better charge separation between alkali metal ion and CN framework.^[39] The addition of Te NRs/NSs was found to further reduce PL intensity substantiating efficient charge transfer between Te and KCN. Interestingly, PL emission of TeKCNIr was almost completly quenched which corroborates an effective charge quenching by Ir atomic sites.

XPS survey scan spectra of CN, KCN and TeKCNIr depicted the presence of all core and sub-core-level peaks corresponding to constituting elements (Figures S15,S16, Supporting Information) The C1s HR-XPS of KCN show characteristics peak for sp^2 hybridized C-(N)₃ and N = C-N carbons for N-linked heptazine network as present in CN framework (Figures \$16,\$17, Supporting Information).^[40] Additionally, a doublet for K2p_{3/2} and K2p_{1/2} components for doped K was also evidently visible.^[41] The N1s spectra of CN and KCN remain almost similar with a slight increase in the intensity of π - π * transition suggesting improved conjugation in CN₂ functionalized and K-doped carbon nitride.^[42] Apart from the uncondensed/residual N = C-Oand C = O peaks in O1s spectra, additional peaks at relatively higher binding energies were associated with residual S-O incorporated from KSCN.^[43] KCNIr with Ir also demonstrated a similar XPS pattern and no detectable signals for Ir were identified due to low atomic concentrations (Figure S18, Supporting Information). The KCN-wrapped Te NRs/NSs (TeKCN) do not show any change in C1s, N1s, and O1s spectra except for additional peaks for surface adsorbed Te-OH functionalities (Figure S19, Supporting Information). The XPS in Te3d region displayed two peak components corresponding to $\text{Te3d}_{5/2}$ and $\text{Te3d}_{3/2}$ peaks at BE \approx 575.9 and 586.4 eV respectively suggesting the presence of Te in the elemental (Te⁰) state.^[44] Conversely, TeKCNIr showed intense Te3d $_{5/2}$ and Te3d $_{3/2}$ signals for the TeO $_2$ chemical state at a relatively higher BE value.^[45] The fact is that IrSA site decoration was performed in the aqueous state which led to the surface oxidation of Te NRs/NSs making Te/TeO₂ core-shell structure. The N1s XPS spectra of TeKCNIr were drastically changed due to the contribution of N atoms from pyrrolidone capping agents on the surface of TeNRs/NSs. Additionally, the Ir4f peaks (4f7/2 and $4f_{5/2}$) were also observed at BE values of 63.9 and 68.5 eV corroborating the presence of Ir sites on the surface of TeKC-NIr catalysts.^[46] TeKCNIrP prepared by using DMF as solvent demonstrates intense TeO₂ peak components because of a high degree of oxidation as DMF removes surface capping agents from Te NRs/NSs.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy using synchrotron-based soft X-ray was performed to further investigate the chemical and structural changes in the materials. Excitation-Emission Matrix Spectroscopy (EEMS) in the energy range of 250 to 2000 eV to identify the constitutional elemental edge demonstrates the presence of C K-edge, N K-edge for CN while KCN displayed an additional K L-edge (Figure 3d,e) due to K doping. Pristine Te NRs/NSs show a very faint Te Medge due to less populated transitions (Figure 3f). The presence of an intense peak for C K-edge suggests dense PVP capping ligands. The C K-edge NEXAFS spectra of CN and KCN revealed strong π^* resonance peaks at 284.4 eV for N = C-N carbons with a small $\pi^*_{C=C}$ contribution from adventitious carbons at 281.8 eV (Figure 3h).^[47] The σ^* region of the C K-edge showed a broad band originating from $\sigma^*_{N-C=N}$ and σ^*_{C-N} excitation.^[48] No distinguishable change in C K-edge spectra was observed after the integration of Te NRs/NSs. The N K-edge NEXAFS spectra of CN exhibited displayed two π^* resonance peaks at 399.2 and 402.1 eV arising from $\pi^*_{C-N=C}$ and π^*_{N-C3} transition of tertiary N-bridged C₆N₇ network (Figure 3i).^[49] A broad band with faint peaks due to σ^* transition of sp² hybridized C-N and C-N = C moieties was also observed substantiating a well-constituted CN framework.^[50] Distinctly, KCN displayed an intense peak at 399.4 eV due to π^* transition of cyanamide (CN₂) and uncondensed N = C-O functionalities. Interestingly, these transitions disappeared in TeKCNIr catalysts which might be due to suppressed π^* transition in NCN/N = C-O interacted Te nanostructures. Pristine Te NRs/NSs displayed a broad absorption band assigned to Te M-edge in the energy range of 577.4-583.8 eV (Figure 3j).^[51] This band was still visible in the TeKCN composite however, the intensity was significantly reduced to a small concentration of Te in the composite.

To validate the presence of isolated Ir sites on the TeKCN structure, AC-HAADF-STEM images of TeKCNIr were collected which displayed bright spots for Ir species in the CN scaffold. Most of the high Z-contrast Ir sites represented the presence of an isolated atomic state, however, small regions with Ir aggregates were also present in the material (Figure 4a-c). The presence of Ir nanoclusters in AC-HAADF-STEM might be due to minor agglomeration during the synthesis stage or exposure/damage of samples to an electron beam (200 keV).^[52] Electron energy loss spectroscopy (EELS) elemental mapping of TeKCNIr displayed intense Te L-edge and O K-edge signals centered on the TeNRs structure (Figure 4d). The presence of intense O K-edge signals centered on Te nanorods demonstrated partial surface oxidation and the presence of Te/TeO2 nanostructure. While C K-edge, N Kedge and K L-edge signals were distributed around the Te/TeO₂ suggesting successful wrapping of KCN (Figure 4d). The presence of KCN-wrapped structures was clearer in Te, K, C, and N composite images. No signals corresponding to Ir were identified due to dilute concentration.

The chemical and coordination structure of Ir species present in the TeKCNIr catalyst was determined using X-ray absorption near-edge structure (XANES) spectroscopy collected using synchrotron-based hard X-ray radiation. The Ir L_3 XANES spectra of TeKCNIr exhibited a sharp rising edge at 11 208 eV originating from the $2p \rightarrow 5d$ ($t_{2g}^{5} \rightarrow e_{g}^{0}$) transition (Figure 4e).^[53] The position of this edge was at higher energy than Ir foil and IrCl₃ (Ir³⁺) and coincided with the IrO₂ edge suggesting the presence of Ir sites as IrO₂ (d56s⁰ state).^[54] Furthermore, the white line intensity of TeKCNIr was significantly increased suggesting reduced electronic density on the Ir site due to partial charge transfer to N atoms in the carbon nitride cavity.^[55] Contrarily, CNIr does not show a significant enhancement in white line intensity suggesting that KCN can more efficiently coordinate with the Ir site.

To evaluate the coordination state and electronic environments Fourier-transformed extended X-ray absorption fine structure





Figure 4. AC-HAADF-STEM images of TeKCNIr at a) 5 nm scale bar showing bright spots for IrSA sites b) Enlarged area of the image a showing IrSA sites distributed in CN matrix. c) at 5 nm scale showing another region with uniform Ir single atom distribution. d) EELS ADF image showing scanned area and EELS elemental mapping for Te, O, N, K, C, RGB composite of Te (red), C (green), K (blue), RGB composite of Te (red), K (green), and N (blue). e) Ir L₃-edge XANES spectra of Ir foil, CNIrSA, IrCl₃, IrO₂, TEKCNIrP and TEKCNIr. f) FT-EXAFS spectra and fitting for Ir foil, IrO₂, CNIr and TEKCNIr. WT EXAFS map of g) Ir foil h) IrO₂ i) CNIr j) TEKCNIr.

(FT-EXAFS) spectra of materials were acquired in Ir L_{III}-edge region (Figure 3f; Figure S22, Supporting Information) The FT-EXAFS spectra of metallic Ir foil displayed a sharp feature at 2.57 Å due to Ir-Ir scattering with another scattering at higher value from distant atoms scattering (Figure 3f).^[56] For IrO₂ powder the first shell Ir-O scattering was observed at 1.62 Å while the second shell Ir-O-Ir interaction was observed at R(Å) value \approx 3.45 Å.^[57] On the other hand, CNIr and TeKCNIr exhibited only one peak at 1.44 and 1.53 Å, respectively attributed to the Ir-O/Ir-N scattering.^[20] Very weak scattering for Ir-Ir or Ir-O-Ir deciphering most of the Ir was present in an isolated state and contribution of agglomerates Ir sites was negligible. To further gain insight into coordination and bonding patterns EXAFS data fitting was executed and obtained values were compared with DFT simulated

models (Tables S1,S2 and Figure S23, Supporting Information). The EXAFS data fitting exhibited the Ir—O bond length of 1.80 and 1.84 Å for CNIrSA and TeKCNIr while Ir-N bond lengths were calculated to be 2.05 and 2.11 Å, respectively. The obtained values closely matched with the DFT constructed model of CNIr and KCNIr and suggested Ir sites were mainly located on KCN surface (Figure S23 and Table S2, Supporting Information). The obtained values were relatively smaller than Ir-Ir (2.71 Å) and Ir-O (1.99 Å) bond lengths in Ir foil and IrO₂ nanoparticles suggesting Ir was distinctly coordinated with N and O atoms. The Ir-O and Ir-N coordination number (C.N.) of TeKCNIr was calculated to be 1.92 and 1.73 suggesting IrN₂O₂ (C.N.–3.65) sites were entirely different than IrO₂ NPs (C.N.–6) and Ir metal (C.N.–12). CNIr demonstrates Ir-N and Ir-O C.N. of 1.97 and 1.83 with a



Figure 5. a) TRPL spectra of CN and TeKCNIr b) Photocurrent density versus time (*J*-*t*) plot during the light on-off cycle c) Photocatalytic H₂ evolution in the presence/absence of TEOA using CN, CNIr, KCN, TeKCN, TeKCNIr after 24 h d) Photocatalytic glycerol conversion and e) glyceraldehyde yield and f) glyceraldehyde selectivity as a function of time under AM1.5G irradiation using Te, TeKCN5, TeKCN10, TeKCN15, CNIr, CN, and TeKCNIr.

total C.N. value of 3.80 which was slightly higher than TeKC-NIr (3.65) indicating an undercoordinated state of IrN_2O_2 sites in TeKCNIrSA. These undercoordinated IrN_2O_2 sites can interact strongly with the adsorbate molecule for accelerated reaction. TeCNIrP catalysts also demonstrate similar features as TeKCNIr except the presence of a small amount of Ir-Ir scattering which suggests DMF promotes agglomeration of Ir sites.

Wavelet transform (WT) EXAFS spectra of Ir foil, IrO₂, CNIr and TeKCNIr were also plotted to understand the electronic structure of Ir species (Figure 4g–j). The WT-EXFAS spectra of Ir foil showed a bright zone at K = 12.90 Å⁻¹ and R = 2.54 Å originating from Ir-Ir scattering while a faint zone at K = 14.17 Å⁻¹ and R = 5.02 Å occurs from scattering from Ir atoms in second coordination shell (Figure 4g).^[58] For IrO₂, scattering from Ir-O first shell coordination gives a broad contour zone at K = 8.19 Å⁻¹ and R = 1.64 Å while Ir-O-Ir second shell scattering was observed at K = 13.59 Å⁻¹ and R = 3.46 Å (Figure 4h).^[59] CNIr displayed a sharp zone at K = 5.38 Å⁻¹ and R = 1.60 Å while K = 5.38 Å⁻¹ and R = 1.61 Å assigned to Ir-N/Ir = O first shell scattering.^[60] The obtained R-space values for CNIr and TeKCNIr were close to

 IrO_2 while K space values were significantly different suggesting IrO_2 entities have distinct electronic environments due to the coordination with N atoms in the C_6N_7 cavity. Further, the absence of any scattering zone at a higher R space value suggests that Ir sites were atomically isolated.

2.2. Photophysical and Photoelectrochemical Performance

The charge recombination dynamics and lifetime of photogenerated charge carriers were determined using time-resolved photoluminescence (TRPL) spectroscopy using a 370 nm excitation pulsed laser (**Figure 5**a and Table S3, Supporting Information). The PL lifetime decay curve of CN and TeKCNIr was best fitted tri-exponentially which agreed well with reported literature on CN-based materials.^[61] The spectra were fitted using the following equations.

$$I(t) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} + A_3 e^{-t/\tau 3}$$
(1)

where, A_1 , A_2 and A_3 represent the normalized amplitudes contribution of decaying components while τ_1 , τ_2 and τ_3 are individual lifetime of each component, respectively. The calculated lifetime value and fractional contributions of decay components are summarized in Table S3 (Supporting Information). The Nlinked C₆N₇ moieties in CN scaffolds contain sp³ and sp² hybridized C-N resulting in the formation of σ and σ^* molecular orbital (MO) and π and π^* MO. Furthermore, the lone pairs on secondary nitrogen (:N-C₂) can also participate in conjugation forming hybrid π +LP bonding and antibonding orbitals. The extended π +LP conjugated network results in the formation of conduction and valence bonds with low bandgap.^[38,61a] The direct band-to-band recombination of $(\sigma^* \rightarrow \sigma \text{ and } \pi^* \rightarrow (LP + \pi))$ photogenerated carriers give rise to the first two shorter lifetime values. The third lifetime with a relatively longer recombination time originated from the $\sigma^* \rightarrow \pi^*$ non-radiative intersystem crossing (ISC) and subsequent $\pi^* \rightarrow (LP + \pi)$ radiative recombination.^[62] The presence of defect states and shallow traps due to uncondensed units also contributes to the third lifetime of carbon nitride.^[63] Interestingly, the TeKCNIr heterostructure demonstrated decreased lifetime for all three components attributed to decreased radiative recombination processes. The decreased lifetime might be due to the presence of sub-energy level defects and interfacial charge transfer.^[64] Additionally, the average lifetime (τ_{avo}) which represents overall recombination was calculated using the following equation.

$$\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$$
(2)

The average lifetime for CN was calculated to be 8.47 ns while the value of cumulative lifetime for TeKCNIr was found to be 7.04 ns. The decreased lifetime suggests decreased radiative recombination processes and indicates better charge transfer in IrSA decorated heterostructure.

To discern the enhanced visible-light-induced charge generation, the photoelectrochemical (PEC) performance was evaluated for the TeKCNIr (Figure 5b and section 3.0 in Supporting Information). The PEC experiments were carried out in a threeelectrode set-up using fluorine-doped tin oxide (FTO) as a conductive substrate followed by deposition of catalysts and used as a photoanode. While Ag/AgCl and Pt were used as reference and counter electrodes. The photocurrent density of the materials with respect to time (J-t curve) was measured at 0.6 V versus Ag/AgCl (1.23 V vs RHE (reversible hydrogen electrode); water oxidation potential) (Figure 5b). The photoanode was irradiated under AM1.5G solar irradiation (100 mW cm⁻²) and light On-Off cycles were performed to validate the true origin of photocurrent from water splitting. Evidently, K doping in the CN lattice and CN₂ functionalization improved the photocatalytic charge generation in the materials reaching a current density of 0.14 mA cm^{-2} compared to pristine CN (0.10 mA cm^{-2}). After the hybridization of KCN with Te nanostructures, TeKCN displayed further improvement in photocurrent density (0.20 mA cm⁻²) deciphering better charge generation and separation in the materials. When TeKCNIr with isolated Ir SA sites was used as a catalyst, the maximum current density of 0.24 mA cm⁻² was achieved which was attributed to efficient charge capture by charge-deficient Ir species. The electrochemical impedance spectroscopy (EIS) Nyquist plot demonstrates a smaller semicircle arc

for TeKCNIr compared to pristine KCN and CN suggesting lower charge transfer resistance (Figure S24, Supporting Information). The Randle circuit obtained by fitting of EIS curve demonstrates decreased charge transport resistance in TeKCNIr (9.57 Ω) compared to pristine CN (11.81 Ω) deciphering better migration of charge carrier in developed heterostructure (Table S4, Supporting Information). Furthermore, the catalytic performance of materials toward hydrogen evolution without and with triethanolamine (TEOA) as a sacrificial donor was also tested to confirm improved charge separation and catalytic performance (Figure 5c). Pristine CN displayed negligible (7.5 μ mol g⁻¹cat) H₂ evolution for pure water splitting after 24 h irradiation with only slight improvement (14.0 µmol g⁻¹cat) in the presence of a TEOA sacrificial donor. In contrast, CNIr exhibited improved performance in the presence of TEOA reaching a total H₂ evolution of 27.7 and 132.4 µmol g⁻¹ cat without and with sacrificial donor, respectively. In contrast, KCN itself displayed a higher H₂ evolution rate reaching a maximum yield of 90 and 361 µmol g⁻¹cat without and with TEOA. Despite a higher photocurrent density, TeKCN was unable to further boost the H₂ evolution rate (19.5 and 339.9 μ mol g⁻¹cat without and with TEOA) which could be due to the lack of plenty of active sites on Te/KCN interface. Interestingly, TeKCNIr heterostructure with Ir atomic sites show a significant improvement in H₂ evolution rate 373.2 and 1595.3 µmol g⁻¹cat with and without TEOA which was \approx 50 and 114 times higher than that of CN.

2.3. Photocatalytic Conversion of Glycerol to Glyceraldehyde

Encouraged by these results, we have explored the scope of TeKC-NIr for the selective oxidation of glycol to glyceraldehyde in aqueous and photocatalytic conditions (section 4.2 in Supporting Information). The product was analyzed by HPLC and ¹H NMR which clearly showed that TeKCNIr promotes facile conversion of glycerol to glyceraldehyde (Figures S25-27, Supporting Information). Time-dependent glycerol conversion demonstrated that pure Te NRs/NSs were almost inactive for the glycerol conversion while CN exhibited sluggish performance with a maximum conversion rate of 9.7% after 24 h under AM1.5G irradiation (Figure 5d). The glyceraldehyde yield using CN as a photocatalyst was found to be 3.2% after 24 h (Figure 5e). CNIr with a decoration of isolated IrN₂O₂ site improved the glycerol conversion (17.9%) and glyceraldehyde yield (10.2%) which undeniably depicts isolated Ir site increased the charge carrier separation and glycerol conversion. Interestingly, TeKCN5 containing KCN and 5% TeNRs/NSs demonstrated a significant improvement in glycerol conversion (37.5%) and glyceraldehyde vield (19.3%). The enhanced activity for TeKCN was attributed to better charge separation in Te and KCN heterostructure and was consistent with the photocurrent density profile. TeKCN10 shows a slight improvement in glycerol conversion (39.4%) and glyceraldehyde yield (21.0%). Further, an increase in Te content to 15% does not improve the catalytic performance of TeKCN heterostructures suggesting TeKCN10 was the optimum catalyst. The glycerol conversion using TeKCN15 was found to be 31% after 24 h. After the decoration of IrN₂O₂ isolated sites on TeKCN10 heterostructure (TeKCNIr), the glycerol conversion rate was slightly improved reaching a value of 45.6% while the glyceraldehyde yield was significantly increased (28%). The increased glyceraldehyde yield



www.advancedsciencenews.com



Figure 6. Photocatalytic a) glycerol conversion b) glyceraldehyde yield and c) glyceraldehyde selectivity under AM1.5G irradiation and 365, 400, 450, 500, 550, 600, and 650 nm LEDs using TeKCNIr catalyst. d) glycerol conversion e) glyceraldehyde yield and f) glyceraldehyde selectivity after 24 h in the presence of BQ, IPA and EDTA as $O_2^{\bullet-}$, \bullet OH and h⁺ scavengers respectively (AM1.5G irradiation). EPR spectra of reaction product using under dark and after 5, 10 min irradiation under AM1.5G irradiation using g) TEMPO as photogenerated hole trapping agent and DMPO as h) superoxide radical i) hydroxyl radical spin labeling agent.

suggests that isolated Ir sites promote selective oxidation of glycerol to glyceraldehyde (Figure 5e). The calculated glyceraldehyde selectivity for CN was 32.5% while glyceraldehyde selectivity for CNIr was found to be 57% which indicates the role of Ir SA sites in improved catalytic selectivity (Figure 5f). The glyceraldehyde selectivity of TeKCN5, TeKCN10 and TeKCN15 was 51.6, 53.2 and 31.0% respectively suggesting TeKCN10 heterostructure itself has better selectivity. When TeKCNIr was used as a catalyst the highest observed selectivity was 61.6%. These observations indicate that the decoration of Ir SA sites provides active centers for improved selectivity. After 24 h reaction, glyceric acid was identified as a major by-product with an overall selectivity of \approx 19.8% while other possible products such as DHA were negligible (Figure S26, Supporting Information). The TeKCNIr selectivity was higher compared to reported state-of-the-art catalysts while most of the catalysts demonstrate DHA as a dominating product (Table **S5**, Supporting Information). Furthermore, the evolved gaseous products were also analyzed which demonstrated H₂ as a major product with a trace of CO₂. After 24 h irradiation, the yield of H₂ was found to be 214.2 µmol g⁻¹cat. While CO₂ was significantly low and was not quantified. The obtained results demonstrate glycerol provides protons for the H₂ generation.

To understand the role of specific energy of light on the photocatalytic activity of TeKCNIr, wavelength-dependent glycerol conversion and glyceraldehyde yield were also calculated. It can be seen from **Figure 6**a,b that solar-simulated AM1.5G irradiation displayed the highest glycerol conversion and glyceraldehyde yield. Among various wavelength LEDs (Power density 1.1 mW cm⁻²), 400 nm LED displayed the highest glycerol conversion of 9.7% with a yield of glyceraldehyde equivalent to 8.4%. On the other hand, at 450 nm wavelength, the glycerol conversion and glyceraldehyde selectivity were 6.3 and 5.6%, respectively. After that, the glycerol conversion gradually depletes as the wavelength of light increases which was due to less energetic electron hole pairs. This suggests that KCN with an

absorption edge of 450 nm generates electron-hole pairs while Te nanostructures facilitate charge separation which is consistent with previous literature.^[12] Interestingly, monochromatic radiation increases the selectivity of glyceraldehyde compared to AM1.5G light (Figure 6c). The glyceraldehyde selectivity using 400, 450, and 365 nm LED was found to be 87.1, 88.6, and 75.2%, respectively. The unusually high selectivity (88.6%) at 450 nm wavelength light attributed to the predominant excitation of charge carriers in KCN structure and has been further discussed in the following sections.

To discern the role of reactive species responsible for the selective oxidation of glycerol to glyceraldehyde, the reaction was carried out using benzoquinone (BQ), isopropyl alcohol (IPA) and ethylene diamine tetraacetic acid (EDTA) as superoxide radial $(O_2^{\bullet-})$, hydroxyl radical (\bullet OH) and hole (h^+) scavengers, respectively (Figure 6d-f). Compared to the reaction without any scavenger (45.6%), using IPA and EDTA the glycerol conversion was slightly decreased to 42.4 and 40.1%, respectively (Figure 6d). When BQ was used as a superoxide radial $(O_2^{\bullet-})$ scavenger the glycerol conversion was decreased to 30.3%. The glyceraldehyde yield and selectivity also follow a similar pattern. A significant drop in the selectivity using BQ suggests O2. - was the main reactive oxygen species (ROS) for the oxidation of glycerol. However, •OH and h⁺ also participate in the reaction, but their relative contribution remains low compared to O2 - radicals. These findings are well in agreement with previous literature which demonstrates that $O_2^{\bullet-}$ radicals promote selective oxidation of organic substrate.^[65] The presence of glyceric acid as a by-product suggests overoxidation of glyceraldehyde can lead to glyceric acid. To understand the influence of oxygen on the reaction, glycerol oxidation in a stainless pressure reactor equipped with a quartz window and 8 bar O₂ (Figure S28, Supporting Information). After 24 h simulated solar light irradiation, the glycerol conversion was found to be 66.3% while the glyceraldehyde selectivity decreased to 26.6% (Figure S29, Supporting Information). The increased glycerol conversion indicates the reduction of O₂ to O₂^{•-} radical anion followed by glycerol oxidation was a more favorable reaction route. However, decreased glyceraldehyde selectivity also substantiates over-oxidation of glyceraldehyde under pressurized O_2 conditions.

To further validate the generation of ROS and electron-hole pairs, electron paramagnetic resonance (EPR) spectroscopy was performed using spin trap agents under dark and light conditions (Figure 6g-i). The EPR spectra acquired using 2,2,6,6tetramethylpiperidine-1-oxyl (TEMPO) and TeKCNIr catalysts under dark conditions exhibited intense triplet with an intensity of 1:1:1 which was signature signals for TEMPO (Figure 6g).^[66] After visible light irradiation, the signal intensity for TEMPO was decreased due to the trapping of photogenerated electrons by TEMPO followed by the formation of EPR silent hydroxyl amine of TEMPOH. The reduced signal intensity under visible light irradiation suggests populated charge carrier generation in the TeKCNIr heterostructure. Furthermore, the EPR experiment carried out using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap showed well resolved quartet (1:1:1:1) due to the formation of DMPO-O₂^{••} species (Figure 6h). The signal intensity was increased after increasing the irradiation time (5 and 10 min) suggesting continuous generation of O2. - species under photocatalytic conditions. Additionally, a quartet with 1:2:2:1 intensity

was also observed deciphering the formation of hydroxyl (\bullet OH) radical during the visible light irradiation (Figure 6i). These observations suggest a direct role of photogenerated electrons, superoxide radical O_2^{\bullet} and hydroxyl radicals (\bullet OH) in the transformation of glycerol to glyceraldehyde. The glycerol oxidation on TeKCNIr proceeds via two electrons and two protons abstraction from glycerol at IrN_2O_2 sites on VB followed by reduction of intermediates at the CB. So, reactions at both CB and VB contribute to product formation. The addition of scavengers reduces the reaction rate either at CB or VB due to competition for active sites, which interferes with charge transfer and proton from glycerol molecule and another dominant reaction pathway might be preferred which reduces the product selectivity.

Temperature programmed desorption (TPD) using probe molecule titration was implemented to understand the nature and counts of Lewis/Brønsted acid and base sites (Figures S30,S31, Supporting Information). TPD using CO₂ (a weak Lewis acid) provides information on Lewis base sites while pyridine being a strong base will titrate all types of acidic sites giving a total acidic site count. Sterically hindered molecule DTBP (2,6-di-tert-butylpyridine) can only titrate Brønsted Acid sites.^[67] The difference between total and Brønsted acid sites provides Lewis acid count (Figure S32, Supporting Information). CO₂-TPD of CN shows a strong desorption peak at 168 °C due to the presence of secondary: N-C₂ nitrogen of heptazine (C_6N_7) ring system and uncondensed: NH/NH₂ (Figure S30a, Supporting Information).^[68] The doping of K⁺ does not change the CO₂ desorption profile (165 °C) suggesting the nature of basic sites and heptazine ring coordination pattern remain almost the same in KCN. The CO₂-TPD of TeKCN shows a parent KCN peak at 161 °C along with a weak shoulder peak at 95 °C. The weak desorption peak at 95 °C might arise due to surface adsorb H₂O molecules (Lewis base) or residual polyvinylpyrrolidone (PVP) on TeNRs/NSs surface. After the decoration of IrN₂O₂ SA sites, the CO₂ desorption peak appeared slightly at higher temperatures (higher basic character). The observed effect might be due to increased charge density on the C6N7 motif from Ir metal to ligand charge transfer (MLCT) and stronger CO₂ adsorption on IrO₂ sites.^[69] Pyridine-TPD of CN, KCN and TeKCN show similar desorption profiles with a major desorption peak at 83, 88 and 86 °C (Figure S30b, Supporting Information). Though CN structure does not have any specific acidic sites, chemisorbed O-H groups on CN can behave as Brønsted acid sites.^[70] The low desorption temperature for pyridine also supports the presence of weakly bonded OH on the CN/KCN's surface. TPD peak at higher temperatures (175-180 °C) was attributed to strongly bonded -OH produced from incomplete condensation of CNs. TeKCNIr shows three weak desorption peaks at 64, 111 and 149 °C. Considering the very weak desorption profile (acid strength) of 64 and 111 °C peaks from chemically adsorbed O-H groups, it can be inferred that the acidic sites should not govern the catalytic activity of TeKCNIr. The peak at a relatively high temperature (149 °C) was attributed to the desorption of pyridine from Ir-O-OH sites formed by hydrolysis of surface adsorbed water. DTBP (2,6di-tert-butylpyridine) TPD also reveals the presence of a similar desorption profile confirming the presence of Brønsted acid sites on TeKCNIr (Figure S31, Supporting Information). The active site count analysis shows TeKCNIr possesses the highest numbers of basic sites (1.0 µmol g⁻¹cat). As expected, Lewis acid count www.advancedsciencenews.com

CIENCE NEWS



Figure 7. a) Band diagram of Te, KCN before and after contact showing the charge flow and plausible mechanism of glycerol oxidation. b) optimized geometry of TeKCN, c) charge density difference iso-surface of TeKCN and d) optimized structures of TeKCNIr.

remains almost constant in all materials and therefore cannot be accounted as the active site in catalysis.

The visible light absorption profile and bandgap energies (E_{α}) of the materials were determined using the Kubelka-Munk function (Figure S33, Supporting Information).^[71] The optical band gap of Te NRs/NSs, CN, KCN, KCNIr, TeKCN, and TeKCNIr was calculated to be 0.32, 2.72, 2.62, 2.66, 1.89, and 1.94 eV respectively. Furthermore, Mott-Schottky analysis of Te, KCN, TeKCN and TeKCNIr demonstrated the flat band potential (E_{fb}) value -0.14, -0.47, -0.31, and -0.52 V respectively versus NHE at pH-0 (Figure S34, Supporting Information). Considering the Fermi level lies close to the CB in n-type materials, these values represent the position of the CB. The position of Fermi level with respect to the vacuum level (E_{vac}) was determined using ultraviolet photoelectron spectroscopy (UPS) work function (WF) spectroscopy (Figure \$35, Supporting Information). The work function (ϕ) value was estimated by subtracting the cut-off energy of secondary electrons ($E_{\rm cut-off}$) from the energy of the He-II UV source (21.21 eV; WF (ϕ) = 21.21– $E_{\text{cut-off}}$) (See SI for more detail).^[72] From the point of inflections, the $E_{cut-off}$ energies of CN, KCN, TeKCN and TeKCNIr were calculated to be 16.30, 16.33, 16.35, and 16.36 eV and the corresponding WF values w.r.t to Evac were 4.91, 4.88, 4.86, and 4.85 eV respectively. Additionally,

the VB) position calculated using XPS valance band (XPS-VB) spectra for CN, KCN, TeKCN and TeKCNIr was 1.98, 1.70, 1.48, and 1.46 eV below the Fermi level (Figure S36, Supporting Information) Based on band energies calculations, the band diagrams of materials were constructed (Figure S37, Supporting Information). The TeNRs/NSs due to the low band gap can absorb in visible to NIR region. Due to the intrinsic p-type nature of bulk Te, it makes a p-n heterojunction with n-type KCN (Figure 7).^[73] After contact, electrons from the conduction band of n-type KCN flow to Te during the Fermi level equilibration and a Type-II (staggered) heterojunction was established. In TeKCN heterojunction, after absorption of visible light, the photogenerated electrons on Te migrate to KCN and resulting electrons reduced O_2 to $O_2^{\bullet-}$. The resulting O₂^{•-} can either directly participate in glycerol oxidation or are transformed to •OH radicals which oxidize glycerol. It can be seen from the VB position of KCN that photogenerated holes do not possess the required oxidation potential to generate •OH from water (2.32 V vs NHE at pH-0).^[74] Therefore observed •OH radicals in the EPR originated from the indirect route via reduction of O₂. However, due to the low oxidation potential of glycerol (0.004 V vs NHE at pH-0), the holes in the VB of KCN can directly participate in glycerol oxidation.^[75] The isolated IrN2O2 SA sites improve the catalytic activity due to their

www.afm-journal.de

excellent hole-capturing ability thus reducing the recombination losses. Additionally, as found from DFT analysis, IrN2O2 sites also work as active sites to bind with glycerol molecules and facilitate its selective oxidation. The stepwise transfer of two holes from IrN₂O₂ sites to surface adsorbed glycerol molecule followed by proton abstraction and reduction of intermediates at the CB led to the generation of glyceraldehyde. The high density of Lewis base site on TeKCNIr also promotes facile electron transfer and reduction of intermediate therefore improving the product yield. The observed high selectivity (88.6%) at 450 nm for TeKCNIr heterostructure can be explained based on populated charge generation in KCN at lower wavelength. At higher wavelength only Te NRs/NSs can be excited, and a significant charge loss takes place at the interface. Furthermore, generated less energetic holes remained confined to Te structure thus holes are unavailable to IrN₂O₂ sites. However, when KCN was excited at a lower wavelength, the photogenerated holes can be efficiently captured by IrN2O2 sites which facilitates selective oxidation of adsorbed glycerol molecules.

SCIENCE NEWS _____ www.advancedsciencenews.com

To understand the structure of materials and charge transfer mechanism in TeKCNIr heterostructure, density functional theory (DFT) was performed using Vienna ab initio simulation package (VASP). A single layer 2×2×1 supercell of CN with 32 nitrogen and 24 carbon atoms was considered with a vacuum layer of 20 Å and its optimized geometry is shown in Figure S38a (Supporting Information). After optimizing the bulk structure of Te structure, its (001) surface is generated and optimized. 3×3×1 supercell of Te surface with 54 atoms is considered to match the size of the g-C₃N₄ supercell and the optimized structure of the Te surface is shown in Figure S38b (Supporting Information) Optimized cell parameters of CN (13.314 Å) and Te surface (12.767 Å) were found to have a mismatch of 4.27%. CN adsorbed on Te surface has been optimized and reported in Figure S39a (Supporting Information). Charge density difference iso-surface for g- C_3N_4 -Te system indicates no significant charge transfer between the g-C₃N₄ and Te (Figure S39b, Supporting Information). On the other hand, charge density difference iso-surface for TeKCN with one K atom placed between the CN and Te shows a significant electron transfer to the C3N4 surface indicating the role of K as a bridge between the Te and C_3N_4 surfaces (Figure 7b,c). Planar averaged electrostatic potential (Φ_{vacuum}) along the normal direction to the surface has been calculated for both CN and TeKCN and the work function was calculated as (e $\Phi_{vacuum} - \mu_{Fermi}$) (Figure S40, Supporting Information). The calculated work function for CN was found to be 6.15 eV whereas it is 4.59 eV for the Te-K-C₃N₄. These results suggest facile charge transfer from Te to CNs surface.

Furthermore, IrO_2 unit were adsorbed over the CN, KCN, TeCN and TeKCN surfaces with two different configurations. In the first configuration, IrO_2 unit is considered to be linear with Ir atom interacting with nitrogen atoms of C_3N_4 and O atoms are placed above and below the C_3N_4 sheet. While in second configuration, both the O atoms of IrO_2 are on the same side of CNs sheet (Figure 7; Figure S23e,f, Table S2, Supporting Information). From the optimized structures, the second configuration was found to be the minimum energy structure. It can be seen from the optimized structure that in TeKCNIr, IrO_2 facing toward the surface can potentially interact with glycerol molecule during oxidation reaction.

3. Conclusion

We have designed an efficient Te/TeO₂ core-shell structure decorated with K-doped carbon nitride (KCN) van der Waal heterojunction by a simple electrostatic interaction approach. The decoration of Ir single atom sites on TeKCN heterojunction by hydrolysis decomposition improved the catalytic conversion of glycerol to glyceraldehyde under solar-simulated light without any sacrificial donor. The catalytic selectivity for glyceraldehyde formation can reach as high as 88% under 450 nm irradiation. AC-HAADF-STEM and WAXS analysis reveal isolated Ir single atoms decorated on KCN 2D structure. Synchrotron-based XANES and EXAFS analysis validate the presence of undercoordinated IrN₂O₂ sites embedded in the CN framework. Due to the presence of low bandgap Te nanostructure, a better charge separation at the Te/KCN nano-heterointerface was achieved resulting in improved catalytic performance. The IrN₂O₂ isolated sites improve the catalytic selectivity for glyceraldehyde formation. Based on scavenger and EPR studies, superoxide radicals and hydroxyl radicals were found to be the main reactive species promoting the selective oxidation of glycerol. The findings presented in the manuscript will galvanize studies to develop active and resilient SACs for the selective transformation of low-value products to commodity chemicals.

Supporting Information

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

Acknowledgements

The authors would like to thank the University of Calgary's CFREF for financial assistance. Drs. Natalie Hamada and Brian Langelier at the Canadian Centre for Electron Microscopy (CCEM), McMaster University are kindly acknowledged for HR-TEM, AC-HAADF, and EELS analysis on the samples. Part of the research described in this paper was performed at the Canadian Light Source (Project: 35G12344), a national research facility of the University of Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the University of Saskatchewan. Drs. Ning Chen, Beatriz Diaz-Moreno, Jay Dynes, Tom Regier, Zachary Arthur and Adam Leontowich are kindly acknowledged for helping in hard/soft X-ray and WAXS analysis.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.K. and J.W. contributed equally to this work. P.K. and A.A. conceived the research, synthesized, and characterized the catalyst, evaluated part of the catalytic performance, interpreted the results, and wrote the initial draft of the manuscript. J.W. performed photocatalytic reactions and analyzed the reaction product. S.R. conducted spectroscopic characterizations and chemical analysis on the catalysts and edited the manuscript. V.J. and S.R. conducted the TPD measurements and analysis on the catalysts.

X.W. helped with EXAFS analysis. H.H., K.K., D.T. helped in the catalyst's synthesis, characterization, and performance evaluation. S.K. performed DFT analysis and compiled results. P.B., P.M.A., J.H. M.G.K. and M.A. supervised the research and edited the manuscript. All co-authors read and approved the final version of the manuscript.

Data Availability Statement

SCIENCE NEWS _____

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

doped carbon nitride, glycerol conversion, photocatalysis, photooxidation, single atom catalysts

Received: November 4, 2023 Revised: February 24, 2024 Published online:

- M. Ebadian, S. van Dyk, J. D. McMillan, J. Saddler, *Energy Policy* 2020, 147, 111906.
- [2] (STARBFVO Animal Fats), By Application (Fuel, Power Generation), By Region (Europe, APAC), And Segment Forecasts, 2022 –2030 Report ID: GVR-1-68038-513-7 2022, 159.
- [3] P. J. M. Lima, R. M. da Silva, C. A. C. G. Neto, N. C. Gomes e Silva, J. E. d. S. Souza, Y. L. Nunes, J. C. Sousa dos Santos, *Biotechnol. Appl. Biochem.* 2022, 69, 2794.
- [4] a) Y. Wang, S. Furukawa, S. Song, Q. He, H. Asakura, N. Yan, Angew. Chem. 2020, 132, 2309; b) M. Anitha, S. Kamarudin, N. Kofli, Chem. Eng. J. 2016, 295, 119; c) D. Liu, J.-C. Liu, W. Cai, J. Ma, H. B. Yang, H. Xiao, J. Li, Y. Xiong, Y. Huang, B. Liu, Nat. Commun. 2019, 10, 1779.
- [5] a) J. Yu, F. Dappozze, J. Martín-Gomez, J. Hidalgo-Carrillo, A. Marinas, P. Vernoux, A. Caravaca, C. Guillard, *Appl. Catal. B* 2021, 299, 120616; b) W. Sun, Y. Zheng, J. Zhu, *Mater. Today Sustain.* 2023, 23, 100465.
- [6] a) J. Wang, P. Kumar, H. Zhao, M. G. Kibria, J. Hu, *Green Chem.* 2021, 23, 7435; b) Y. Markushyna, C. A. Smith, A. Savateev, *Eur. J. Organic Chem.* 2020, 2020, 1294.
- [7] a) H. Kasap, D. S. Achilleos, A. Huang, E. Reisner, J. Am. Chem. Soc.
 2018, 140, 11604; b) S. Wu, H. Yu, S. Chen, X. Quan, ACS Catal. 2020, 10, 14380; c) M. Zhang, X. Bai, D. Liu, J. Wang, Y. Zhu, Appl. Catal. B 2015, 164, 77.
- [8] V. W.-h. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum, B. V. Lotsch, *Nat. Commun.* 2016, 7, 12165.
- H. Yu, R. Shi, Y. Zhao, T. Bian, Y. Zhao, C. Zhou, G. I. Waterhouse, L. Z. Wu, C. H. Tung, T. Zhang, *Adv. Mater.* 2017, *29*, 1605148.
- [10] D. Zhao, C. L. Dong, B. Wang, C. Chen, Y. C. Huang, Z. Diao, S. Li, L. Guo, S. Shen, Adv. Mater. 2019, 31, 1903545.
- [11] a) G.-Q. Liu, Y. Yang, Y. Li, T. Zhuang, X.-F. Li, J. Wicks, J. Tian, M.-R. Gao, J.-L. Peng, H.-X. Ju, *Nat. Commun.* **2021**, *12*, 4296; b) Y. Wang, G. Qiu, R. Wang, S. Huang, Q. Wang, Y. Liu, Y. Du, W. A. Goddard III, M. J. Kim, X. Xu, *Nat. Electron.* **2018**, *1*, 228.
- [12] B. Qiu, C. Wang, J. Wang, Z. Lin, N. Zhang, L. Cai, X. Tao, Y. Chai, *Mater. Today Energy* **2021**, *21*, 100720.
- [13] P. Kumar, D. Laishram, R. K. Sharma, A. Vinu, J. Hu, M. G. Kibria, *Chem. Mater.* 2021, 33, 9012.
- [14] S. Guo, Z. Zhu, X. Hu, W. Zhou, X. Song, S. Zhang, K. Zhang, H. Zeng, *Nanoscale* **2018**, 10, 8397.

- [15] a) S. K. Kaiser, Z. Chen, D. Faust Akl, S. Mitchell, J. Perez-Ramirez, *Chem. Rev.* 2020, 120, 11703; b) J. Zhang, H. Yang, B. Liu, *Adv. Energy Mater.* 2021, 11, 2002473.
- [16] a) J. Fu, J. Lym, W. Zheng, K. Alexopoulos, A. V. Mironenko, N. Li, J. A. Boscoboinik, D. Su, R. T. Weber, D. G. Vlachos, *Nat. Catal.* 2020, *3*, 446; b) S. De, A. S. Burange, R. Luque, *Green Chem.* 2022, *24*, 2267; c) P. Kumar, M. Khan, J. Hu, M. G. Kibria, in *Advanced Catalysis for Drop-in Chemicals*, Elsevier, Amsterdam, The Netherlands 2022, p. 63.
- [17] L. Xiong, H. Qi, S. Zhang, L. Zhang, X. Liu, A. Wang, J. Tang, Adv. Mater. 2023, 35, 2209646.
- [18] P. Kumar, T. A. Al-Attas, J. Hu, M. G. Kibria, ACS Nano 2022, 16, 8557.
- [19] J. Deng, C. Zhou, Y. Yang, B. Nan, L. Dong, L. Cai, L. Li, Z.-J. Wang, X. Yang, Z. Chen, *Chem. Eng. J.* **2023**, 462, 142282.
- [20] J. Chen, P. Cui, G. Zhao, K. Rui, M. Lao, Y. Chen, X. Zheng, Y. Jiang, H. Pan, S. X. Dou, Angew. Chem., Int. Ed. 2019, 58, 12540.
- [21] Z. Li, Y. Chen, Chem. Commun. 2022, 58, 13983.
- [22] D. Zhao, Z. Chen, W. Yang, S. Liu, X. Zhang, Y. Yu, W.-C. Cheong, L. Zheng, F. Ren, G. Ying, J. Am. Chem. Soc. 2019, 141, 4086.
- [23] Y. Yin, Y. Zhang, T. Gao, T. Yao, J. Han, Z. Han, Z. Zhang, Q. Wu, B. Song, *Mater. Chem. Phys.* **2017**, *194*, 293.
- [24] H. Cui, K. Zheng, Z. Xie, J. Yu, X. Zhu, H. Ren, Z. Wang, F. Zhang, X. Li, L.-Q. Tao, ACS Appl. Mater. Interfaces 2020, 12, 47704.
- [25] C. Shen, Y. Liu, J. Wu, C. Xu, D. Cui, Z. Li, Q. Liu, Y. Li, Y. Wang, X. Cao, ACS Nano 2019, 14, 303.
- [26] Y. Du, G. Qiu, Y. Wang, M. Si, X. Xu, W. Wu, P. D. Ye, Nano Lett. 2017, 17, 3965.
- [27] P. Kumar, E. Vahidzadeh, U. K. Thakur, P. Kar, K. M. Alam, A. Goswami, N. Mahdi, K. Cui, G. M. Bernard, V. K. Michaelis, J. Am. Chem. Soc. 2019, 141, 5415.
- [28] V. W.-h. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum, B. V. Lotsch, *Nat. Commun.* 2016, 7, 12165.
- [29] Y. Yang, S. Wang, Y. Jiao, Z. Wang, M. Xiao, A. Du, Y. Li, J. Wang, L. Wang, Adv. Funct. Mater. 2018, 28, 1805698.
- [30] C. Ott, F. Reiter, M. Baumgartner, M. Pielmeier, A. Vogel, P. Walke, S. Burger, M. Ehrenreich, G. Kieslich, D. Daisenberger, Adv. Funct. Mater. 2019, 29, 1900233.
- [31] a) P. Kumar, S. Mulmi, D. Laishram, K. M. Alam, U. K. Thakur, V. Thangadurai, K. Shankar, *Nanotechnology* **2021**, *32*, 485407; b) A. Chowdhury, D. C. Cameron, M. Hashmi, *Thin Solid Films* **1998**, *332*, 62.
- [32] G. Rao, H. Fang, T. Zhou, C. Zhao, N. Shang, J. Huang, Y. Liu, X. Du, P. Li, X. Jian, *Adv. Mater.* **2022**, *34*, 2204697.
- [33] M. Smirnov, V. Kuznetsov, E. Roginskii, J. Cornette, M. Dutreilh-Colas, O. Noguera, O. Masson, P. Thomas, J. Physics Condens. Matter 2018, 30, 475403.
- [34] T. Miller, A. B. Jorge, T. Suter, A. Sella, F. Corà, P. McMillan, Phys. Chem. Chem. Phys. 2017, 19, 15613.
- [35] a) J. Lu, Y. He, C. Ma, Q. Ye, H. Yi, Z. Zheng, J. Yao, G. Yang, *Adv. Mater.* **2023**, *35*, 2211562; b) B. Qiu, C. Wang, J. Wang, Z. Lin, N. Zhang, L. Cai, X. Tao, Y. Chai, *Mater. Today Energy* **2021**, *21*, 100720.
- [36] F. Goettmann, A. Fischer, M. Antonietti, A. Thomas, Angew. Chem., Int. Ed. 2006, 45, 4467.
- [37] P. Sun, G. Monaco, P. Zalden, K. Sokolowski-Tinten, J. Antonowicz, R. Sobierajski, Y. Kajihara, A. Q. Baron, P. Fuoss, A. C. Chuang, *Proc. Natl. Acad. Sci* 2022, 119, e2202044119.
- [38] Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang, J. Qiu, Sci. Rep. 2013, 3, 1.
- [39] K. L. Corp, C. W. Schlenker, J. Am. Chem. Soc. 2017, 139, 7904.
- [40] W. Wang, H. Zhang, S. Zhang, Y. Liu, G. Wang, C. Sun, H. Zhao, Angew. Chem., Int. Ed. 2019, 58, 16644.
- [41] W. Liu, P. Wang, J. Chen, X. Gao, H. Che, B. Liu, Y. Ao, Adv. Funct. Mater. 2022, 32, 2205119.

16163028, 0, Downloaded from https://onlineLibrary.wiley.com/doi/10.1002/adfm.202313793, Wiley Online Library on [21/03/2024], See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [42] Y. Chen, X. Liu, L. Hou, X. Guo, R. Fu, J. Sun, Chem. Eng. J. 2020, 383, 123132.
- [43] a) D. Laishram, S. Zeng, K. M. Alam, A. P. Kalra, K. Cui, P. Kumar, R. K. Sharma, K. Shankar, *Appl. Surf. Sci.* 2022, 592, 153276; b) H. Wang, Y. Bian, J. Hu, L. Dai, *Appl. Catal. B* 2018, 238, 592.
- [44] Y. Zhang, J. Guo, Y. Xu, W. Huang, C. Li, L. Gao, L. Wu, Z. Shi, C. Ma, Y. Ge, *Nanoscale Horiz*. **2020**, *5*, 847.
- [45] Y. Ren, R. Sun, X. Yu, R. Wang, W. Zhang, X. Zhu, Y. Ma, L. Ma, Mater. Adv. 2023, 4, 4455.
- [46] M.-Q. Yang, K.-L. Zhou, C. Wang, M.-C. Zhang, C.-H. Wang, X. Ke, G. Chen, H. Wang, R.-Z. Wang, J. Mater. Chem. A 2022, 10, 25692.
- [47] X. Guan, M. Fawaz, R. Sarkar, C.-H. Lin, Z. Li, Z. Lei, P. D. Nithinraj, P. Kumar, X. Zhang, J.-H. Yang, J. Mater. Chem. A 2023, 11, 12837.
- [48] N. Meng, W. Zhou, Y. Yu, Y. Liu, B. Zhang, ACS Catal. 2019, 9, 10983.
- [49] Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S. Z. Qiao, Nat. Commun. 2014, 5, 3783.
- [50] C. Han, L. Du, M. Konarova, D.-C. Qi, D. L. Phillips, J. Xu, ACS Catal. 2020, 10, 9227.
- [51] D. Telesca, Y. Nie, J. Budnick, B. Wells, B. Sinkovic, Phys. Rev. B 2012, 85, 214517.
- [52] S. K. Kaiser, R. Lin, S. Mitchell, E. Fako, F. Krumeich, R. Hauert, O. V. Safonova, V. A. Kondratenko, E. V. Kondratenko, S. M. Collins, *Chem. Sci.* 2019, *10*, 359.
- [53] J. Zhao, S. Ji, C. Guo, H. Li, J. Dong, P. Guo, D. Wang, Y. Li, F. D. Toste, *Nat. Catal.* **2021**, *4*, 523.
- [54] H. Yang, X. Wang, Q. Liu, A. Huang, X. Zhang, Y. Yu, Z. Zhuang, G. Li, Y. Li, Q. Peng, J. Am. Chem. Soc. 2023, 145, 6658.
- [55] a) X. Zheng, J. Tang, A. Gallo, J. A. Garrido Torres, X. Yu, C. J. Athanitis,
 E. M. Been, P. Ercius, H. Mao, S. C. Fakra, *Proc. Natl. Acad. Sci* 2021, 118, e2101817118; b) H. N. Nong, T. Reier, H.-S. Oh, M. Gliech, P. Paciok, T. H. T. Vu, D. Teschner, M. Heggen, V. Petkov, R. Schlögl, *Nat. Catal.* 2018, 1, 841.
- [56] M. Xiao, J. Zhu, G. Li, N. Li, S. Li, Z. P. Cano, L. Ma, P. Cui, P. Xu, G. Jiang, Angew. Chem., Int. Ed. 2019, 58, 9640.
- [57] J. Gao, C.-Q. Xu, S.-F. Hung, W. Liu, W. Cai, Z. Zeng, C. Jia, H. M. Chen, H. Xiao, J. Li, J. Am. Chem. Soc. 2019, 141, 3014.

[58] H. You, D. Wu, D. Si, M. Cao, F. Sun, H. Zhang, H. Wang, T.-F. Liu, R. Cao, J. Am. Chem. Soc. 2022, 144, 9254.

www.afm-journal.de

- [59] W. Zhao, F. Xu, Z. Wang, Z. Pan, Y. Ye, S. Hu, B. Weng, R. Zhu, Small 2022, 18, 2205495.
- [60] D. Liu, Y. Zhao, C. Wu, W. Xu, S. Xi, M. Chen, L. Yang, Y. Zhou, Q. He, X. Li, *Nano Energy* **2022**, *98*, 107296.
- [61] a) R. Godin, Y. Wang, M. A. Zwijnenburg, J. Tang, J. R. Durrant, J. Am. Chem. Soc. 2017, 139, 5216; b) D. Zhao, Y. Wang, C.-L. Dong, Y.-C. Huang, J. Chen, F. Xue, S. Shen, L. Guo, Nat. Energy 2021, 6, 388.
- [62] C. Li, E. Hofmeister, I. Krivtsov, D. Mitoraj, C. Adler, R. Beranek, B. Dietzek, ChemSusChem 2021, 14, 1728.
- [63] E. Mitchell, A. Law, R. Godin, Chem. Commun. 2021, 57, 1550.
- [64] M. Y. Ye, Z. H. Zhao, Z. F. Hu, L. Q. Liu, H. M. Ji, Z. R. Shen, T. Y. Ma, Angew. Chem., Int. Ed. 2017, 56, 8407.
- [65] Z. Huang, N. Luo, C. Zhang, F. Wang, Nat. Rev. Chem. 2022, 6, 197.
- [66] J. Ma, D. Jin, Y. Li, D. Xiao, G. Jiao, Q. Liu, Y. Guo, L. Xiao, X. Chen, X. Li, Appl. Catal. B 2021, 283, 119520.
- [67] a) J. N. Hall, P. Bollini, ACS Catal. 2020, 10, 3750; b) W. T. Broomhead, Y.-H. C. Chin, ACS Catal. 2024, 14, 2235.
- [68] Y. Li, S. Ouyang, H. Xu, W. Hou, M. Zhao, H. Chen, J. Ye, Adv. Funct. Mater. 2019, 29, 1901024.
- [69] H. Zhang, G. Liu, L. Shi, J. Ye, Adv. Energy Mater. 2018, 8, 1701343.
- [70] R. G. Pavelko, H. Daly, C. Hardacre, A. A. Vasiliev, E. Llobet, Phys. Chem. Chem. Phys. 2010, 12, 2639.
- [71] S. Gao, Q. Zhang, X. Su, X. Wu, X.-G. Zhang, Y. Guo, Z. Li, J. Wei, H. Wang, S. Zhang, J. Am. Chem. Soc. 2023, 145, 9520.
- [72] P. Kumar, P. Kar, A. P. Manuel, S. Zeng, U. K. Thakur, K. M. Alam, Y. Zhang, R. Kisslinger, K. Cui, G. M. Bernard, *Adv. Opt. Mater.* **2020**, *8*, 1901275.
- [73] a) M. Lin, H. Chen, Z. Zhang, X. Wang, *Phys. Chem. Chem. Phys.* 2023, 25, 4388; b) R. Zhuo, Y. Wang, D. Wu, Z. Lou, Z. Shi, T. Xu, J. Xu, Y. Tian, X. Li, *J. Mater. Chem. C* 2018, 6, 299.
- [74] F. Xiao, Z. Wang, J. Fan, T. Majima, H. Zhao, G. Zhao, Angew. Chem., Int. Ed. 2021, 60, 10375.
- [75] Z. H. Al-Azri, W.-T. Chen, A. Chan, V. Jovic, T. Ina, H. Idriss, G. I. Waterhouse, J. Catal. 2015, 329, 355.