

Boosting Selective Nitrogen Reduction via Geometric Coordination Engineering on Single-Tungsten-Atom Catalysts

Yu Gu, Baojuan Xi, Wenzhi Tian, Hua Zhang, Qiang Fu, and Shenglin Xiong*

Atomic interface regulation that can efficiently optimize the performance of single-atom catalysts (SACs) is a worthwhile research topic. The challenge lies in deeply understanding the structure-properties correlation based on control of the coordination chemistry of individual atoms. Herein, a new kind of W SACs with oxygen and nitrogen coordination (W-NO/NC) and a high metal loading over 10 wt% is facilely prepared by introducing an oxygenbridged [WO₄] tetrahedron. The local structure and coordination environment of the W SACs are confirmed by high-angle annular dark-field scanning transmission electron microscopy, X-ray photoelectron spectroscopy, and extended X-ray absorption fine structure. The catalyst shows excellent selectivity and activity for the electrochemical nitrogen reduction reaction (NRR). Density functional theory calculation reveals that unique electronic structures of the N and O dual-coordinated W sites optimize the binding energy of the NRR intermediate, resulting in facilitating the electrocatalytic NRR. This work opens an avenue toward exploring the correlation between coordination structure and properties.

1. Introduction

Owing to the maximized atomic utilization and unique quantum size effects, single-atom catalysts (SACs) have been attracting intensive interests in the field of electrocatalysis.^[1–4] Meanwhile, the geometry and local electronic structures of SACs can be regulated by changing the metal atoms (Pt, Mn, Ni, Mo, etc.), adjusting the coordination anions (C, N, O, S, etc.) and coordination numbers, which significantly improves catalytic property of active centers and enables flexible reaction tenability.^[5–11] The adsorption of N₂ in the N₂ reduction reaction (NRR) and the adsorption of H in the hydrogen evolution reaction (HER) on catalytic active sites are competitive. The atomically dispersed MoN_1C_2 catalyst possessed excellent activity for HER,^[12,13] while MoN_3 is reported to be highly

Dr. Y. Gu, Prof. B. J. Xi, Dr. W. Z. Tian, H. Zhang, Prof. Q. Fu, Prof. S. L. Xiong Key Laboratory of Colloid and Interface Chemistry Ministry of Education School of Chemistry and Chemical Engineering State Key Laboratory of Crystal Materials Shandong University Jinan 250100, P. R. China E-mail: chexsl@sdu.edu.cn

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selective for NRR.^[14,15] For CO₂ reduction reaction, SACs usually promote the reduction of CO₂ to CO by two-electron reaction pathway,^[16] while cobalt single atoms immobilized by phthalocyanine ligands is more inclined to generate methanol with a Faraday efficiency as high as 40%.[17] Therefore, there is an urgent need to explore new catalytically active configurations for inducing superior activities to achieve distinctive electrocatalysis performance.^[18] However, due to the limitation of synthetic approaches and the immaturity of atomic-scale control technology, it is difficult to engineer the targeted SACs and adjustable structure.^[19] Besides, difficulties in judging the accurate coordination environment and active sites is not conducive to rationalize structure and performance relationship.^[6] Moreover, isolated metal atoms tend to aggregate during hightemperature treatment. The challenge is

posed on synthesizing high load (>10 wt%) SA electrocatalysts with large-scale production.^[8,19] Therefore, the necessary break-through in SAC-based electrocatalysis is controlling the coordination chemistry of metal single atoms, especially with high metal loading, and in-depth insight into the structure–property relationships.^[20,21]

The electrocatalytic NRR is a sustainable alternative to the energy-intensive Haber-Bosch ammonia production process.^[22] The kinetic dilemma of NRR is derived from the antagonistic relationship between N2 activation and NHx intermediates (x = 0 to 2) transformation. According to previous theoretical investigations, in a series of pure metal catalysts, the W atoms have high NRR activity and selectivity for N₂ fixation.^[10,23] Chen et al. theoretically studied a series of single metal atoms on g-C₃N₄ substrate and found that W@C₃N₄ exhibit the outstanding NRR catalytic activity with a low limiting potential, and can well suppress the competing HER.^[24] Du et al. reported that the excellent NRR catalytic activity of W atoms anchored on N-doped graphene is derived from the inherent properties of W atoms, such as significant positive charge, large spin moment, moderate binding energy strength of NRR intermediates.^[23] However, W atom catalysts can strongly activate N₂, but impede the conversion of NH_x intermediates. ^[10] To the best of our knowledge, there have been no reports to experimentally investigate the application of single-atom W in the NRR. So, much effort should be made to identify the active sites and overcome the scaling relationship by exploring diverse coordination structures of single-atom W. The introduction of O





coordination weakens the W–N bond strength, thereby optimizing the binding energy of the adsorbed intermediate, and reconciles the contradictory relationship between N_2 activation and intermediate transformation.

In this work, we successfully prepared a new kind of W SACs using Na_2WO_4 containing oxygen-bridged [WO₄] tetrahedra^[25] as the metal source by the combination of coordination polymer strategy and self-templating method. Melamine– formaldehyde resin (MFR) is used to adsorb metal ions to fabricate W atomically dispersed coordination polymer, which was subsequently assembled with a graphene oxide (GO) matrix via intermolecular interactions. Due to the combined resinchelating and self-templating method, the metal loading can be higher than 10 wt%. The W-NO/NC configuration of O,Ncoordinated W single atoms is distinct from the reported M–N configuration reported by traditional methods. the source of metal in the catalyst which can introduce metal– O sites and inhibit agglomeration of metal atoms during the pyrolysis process. Due to its many secondary and tertiary amine groups that can effectively chelate a large amount of metal ions (Figure S1, Supporting Information),^[26] the MFR is selected to coordinate with W precursors to form a coordination polymer named as W-MFR. The obtained W-coordinated polymer was subsequently assembled with graphene oxide (GO) template via intermolecular interactions,^[27] and then underwent carbonization at 600 °C for 2 h under vacuum to afford the final highloading W single atoms coordinated by N/O and supported on nitrogen-doped carbon (denoted as W-NO/NC).

As exhibited in Raman spectra (Figure S2, Supporting Information), the I_D/I_G value increased from 1.13 for NC to 1.26 for W-NO/NC, which indicates that the incorporation of W atoms can arouse more intrinsic disorders in W-NO/NC. Furthermore, the Brunauer–Emmett–Teller surface areas of W-NO/NC and NC are 126 and 76 m² g⁻¹, respectively (Figure S3a,c, Supporting Information), and the main pore size is centered at about 3.5 nm (Figure S3b,d, Supporting Information). These results suggest that W atoms can effectively inhibit the agglomeration between graphene sheets and MFR, and generate a considerable amount of voids, which provide abundant

2. Results and Discussions

Synthesis of the high-loading W SACs is illustrated in **Figure 1**a (see details in the Supporting Information). Specifically, oxygen-containing metal salts with separated units are used as



Figure 1. a) Illustration of the formation of W-NO/NC. b) TEM image. c,d) Aberration-corrected HAADF-STEM images. e) HAADF-STEM image and the corresponding EDX element mappings showing the distribution of C (red), O (blue), N (green), and W (yellow). Scale bars: b) 25 nm; c) 5 nm; d) 2 nm.





coordination sites for the uniform distribution of W single atoms. The X-ray diffraction (XRD) patterns (Figure S4, Supporting Information) of W-NO/NC and NC both indicate two broad diffraction peaks attributable to the (002) and (101) planes of graphitic carbon. Notably, no diffraction peaks corresponding to metallic W or its oxide crystal structures can be detected. As can be seen from transmission electron microscopy (TEM; Figure 1b; Figure S5, Supporting Information), the W-NO/NC shows only some wrinkled graphene nanosheets and no nanoparticles are found in the selected detection range. High-angle annular dark-field scanning TEM (HAADF-STEM) was applied to investigate the existence forms of W atoms. Numerous bright dots could be distinctly observed from the aberration-corrected HAADF-STEM image with atomic resolution in Figure 1c,d, indicating isolated tungsten atoms. The representative energydispersive X-ray spectrum (EDX) elemental mappings of the W-NO/NC sample in Figure 1e further confirm the uniform

spatial distribution of W atoms over the entire substrate along with N, C, and O, coinciding with the X-ray photoelectron spectroscopy (XPS) results (Figure S6, Supporting Information). The W content was about 10.2 wt% as determined by inductively coupled plasma mass spectrometry (ICP-MS).

To further reveal the electronic structure evolution and the local coordination chemistry of W-NO/NC, High-resolution XPS and X-ray absorption fine structure (XAFS) analyses were carried out. As shown in **Figure 2**a, the W 4f XPS spectrum of W-NO/NC exhibits two peaks at 35.4 and 37.5 eV ascribed to the W 4f_{5/2} and W 4f_{7/2}.^[28] For comparison, W-N/NG sample was synthesized via the similar preparation method except using a metal-cation salt (WCl₆) as the metal source (Figures S7–S9, Supporting Information). The above two bands of W 4f have some shift toward high binding energy in W-NO/NC compared to W-N/NC, representing the higher oxidation state of W atoms in W-NO/NC (Figure S10a, Supporting Information). The subtle



Figure 2. a-c) High-resolution W 4f (a), O 1s (b), and N 1s (c) XPS spectra of W-NO/NC and NC. d) XANES and e) k^3 -weighted FT-EXAFS curves of the W-NO/NC at W L₃-edge; f) WT-EXAFS of the W-NO/NC and the references; and g) k^3 -weighted FT-EXAFS fitting curves of the W-NO/NC at W L₃-edge. h) Atomic structure model of the W-NO/NC.

displacement reflects the altering of local electronic structure for W-NO/NC system. It is notable that in the high-resolution O 1s spectrum of W-NO/NC, an obvious peak corresponding to W-O bond is observed,^[25] which is not found in NC and W-N/NC (Figure 2b and Figure S10b, Supporting Information). Obviously, the metal atoms in W-N/NC are anchored in NC by N atoms, while the W atoms in W-NO/NC has two coordinations: W–O and W–N. Usually, the metal atoms are dispersed on N-doped carbon substrate in form of metal-N-C. Tungsten oxides tend to be converted into the corresponding nitrides in NH₃ atmosphere at high temperature.^[29] As is well known, with regard to the tungstate member, the structure of isolated tungsten oxide remains extremely unstable; then the weaker W-O bonds cannot well survive during the high temperature pyrolysis compared with W-N bonds (Figure S11, Supporting Information).^[25,30] The single W atoms were partially reduced by the generated ammonia during the pyrolysis of W-MFR precursor and lost the binding O atoms.^[31] W-NO/NC shows a negligible difference in the XPS spectra of N and C from those of the NC sample (Figure 2c and Figure S12, Supporting Information), indicating the introduction of metal barely affects the status of those elements.

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In Figure 2d, the XANES spectrum of W L3-edge revealed that the white-line intensity of the W-NO/NC is situated between those of W foil and WO₂, indicating a cationic environment. The peak around 10,210 eV is due to the electronic transition from 2p_{3/2} to unoccupied 5d orbital.^[32,33] More detailed local coordination chemistry on W sites in W-NO/NC can be obtained from extended XAFS (EXAFS) analysis. As displayed in the FT-EXAFS spectra of W L₃-edge (Figure 2e), W-NO/ NC possessed only one sharp peak located at 1.31 Å assigned to the W-O/N coordination. Additionally, no W-W peak can be detected for W-NO/NC, confirming the atomic dispersion of single W sites, in line with the STEM observation. Wavelet transform (WT) EXAFS was further conducted because of the high sensitivity in both k and R ranges. The WT contour plots of W-NO/NC exhibited one intensity peak at 5.2 Å⁻¹, which is close to that in WO3 and the signals derived from W-W contribution are invisible (Figure 2f). Therefore, the W species in W-NO/NC were confirmed to be isolated atomically distributed. EXAFS fittings (Figure 2g, Figures S13 and S14, Supporting Information) and the fitted parameters (Table S1, Supporting Information) display that the isolated W atoms were coordinated with two O atoms and two N atoms (Figure 2h). The average bond lengths for W-N and W-O were 1.86 and 1.77 Å, respectively. Here, it should be noted that the EXAFS analysis obtained is the average coordination result. Other WN_xO_y with slightly different coordination exists in the material inevitably, due to the existence of disorder, edge and in-plane sites.

To reveal the relationship between NRR activity and local coordination structure, we evaluate these two structures of single-atom W sites from density functional theory (DFT) calculations. The bond lengths of the N₂ molecules adsorbed on W-N₂O₂ and W-N₄ are prolonged from 1.120 Å (molecular N₂) to 1.158 and 1.151 Å (**Figure 3**a). The Bard charge analysis exhibits that more electrons are transferred from W in W-N₂O₂ (0.50 e) to adsorbed N₂ molecules than W in W-N₄ (0.47 e), while losing fewer electrons than W in W-N₄ (Figure 3b). The corresponding charge density difference shows that the coordination atom O

in W-N₂O₂ with greater electronegativity enhances the localization around of W (Figure 3c). However, for W-N₄, the negative charge is shared by the coordinated nitrogen atoms, thus impeding charge occupy the anti-bounding orbitals of N₂ molecule. Therefore, W atom in W-N₂O₂ is more conducive to polarization and activation of N₂ molecules, and facilitate to trigger the subsequent reduction reactions by a proton.

We then calculated catalyzed NRR pathways on W-N2O2 and W-N₄ models (Figures S15 and S16, Supporting Information). The distal pathway would be more favorable because of higher energy barriers (1.59 eV) of the alternative pathway (Figure S17, Supporting Information). Therefore, we focus on the distal pathway of W SAC (Figure 3d,e). Notably, since the free energy level of *NNH is low, the first protonation step is not the potential determination step (PDS) of W SAC. Instead, the last hydrogenation step (*NH₂ + H⁺ + $e^- \rightarrow NH_3(g)$) becomes PDS, which is consistent with previous theoretical studies for W SAC.^[10,23,24] Compared to $W-N_4$ (1.32 eV), $W-N_2O_2$ showed the lower ΔG_{*NH_2} (1.11 eV). It should be noted that though the desorption of *NH3 is endothermic, the protonation of *NH₃ would form NH₄⁺ in solution, which is expected to be a favorable step.^[34] The HER is the major challenge for the NRR, which can seriously reduce the Faradaic efficiency (FE) of NRR. The difference between the limiting potentials for NRR and HER is a descriptor for assessing the catalytic selectivity of W SAC (Figure 3f). Compared with W-N₄, although the $U_{\rm L}$ (HER) of W-N₂O₂ is slightly smaller (Figure S18, Supporting Information), it has more positive $[U_L(NRR) - U_I(HER)]$ values, which demonstrate the higher selectivity toward NRR. The projected density of states (PDOS) show that the 2π orbital near the Fermi level of the N₂ molecule is strongly split and obvious overlap with the W d orbital (Figures S19 and S20, Supporting Information). The powerful $d-2\pi^*$ coupling can activate the N₂ molecule to be of radical nature, which is active for hydrogenation. The nature of bonding between W and N can be further understood by projected crystal orbital Hamilton populations (pCOHP) analyses (Figure 3g,h). The bonding orbitals of W-N in W-N2O2 (ICOHP: -5.31) are less occupied than in W-N4 (ICOHP: -5.89), indicating that the interaction between N and W is weaker in W-N₂O₂. Therefore, W-N₂O₂ has weaker adsorption of *N intermediates (Figure 3i), which is more conducive to the release of the second ammonia molecule than W-N₄. These further confirmed that the introduction of O coordination can enhance the activity and selectivity on the W active site.

Electrochemical measurements of W-NO/NC were conducted in 0.5 \mbox{M} LiClO₄ by a H-type two-compartment cell. Before each NRR test, the feeder gas purification system was employed to purify the N₂ (¹⁴N₂ or ¹⁵N₂) and Ar gas to eliminate the interference of impurities. All experiments were carried out in strict accordance with the recommended protocol.^[35] The controlled experiments and isotope measurements were performed to ensure that the N source originates. The yielded NH₃ and possible by-product (N₂H₄) were detected by the indophenol blue method and Watt–Chrisp method.^[36,37] The corresponding calibration curves are shown in Figures S21–S23 (Supporting Information). The current density of the LSV curve under N₂ is higher than under Ar, indicating that W-NO/NC are active for NRR catalysis (**Figure 4a**). Figure S24 (Supporting Information) shows time-dependent current density curves of www.advancedsciencenews.com

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Figure 3. a) Adsorption configuration of an N₂ molecule on W-N₂O₂ and W-N₄ and b) corresponding Bader charge analysis and c) charge density differences (cyan represents holes and yellow represents electrons). d,e) Free energy diagrams of W-N₂O₂(d) and W-N₄ (e). f) Liming potential (U_L) versus [U_L (NRR)– U_L (HER)] of W-N₂O₂ and W-N₄, in which the red dashed line indicates the corresponding value of the metal-based benchmark. g,h) Projected density of states (PDOS) and projected crystal orbital Hamilton populations (COHP) of W-N₂O₂(g) and W-N₄ (h). i) Illustration of the correlation between integrated COHP (ICOHP) and the $\Delta G_{\pi N}$.

W-NO/NC at various potentials for 2 h. Related UV–vis absorption spectra of the electrolytes are shown in Figures S25 and S26 (Supporting Information), suggesting NRR process occurs at potential ranges from -0.60 to -0.85 V. The corresponding NH₃ yields and Faradaic efficiency (FE) under these potentials are plotted in Figure 4b. As observed, W-NO/NC offers a maximum NH₃ yield of 12.62 µg h⁻¹ mg⁻¹_{cat} and a highest FE of 8.35% at -0.70 V, superior to some single–atom catalysts (Table S3, Supporting Information) and reported NRR electrocatalysts in aqueous electrolytes (Table S4, Supporting Information). Furthermore, W-NO/NC exhibited a far higher selectivity and NH₃ yield than that of W-N/NC and NC, indicating that metal sites with N and O coordination are the main source of

activity (Figure 4c). Of note, NH₃ is the only product without the presence of N₂H₄ in the final product (Figure S27, Supporting Information), implying W-NO/NC has excellent selectivity for NRR.^[38] Additionally, the isotope-labeling experiments were carried out, and ¹⁵NH₄⁺ with the characteristic double peaks was detectable in ¹⁵N₂-saturated electrolyte (Figure 4d). These results confirm that the detected NH₃ was really produced from the electrochemical reduction of N₂, rather than from NH₃ or NO₃⁻ contaminants. We also examined the stability of W-NO/NC, NH₃ yields and FEs remained essentially stable during recycling tests for five times (Figure 4e). The 24 h electrochemical stability test of W-NO/NC at –0.70 V shows only a slight decrease in current density (Figure S28, Supporting ADVANCED SCIENCE NEWS _____





Figure 4. a) LSV curves of W-NO/NC in Ar- and N₂-saturated 0.5 \times LiClO₄ with a scan rate of 2 mV s⁻¹. b) Corresponding NH₃ yields and FEs for W-NO/NC at all potentials. c) Amount of NH₃ generated over W-NO/NC, W-N/NC, and NC at -0.70 V. d) ¹H NMR spectra of both ¹⁴NH₄⁺ and ¹⁵NH₄⁺ produced from the NRR tests using ¹⁴N₂ or ¹⁵N₂ as N₂ source. e) NH₃ yields and FEs at -0.70 V during recycling test for five times. f) NH₃ yields and FEs at -0.70 V for 2 h over initial and post-NRR W-NO/NC subjected to 24 h operation.

Information). After 24 h of stability test of W-NO/NC, it was found that the yield of NH₃ and FE did not decrease significantly (Figure 4f). Importantly, the control experiments were performed in N₂-saturated solution under open-circuit potential and Ar-saturated solution at -0.70 V; no NH₃ was detected (Figure S29, Supporting Information). In the NRR alternating cycles test, NH₃ is only generated in the N₂-saturated solution (Figure S30, Supporting Information).

3. Conclusion

We report here a new kind of W SACs with a unique O,N coordination for elevating the NRR activity and depressing the HER activity simultaneously. A high metal loading more than 10 wt% was achieved due to the combined resin-chelating and self-template method. The isolation and local environment were identified by HAADF-STEM and EXAFS characterizations at the atomic level. The combination of electrochemical tests and theoretical calculations confirm the W single atoms were the activity origin of the highly NRR activity, and reveal the critical role of the specific local coordination to influence the adsorption behavior and reaction selectivity. This work potentially offers a versatile synthesis approach for well-defined and high-metal-loading SACs, and systematically investigates the influence of local coordination environments on electrocatalytic activity and selectivity.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

coordination chemistry, high loading, nitrogen reduction reaction, single-atom catalysts, single tungsten atoms

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