

# Electrochemical activation of C–H by electron-deficient W<sub>2</sub>C nanocrystals for simultaneous alkoxylation and hydrogen evolution

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## Article

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# Abstract

Activation of C – H bonds is maybe the central challenge in organic chemistry and usually the key step for the retro-synthesis of functional natural products and medicines from abundant hydrocarbons due to the high chemical stability of C – H bonds. Electrochemical methods are now recognized as a powerful alternative for C – H activation, but this approach usually requires high overpotential and homogeneous mediators. Here, we designed electron-deficient  $W_2C$  nanocrystal-based electrodes to boost the heterogeneous activation of C – H bonds under mild conditions via an additive-free, purely heterogeneous electrocatalytic strategy. The electron density of  $W_2C$  nanocrystals was tuned by constructing Schottky heterojunctions with nitrogen-doped carbon support to facilitate the preadsorption and activation of benzylic C – H bonds of ethylbenzene on the  $W_2C$  surface, enabling a high turnover frequency ( $18.8 \text{ h}^{-1}$ ) at a comparably low work potential (2 V versus SCE). The pronounced electron deficiency of the  $W_2C$  nanocatalysts substantially facilitates the direct deprotonation process to ensure long-term electrode durability without self-oxidation. The efficient oxidation process also boosts the balancing hydrogen production from as-formed protons on the cathode by a factor of 10 compared to an inert reference electrode. The whole process meets the requirements of atomic economy and electric energy utilization in terms of sustainable chemical synthesis.

## Introduction

Direct activation of C–H bonds via selective oxidation of *hydrocarbons* is of great interest for organic hydrocarbons<sup>1,2</sup>. As a typical and important transformation path of C–H bonds, selective dehydrogenation of C–H bonds has been widely used for the production of high value-added compounds such as alcohols, and ketones and ethers<sup>3-5</sup>. However, the chemical stability of C–H bonds without activating neighborhood effects makes C–H activation quite challenging, and either extreme and rather toxic oxidants as chromium or selenium compounds or noble-metal-catalysts (based on rhodium or palladium) at high temperatures have to be applied to obtain acceptable conversions<sup>6-8</sup>. Moreover, the as-formed side product water from the cleavage of C–H bonds via oxydehydrogenation is free of value. As a result, novel and sustainable strategies are highly desirable to further decrease the economic and environmental footprints of C–H activation processes.

Electrochemical transformation is recognized as an environmentally friendly method for the production of various functional molecules driven by electricity under mild conditions<sup>9-11</sup>. Pioneering works of electrochemical synthesis using homogeneous catalysts have demonstrated the advantages of this technique for C–H activation<sup>11</sup>, which includes selective oxidation<sup>12</sup>, amination<sup>13</sup>, epoxidation<sup>14</sup> and dehydrogenative coupling reactions<sup>15</sup>. Most of these reactions have high atom economy and excellent compatibility with flow reactors for continuous synthesis<sup>16,17</sup>. The current strategies to boost the transformation of specific substrates mainly rely on the involvement of functional additives<sup>11</sup> (e.g., organic ligands, bases and mediators), a high work potential and/or sacrificial transition metal electrodes<sup>18</sup>, which all will severely limit real-industry applications. Principally, the preparation of cost-

effective and active electrode materials is at least as important as the development of a new methodology for selective C–H bonds activation<sup>19-26</sup>, and only non-targeted, commercial first generation electrodes (such as carbon rod, platinum and reticulated vitreous carbon) are applied as the current collectors in electrochemical organic synthesis at the moment. The significant progress reported using well-designed reaction-specified electrodes in improving the catalytic activity for water splitting, nitrogen reduction reactions and even carbon dioxide reduction reactions<sup>27-30</sup> further manifests the huge gap between the design of novel electrode materials and the requirements of sustainable electrochemical organic synthesis.

Herein, we present the proof-of-concept application of electron-deficient  $W_2C$  nanocrystal-based electrodes for the highly efficient electrochemical activation of C–H bonds, highlighting the key importance of the modified physicochemical properties of electrode materials in boosting additive-free C–H activation reactions. A nanoheterojunction composed of  $W_2C$  nanocrystals and nitrogen-doped carbons has been rationally designed to control the number of electrons flowing from  $W_2C$  nanocrystals to nitrogen-doped carbons by increasing the doping concentration in the carbon supports to enhance the interfacial Schottky effect. The as-formed electron-deficient  $W_2C$  nanocrystal-based electrode acts as a functional anode to simultaneously facilitate the alkoxylation of ethylbenzene with methanol on the anode and the balancing hydrogen evolution reaction on the cathode. Both the experimental and theoretical results indicate the key role of the electron deficiency of the  $W_2C$  nanocrystals in capturing ethylbenzene on the anode to substantially increase the reaction rates of alkoxylation and hydrogen evolution reaction processes simultaneously and ensure the long-term stability of the anode without scarifying the current collector.

The  $W_2C/NC$  catalysts were prepared via a modified nanoconfinement method (Supplementary Fig. 1) from a mixture of dicyandiamide and ammonium tungstate, followed by  $N_2$ -protected thermal pyrolysis at high temperatures. The nitrogen contents (x at.%) of the  $W_2C/N_xC$  samples could be tuned from 3.0 via 2.3 to 1.4 at.% (Supplementary Fig. 2 and Table 1) by elevating the condensation temperatures from 1000 to 1200 °C (for experimental details please see the experimental section). The morphology (Supplementary Fig. 3), surface area (Supplementary Fig. 4) and W content (Supplementary Table 1) of  $W_2C/N_xC$  samples are well maintained, as reflected by their scanning electron microscopy (SEM) images. Transmission electron microscopy (TEM) observations (Fig. 1a-c and Supplementary Fig. 5-7) further reveal the presence of few-layer-graphene-supported  $W_2C$  nanocrystals with a mean size of 2.5 nm (Fig. 1a and Supplementary Fig. 8) and a typical lattice fringe of 0.24 nm (Fig. 1b), which corresponds to the (002) plane of  $\alpha$ - $W_2C$ <sup>31,32</sup>. The formation of  $W_2C$  is doubly confirmed by its X-ray diffraction (XRD) pattern (Supplementary Fig. 9), matching well with that of typical  $\alpha$ - $W_2C$  (JCPDS# 35-776)<sup>31</sup>. Detailed elemental mapping images (Fig. 1c) exhibit nanometer-sized W-rich areas with a homogeneous distribution of N atoms along with the whole carbon support, indicating an integrated structure of  $W_2C$  nanocrystals on the nitrogen-doped carbons.

The highly coupled structure of  $W_2C/NC$  dyads makes it possible to form a rectifying interface for modulation of the electron density of  $W_2C$  nanocrystals. The density functional theory (DFT) calculation results (Supplementary Fig. 10,11) predict electron transfer from  $W_2C$  to nitrogen-doped carbons, resulting in more pronounced electron-deficient regions in  $W_2C$  nanocrystals suggested by the charge density difference (CDD) stereograms (Fig. 1d) of the same  $W_2C$  model supported on pristine carbons ( $W_2C/C$ ). The mean number of electrons transferred from the  $W_2C$  nanocrystal to the nitrogen-doped carbon support (Fig. 1e) increases from 0.338 to 0.397 as more nitrogen atoms (from 1.4 to 3.0 at.%) are doped into the carbon support models (Supplementary Fig. 12), which were constructed based on the X-ray photoelectron spectroscopy (XPS) analysis results<sup>33</sup>. As depicted in Fig. 1f, the nanoheterojunction of  $W_2C$  and NC has a rectifying contact, with electrons flowing from the  $W_2C$  side with a lower Fermi level ( $E_F$ ) to the NC side, generating electron-deficient  $W_2C$  due to the interfacial Schottky barrier<sup>34,35</sup>. Indeed, the electron donation from the  $W_2C$  nanocrystals to the nitrogen-rich carbon supports is experimentally confirmed by the gradual shift in W 4f XPS peaks to higher energy (Fig. 1g) from 34.2 via 34.4 to 34.5 eV for  $W_2C/N_{1.4}C$ ,  $W_2C/N_{2.3}C$  and  $W_2C/N_{3.0}C$ , respectively, resulting in gradually increased work functions (Fig. 1h and Supplementary Fig. 13) from 5.4 via 5.6 to 5.7 eV. A similar trend for the electron density of  $W_2C$  nanocrystals in  $W_2C/N_xC$  samples is also demonstrated by the most positive W M4,5 peak (Supplementary Fig. 14) of the  $W_2C/N_{3.0}C$  materials among all samples<sup>36</sup>. All of the above results indicate the formation of electron-deficient  $W_2C$  nanocrystals and the successful further enhancement of electron deficiencies by increasing the nitrogen contents in the carbon supports.

Inspired by the success in modifying the electron density of  $W_2C$  nanocrystals, we further evaluated the possible catalytic activity of  $W_2C/N_xC$  catalysts for electrochemical alkoxylation of ethylbenzene with methanol under mild conditions as a model reaction. Considering that the reported methods for alkoxylation of C–H bonds usually require highly active additives/oxidants and/or a high reaction temperature, we initially tested the possibility of additive-free alkoxylation of ethylbenzene with methanol using only a simple electrolyte containing lithium perchlorate and  $W_2C/N_xC$ -based electrodes under ambient conditions (Fig. 2 and Supplementary Fig. 15). No product was detected without applying a working potential for various electrodes in our electrochemical system (Supplementary Fig. 16), illustrating that the methoxylation reaction cannot proceed spontaneously. Surprisingly, a complete conversion of ethylbenzene can be achieved on the  $W_2C/N_{3.0}C$  electrode with high selectivity to the target product (1-methoxyethyl)benzene (Fig. 2a,b and Supplementary Fig. 17) and a total carbon balance of approximately 95%, confirming the possibility of highly efficient alkoxylation of C–H bonds on a well-designed heterogeneous electrode without sacrificing additives. The fact that control electrodes with the same amount of bare NC sample,  $W_2C$  catalyst or a mechanical mixture of the two components (Fig. 2e) give much lower conversions of ethylbenzene than the  $W_2C/N_{3.0}C$  electrode under fixed conditions further indicates a synergistic effect between  $W_2C$  and  $N_{3.0}C$  components in facilitating the transformation of ethylbenzene.

Unlike the oxidative alkoxylation reaction of C–H bonds by using various oxidants for dehydrogenation to generate water<sup>37</sup>, our heterogeneous electrochemical system could achieve the full use of as-formed protons from the activation of C–H bonds and methanol for subsequent hydrogen evolution reactions, generating hydrogen gas bubbles on the cathode (Supplementary Fig. 18). Moreover, the calculated Faradaic efficiencies (Fig. 2d and Supplementary Fig. 19) are similar for the conversion of ethylbenzene to (1-methoxyethyl)benzene on the  $W_2C/N_{3.0}C$  anode ( $F_E$ : 42-46%) and hydrogen production on the Ti cathode ( $F_E$ : 42-55%), implying a cascade transformation of protons generated from the anode into hydrogen gas on the cathode. Even with an excess amount of methanol in the reactor, only a trace amount of formaldehyde (0.006 mmol) formed during the conversion of 0.5 mmol of ethylbenzene (Supplementary Fig. 20), well explaining the comparable Faradaic efficiencies for the reactions on anode and cathode without the obvious contribution of methanol dehydrogenation to the total  $F_E$  for hydrogen evolution reactions. Remarkably, the electron-deficient  $W_2C$  in the  $W_2C/N_{3.0}C$ -based electrode substantially promotes the hydrogen evolution rate on the Ti cathode to 880  $\mu\text{mol}$  (Fig. 2c), which is above 10 times that on the same Ti cathode (85  $\mu\text{mol}$ ) when using bare carbon cloth as the anode. The constant current density of the  $W_2C/N_{3.0}C$  anode under fixed conditions with different cathodes (Fig. 2f), including Pt mesh, Ti mesh and carbon rod, further demonstrates that the activation and deprotonation of ethylbenzene on the  $W_2C/N_{3.0}C$  electrode is the rate dominating step for the whole reaction. Indeed, the alkoxylation reaction could be selectively quenched by butylated hydroxytoluene (BHT) (Supplementary Fig. 21), indicating a radical-based pathway on the  $W_2C/N_{3.0}C$  anode, as indicated in Fig. 2a<sup>18</sup>.

The role of the electron-deficient  $W_2C$  nanocrystals and the interfacial effect of the heterojunction catalysts on the electrochemical alkoxylation of C–H bonds were simulated via theoretical calculations and then validated by experimental evidence (Fig. 3). The optimized geometry (Fig. 3a,c) of ethylbenzene presents preferred adsorption of benzylic C–H bonds on the  $W_2C$  surface dependent of the electron-deficiency of  $W_2C$ , indicating the feature role of  $W_2C$  as an active component. This role was further validated by more negative onset potentials (<1.4 V versus SCE) for the electrochemical alkoxylation reaction on  $W_2C/N_xC$  anodes than that (>1.6 V versus SCE) of the bare carbon cloth electrode (Supplementary Fig. 22). However, the polarization of adsorbed C–H bonds is enhanced by the electron-deficient surface of the  $W_2C-0.08e^-$  model, as reflected by the more pronounced electron density difference (Hirshfeld charge) of the preadsorbed C–H bonds (Fig. 3c and Supplementary Fig. 23) and a much lower calculated adsorption energy for ethylbenzene (Fig. 3e). Such strong adsorption of ethylbenzene molecules over the electron-deficient  $W_2C$  surface was then experimentally validated by the temperature-programmed desorption (TPD) analysis results (Fig. 3f), exhibiting gradually elevated adsorption capacities over those of more electron-deficient  $W_2C/N_xC$  samples with similar surface areas. It should be noted that the bare carbon support (NC sample in Fig. 3f) provides a low adsorption capacity, only 21% of the best-in-class  $W_2C/N_{3.0}C$  sample (Supplementary Fig. 24). More importantly, the electron deficiency-induced adsorption behavior of ethylbenzene on the final  $W_2C/N_xC$ -based anodes under a fixed bias in the electrochemical reactor was well expressed with the same trend in adsorption capacities (Fig. 3g) as that revealed by TPD results, making successive C–H dissociation process more favorable.

Indeed, the stronger interaction between preadsorbed ethylbenzene molecules and electron-deficient  $W_2C$  significantly reduces the Gibbs free energy of each step of the whole alkoxylation reaction pathway (Fig. 3e). The dissociation of C–H bonds of ethylbenzene on the electron-deficient  $W_2C$  catalyst ( $W_2C-0.08e^-$  model) is the rate-limiting step with a free energy change of only 0.34 eV, and the subsequent coupling of  $*C_8H_9$  and  $*CH_3O^*$  ( $*C_8H_9^* + *CH_3O^*$ ) and desorption of as-formed (1-methoxyethyl)benzene ( $*C_9H_{12}O$ ) proceed automatically. With similar configurations, the last three steps for the catalytic conversion of preadsorbed ethylbenzene molecules on the pristine  $W_2C$  catalyst ( $W_2C$  model) are thermodynamically uphill with a larger free energy change of 0.4 eV for the ( $*C_8H_9^* + *CH_3O^*$ ) step, again indicating the key role of electron density in facilitating the whole reaction and desorption processes on the  $W_2C$  surface. This electron-deficiency-dependent promotion effect on the activity of  $W_2C$  was then unambiguously confirmed by the gradually increased catalytic activities (Fig. 3h) and  $F_E$  values (Fig. 3i) for producing (1-methoxyethyl)benzene on more electron-deficient  $W_2C/N_xC$ -based anodes under fixed work potential.

The  $W_2C/N_{3.0}C$  anode also shows excellent electrochemical stability for long-term use. The composition (Supplementary Fig. 25) and morphology (Supplementary Fig. 26) of the used  $W_2C/N_{3.0}C$  materials were maintained well. Most importantly, the  $W_2C/N_{3.0}C$  anode can be recycled at least four times without an obvious decrease in  $F_E$  (41-46%) (Fig. 4b and Supplementary Fig. 27). It should be noted that inert metal anodes for alkoxylation of ethylbenzene, including stable metals (exemplified by Ti mesh) and active metals (exemplified by Ni plate), decompose rapidly within 5 h (Fig. 4a and Supplementary Fig. 28), illustrating the key importance of the high activity of the  $W_2C/N_{3.0}C$  anode to keep itself from corroding. As a durable anode, the electron-deficient  $W_2C$  electrode exhibits satisfying activity for electrochemical alkoxylation of various aromatic C–H bonds using a series of aliphatic alcohols (Supplementary Table 2) with good to high conversions and high selectivity in 18 h, suggesting an excellent tolerance of our electrode material to various functional groups. As the best-in-class anode in this work, the  $W_2C/N_{3.0}C$  electrode provides a high turnover frequency (TOF) value of  $18.8 h^{-1}$ , which is comparable to or even higher than the reported values, mostly of homogeneous catalysts, for similar alkoxylation reactions (Fig. 4c and Supplementary Table 3-5)<sup>38,39</sup>.

In summary, we have demonstrated the key role of electron-deficient  $W_2C$  nanocrystals as electrode materials in boosting the activity and durability for electrochemical activation of C–H bonds via a heterogeneous pathway. We successfully tuned the electron density of  $W_2C$  nanocrystals by constructing Schottky heterojunctions with nitrogen-doped carbons to achieve preferred adsorption of benzylic C–H bonds of ethylbenzene on the  $W_2C$  surface and facilitate subsequent C–H activation, which is the rate-limiting step. Unlike conventional oxidative alkoxylation to generate water, the as-formed protons on the  $W_2C$  anode could be simultaneously converted to hydrogen gas in our additive-free electrochemical

reactor under mild conditions. This two-birds-with-one-stone strategy illustrates the significant potential of powerful designer electrode materials to substantially increase catalytic efficiency, atomic economy and electricity utilization for organic electrosynthesis and hydrogen energy production in one electrocatalytic system. In addition to the hydrogen evolution reaction, the reduction process might be compatible with other important reactions (e.g. carbon dioxide reduction reaction or  $N_2/NO_x$  reduction reactions) to create novel or more complex cascade reaction pathways for the production of high value-added compounds from abundant hydrocarbons and even waste gases. This work may also boost the development of zero-additive and zero-emission electrosynthesis systems through the design of novel electrode materials.

## Methods

**Synthesis of  $W_2C/N_xC$ :** All chemicals were analytical grade and used as received without further purification. A homogenous mixed solution including  $(NH_4)_6H_2W_{12}O_{40} \cdot nH_2O$  (0.75 g), DCDA (15 g) and deionized water (150 mL) was heating at 80 °C, and the mixed solution was evaporated at a constant temperature with stirring. The obtained mixture after evaporating water was transferred into a cylindrical crucible with lid, and heated at 1000, 1100 and 1200 °C for 2 h with a heat rate of 2.5 °C  $min^{-1}$  under high purity nitrogen atmosphere. The final products after cooling down to room temperature were named  $W_2C/N_xC$  (x represents the nitrogen contents) and used for further experiments and characterizations.

The control group of nitrogen-doped carbon (NC) was prepared with the same procedure as  $W_2C/N_xC$  without metal precursor. And  $W_2C$  and NC mixture was obtained by mixing  $W_2C$  powder and NC mechanically.

**Materials Characterization:** Powder X-ray diffraction patterns (XRD) was performed using a Bruker D8 Advance X-ray diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$ ) and operated at a scan rate of 6°  $min^{-1}$ . Scanning electron microscopy (SEM) were operated on FEI Nova NanoSEM 450 field emission scanning electron microscope. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) analysis were measured on a JEM-2100F microscope with an acceleration voltage of 200 kV. Temperature programmed desorption (TPD) was carried out on a Micromeritics Autochem II chemisorption analyzer with ethylbenzene probe molecules at 110 °C. Nitrogen adsorption-desorption isotherms were acquired on Quantachrome NOVA-2200e at 77 K. Prior to the measurement, the samples were degassed at 200 °C for 12 h with a gas flow of nitrogen. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) experiments were recorded at a Kratos Axis Ultra DLD spectrometer and ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific), respectively. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurement was conducted on an iCAP6300 spectrometer for tungsten element analysis.

**Electrochemical measurements:** All of the electrochemical experiments were performed in a standard three-electrode system on an electrochemical station (CHI 660E, Shanghai CH Instruments Company).

Working electrodes were composed of catalysts supported by carbon cloth. The catalyst ink was prepared by sonicating and dispersing 5 mg of catalyst into a solution containing 700  $\mu\text{L}$  of ethanol, 350  $\mu\text{L}$  of deionized water and 160  $\mu\text{L}$  of 5% Nafion solution. The working electrodes were prepared by evenly dipping 150  $\mu\text{L}$  of ink onto carbon cloth ( $1 \times 1 \text{ cm}$ ) and dried at  $120 \text{ }^\circ\text{C}$  for 1 h in the oven. Titanium (Ti) mesh with a size of  $1 \times 1 \text{ cm}$  and saturated calomel electrode (SCE) were employed as counter and reference electrode, respectively. The control electrodes with different sample loading were prepared by dipping 50, 100 and 200  $\mu\text{L}$  of ink on carbon cloth, respectively. The electrocatalytic reactions were conducted in 15 mL of methanol with 61  $\mu\text{L}$  of ethylbenzene (0.5 mmol) and 0.106 g of lithium perchlorate (1 mmol) at room temperature in a home-made electrolyzer, in which methanol was not only used as solvent, but also simultaneously used as reactant. The electrocatalytic stability tests of catalyst for the reaction between ethylbenzene and methanol were evaluated using the same reaction potential for four consecutive cycles, and electrodes would have to dry at  $120 \text{ }^\circ\text{C}$  before the next reaction.

Electrode adsorption experiments were conducted in electrolyzer containing 1.5 mmol of ethylbenzene, 15 mL of methanol and 1 mmol of lithium perchlorate with  $\text{W}_2\text{C}/\text{N}_x\text{C}$  anodes, Ti mesh cathode and saturated calomel electrode. To accurately measure the adsorption volume of ethylbenzene before transforming (1-methoxyethyl)benzene, we performed at 2 V versus SCE for 10 min. After the completion of adsorption, the residual volume of ethylbenzene in solution was obtained by extraction and analyzed in gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010SE) with dodecane as internal standard. And the adsorption volume for ethylbenzene on  $\text{W}_2\text{C}/\text{N}_x\text{C}$  ( $C_{\text{ads}}$ ) was calculated using the equation of  $n_{\text{ads}} = n_{\text{ini}} - n_{\text{res}}$  ( $n_{\text{ini}}$  and  $n_{\text{res}}$  represent the initial and residual contents in solution, respectively)<sup>40</sup>.

**Products analysis:** After the reaction, 500  $\mu\text{L}$  of solution was firstly taken from electrolyzer and transferred into an extracted solution containing 500  $\mu\text{L}$  of dichloromethane, 500  $\mu\text{L}$  of deionized water and 0.2  $\mu\text{L}$  of dodecane, and then dried by magnesium sulfate anhydrous. Finally, the extracted solution was analyzed in GCMS to determine the components of products and calculate the conversion and selectivity.

The Faradaic efficiency ( $F_E$ ) was calculated as follow:

$$F_E = \frac{N_i \cdot n \cdot F}{Q}$$

where  $N_i$  is the number of moles for the specific product (mole);  $n$  is the number of electrons exchanged for product formation, which is 2 e in this reaction;  $F$  is the Faradaic constant of  $96487 \text{ C mol}^{-1}$ ;  $Q$  is the passed charge.

Turnover frequency (TOF) was defined by the following equation:

$$TOF = \frac{n}{N \cdot h}$$

where  $n$  is the number of moles for product;  $N$  is the number of moles of active metal sites determined from ICP-AES.

**Theoretical calculation:** The Spin polarization density functional theory (DFT) calculations were performed by the DMol3 program on Materials Studio. The generalized gradient approximation method with Perdew-Burke-Ernzerhof functional (GGA-PBE) was used for describing the exchange-correlation interaction among electrons<sup>41</sup>. The double numerical plus polarization (DNP) basis set was employed, while an accurate DFT semi-core pseudopotentials (DSPP) was adapted to describe the metal atoms<sup>42,43</sup>. The  $6 \times 6 \times 1$  k-points was used for sampling the Brillouin zone. Hexagonal  $W_2C$  (0001) facets were modeled in terms of the slabs of  $5 \times 5$  supercells with  $14.76 \times 14.76 \text{ \AA}$  and  $120^\circ$  and  $W_2C$  cluster model was placed above a  $6 \times 6$  supercell of graphene lattice<sup>44</sup>. The vacuum slab was set as  $20 \text{ \AA}$  to calculate all periodical models. The contents of graphitic N and pyridinic N in the graphene lattice were estimated according to the XPS elements analysis results.

The Gibbs free energy change ( $\Delta G$ ) for each step of ethylbenzene activation was calculated as follows:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S (T = 298.15 \text{ K})$$

where  $\Delta E$ ,  $\Delta ZPE$  and  $\Delta S$  are the changes in the reaction energy, zero-point energy and entropy, respectively.

### Data availability

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

## Declarations

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### Author contributions

X.-H.L. and X.L. designed the experiments. X.L. conducted the preparation of the  $W_2C/N_xC$  catalysts and electrodes and carried out all of the corresponding characterizations and performance tests. X.-H.L. and X.L. co-wrote the original manuscript. X.L. and S.-N.Z. helped to conduct theoretical calculations and results analysis. D.X., J.-J.Z., Y.-X.L., G.-Y.Z., H.S., Z.-H.X. and X.L. helped to conduct the experiments and

characterizations. X.-H.L., J.-S.C. and M.A. oversaw all of the research phases and revised the manuscript. All of the authors discussed the results and commented on the manuscript.

## Competing interests

The authors declare no competing interests.

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