Gold-like activity copper-like selectivity of heteroatomic transition metal carbides for electrocatalytic carbon dioxide reduction reaction

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An overarching challenge of the electrochemical carbon dioxide reduction reaction (eCO₂RR) is finding an earth-abundant, highly active catalyst that selectively produces hydrocarbons at relatively low overpotentials. Here, we report the eCO₂RR performance of two-dimensional transition metal carbide class of materials. Our results indicate a maximum methane (CH₄) current density of −421.63 mA/cm² and a CH₄ faradic efficiency of 82.7% ± 2% for di-tungsten carbide (W₂C) nanoflakes in a hybrid electrolyte of 3 M potassium hydroxide and 2 M choline-chloride. Powered by a triple junction photovoltaic cell, we demonstrate a flow electrolyzer that uses humidified CO₂ to produce CH₄ in a 700-h process under one sun illumination with a CO₂RR energy efficiency of about 62.3% and a solar-to-fuel efficiency of 20.7%. Density functional theory calculations reveal that dissociation of water, chemisorption of CO₂ and cleavage of the C-O bond—the most energy consuming elementary steps in other catalysts such as copper—become nearly spontaneous at the W₂C surface. This results in instantaneous formation of adsorbed CO—an important reaction intermediate—and an unlimited source of protons near the tungsten surface sites that are the main reasons for the observed superior activity, selectivity, and small potential.
The electrocatalytic carbon dioxide reduction reaction (eCO2RR) driven by renewable energy has great potential for the sustainable production of chemicals and fuels at the gigaton scale that can be used any time, any place. It also offers a promising way to store energy in chemical bonds due to having nearly two orders of magnitude higher energy density compared to the most advanced battery technologies. However, reducing CO2 to value-added chemicals is both costly and slow based on intrinsic thermodynamics and kinetics, making the goal of an effective and feasible process a real challenge.

Conventional pure metal catalysts such as gold (Au), palladium (Pd), silver (Ag), and newly developed transition metal dichalcogenides (TMDCs) are known to exhibit high activities for the CO2RR in different electrolytes. Other catalysts such as copper (Cu) and Cu-based catalysts have the ability to reduce CO2 to various chemicals such as methane (CH4), ethylene (C2H4), formic acid (HCOOH), methanol (CH3OH), and ethanol (C2H5OH) as an intermediate product. Other catalysts such as copper (Cu) and Cu-based catalysts have the ability to reduce CO2 to various chemicals such as methane (CH4), ethylene (C2H4), formic acid (HCOOH), methanol (CH3OH), and ethanol (C2H5OH). Despite their good selectivity, these catalysts require high potentials—excess energy—to achieve suitable current densities—reaction rates—impeeding their use for effective production of chemicals and fuels.

Heteroatomic transition metal carbide (TMC) catalysts, also known as MXenes, have recently received great attention for various electrocatalytic reactions due to their unique structural and electronic properties. In particular, M2C (M denotes transition metals) exhibit high activity for the CO2RR of TMCs compared to Cu NPs at different potentials. The TMC NFs i.e., W2C, Mo2C, Nb2C, and V2C were synthesized using a carburization process followed by the liquid exfoliation technique. The electrocatalytic performance of TMC NFs with similar crystallite sizes were then studied in a three-electrode cell and compared with Au and Cu nanoparticles (NPs), conventional catalysts for this reaction, under identical experimental conditions. To improve the CO2RR performance in competing with hydrogen evolution reaction (HER), we have employed a mixture of 3 M potassium hydroxide (KOH) and 2 M choline chloride (CC) solution (KOH:CC 3 M:2 M) as the electrolyte in this study.

The linear sweep voltammetry (LSV) experiments and a real-time product stream analysis show that CO2RR on the W2C surface starts at a potential of ~122.7 mV vs reversible hydrogen electrode (RHE) by producing CO and H2 and reach maximum CO2RR current density (j(CO2RR)) of ~548.9 mA/cm2 at ~1.05 V vs RHE (Supplementary Figs. 2–4 and Fig. 1a). As shown in Fig. 1a, j(CO2RR) of ~421.63 mA/cm2 is obtained for W2C NFs at a potential range of ~0.45 to ~1.05 V vs RHE for W2C, Mo2C, Nb2C, and V2C NFs and a potential range of ~0.55 to ~1.05 V vs RHE for V2C NFs where CH4 is identified as the main product.

Figure 1b illustrates CH4 formation current densities (j(CH4), mA/cm2) of the TMC NFs compared to Cu NPs, a conventional catalyst for hydrocarbon production. The partial current densities of different products (i.e., H2, CO, CH4, C2H4, CH3OH, and C2H5OH) were calculated by multiplying FE and total current densities at different potentials (Supplementary section 3 and Supplementary Fig. 3). As shown in Fig. 1b, a maximum j(CH4) of ~421.63 mA/cm2 is obtained for W2C NFs at a potential of ~1.05 V vs RHE where Nb2C NPs, Mo2C NPs, and V2C NFs show values of ~219.16, ~211.33, and ~147.56 mA/cm2, respectively, at this potential. We also compared the CH4 formation current densities of TMCs compared to Cu NPs at different potentials (E(VRE)) under identical experimental conditions.

Results and discussion

The TMC NPs i.e., W2C, Mo2C, Nb2C, and V2C were synthesized using a carburization process followed by the liquid exfoliation technique. The electrocatalytic performance of TMC NFs with similar crystallite sizes were then studied in a three-electrode cell and compared with Au and Cu nanoparticles (NPs), conventional catalysts for this reaction, under identical experimental conditions. To improve the CO2RR performance in competing with hydrogen evolution reaction (HER), we have employed a mixture of 3 M potassium hydroxide (KOH) and 2 M choline chloride (CC) solution (KOH:CC 3 M:2 M) as the electrolyte in this study.

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formation activity of TMCs i.e., W$_2$C, Nb$_2$C, Mo$_2$C, and V$_2$C NFs with state-of-the-art catalysts in the literature by calculating their maximum CH$_4$ formation current densities ($j_{\text{CH}_4}$) (Supplementary Table 2)\textsuperscript{46,53-54}. Supplementary Table 2b indicates that the $j_{\text{CH}_4}$ of W$_2$C NFs is 3.6 and 4.2 times higher than recently studied La$_2$CuO$_3$ ($\sim$117 mA/cm$^2$ at $-1.4$ V vs RHE)\textsuperscript{33} and Cu–N (\textasciitilde100 mA/cm$^2$ at $-1.0$ V vs RHE)\textsuperscript{48}, respectively. The partial current densities of other hydrocarbon products i.e., C$_2$H$_4$, CH$_2$OH, and C$_2$H$_5$OH are also shown in Supplementary Fig. 3 (Supplementary section 3).

To evaluate the intrinsic activity of W$_2$C NFs, we measured CH$_4$ formation turnover frequency (TOF$_{\text{CH}_4}$) by normalizing its activity to the number of active atoms at the surface using the roughness factor method and compared it with the other catalysts in this study (Supplementary section 5). Our calculations indicate a TOF$_{\text{CH}_4}$ of 10.42 s$^{-1}$ at a potential of $-1.05$ V vs RHE for W$_2$C NFs; by comparison, TOF$_{\text{CH}_4}$ of 4.54, 3.74, and 2.79 s$^{-1}$ were calculated for Mo$_2$C NFs, Nb$_2$C NFs, and V$_2$C NFs, respectively. The calculated TOF$_{\text{CH}_4}$ of W$_2$C NFs at the potential of $-1.05$ V vs RHE is about two orders of magnitude higher than that of Cu NPs for the formed products (i.e., CO, CH$_4$, etc.)\textsuperscript{55}, suggesting a steeper Tafel slopes, and therefore a weaker potential dependence of the TMCs show all Bragg peaks of W$_2$C, Mo$_2$C, Nb$_2$C, and V$_2$C (Supplementary section 2)\textsuperscript{46,48}.

Furthermore, we performed a comparative mechanistic study by calculating Tafel slopes for different products to gain insight about the eCO$_2$RR mechanism of the TMCs i.e., W$_2$C, Mo$_2$C, Nb$_2$C, and V$_2$C NFs in the two-compartment three-electrode electrochemical cell (Supplementary section 6 and Supplementary Fig. 8)\textsuperscript{58}. Our Tafel plot analyses show that the TMC NFs possess steeper Tafel slopes, and therefore a weaker potential dependence compared with Cu NPs for the formed products (i.e., CO, CH$_4$, and C$_2$H$_4$) (Supplementary Fig. 8).\textsuperscript{58} The Tafel plot analyses suggest a different CO$_2$RR mechanism for TMC NFs than that of Cu catalysts where C–O bond scission is the rate-determining step\textsuperscript{58}. To gain more insight to the remarkable performance of these catalysts for electrocatalytic CO$_2$RR, the structural and physicochemical properties of TMC NFs were characterized at molecular and atomic scales by performing X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy (STEM) (Supplementary sections 7–9). At first, we have performed XPS experiments to analyze the surface chemistry of TMC NFs. XPS analysis (Supplementary Fig. 9) indicates that our NF samples contain metallic TMCs, with little or no evident surface oxidation. The results show that the chemical composition of the surface, the empirical formula of M$_2$C (M: transition metal, C: Carbide), and the oxidation state of $+2$ for the transition metals i.e., W, Mo, Nb, and V are similar in all synthesized TMCs (Supplementary section 7). The lattice structure and crystallite size of the TMC NFs were then studied by performing XRD experiments. The XRD pattern of W$_2$C NFs shows a sharp peak at 39.91° along with three pronounced peaks at 34.84°, 38.54°, and 52.65° corresponding to (101), (100), (002), and (102) crystal surfaces of W$_2$C, respectively. The XRD spectra of the TMCs show all Bragg peaks of W$_2$C, Mo$_2$C, Nb$_2$C, and V$_2$C NFs; verifying their homogenous and pure structures. The XRD results indicate a constant dominant lattice plane of (101) and a similar average crystallite size of 25.4 ± 5 nm for all synthesized TMCs (Supplementary Fig. 10)\textsuperscript{59–61}.

Furthermore, we performed atomic-scale STEM experiments to study surface atom coordination, crystallite sizes, and dominant plane structures of TMC NFs (Supplementary Figs. 11–18). Figure 2a–d shows STEM results of W$_2$C NFs. Figure 2a, b indicate high-angle annular dark-field (HAADF) image and corresponding fast Fourier transforms (FFT) of W$_2$C NFs in the <101> zone axis. The atomic models of the <101> zone axis and bright-field (BF) image of W$_2$C NFs are represented in Fig. 2c and d, respectively. Figure 2d indicates the carbon atomic columns in the red box and the intensity profile across the red box region showing that the distance between two carbon atoms is 2.55 Å. The STEM results of other TMCs i.e., Mo$_2$C, Nb$_2$C, and V$_2$C NFs are explained in Supplementary section 9. The STEM and XRD results of synthesized TMC NFs confirm that the structure of these materials is a perfect match with the standard 1T structure, suggesting a tetragonal symmetry and octahedral coordination of the atoms (Fig. 2c)\textsuperscript{43,62}. Figure 2e indicates the schematic of 1T structure TMC NFs showing tetragonal symmetry, one layer per repeat unit with octahedral coordination. The lattice constant $a$ is in the range of 3.07 to 3.15 Å for synthesized TMC NFs. The stacking index $b$ indicates the interlayer spacing which is in the range of 4.53 to 5 Å for synthesized TMCs. As shown in Fig. 2e, 1T atomic coordination provides metal-terminated surface atoms that are known to be favorable binding sites of adsorbed intermediates in eCO$_2$RR\textsuperscript{43,62}. Our atomic and molecular scale structural analyses indicate that the synthesized TMC NFs have fairly similar structural properties e.g., (1T) crystalline structure with a dominant plane of (101), crystallite sizes, and atomic coordination.

To further discern the difference between the observed electrocatalytic performance of the TMCs, we have studied their electronic properties by performing electrochemical impedance spectroscopy (EIS) (Supplementary section 11) and, work function measurements using ultraviolet photoelectron spectroscopy (UPS) (Supplementary section 12). At first, we have employed the EIS experiments to compare the overall electron-transfer properties of the TMC catalysts in the double layer region (Supplementary section 11). To do this, TMC NFs with similar structural and physical properties e.g., sizes, shapes, and mass loadings (0.1 mg/cm$^2$) coated on glass carbon were used as the working electrodes. This results in similar roughness, morphology, intrinsic capacitance, and exposed surface area of the studied samples confirmed by our characterization results (Supplementary sections 5–10). The EIS experiments have been performed at a potential of $-310$ mV vs RHE for all TMCs under identical experimental conditions (Supplementary section 11). Figure 2f shows the fitted EIS spectra of each TMC catalyst using Randles circuit model, indicating a smaller charge transfer resistance ($R_{ct}$) for W$_2$C NFs (~17 ohm) compared to the other TMCs, i.e., Mo$_2$C NFs (~25 ohm), Nb$_2$C NFs (~33 ohm), and V$_2$C NFs (~38 ohm)\textsuperscript{63}. The UPS method also was used to compare the surface work function of TMCs (Fig. 2g). The results indicate a lower work function for W$_2$C NFs (0.2 to 0.84 eV) compared to Mo$_2$C NFs (3.92 eV), Nb$_2$C NFs (4.44 eV), and V$_2$C NFs (4.55 eV). The charge transfer resistance obtained by EIS experiments and the surface work function value measured by UPS experiments suggests the superior activity of W$_2$C NFs compared to other TMCs in this study i.e., Mo$_2$C, Nb$_2$C, and V$_2$C NFs.

In addition to our experimental observations, we have performed density functional theory (DFT) calculations to gain more insight to the electronic and catalytic properties of M$_2$C compounds. The aim is to address the enhanced activity and selectivity of these TMCs and to explore both electrochemical (i.e., driven) and chemical (i.e., favorable or spontaneous) processes that distinguish them from other catalysts, such as Au and Cu.

With respect to activity, the electronic density of states (DOS) indicate that transition metal $d$ states dominate at the Fermi level of these TMCs, much more so than elemental Au, another high
activity catalyst. Bader charge calculations indicate that metal atoms at the TMC surface are significantly more reduced compared to the bulk atoms (Fig. 2h and Supplementary Fig. 24). These results indicate the increased availability of electrons at metal-rich TMC surfaces, which may increase the catalytic activity of TMC NFs.

With respect to the increased selectivity of TMC NFs, especially for CH4 production, we have explored the CO2RR pathway on the W2C (101) surface in detail by using DFT calculations. Focusing initially on electrochemical processes, we employed the computational hydrogen electrode (CHE) model64–66 (Supplementary Tables 7–10) to explore the stepwise electronic reduction and protonation of adsorbed species in the low molecular coverage limit. The lowest free energy pathway to produce CH4 with only electrochemical steps is shown in Fig. 3 and Supplementary Fig. 27. The same steps with only a slight adjustment for experimental Faradaic efficiencies for the production of CH4 (and consequently CO) and an excess of surface protons. This may explain the high Faradaic efficiencies for the production of both H2 and CO at low potentials (see Supplementary section 3 and Supplementary Table 1). However, once a limiting potential (~0.74 V estimate) is reached, the readily protonated products of adsorbed CO that produce CH4 are no longer hindered by a build-up of adsorbed byproducts (O* then OH*), which can now be protonated and released from the surface.

We can divide the complex, multistep reaction into two key parts: initial conversion of adsorbed CO2 to adsorbed CO, followed by conversion of adsorbed CO to CH4 with the release of H2O (see Fig. 3 and Supplementary Fig. 27). As indicated in
Fig. 3 Minimum energy path for the electrochemical CO₂ conversion into CH₄ on the surface of W₂C NFs. Only electrochemical steps are shown. The parts of the reaction where chemical and electrochemical steps are essential are highlighted by colors. The favorable reactions of key chemical steps are provided (for free energies of these reactions, see Table S9). The intermediates are indicated. Gibbs free energies for reaction at zero potential vs RHE are given in eV.

**Chemical & Electrochemical Steps**

- **W₂C**
  - CO₂ → CO + H₂O
  - CO₂ + H₂O → CO₂⁻ + H₂ + OH⁻
  - H₂O → H⁺ + OH⁻

**Electrochemical Steps**

- HO⁻ + CO₂ → HOCO⁻
  - HO⁻ + H₂O → H₂O + CO₂⁻
  - CH₃O⁻ → CH₃OH
  - CH₃OH → CH₄ + H⁺ + OH⁻

Fig. 3, the first part, generation of adsorbed CO₂ can be achieved by chemical or electrochemical means. We have direct and favorable chemical conversion of adsorbed CO₂ to adsorbed CO and O on W₂C (101), but also two electrochemical pathways: production of HO⁻−CO₂ in a single step (+0.66 eV, Fig. 3) or an alternative initially favorable protonation to OCHO⁻ by two uphill electrochemical steps producing the first OCH₂O⁻ by the release of H₂ and the final product of HO⁻−CO₂ with a similar free energy cost (+0.68 eV, Supplementary Fig. 27 and Supplementary Table 10). A final electrochemically driven protonation of HO⁻−CO₂ favorably releases H₂O and leaves CO²⁻.

With chemically or electrochemically generated adsorbed CO₂, we can proceed to the second part of the overall reaction to produce CH₄ from CO₂, which involves multiple favorable protonation steps. The W₂C catalyst distinguishes itself. The electrochemical activation of CO₂ → HCO⁻ remains thermodynamically favorable (ΔG = −0.26 eV) on W₂C (101), whereas on other catalysts, such as Cu, this process is usually uphill with the potential ranging from −0.74 to −0.97 V vs RHE(96,70). Moreover, due to the spontaneous water dissociation, the direct H⁺ transfer step CO⁻ + H₂O → HCO⁻ on W₂C could be even more favorable with a resultant ΔG = −0.433 eV (Supplementary Table 10). The next two electrochemical steps are downhill (ΔG = −0.04 and −0.58 eV): the first forming the unstable methoxy radical CH₃O⁻ with oxygen attached to a surface W atom; the second leading to spontaneous dissociation into the methyl radical CH₃ and a surface oxygen atom O⁻. The electrochemical conversion of the surface CH₃ into CH₄ is favorable (ΔG = −0.43 eV) and the protonation of the surface oxygen O⁻ is only slightly uphill (ΔG = +0.03 eV). As we already stated, for the overall reaction CO₂ + 8H⁺/e⁻ → CH₄ + 2H₂O on W₂C (101) it is the final protonation of OH⁻ to release H₂O that is the limiting step (ΔG = +0.74 eV).

We also compared W₂C with the other TMCs studied by calculating the energies of adsorption of water and CO₂ as well as the potentials of the rate-determining step (i.e., protonation of OH⁻) for Nb₂C, Mo₂C, and V₂C (Supplementary Table 11). Our calculations indicate that these TMCs also strongly chemisorb CO₂ with adsorption energies of −1.32, −1.62, and −0.96 eV, respectively. Moreover, Nb₂C also shows favorable C−O bond scission of adsorbed CO₂. Additionally, Nb₂C, Mo₂C, and V₂C strongly adsorb water with the energies of −1.87, −1.23, and −0.59 eV, respectively, where Nb₂C is the only other catalyst that dissociates water. In contrast to W₂C, the energies required for the protonation of OH⁻ are higher: +1.17, +1.25, and +0.85 eV for Nb₂C, Mo₂C, and V₂C, respectively (Supplementary Table 11). Therefore, we can conclude that, within this set of four TMCs, W₂C possesses the optimal characteristics for efficient completion of CO₂RR: (1) sufficiently strong adsorption of CO₂, (2) spontaneous dissociation of water, and (3) the lowest limiting potential for OH⁻ protonation. We conclude that the performance of Nb₂C is reduced due to its stronger water adsorption, resulting in the protonation of OH⁻ requiring more energy. We would expect Mo₂C to have a lower surface coverage of protons and higher costs for the protonation of OH⁻. The weakest CO₂ adsorption on V₂C decreases its surface coverage, making it the worst TMC catalyst here, despite its relatively small limiting reaction potential of protonation of OH⁻.

As we mentioned before, for W₂C the realistic network of pathways towards CH₄ consists of a potential-dependent combination of competing chemical and electrochemical steps with the actual limiting potential being in the range from −0.483 to −0.744 V vs RHE (see the full path. Supplementary Fig. 27), which is consistent with our three-electrode electrochemical experimental results (Supplementary section 3 and Supplementary Table 1). A steeper Tafel slope for CH₄ formation on W₂C than other TMCs and Cu (Supplementary Fig. 8) also indicates the competition between reactions for the active sites on the catalyst surface. Specifically, the spontaneous water dissociation on W₂C (101) explains the ease of the HER in our nonacidic electrolyte where the source of protons is normally water. A weak potential dependence of the partial CO current and its small overpotential also originate from the interplay between chemical and electrochemical steps (see Supplementary Information for details).

Experimentally, we have studied the effect of CC on the activity and selectivity of the TMC catalysts. To do this, we have performed electrochemical CO₂RR in different CC concentrations of i.e., 0.01, 0.1, 1, and 2 M mixed with 3 M KOH (Supplementary section 14). Figure 4 shows CO₂RR overall current density and different products (i.e., CH₄, C₂H₄, CO, alcohols-CH₃OH, and C₂H₅OH- and H₂) partial current densities for W₂C NFs in different CC concentration electrolytes. Figure 4a indicates that by increasing the concentration of CC in the electrolyte the CO₂RR current density (j[CO₂RR]) increases and reaches a maximum value of −548.89 mA/cm² at a potential of...
−1.05 V vs RHE for 2 M of CC. The obtained value is about 32, 24, and 17, 9% higher than that of 0, 0.01, 0.1, and 1 M of CC, respectively. Moreover, a maximum CH₄ formation current density ($j_{CH_4}$) of −421.63 mA/cm² is obtained for 2 M CC at a potential of −1.05 V vs RHE that is about 1.41, 1.29, 1.19, and 1.1 times higher than that of 0, 0.01, 0.1, and 1 M, respectively (Fig. 4b).

The results also indicate using W₂C NFs, maximum partial current densities of other products i.e., C₂H₄ ($j_{C_2H_4}$ of −35.84 mA/cm²), CO ($j_{CO}$ of −78.48 mA/cm²), and alcohols ($j_{Alcohols}$ of −12.81 mA/cm²; −6.84 mA/cm² for CH₃OH and −5.97 mA/cm² for C₂H₅OH) were obtained at the potential of −1.05 V vs RHE in 2 M CC (Fig. 4b–d). In contrast, the measured H₂ partial current densities indicate that by adding a higher concentration of CC to the electrolyte solution the rate of H₂ production decreases significantly where a minimum H₂ formation current density of −4.48 mA/cm² was obtained for 2 M CC at a potential of −0.85 V vs RHE that is 12.31, 8.97, 6.76, 3.23 times lower than that of 0, 0.01, 0.1, and 1 M CC, respectively.

These results suggest that adding CC to the 3 M KOH electrolyte suppresses the competing HER and increases the formation of CO₂RR products more specifically CH₄. The stability of the CC electrolytes was studied by conducting nuclear magnetic resonance (NMR) and $^{13}$CO₂ isotope experiments (Supplementary sections15 and 16). The $^1$H and $^{13}$C NMR spectra reveal similar peak areas and chemical shifts for fresh and used electrolytes indicating no generation of new diamagnetic species or change in the CC structure under an applied potential of −1.05 V vs RHE (Supplementary Figs. 38, 39). The $^{13}$CO₂ isotope experiments also show that the CO₂ gas present inside the electrolyte is the only source of the formed products in the electrochemical CO₂RR (Supplementary Fig. 41). These results confirm that CC with different concentrations i.e., 0, 0.01, 0.1, 1, and 2 M remains stable at the range of applied potentials in the electrochemical CO₂RR experiments.

Next, we studied the performance of W₂C NFs in our developed solid polymer electrolyte flow electrolyzer for continuous electrochemical CO₂RR using this catalyst as the cathode (Supplementary section 17). The flow electrolyzer used in this study consists of a two-compartment electrochemical setup with an active area of 5 cm² coated with W₂C NFs at the cathode and iridium oxide nanoparticles (IrO₂ NPs) as the anode and were then fed with humidified CO₂ and KOH:CC (3 M:2 M) electrolyte, respectively (Supplementary section 17).
To study the CO$_2$RR performance of W$_2$C NFs in the flow electrolyzer, we performed chronoamperometry (CA) experiments at different cell potentials ranging from $-1.5$ to $-2.3$ V for W$_2$C NFs (Supplementary section 17). As shown in Fig. 5a, the results show that at a cell potential of $-1.5$ V, hydrogen (H$_2$, FE of $54.9\% \pm 1.4$) and CO (FE of $40.1\% \pm 1.8$) are the dominant products. However, our measurements indicate that by increasing the cell potential a system becomes more selective for CH$_4$ formation with the maximum FE of $82.7\% \pm 2$ at a cell potential of $-2.1$ V. At this potential, W$_2$C NFs slightly produce other products such as C$_2$H$_4$, C$_2$H$_5$OH, C$_2$H$_3$OH, CO, and H$_2$ with FEs of 5.6, 1.4, 1.2, 6.1, and 1.4, respectively. Figure 5b shows the maximum CH$_4$, C$_2$H$_4$, C$_2$H$_5$OH, and C$_2$H$_3$OH current densities of $-421.28$, $-5.27$, $-5.95$, and $-5.19$ mA/cm$^2$ at the cell potential of $-2.3$ V, respectively, confirming high selectivity of W$_2$C NFs towards CH$_4$ as the main product.

Next, we coupled the electrolyzer to a triple junction photovoltaic (TJ-PV) cell with a maximum efficiency of $34.3\%$ to determine the CO$_2$RR performance and energy efficiency of W$_2$C NFs in a solar-driven device (Supplementary section 18). The j-V characteristic curve of the TJ-PV cell under one sun illumination (100 mW/cm$^2$) using a sun simulator light source is shown in Supplementary Fig. 48. The operating point is chosen to provide a photo-potential fluctuation between $-2.08$ and $-2.12$ V, confirming the high stability of W$_2$C NFs for CO$_2$RR.

The measured sun to CO$_2$RR products (CO, CH$_4$, C$_2$H$_4$, C$_2$H$_5$OH, and C$_2$H$_3$OH) as well as total solar-to-fuel efficiency (SFE) of W$_2$C NFs over a 700-h process are shown in Fig. 5d (Supplementary section 18). As shown in this figure, an average sun to the CH$_4$ production efficiency of $17.3\%$ with negligible variation ($2\%$) is achieved during the 700-h continuous process. Considering other products, W$_2$C NFs show an SFE of $20.7\%$.

We also calculated the energy efficiency of CO$_2$RR in our developed flow electrolyzer and compared it with state-of-the-art catalytic systems in the literature (Supplementary section 17). As shown in this figure (Supplementary Fig. 47), the maximum energy efficiency of $62.3\%$ was obtained for our developed flow electrolyzer using W$_2$C catalyst that is about 67 and 73% more efficient than Cu$_{ab}$ (37.4%)$^{50}$ and recently developed Cu-CIPH (36.1%)$^{72}$ catalytic systems, respectively.

In summary, we have synthesized four members of TMCs with a formula of M$_2$C, i.e., W$_2$C, Mo$_2$C, Nb$_2$C, and V$_2$C NFs using the carburization method followed by the liquid exfoliation technique and tested their catalytic performance for eCO$_2$RR in KOH:CC (3 M:2 M) electrolyte. The electrocatalytic performance studies of TMCs shows these materials are mainly selective for CH$_4$ formation with W$_2$C NFs having the best CO$_2$RR activity compared to the studied catalysts. For instance, a CO$_2$RR current density of $-548.89$ mA/cm$^2$ and a maximum CH$_4$ current density of $-421.63$ mA/cm$^2$ at the potential of $-1.05$ V vs RHE were observed for W$_2$C NFs. Our electrochemical results also indicate that adding CC to the electrolyte enhances the formation of CO$_2$RR products by suppressing the HER for all studied TMCs. Moreover, the NMR and $^{13}$CO$_2$ isotope experiments confirm that the CC remains stable during the electrochemical experiments. Atomic and molecular scale characterizations such as XPS, XRD, and STEM indicate that all synthesized TMCs have a similar

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**Fig. 5 Electrocatalytic performance and stability of W$_2$C NFs in the solid polymer electrolyte flow electrolyzer.** **a** Faradaic efficiency (FE) measurements of H$_2$, CO, CH$_4$, C$_2$H$_4$, methanol (MeOH), and ethanol (EtOH) for W$_2$C NFs at different cell potentials. The error bars represent standard deviations of four independent experiments. **b** Partial current density for each product as a function of cell potential. **c** Measured total current densities and cell potentials of the solar-driven solid polymer electrolyte flow electrolyzer under one sun illumination provided by the TJ-PV cell over time. **d** Total sun to fuels efficiency and sun to CH$_4$ production efficiency in the solar-driven solid polymer electrolyte flow electrolyzer over time.
Electrochemical characterization of W2C NFs with a known responsivity calibration curve. Our results indicated a custom-made sun simulator light source and an InGaAs photodiode (Thorlabs, DET400A) demonstrated solar-driven power densities of 20.7%, respectively, under one sun illumination. The performance of TMC NFs i.e., W2C, Mo2C, Nb2C, and V2C NFs and compared with that of Au and Cu NPs. The CA experiments were carried out in the range of −0.483 to −0.744 V vs RHE. Using W2C NFs, we have demonstrated a solar-driven fuel cell that can work up to 700 h with a solar to CH4 efficiency of 14.5% and 20.7%, respectively, under one sun illumination. The demonstrated solar-driven fuel cell utilizing a non-precious metal catalyst (W2C NFs) in this study achieves maximum efficiency of 62.3% making it a good candidate to approach the commercially relevant intrinsic renewable electrical energy.

**Methods**

**Synthesis of TMCs.** TMCs were prepared by carburization process in a dual-zone tubular furnace with a controlled flow of CH4 and H2 mixture (volumetric ratio CH4:H2 of 1:9) at a temperature of 973 K. The obtained bulk powders were then collected and ground to fine powders in a mortar and pestle. Next, a certain amount of TMC powders were processed in isopropyl alcohol using an ultrasonic liquid processor (Sonics VibraCell VCX-130) to obtain a solution of TMC NFs. The resulting solution was further centrifuged and the top two-third of the solutions were collected and stored as the TMCs in a vial for cathode electrode preparation. A detailed explanation is provided in Supplementary section 1.

**Electrochemical setup.** A two-compartment three-electrode electrochemical cell was used to perform the fundamental study for cathodic half-cell reaction using the synthesized W2C, Mo2C, Nb2C, and V2C NFs and compared with them and Au and Cu NPs. In the three-electrode cell study, the working electrode was prepared by drop-casting the catalysts (mass loading of 0.1 mg) on a glassy carbon electrode with a geometric surface area of 1 cm². The catalyst loading on the electrode was precisely controlled to be 0.1 mg/cm² on the glassy carbon electrode. Platinum (Pt) gauze 52 mesh (Alfa Aesar) and Ag/AgCl (BAS) were used as counter and reference electrodes, respectively. The cathode and anode parts of the cell were separated through an anion exchange membrane (Sustain X37-50 Grade RT, Dioxide Materials). All experiments were performed in a CO2 saturated KOH:CC (3 M:2 M) electrolyte with a pH of 14.5 ± 0.1. A two-compartment zero-gap solid polymer electrolyte flow cell was used to study the electrochemical performance where the working and counter electrodes are separated using an anion exchange membrane. Working electrodes (cathode) were prepared by brush-coating the solution of studied catalysts (W2C NFs, Au NPs, and Cu NPs) on the gas diffusion layer (GDL, Sigracet 39 BC, Fuel Cell Store) electrodes with a geometrical surface area of 5 cm². The counter electrode (anode) was prepared using a similar procedure where InO2 powder (Sigma Aldrich) was used as the catalyst solution. The actual loadings of 0.1 ± 0.01 mg/cm² were determined by weighing the dry GDLs before catalyst deposition and coated GDLs after being dried in a vacuum oven overnight. As a separator in our experiments, we used an anion exchange membrane (Sustain X37-50 Grade RT, Dioxide Materials) which was treated in 1 M KOH overnight at 75 °C and then washed with deionized water prior to use. Anolyte flow of KOH:CC (3 M:2 M) with a flow rate of 20 ml/min was fed to the anode compartment using a peristaltic pump (Masterflex, Cole-Parmer). A mass flow controller (SmartTrak 50, Sierra, calibrated with CO2 gas) was used to control the fuel cell operation at a flow rate of 0.23 ± 0.01 ml/s.

**PV cell characterization.** A solar-powered cell was assembled by connecting the solid polymer electrolyte flow electrolyzer to a triple junction photovoltaic cell (TJ-PV) solar cell. The TJ-PV cell was characterized at different sun illuminations using a custom-made sun simulator light source and an InGaAs photodiode (Thorlabs, PDG03-AL) with a known responsivity calibration curve. Our results indicated a maximum efficiency of 34.32% under one sun illumination used in our study.

**Electrochemical characterization.** Electrochemical experiments were performed using a Biologic Potentiostat SP-150. The CA technique was used to study the performance of TMC NFs i.e., W2C, Mo2C, Nb2C, and V2C NFs and compared with that of Au and Cu NPs. The CA experiments were carried out in the range of −0.483 to −1.05 V vs RHE. All experiments were performed under identical experimental conditions. The LSV technique was used to study the fundamentals of the cathodic half-cell reaction in the three-electrode cell setup. LSV curves were obtained by sweeping the potential between +0.2 and −1.05 V vs RHE with a scan rate of 20 mV/s. The conversion of Ag/AgCl reference electrode potential to the RHE scale was calculated using the Nernst equation considering the pH of the solution (pH = 14.5).

**Product characterization.** A gas chromatography system (GC, SRI, 8610 C) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) was used to detect and quantify the electrochemical CO2RR products. Ultra-purity high helium (He) and nitrogen (N2) gases (99.999%, Airgas) were used as the carrier gas to identify any possible type of product. The signal response of the FID and TCD to each gaseous product (e.g., CH4, CO, CH2=CH2, C2H4, and CH3OH) was calibrated by feeding standard samples into the mass spectrometer. An electron energy of 70 eV was used for ionization of all species, with an emission current of 500 µA. All mass-selected product cations were detected by a secondary electron multiplier with a detector voltage of 1200 V for maximizing the signal-to-noise ratio of the products.

**X-ray diffraction (XRD).** The XRD technique was used to identify the phase purity and crystallinity of all studied catalysts (W2C, Mo2C, Nb2C, and V2C NFs, Au NPs, and Cu NPs) using a Bruker D2 PHASER diffractometer in Bragg-Brentano geometry employing a Ni filtered Cu Ka radiation (1.5405 Å). The XRD patterns were obtained using a LynxEye linear position-sensitive detector and a step width of 0.2° with a counting time of 1 s/step.

**X-ray photoelectron spectroscopy (XPS).** A Thermo-Scientific ESCALAB 250Xi instrument equipped with an electron flood and scanning ion gun was used to identify the oxide states of the W2C NFs. All obtained spectra were analyzed using Thermo-Advantage software, considering the standard carbon peak at 284.8 eV and relative sensitivity factors.

**Ultraviolet photoelectron spectroscopy (UPS).** Surface work function measurements were carried out using the UPS technique. All UPS data were acquired with a Thermo-Scientific ESCALAB 250Xi instrument using He I (21.2 eV) ultraviolet radiation and a pass energy of 8.95 eV.

**Scanning transmission electron microscopy (STEM).** W2C NFs were characterized at the atomic scale using a spherical aberration-corrected JEM-ARM 200CF STEM with a cold field emission gun operating at 200 kV. HAADF detector with 22 mrd inner-detector angle and BF detector were utilized to obtain the atomic resolution images.

**Theoretical study.** We performed a comparative DFT analysis for the observed catalytic activity and reactivity of W2C NFs with Au and other TMCs using the SIESTA package, with Perdew–Burke–Ernzerhof functional with a double-zeta with polarization (DZP) localized basis set and the norm-conserving Troullier– Martins pseudopotentials. Calculations of DOS for bulk and slab geometries of Au and TMCs were performed using the Effective Screening Method (ESM) for Brillouin zones of the unit cells sampled by Monkhorst-Pack k-point grids of size 9 × 9 × 9 and 1 × 9 × 9, respectively, together with a plane-wave cutoff of 300.0 Ry. The optimization of the atomic positions and cell parameters were carried out using a conjugate-gradient algorithm until a maximum atomic force tolerance of 0.04 eV/Å and a maximum stress component along each periodic direction of lower than 1 GPa were achieved. The Vienna ab initio Simulation Package (VASP, version 5.4.4) with PAW (projector augmented wave method) and Perdew–Burke–Ernzerhof exchange-correlation functionals were used to analyze the calculated free energies of different reaction molecular species on the (100) surface of M2C (M = W, V, Mo, Nb). All the VASP calculations were performed for neutral non-spin-polarized systems and a dipolar electrostatic correction was used along the normal to the surface of the slab. Next, we used the tetrahedron method with Blochl corrections and 1 × 3 x 3 Monkhorst-Pack k-point sampling for the calculations of total electronic energy (smearing σ = 0.1). The adsorption free energies were then used within the CHE model to evaluate the lowest free energy pathways and the limiting reaction potentials.
20. Zhang, Z. et al. Rational design of bi nanoparticles for efficient solar-driven CO2 electroreduction at low overpotential. *Energy Environ. Sci.* 12, 1334–1340 (2019).

21. Todoroki, N. et al. Surface atomic arrangement dependence of electrochemical CO2 reduction on molybdenum disulfide. *Adv. Energy Mater.* 9, 1803536 (2019).

22. Back, S., Yeom, M. S. & Jung, Y. Active sites of Au and Ag nanoparticle catalysts for CO2 electroreduction to CO. *ACS Catal.* 5, 5098–5106 (2019).

23. Kim, K. S., Kim, W. J., Lim, H. K., Lee, E. K. & Kim, H. Tuned chemical bonding ability of Au at grain boundaries for enhanced electrochemical CO2 reduction. *ACS Catal.* 6, 4443–4448 (2016).

24. Tso, Z., Wu, Z., Yuan, X., Wu, Y. & Wang, H. Copper–gold interactions enhancing formate production from electrochemical CO2 reduction. *ACS Catal.* 9, 10894–10898 (2019).

25. Morales-Guio, C. G. et al. Improved CO2 reduction activity towards C2+ alcohols on a tandem gold on copper electrocatalyst. *Nat. Catal.* 1, 764–771 (2018).

26. Liu, M. et al. Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration. *Nature* 537, 382 (2016).

27. Asadi, M. et al. Highly efficient solar-driven carbon dioxide reduction on molybdenum disulfide catalyst using choline chloride-based electrolyte. *Adv. Energy Mater.* 9, 1803536 (2019).

28. Nittori, S. et al. Progress and perspectives of electrochemical CO2 reduction on copper in aqueous electrolyte. *Chem. Rev.* 119, 7610–7672 (2019).

29. Dinh, C. T. et al. Electroreduction to ethylene via hydroxide-mediated copper catalysts at an abrupt interface. *Science* 360, 783–787 (2018).

30. Li, F. et al. Molecular tuning of Cu2+-to-ethylene conversion. *Nature* 577, 509–513 (2020).

31. Wakerley, D. et al. Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface. *Nat. Mater.* 18, 1222–1227 (2019).

32. Jiang, K. et al. Metal ion cycling of Cu foil for selective C–C coupling in electrochemical CO2 reduction. *Nat. Catal.* 1, 111–118 (2018).

33. Zhang, X., Sun, X., Guo, X. S., Bond, A. M. & Zhang, J. Formation of lattice-dislocated bismuth nanowires on copper foam for enhanced electrocatalytic CO2 reduction at low overpotential. *Energy Environ. Sci.* 12, 1334–1340 (2019).

34. Iijima, G., Inomata, T., Yamaguchi, H., Ito, M. & Masuda, H. Role of a hydroxide layer on Cu electrodes in electrochemical CO2 reduction. *ACS Catal.* 9, 6305–6319 (2018).

35. Liang, Z. et al. Copper-on-nitride enhances the stable electrocatalysis of multi-carbon products from CO2. *Nat. Commun.* 9, 3828 (2018).

36. Garza, A. J., Bell, A. T. & Head-Gordon, M. Mechanism of CO2 reduction at copper surfaces: pathways to C2 products. *ACS Catal.* 8, 1490–1499 (2018).

37. Ringel, S. et al. Understanding cation effects in electrochemical CO2 reduction. *Energy Environ. Sci.* 12, 3001–3014 (2019).

38. Li, C. W. & Kanan, M. W. CO2 reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu2O films. *J. Am. Chem. Soc.* 134, 7231–7234 (2012).

39. Gogotsi, Y. & Anasori, B. The rise of MXenes. *Nanoscale* 13, 8491–8494 (2019).

40. Anasori, B. et al. Two-dimensional, ordered, double transition metals carbides (MXenes). *Nanoscale* 9, 9507–9516 (2015).

41. Hantanarisakul, K. & Gogotsi, Y. Electronic and optical properties of 2D transition metal carbides and nitrides (MXenes). *Adv. Mater.* 30, 1804779 (2018).

42. Esmaeilrad, M., Kondori, A., Ruiz Belmonte, A. & Asadi, M. Electrocatalysis of carbon dioxide to methane enabled by molybdenum carbide nanocatalyst. *ECS Meet. Abstr.* MA2020-02, 3234 (2020).

43. Lei, J., Kutana, A. & Yakobson, B. I. Predicting stable phase monolayer Mo2C (MXene), a superconductor with chemically-tunable critical temperature. *J. Mater. Chem. C* 5, 3438–3444 (2017).

44. Lewandowski, M., Szmya, A., Sayag, C. & Beaumier, P. Applied catalysis B: environmental atomic level characterization and sulfur resistance of unsupported W2C during dibenzothiophene hydrodesulfurization. *Chem. Sci.* 5, 180477 (2014).

45. Kondori, A. et al. Identifying catalytic active sites of trimolybdenum phosphide (Mo3P) for electrochemical hydrogen evolution. *Adv. Energy Mater.* 9, 1900516 (2019).

46. Esmaeilrad, M. et al. Oxygen functionalized copper nanoparticles for solar-driven conversion of carbon dioxide to methane. *Nanoscale* 14, 2099–2108 (2020).

47. Vasilyev, D. V. & Dyson, P. J. The role of organic promoters in the electroreduction of carbon dioxide. *ACS Catal.* 11, 1392–1405 (2021).

48. Zhang, T. et al. Highly dispersed, single-site copper catalysts for the electroreduction of CO2 to methane. *J. Electroanal. Chem.* 875, 113862 (2020).

49. Wu, J. et al. A metal-free electrocatalyst for carbon dioxide reduction to multi-carbon hydrocarbons and oxygenates. *Nat. Commun.* 7, 13369 (2016).

50. De Gregorio, G. L. et al. Facet-dependent selectivity of Cu catalysts in electrochemical CO2 reduction at commercially viable current densities. *Nat. Catal.* 10, 4854–4862 (2020).

51. Chen, S. et al. Highly selective carbon dioxide electroreduction on structure-evolved copper perovskite oxide toward methane production. *ACS Catal.* 10, 4640–4646 (2020).

52. Wang, X. et al. Efficient methane electrolysers enabled by tuning local CO2 availability. *J. Am. Chem. Soc.* 142, 3525–3531 (2020).

53. Weng, Z. et al. Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction. *Nat. Commun.* 9, 415 (2018).

54. Mathur, K., Beberwyck, B. J. & Alivisatos, A. P. Enhanced electrochemical methanation of carbon dioxide with a dispersible nanoscale copper catalyst. *J. Am. Chem. Soc.* 136, 13319–13325 (2014).
55. Jones, J. P., Prakash, G. K. S. & Olah, G. A. Electrochemical CO2 reduction: recent advances and current trends. *Inorg. Chem.* 54, 1451–1466 (2015).
56. Kuhl, K. P., Cave, E. R., Abrain, D. N. & Jaramillo, T. F. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* 5, 7050–7059 (2012).
57. Hoang, T. T. H. et al. Nanoporous copper–silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO2 to ethylene and hydrogen. *J. Am. Chem. Soc.* 140, 5791–5793 (2018).