Heteroatom-Mediated Interactions between Ruthenium Single Atoms and an MXene Support for Efficient Hydrogen Evolution

Vinoth Ramalingam, Purushothaman Varadhan, Hui-Chun Fu, Hyunho Kim, Daliang Zhang, Shuangming Chen, Li Song, Ding Ma, Yun Wang, Husam N. Alshareef,* and Jr-Hau He*

Single atom catalysts (SACs) have emerged as a promising candidate in the field of heterogeneous catalysis. Unlike metal nanoparticles or bulk metal catalysts, SACs are atomically dispersed and isolated metal active sites that are coordinatively unsaturated. Furthermore, they demonstrate the quantum confinement effect and display metal–support interactions. These unique characteristics have made SACs an ideal catalyst for CO oxidation, the oxygen reduction reaction, the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), various hydrogenation reactions, CO2 reduction, and other electrochemical applications. The catalytic activity and selectivity of SACs not only depend on the nature of the single atom but also on the solid supports that are used to disperse the metal. Therefore, it is essential to...
choose an appropriate support to ensure strong interactions between the isolated SACs and the substrate in order to achieve the desired catalytic activity and selectivity. Thus far, graphene nanosheets, carbon nanotubes, and other carbon materials and metal oxides have been widely used as supports for SACs.\(^{[5-7]}\) Unfortunately, these materials tend to be either poor electrical conductors, electrochemically inert, or hydrophobic, which hampers the practical application of SACs for water-based electrochemical reactions.\(^{[8,9]}\) Thus, it is crucial to identify a solid support with excellent conductivity that is also electrochemically active and hydrophilic in order to better host isolated single atoms for electrocatalytic applications.

MXenes, a new class of 2D transition metal carbides/nitrides, feature exceptional properties, including (i) excellent electronic conductivity with efficient charge transport, (ii) catalytically active basal planes with exposed metal sites, (iii) hydrophilic surface functionalities (\(T_x = O, -OH, \text{ and } -F\) groups), and (iv) a unique layered structure consisting of conductive transition metal carbides, or metal nitrides.\(^{[10,11]}\) These attractive properties render MXenes as superior candidates for facilitating various electrochemical applications, including supercapacitors, Li-ion or Li-sulfur batteries, and electrocatalytic OER and HER.\(^{[10,12,13]}\) Notably, conductive transition-metal-carbide-based MXenes can facilitate fast electron transport to electrochemically active sites to facilitate electrochemical reactions. In addition, MXenes intercalated with water molecules can enhance ion transport in liquid electrolytes.\(^{[14]}\) Recently, Li et al. have demonstrated the reactive metal–support interactions (RMSI) between Pt nanoparticles and transition metal carbide MXenes in which Pt nanoparticles directly bonded with the metal sites of the MXene and formed a bimetallic alloy and ordered intermetallic structures for \(H_2O\) and \(C-H\) activation applications, respectively.\(^{[15,16]}\) Likewise, Zhang et al. have immobilized the Pt single atoms in the Mo vacancies of \(Mo_2TiC_2T_x\) and further stabilized the Pt single atoms via the formation of Pt–C–CO complex with the surrounding carbon atoms from \(Mo_2TiC_2T_x\) MXene.\(^{[17]}\) However, the coordination interaction between metal single atoms and MXene remains unexplored. Therefore, it is important to understand the strong coordination interactions between single atoms and MXene support via heteroatom sites and the corresponding catalytic activity.

Herein, we report the coordination interaction between isolated ruthenium single atoms (Ru\(_{\text{SA}}\)) and a 2D titanium carbide (Ti\(_3\)C\(_2\)T\(_x\)) MXene support through the nitrogen (N) and sulfur (S) heteroatom dopants. The Ru\(_{\text{SA}}\) are stabilized on the MXene support via the formation of Ru–N and Ru–S bonds with the N and S atoms. The Ru\(_{\text{SA}}\)-coordinated N and S species in Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) remarkably enhances the catalytic activity for HER in acidic solution. Interestingly, integrating this Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst with a \(n^n^p^1\)-Si photocathode results in an exceptionally high photocurrent density of 37.6 mA cm\(^{-2}\) upon AM 1.5G illumination, outperforming the photocurrent density value of most precious noble metal integrated Si-based photocathodes reported elsewhere. Density functional theory (DFT) calculations reveal that the coordination interaction of Ru\(_{\text{SA}}\) alters the electronic structure of the Ti\(_3\)C\(_2\)T\(_x\) MXene support to achieve an optimal Gibbons hydrogen adsorption free energy (\(\Delta G^{\text{ads}}\)) of close to zero, which is favorable for enhanced HER performance. We believe the findings of this study can be applied to other members of the MXene family for the rational design of highly efficient catalysts at the atomic or molecular levels.

A schematic representing the synthesis of the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst is depicted in Figure 1a. The Ti\(_3\)C\(_2\)T\(_x\) MXene is prepared from MAX phase (M: transition metal, A: main group element, X: C and/or N) Ti\(_3\)AlC\(_2\) using a lithium fluoride (LiF)/hydrochloric (HCl) acid mixture to selectively remove the Al layers from the MAX phase and thereby produce few-layered Ti\(_3\)C\(_2\)T\(_x\) MXene (Figure 1a). To prepare the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) electrocatalyst, we mixed Ti\(_3\)C\(_2\)T\(_x\), RuCl\(_3\)-xH\(_2\)O, and thiourea together and then freeze-dried this material to produce a foam. The oxygen-rich surface functional groups (O and OH groups) on the Ti\(_3\)C\(_2\)T\(_x\) sheets are expected to interact with or adsorb the Ru cations, which promotes the incorporation of Ru\(_{\text{SA}}\) onto the Ti\(_3\)C\(_2\)T\(_x\) support.\(^{[18]}\) Moreover, the freeze-drying process not only prevents the restacking of the Ti\(_3\)C\(_2\)T\(_x\) MXene sheets but also helps to achieve the homogeneous distribution of Ru metal ions on the substrate.\(^{[18]}\) We then annealed this foam at 500 °C under inert atmosphere, which leads to the simultaneous doping of N, S, and Ru\(_{\text{SA}}\) onto the Ti\(_3\)C\(_2\)T\(_x\) sheets. Transmission electron microscopy (TEM) images of the bare Ti\(_3\)C\(_2\)T\(_x\) MXene nanosheet indicates the successful removal of the Al layer from the Ti\(_3\)AlC\(_2\) starting material (Figure S1a,b, Supporting Information). Field emission-scaning electron microscopy (FESEM) of the final Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) product reveals the formation of a well-defined 2D nanosheet structure (Figure 1b). Likewise, TEM images further confirm the layered structure of Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\), which features smooth surfaces and edges (Figure 1c,d). No obvious Ru nanoparticle formation was observed in Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\). Figure 1e displays a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst, in which the small, homogeneously distributed bright spots of <1 nm in size confirm the presence of atomically dispersed Ru\(_{\text{SA}}\) isolated on the Ti\(_3\)C\(_2\)T\(_x\) support. We estimated the ruthenium loading to be 1.2 wt% based on inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis. Furthermore, scanning transmission electron microscopy-energy dispersive X-ray (STEM-EDX) mapping shows the existence and uniform distribution of Ti, C, O, N, S, and Ru elements in the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst (Figure 1f,g); the corresponding STEM-EDX profile is shown in Figure S2, Supporting Information. These results strongly suggest the homogeneous distribution of isolated Ru\(_{\text{SA}}\) in the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst.

The X-ray diffraction (XRD) patterns of Ti\(_3\)C\(_2\)T\(_x\) MXene show that a strong (002) peak is shifted to a lower angle (2θ = 9°) compared to that of the Ti\(_3\)AlC\(_2\) starting material, suggesting the successful etching of Al layers from the MAX phase and the formation of the MXene structure (Figure S3, Supporting Information).\(^{[19]}\) We performed X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure spectroscopy (XAFS) to investigate the existence and electronic states of single Ru atoms in the Ru\(_{\text{SA}}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst. The existence of Ti, C, O, and F elements in the survey scan indicates the successful preparation of the Ti\(_3\)C\(_2\)T\(_x\) MXene (Figure S4a, Supporting Information), which is further supported by the Ti–C bond observed in the high-resolution C1s spectrum and the intense Ti\(^{3+}\) peak identified in the high-resolution Ti2p spectrum (Figure S4b,c, Supporting Information). The survey
scan spectra of the RuSA-N-S-Ti3C2Tx catalyst show the presence of Ti, C, O, N, S, and Ru elements, indicating the doping of Ru, N, and S on the Ti3C2Tx MXene (Figure S5, Supporting Information). Figure 2a shows the high-resolution C1s and Ru3d XPS spectra of RuSA-N-S-Ti3C2Tx and a control made without Ru (N-S-Ti3C2Tx). The binding energy peaks identified for RuSA-N-S-Ti3C2Tx at 281.8, 282.2, 285.0, 285.7, 286.6, and 288.4 eV correspond to C–Ti–N, C–Ti, graphitic C–C, C–N, C–O, and C=O, respectively.[20] Compared with N-S-Ti3C2Tx, an additional small peak observed for RuSA-N-S-Ti3C2Tx at 280.6 eV located between the oxidation state of Ru(0) and Ru4+ indicates the different oxidation states of Ru in RuSA-N-S-Ti3C2Tx.[21] Moreover, it is difficult to distinguish the Ru3d3/2 peak from the graphitic C–C signals because of spectral overlap in the energy range around 285.0 eV.[21] The high-resolution N1s XPS spectrum of N-S-Ti3C2Tx shows peaks at 396.3, 397.5, 398.8, and 399.4 eV, which are assigned to Ti–N, pyridinic–N, N–Ti–O, and pyrrolic–N bonds, respectively (Figure S6, Supporting Information).[22,23] However, the pyrrolic–N component of RuSA-N-S-Ti3C2Tx is observed at 400.2 eV, which is ≈0.8 eV higher than the pyrrolic–N of N-S-Ti3C2Tx (Figure 2b) possibly due to the chemical interaction between RuSA and the surrounding N atoms on the support.[21] Meanwhile, the high-resolution S2p spectrum of RuSA-N-S-Ti3C2Tx can be deconvoluted into six different components, including S–Ti (160.6 eV), chemisorbed S (161.8 eV), S–Ru (162.5 eV), S–C (163.8 and
The Ru–N bond and S–Ru bond identified in the high-resolution N1s and high-resolution S2p XPS results clearly confirm that the RuSA are coordinated with both N and S in RuSA-N-S-Ti3C2Tx.

The Ti2p and Ru3p XPS spectra of Ru SA-N-S-Ti3C2Tx are shown in Figure S7 (Supporting Information). A binding energy peak identified at 455.1 eV is assigned to Ti–C bonds in Ti3C2Tx. Two peaks located at 456.6 and 462.5 eV are related to the Ti3+ signal of Ti3C2Tx. In addition, the peaks at 455.7, 458.8, and 464.3 eV correspond to Ti–N, Ti–OH, and Ti–O bonds, respectively. A peak at 461.4 eV is attributed to Ru(0) or Ti2+. To gain insight into the dispersion of Ru species on RuSA-N-S-Ti3C2Tx, we investigated the chemical state and coordination environment of the RuSA using X-ray absorption fine structure spectroscopy (XAFS). The Fourier transform-X-ray absorption fine structure (FT-EXAFS) spectrum of RuSA-N-S-Ti3C2Tx exhibits a superimposed peak at 1.67 Å, which can be ascribed to both Ru–N(O) and Ru–S scattering pairs (Figure 2d). Compared to Ru foil and RuO2, the absence of Ru–Ru and Ru–O scattering pairs in RuSA-N-S-Ti3C2Tx indicates the existence of atomically dispersed RuSA isolated on the MXene support (Figure 2d). Furthermore, we performed quantitative EXAFS curve fitting analysis to study the bonding environment of the RuSA (Figure 2e). As displayed in Table S1 (Supporting Information), the coordination number of Ru–N(O) bonding in the first coordination bonding sphere is estimated to be 2.09 Å. Moreover, an additional coordination sphere with a coordination number of 2.37 Å is attributed to the Ru–S bonding configuration. These results confirm the successful coordination of RuSA with both N and S in RuSA-N-S-Ti3C2Tx, which is consistent with the XPS results. Figure 2f shows the normalized Ru k-edge X-ray absorption near edge structure (XANES) spectra of Ru foil, RuO2, and RuSA-N-S-Ti3C2Tx. The Ru k-edge XANES profile of RuSA-N-S-Ti3C2Tx is entirely different from those of the Ru foil and RuO2 XANES profiles, indicating the different oxidation state of RuSA and further confirming the chemical coordination of RuSA with N and S species. Therefore, the EXAFS and XANES results confirm the strong electronic coupling between isolated RuSA and the Ti3C2Tx MXene support via N and S atoms. Figure 3a shows the HER polarization curves of bare carbon paper (CP), Ti3C2Tx, N-S-Ti3C2Tx, RuSA-Ti3C2Tx, and RuSA-N-S-Ti3C2Tx catalysts in 0.5 m H2SO4 electrolyte. As shown in Figure 3a, the current densities of RuSA-Ti3C2Tx and RuSA-N-S-Ti3C2Tx catalysts are not in the baseline at zero overpotential, which might be due to the potential hydrogen adsorption effect of precious Ru metal and the capacitance effect of nanocarbons from Ti3C2Tx MXene support that influence the current starting points not at zero. The Ti3C2Tx, N-S-Ti3C2Tx, and sulfate species (168.0 eV) (Figure 2c). The Ru–N bond and S–Ru bond identified in the high-resolution N1s and high-resolution S2p XPS spectra of N-S-Ti3C2Tx and RuSA-N-S-Ti3C2Tx. The FT-EXAFS spectra of Ru foil show a main Ru–Ru peak at 2.44 Å (which corresponds to the Ru–Ru shell with a coordination number of 2.68 Å, based on fitting), while RuO2 displays two peaks at 1.47 and 3.0 Å (which correspond to the Ru–O shell with coordination numbers of 1.90 and 2.02 Å, respectively, based on fitting) and RuSA-N-S-Ti3C2Tx shows a Ru–N(O)/S peak at 1.67 Å (which corresponds to the Ru–N/O and Ru–S shells with the coordination numbers of 2.09 and 2.37 Å, respectively, based on fitting). The normalized Ru k-edge XANES spectra of Ru foil, RuO2, and RuSA-N-S-Ti3C2Tx.
and RuSA-Ti3C2T_x catalysts feature large overpotential values of 673, 453, and 215 mV, respectively, to reach a current density of 10 mA cm^{-2}. Remarkably, RuSA-N-S-Ti3C2T_x catalysts exhibit an onset potential of nearly zero (η_{onset}) and the smallest overpotentials of 76 and 237 mV to attain 10 and 100 mA cm^{-2}, respectively, indicating the exceptional electrocatalytic HER performance of RuSA-N-S-Ti3C2T_x, which we believe is due to the chemical interactions of the RuSA and MXene support. The Pt control sample exhibits an overpotential of 53 and 81 mV to reach the current densities of 10 and 100 mA cm^{-2}, respectively.

In order to study the effect of the heteroatom dual dopants (i.e., N and S) on the HER performance, we prepared the same catalyst only doped with just N (i.e., RuSA-N-Ti3C2T_x) under identical experimental conditions using urea as the N source for the control experiment. The RuSA-N-Ti3C2T_x has an overpotential of 151 mV at 10 mA cm^{-2} (Figure S8, Supporting Information), which is ≈75 mV higher than RuSA-N-S-Ti3C2T_x, indicating the improved catalytic performance when S atoms are also doped into the MXene substrate. The high electronegativity and different atomic radii of the N and S atoms allow them to act as two different binding sites for the formation of the RuSA, which helps to drive the enhanced HER catalytic activity. [28] We also studied the reaction kinetics of the catalysts during the HER process by extracting the slope values from the Tafel plots (Figure 3b). The RuSA-N-S-Ti3C2T_x catalyst shows a Tafel slope of 90 mV dec^{-1}, suggesting that the RuSA-N-S-Ti3C2T_x catalyst follows the Volmer–Heyrovsky mechanism that combines a fast initial discharge reaction step (Volmer reaction: \( \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_ads + \text{H}_2\text{O} \)) followed by a slow electrochemical desorption reaction step.
A high Tafel value of 90 mV dec\(^{-1}\) noted for Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) could result from the Ti\(_3\)C\(_2\)T\(_x\) MXene support. In contrast, this Tafel value is higher than the Tafel values of previously reported Ru-based electrocatalysts.\(^{[23]}\) However, the value is similar to those reported for MXene based HER catalyst [Ti\(_3\)CT\(_x\) (88 mV dec\(^{-1}\)) and Mo\(_2\)CT\(_x\) (82 mV dec\(^{-1}\))],\(^{[31,32]}\) suggesting that the HER active sites not only originate from Ru\(_{SA}\) but also arise from the electrochemically active Ti\(_3\)C\(_2\)T\(_x\) MXene to some extent. We further evaluated the HER performance of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) in alkaline and neutral pH electrolytes and found that overpotentials of 99 and 275 mV are required to achieve a current density of 10 mA cm\(^{-2}\), respectively, indicating the outstanding HER activity of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst under various pH conditions (Figure 3c,d). Figure 3e shows the electrochemical impedance spectra (EIS) of Ti\(_3\)C\(_2\)T\(_x\), N-S-Ti\(_3\)C\(_2\)T\(_x\), and Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) measured in 0.5 m H\(_2\)SO\(_4\). The Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) has a smaller charge transfer resistance than Ti\(_3\)C\(_2\)T\(_x\) and N-S-Ti\(_3\)C\(_2\)T\(_x\), which shows the HER process occurs effectively at the interface between the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) surface and electrolyte. The HER performance of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) is retained up to 3000 cyclic voltammetry (CV) cycles with negligible negative shift (=17 mV) in the overpotential (Figure S9, Supporting Information), indicating the long-term stability of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\). In addition, the resultant Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst provides excellent long-term stability in acidic electrolyte with negligible degradation in HER performance after 16 h of reaction time, which further reveals that the Ru\(_{SA}\) are well preserved on the MXene support (Figure S10, Supporting Information). Moreover, the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst was also stable up to 4000 and 1000 CV cycles under alkaline and neutral electrolytes, respectively (Figure S11a,b, Supporting Information). The EIS spectra of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst before and after CV cycling in alkaline and neutral electrolytes show only a slight increase in the charge transfer resistance even after several CV cycles (4000 cycles in alkaline electrolyte and 1000 cycles in neutral electrolyte) (Figure S11c,d, Supporting Information). The long-term chemical stability of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) could be attributed to the thiourea-assisted carbonization that occurs during the synthesis of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst upon thermal annealing under inert atmosphere.\(^{[13]}\) The carbonization process largely prevents the MXene surface from oxidation and thereby preserves the MXene structure during the HER process.\(^{[14]}\) Moreover, the Ru\(_{SA}\) are strongly bonded with the MXene support via N and S binding sites, as evidenced from the XAFS results. Overall, the electrochemical results suggest that Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) is an efficient and stable electrocatalyst for HER.

To gain more insight into the enhanced HER performance, we calculated the double-layer capacitance (\(C_{dl}\)) of the catalysts from the CV measurements obtained in 0.5 m H\(_2\)SO\(_4\). Figure 3f depicts the CV curves of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) at different scan rates ranging from 5 to 100 mV s\(^{-1}\). Similarly, the CV curves of Ti\(_3\)C\(_2\)T\(_x\) at different scan rates are shown in Figure S12 (Supporting Information). We determined the \(C_{dl}\) value of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) to be 31 mF cm\(^{-2}\), which is 62 times higher than that of Ti\(_3\)C\(_2\)T\(_x\) (0.5 mF cm\(^{-2}\)) (Figure 3g), indicating the high electrochemically active area with exposed catalytic active sites available on Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\), which are favorable for boosting the HER performance. Turnover frequency (TOF) is an important factor used to evaluate the HER activity of a catalyst. We calculated the TOF value of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) in 0.5 m H\(_2\)SO\(_4\) electrolyte based on the ICP-OES analysis (TOF calculation details are provided in the Supporting Information). Based on these results, we estimated the TOF values of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) at 100, 150, and 200 mV to be 0.52, 0.87, and 1.50 s\(^{-1}\), respectively (Figure 3h). The TOF values of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) are comparable with reported transition metal-based HER catalysts in acidic electrolyte (Figure 3h),\(^{[35–41]}\) suggesting the exceptional activity of the catalyst.

To the best of our knowledge, this reported HER performance is superior to that of other MXene-based HER catalysts reported thus far (Table S2, Supporting Information). As shown in Figure 3i, the HER performance of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) is also comparable with many recently reported precious transition metals based HER electrocatalysts in acidic solution (Table S3, Supporting Information). For comparison, we prepared different metals (Fe, Co, Ni, and Pt) anchored to the Ti\(_3\)C\(_2\)T\(_x\) MXene catalyst under the same experimental conditions and compared their HER performance to Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) (Figure 3j). Among them, Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) was found to be a superior HER catalyst, with the lowest overpotential value compared to that of Fe-N-S-Ti\(_3\)C\(_2\)T\(_x\), Co-N-S-Ti\(_3\)C\(_2\)T\(_x\), Ni-N-S-Ti\(_3\)C\(_2\)T\(_x\), and Pt-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalysts in acidic electrolyte. To understand the catalytic active sites in the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) electrocatalyst, we conducted a potassium thiocyanate ion (KSCN\(^−\)) test in 0.5 m H\(_2\)SO\(_4\). It is widely known that KSCN\(^−\) ions have the ability to block metal sites under acidic conditions.\(^{[21,42]}\) Therefore, we measured the HER polarization curves of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst before and after the addition of KSCN\(^−\) ions to the 0.5 m H\(_2\)SO\(_4\) electrolyte (Figure S13, Supporting Information). The addition of 40 × 10\(^{-3}\) m KSCN\(^−\) ions increases the overpotential from 235 to 400 mV in order to reach a current density of 80 mA cm\(^{-2}\). Further increasing the KSCN\(^−\) ion concentration to 80 × 10\(^{-3}\) m does not further affect the performance, which indicates that all isolated metal sites were blocked by the KSCN\(^−\) ions. However, the overpotential achieved after KSCN\(^−\) addition is still lower than the overpotential of Ti\(_3\)C\(_2\)T\(_x\) MXene, suggesting that Ru\(_{SA}\) are not the sole source of active sites for the enhanced HER performance of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst. In order to further understand the effective role of Ti\(_3\)C\(_2\)T\(_x\) as a potential support for HER, we used reduced graphene oxide (rGO) as an alternative substrate to anchor the Ru\(_{SA}\). The Ru-N-S-rGO catalyst offers an overpotential of 231 mV at 10 mA cm\(^{-2}\), which is 155 mV higher overpotential than Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\), suggesting the effective role of the MXene as a solid support for catalytic reactions (Figure S14, Supporting Information).

Based on our XPS and XAFS results, we performed DFT calculations to better understand the fundamental mechanism and hydrogen binding energies of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst for HER. Figure S15 (Supporting Information) shows the top and side view of the atomic model of a layer of Ti\(_3\)C\(_2\)T\(_x\) that we used in our DFT calculations. In general, the hydrogen adsorption energy on a catalyst surface is a key descriptor for studying the HER catalytic performance, in which an ideal catalyst should possess an optimal hydrogen adsorption energy value close to that of Pt (i.e., close to zero).\(^{[43]}\) The proposed
The calculated Gibbs hydrogen adsorption free energy (\(\Delta G\)) values of -0.86, -0.41, and -0.25 eV, respectively, indicating the strong H adsorption behavior on these catalysts and thus the high energy barriers for the formation and desorption of H\(_2\). Impressively, Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) achieves an optimal \(\Delta G_{\text{ads}}\) value of 0.08 eV, which is much closer to zero, highlighting the favorable H adsorption–desorption and subsequent H\(_2\) production characteristics of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\), enabling it to effectively drive the overall HER process. The optimal \(\Delta G_{\text{ads}}\) achieved by the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst could be attributed to the chemical interaction between the Ru\(_{SA}\) and MXene support, as evidenced from the XAFS results. Figure S16 (Supporting Information) shows the partial density of states (PDOS) of Ru\(_{SA}\) in Ru\(_{SA}\)-Ti\(_3\)C\(_2\)T\(_x\), Ru\(_{SA}\)-N-Ti\(_3\)C\(_2\)T\(_x\), and Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\). The yellow regions of the PDOS diagrams show how doping of Ru\(_{SA}\) induces charge transfer between the Ru\(_{SA}\) and MXene and thereby creates nonbonding states around the Fermi energy level. The lower intensity of the nonbonding states and change in density of states indicate that the isolated Ru atoms optimize the catalytic activity, which matches the trend of \(\Delta G_{\text{ads}}\). Furthermore, the total density of states (TDOS) analysis confirms that Ti\(_3\)C\(_2\)T\(_x\) can be used as a solid support with good electronic conductivity. As depicted in Figure 4c, the TDOS of Ti\(_3\)C\(_2\)T\(_x\), N-S-Ti\(_3\)C\(_2\)T\(_x\), Ru\(_{SA}\)-Ti\(_3\)C\(_2\)T\(_x\), Ru\(_{SA}\)-N-Ti\(_3\)C\(_2\)T\(_x\), and Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) demonstrates that all the systems possess metallic characteristics, which is beneficial for the electrocatalytic HER. Overall the DFT results strongly suggest that the decoration of Ru\(_{SA}\) onto the MXene support alters the electronic structure of Ru\(_{SA}\) with optimal \(\Delta G_{\text{ads}}\) to effectively facilitate the HER process.

Photoelectrochemical (PEC) water splitting is one of the economically viable approaches for producing clean solar hydrogen.\(^{[44,45]}\) We integrated the Ti\(_3\)C\(_2\)T\(_x\) and Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) electrocatalysts with n\(^{\text{np}}\)-Si photocathode to evaluate their PEC \(\text{H}_2\) production performance (see more details in PEC measurements section in Supporting Information). The PEC device structure of the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\)/n\(^{\text{np}}\)-Si photocathode is shown in Figure 5a. It has been previously shown that the drop-casting of Ti\(_3\)C\(_2\)T\(_x\) MXene can easily form a Schottky junction with n-Si by just van der Waals forces.\(^{[46]}\) Therefore, we were able to directly drop-cast the Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst onto the n\(^{+}\) side of the Si photocathode. The work function and band alignment of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\)/n\(^{\text{np}}\)-Si photocathode were investigated using ultraviolet photoelectron spectroscopy (UPS) (Figure S17, Supporting Information). The secondary electron cutoff energy obtained from the UPS spectra can be subtracted from the incident UV photon energy (He I excitation energy of 21.21 eV) to calculate the work function of the materials.\(^{[46]}\) In case of n\(^{\text{np}}\)-Si, the secondary electron cutoff energy is 17.26 eV and its corresponding work function is calculated to be 21.21–17.26 eV = 3.95 eV (the inset in Figure S17, Supporting Information). However, the secondary electron cutoff energy of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) shift toward low binding energy (16.96 eV) compared to n\(^{\text{np}}\)-Si, the work function of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) is estimated to be 21.21–16.96 eV = 4.25 eV that is higher than the work function of n\(^{\text{np}}\)-Si. Moreover, the work function of Ru\(_{SA}\)-N-S-Ti\(_3\)C\(_2\)T\(_x\) catalyst is comparable with the previously reported work function values for Ti\(_3\)C\(_2\)T\(_x\) MXene.\(^{[46,47]}\) Based on the work functions, we proposed the band structure diagram...
for Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$/n‘np’-Si photocathode (Figure 5b).
As shown in Figure 5b, upon light illumination, the photogenerated electrons from n‘np’-Si photocathode can promptly migrate to the Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$ catalyst surface because of their difference in the work functions. Thus, the continuous shuttle of these photogenerated electrons to the active sites of Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$ catalyst can prevent the charge carrier recombination on Si and Si/Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$ interface and thereby efficiently enhances the PEC H$_2$ production performance. Figure 5f displays the current density–voltage (J–V) characteristic curves of the Ti$_3$C$_2$T$_x$ and Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$ electrocatalysts integrated on the n‘np’-Si photocathode (0.5 m H$_2$SO$_4$, scan rate: 20 mV s$^{-1}$, AM 1.5 illumination). g,h) Comparison of the photocurrent density and onset potential of the Ru$_{53A}$-N-S-Ti$_3$C$_2$T$_x$/n‘np’-Si photocathode with previously reported earth-abundant and transition-metal-based electrocatalysts integrated with Si-based photocathodes.
of the Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$/nnp-Si photocathode is due to the excellent HER activity of the Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ electrocatalyst. As shown in Figure 5g, the photocurrent density value of Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$/nnp-Si photocathode is even better than most transition metals and earth-abundant HER catalysts integrated on Si-based photocathodes reported thus far (Table S5, Supporting Information). In addition, the onset potential of the Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$/nnp-Si photocathode is comparable with most reported transition metals and earth-abundant HER electrocatalysts coupled to Si photocathodes (Figure 5h, Table S5, Supporting Information). The PEC results shown herein demonstrate that the integration of a hydrophilic and electrically conductive MXene-based electrocatalyst with a Si photocathode could provide a scalable approach toward developing high-performance Si photocathodes for solar-driven PEC water splitting applications.

In summary, we have demonstrated that Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ is an efficient and stable HER electrocatalyst. The HER performance of Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ is superior to other previously reported MXene-based HER catalysts and most transition-metal-based HER catalysts. XAFS and DFT simulation studies reveal that the remarkable HER catalytic activity of Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ is mainly due to the catalytically active interfaces of the Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ MXene support and its optimal $\Delta G_{\text{H}^+}$. Furthermore, incorporating the Ru$_{54}$N-S-Ti$_3$C$_2$T$_x$ catalyst into a nnp-Si photocathode significantly boosts the photocurrent density to 37.6 mA cm$^{-2}$, which is 10 times higher than that of the Ti$_3$C$_2$T$_x$/nnp-Si photocathode. Both experimental and theoretical studies clearly demonstrate that the catalytic properties of MXenes can be tailored via metal–support interactions.

Supporting Information

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

Acknowledgements

This work was supported by the King Abdullah University of Science and Technology (KAUST). The authors acknowledge the startup fund of City University of Hong Kong. The authors thank the Australian Research Council for funding this work under the Discovery Grant program. This research was undertaken on the supercomputers in the National Computational Infrastructure (NCI) in Canberra, Australia, which was supported by the Australian Commonwealth Government, and the Pawsey Supercomputing Centre in Perth with funding from the Australian government and the Government of Western Australia.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

hydrogen evolution, MXene, photocathodes, single atom catalysts

Received: June 17, 2019
Revised: September 12, 2019
Published online: