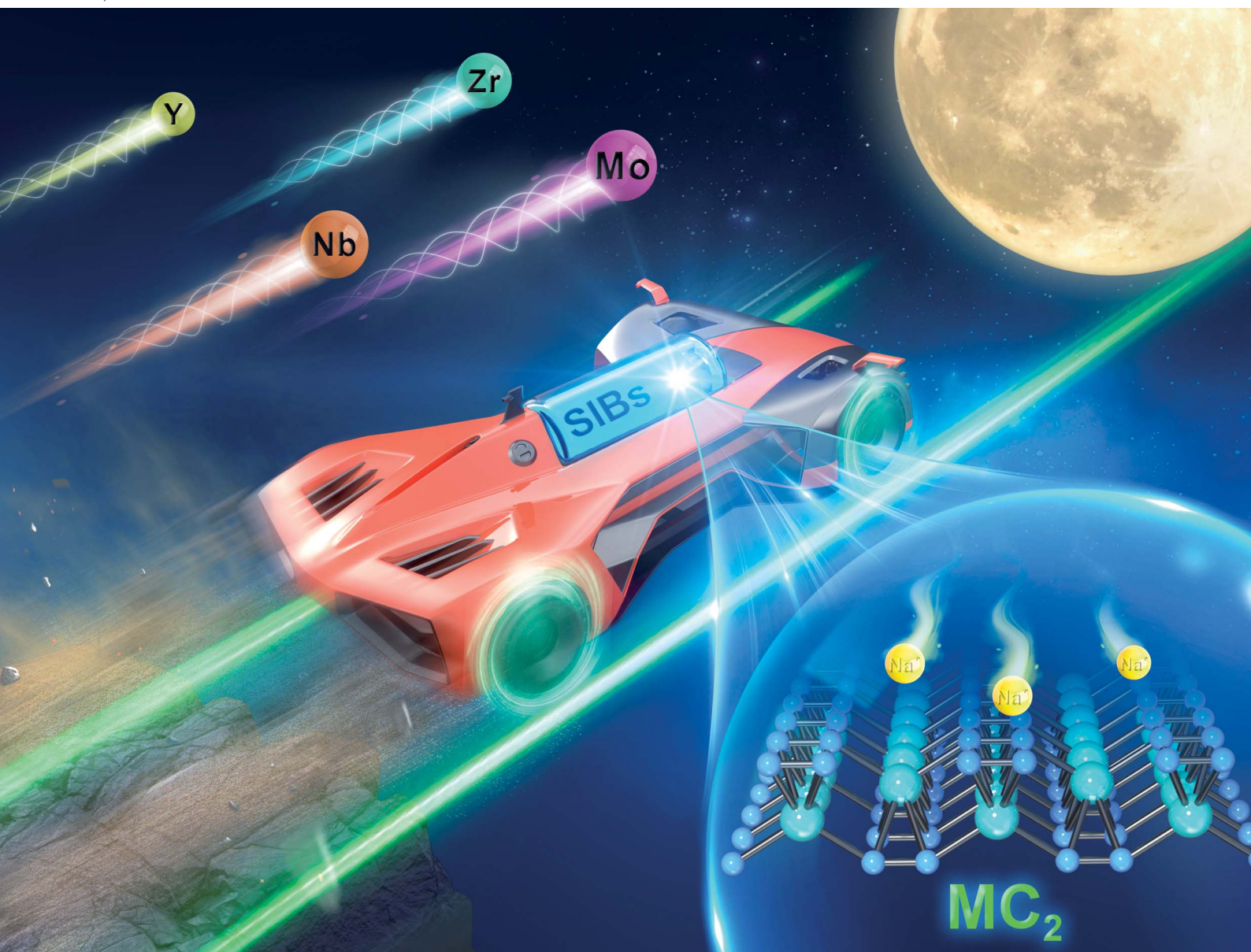


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**PAPER**

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# MC<sub>2</sub> (M = Y, Zr, Nb, and Mo) monolayers containing C<sub>2</sub> dimers: prediction of anode materials for high-performance sodium ion batteries†

Zhanzhe Xu,<sup>a</sup> Xiaodong Lv,<sup>\*bcd</sup> Wenyue Gu<sup>a</sup> and Fengyu Li<sup>ID</sup> <sup>\*a</sup>

Seeking novel high performance anode materials for sodium ion batteries (SIBs) is an attractive theme in developing energy storage devices. In this work, by means of density functional theory computations, we predicted a family of MC<sub>2</sub> (M = Y, Zr, Nb, and Mo) monolayers containing C<sub>2</sub> dimers to be promising anode materials for SIBs. The stability, electronic structure, and adsorption/diffusion/storage behavior of sodium atoms in MC<sub>2</sub> (M = Y, Zr, Nb, and Mo) monolayers were explored. Our computations revealed that Na adsorbed MC<sub>2</sub> (M = Y, Zr, Nb, and Mo) monolayers show metallic characteristics that give rise to excellent electrical conductivity and Na mobility with low activation energies for diffusion (0.21, 0.04, 0.20, and 0.22 eV, respectively) in these materials, indicative of a high charge/discharge rate. In addition, the theoretical capacities of Na-adsorbed on YC<sub>2</sub>, ZrC<sub>2</sub>, NbC<sub>2</sub>, and MoC<sub>2</sub> monolayers are 478, 697, 687, and 675 mA h g<sup>-1</sup>, respectively, higher than that of commercial graphite (284 mA h g<sup>-1</sup>), and the open-circuit voltages are moderate (0.11–0.25 V). Our results suggest that MC<sub>2</sub> (M = Y, Zr, Nb, and Mo) monolayers have great potential to serve as anode materials for SIBs.

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## 1. Introduction

The global demand for advanced energy storage and conversion technologies, especially electrochemical energy technologies, is growing rapidly. Among them, rechargeable batteries, such as lithium-ion batteries (LIBs), are widely used in mobile electronic and electrified vehicles.<sup>1–3</sup> However, LIBs can meet the tough demands of energy storage and conversion applications,

yet the limited abundance (only 20 ppm) and expensiveness of lithium are not the best choices for application in large-scale energy storage systems and sustainability.<sup>4,5</sup> Fortunately, sodium-ion batteries (SIBs) were confirmed as low-cost alternatives to lithium-ion batteries (LIBs) in energy storage applications, on account of the natural abundance, high energy density and similar intercalation chemistry to lithium, suggesting that some mature technologies in LIBs can be translated to SIBs, and SIBs are promising candidates for next generation rechargeable batteries.<sup>6</sup>

Cathode materials with high electrochemical performance for SIBs have been extensively studied experimentally and theoretically, such as layered transition metal oxide compounds, polyanionic compounds, Prussian blue analogues, and sodium-based layered materials.<sup>7,8</sup> However, anode materials matching well LIB systems are not suitable for SIBs due to the bigger ionic radius and the higher redox potential of Na<sup>+</sup> ions vs. Li<sup>+</sup>. For instance, graphite is not available in SIBs, because the interlayer distance of graphite is too small to accommodate sodium, leading to a larger mismatched layer spacing and poor capacity.<sup>9,10</sup> Thus, the design and exploration of suitable electrode materials for SIBs are greatly desired.

In recent years, two-dimensional (2D) materials as electrodes have attracted great attention due to their excellent properties, including good mechanical flexibility, rich active sites, large exposed surface area for electrochemical processes, and expanded interlayer spacing.<sup>11,12</sup> For example, transition metal chalcogenides (TMDs),<sup>13–15</sup> oxides (TMOs),<sup>16,17</sup> borides (MBenes),<sup>18,19</sup> transition metal carbides or nitrides

<sup>a</sup>School of Physical Science and Technology, Inner Mongolia University, Hohhot, 010021, China. E-mail: fengyuli@imu.edu.cn

<sup>b</sup>CAS Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China. E-mail: lvxiaodong@nimte.ac.cn

<sup>c</sup>Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

<sup>d</sup>Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou 341000, People's Republic of China

† Electronic supplementary information (ESI) available: Lattice constants of the MC<sub>2</sub> monolayers; bond length and thickness of the MC<sub>2</sub> monolayers; the calculated phonon spectra of the MC<sub>2</sub> monolayers; the FPMD simulations at the end of 5 ps at 300 K; the electronic localization function (ELF) of the MC<sub>2</sub> monolayers; the partial density of states (TDOS and PDOS) of the MC<sub>2</sub> monolayers; the partial density of states (PDOS) of Na-adsorbed MC<sub>2</sub> monolayers; the variation of the path-I diffusion lengths of Na on the MC<sub>2</sub> monolayers with the lattice constants of MC<sub>2</sub>; the energy profile (left plane) and diffusion pathways (right plane) of Na diffusing on the TiC<sub>2</sub> monolayer; the formation energy (*E<sub>f</sub>*) of Na<sub>x</sub>MC<sub>2</sub> with respect to MC<sub>2</sub> monolayers and Na bulk bcc metal; the configurations and their optimized adsorption energies (eV) for Na<sub>x</sub>NbC<sub>2</sub>; the side views of the Na-intercalated MC<sub>2</sub> monolayer at the end of 5 ps FPMD simulations at 300 and 500 K, respectively. See DOI: 10.1039/d1na00422k



(MXenes),<sup>20,21</sup> and main group binary compounds ( $B_2S$ ,  $BN_2$ ,  $SiS$ ,  $SnP_3$ , *etc.*)<sup>22–25</sup> have been theoretically and experimentally explored as anode materials. Among these materials, 2D MXenes have experienced rapid development as anode materials after the successful exfoliation of  $Ti_3C_2$  nanosheets in 2011,<sup>26</sup> due to their superior electrical conductivity, high performance rate, and high specific capacities.<sup>27–30</sup> So far, metal-rich 2D MXene-based materials (*i.e.*  $Ti_2C$ ,<sup>31</sup>  $V_2C$ ,<sup>32</sup>  $Nb_2C$ ,<sup>33</sup>  $Mo_2C$ ,<sup>34</sup>  $Cr_2C$ ,<sup>35</sup>  $Mn_2C$ ,<sup>36</sup> *etc.*) have been extensively studied as anode materials for LIBs and SIBs. However, the major problems with MXenes are surface functionalization and metal atoms exposed on the surface commonly to suppress sodium adsorption, which largely reduce the storage capacity and the performance of batteries.<sup>21</sup>

In this regard, Wang *et al.*<sup>37</sup> proposed a novel carbon-rich 2D metal carbide (MC), namely  $TiC_2$  monolayer, which consists of unique  $C_2$  dimers (Fig. 1a) and exhibits high structural stability. The Li capacity, open-circuit voltage (OCV), and diffusion barrier were calculated to be  $622 \text{ mA h g}^{-1}$ , 0.96 V, and 0.11 eV, respectively, indicating that the  $TiC_2$  monolayer is a promising anode material for LIBs. Subsequently, other transition metal carbide ( $VC_2$ ,<sup>38,39</sup>  $TaC_2$ ,<sup>40</sup>  $MnC_2$ ,<sup>41</sup>  $ScC_2$ ,<sup>42</sup> and  $WC_2$  (ref. 43)) monolayers with a similar configuration were also theoretically investigated as LIB and SIB anode materials. In particular, Zhao *et al.*<sup>44</sup> found that an  $FeC_2$  monolayer containing isolated  $C_2$  dimers with ferromagnetic and half-metallic properties was possible to be synthesized by chemically exfoliating the bulk counterpart of  $ThFeC_2$ .

Therefore, the proposal of C-rich  $MC_2$  monolayers may offer a new strategy for the rational design of 2D anode materials for SIBs. In this work, four  $C_2$ -containing  $MC_2$  ( $M = Y, Zr, Nb$  and  $Mo$ ) monolayers were systematically explored by means of DFT computations. According to our calculations of cohesive energy, phonon dispersion, first-principles molecular dynamics (FPMD) stimulation, mechanical parameters, and sodium adsorption/diffusion/capacity, the four examined monolayers

were confirmed to exhibit great thermodynamic, dynamic, thermal, and mechanical stability, excellent electronic conductivity and outstanding electrode performance as a SIB anode material. In particular, the  $ZrC_2$  monolayer exhibits superior electrochemical performance with high theoretical storage capacity ( $699 \text{ mA h g}^{-1}$ ) and small diffusion energy barriers (0.04 eV) for Na atoms.

## 2. Computational methods

In this study, the structural relaxation and performance calculations were based on density functional theory (DFT) methods within the Vienna *ab initio* simulation package (VASP).<sup>45–47</sup> The general gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional and a plane wave basis set with an energy cut-off of 500 eV were employed.<sup>48,49</sup> Monkhorst–Pack meshes<sup>50</sup> of  $11 \times 11 \times 1$  and  $5 \times 5 \times 1$   $k$ -points were used to sample the two-dimensional Brillouin zone for the unit cell and supercell relaxation and electronic structure calculations, respectively. An inter-layer vacuum space of 20 Å was used to avoid the interactions of mirror images in adjacent layers. All the structures are fully relaxed until the convergence tolerances for the energy and force on each atom were less than  $1.0 \times 10^{-5}$  eV and 0.02 eV Å<sup>-1</sup>, respectively. All the atomic structures and charge density distributions were visualized by using the VESTA package.<sup>51</sup>

The dynamic stability of  $MC_2$  ( $M = Y, Zr, Nb$ , and  $Mo$ ) monolayers was evaluated by recording the phonon spectrum with the PHONOPY code<sup>52</sup> on the basis of density functional perturbation theory (DFPT). Thermal stabilities were assessed by performing first-principles molecular dynamics (FPMD) simulations (a  $4 \times 4 \times 1$  supercell, 96 atoms) in the NVT ensemble lasting for 5 ps with a time step of 1 fs at room temperature (300 K), and the temperature was controlled by the Nosé–Hoover method.<sup>53</sup> By using the climbing-image nudged elastic band (CI-NEB) approach,<sup>54,55</sup> the diffusion energy barrier

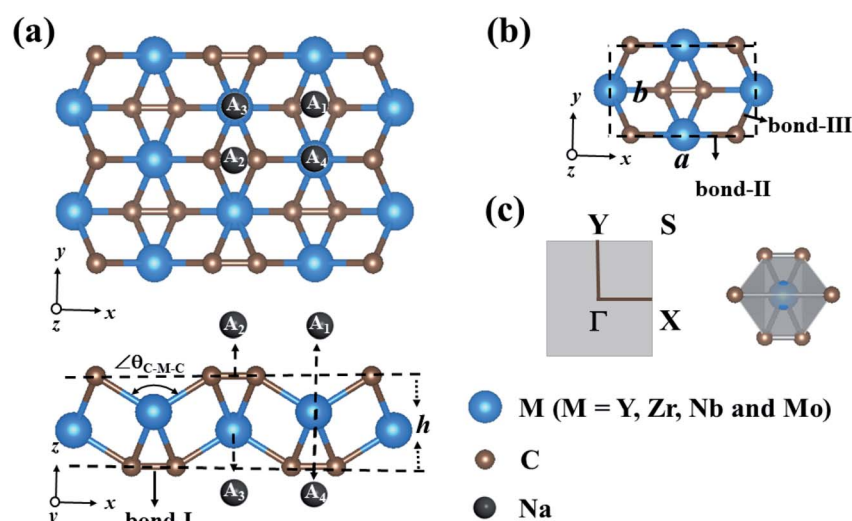


Fig. 1 (a) The geometric structure of the  $2 \times 2 \times 1$  supercell of the  $MC_2$  ( $M = Y, Zr, Nb$ , and  $Mo$ ) monolayers (top and side views); (b) the unit cell is highlighted by the black dashed lines; (c) the Brillouin zone of the  $MC_2$  monolayers and the edge-shared  $MC_6$  octahedral structure.



and the minimum energy pathways of Na atom diffusing on  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers were calculated. The charge distribution and transfer were analyzed by the Bader charge method.<sup>56</sup>

### 3. Results and discussion

#### 3.1 Geometric structure of the $\text{MC}_2$ ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers

The optimized structures of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers are displayed in Fig. 1a. From the top view, these monolayers exhibit a rectangular lattice with the space group  $Pm\bar{m}n$  symmetry, where carbon atoms are in the form of  $\text{C}_2$  dimers, and each unit cell contains two M atoms and four C atoms (Fig. 1b). From the side view, the crystal structure of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers possesses a tetra-layer structure with two M layers sandwiched between two C layers, in which each M atom bonds with six neighboring C atoms, while each C atom is shared by one C of the same  $\text{C}_2$  dimer and three adjacent M atoms, forming an edge-shared  $\text{MC}_6$  octahedral structure without M atoms exposed on the surface (Fig. 1c).

Table 1 summarizes the optimized structural parameters of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers, including the lattice constants ( $a$  and  $b$ ), bond lengths of C–C (bond I), M–C (bond II along the  $x$  axis and bond-III along the  $y$  axis) and thickness ( $h$ ), and the evolution trend was plotted for different  $\text{MC}_2$  monolayers with transition metal atoms ( $M$ ) from  $\text{Y} \rightarrow \text{Mo}$  (Fig. S1 and S2†). The lattice constants ( $4.84 \leq a \leq 5.80 \text{ \AA}$  and  $3.01 \leq b \leq 4.28 \text{ \AA}$ ) are close to those of  $\text{VC}_2$  ( $a = 4.62 \text{ \AA}$  and  $b = 3.28 \text{ \AA}$ ),<sup>38</sup>  $\text{FeC}_2$  ( $4.54 \text{ \AA}$  and  $2.89 \text{ \AA}$ ),<sup>44</sup> and  $\text{ScC}_2$  ( $5.39 \text{ \AA}$  and  $4.12 \text{ \AA}$ ).<sup>42</sup> The remarkable feature we can see is that structural parameters, such as lattice constants ( $a$  and  $b$ ), bond lengths M–C ( $d_{\text{M-C}}$ ) and bond angle ( $\angle \theta_{\text{C-M-C}}$ ), decrease from  $5.77$  to  $4.84 \text{ \AA}$  ( $4.45$  to  $3.03 \text{ \AA}$ ),  $2.39$  to  $2.03 \text{ \AA}$  ( $2.51$  to  $2.26 \text{ \AA}$ ) along the  $x$  ( $y$ )-direction and  $138.14^\circ$  to  $119.28^\circ$  from  $\text{Y} \rightarrow \text{Mo}$  (Fig. S3†), mainly originating from the decrease of the atomic radius from  $\text{Y}$  to  $\text{Mo}$ . However the others, including bond lengths C–C ( $d_{\text{C-C}}$ ) and thickness ( $h$ ), increase ( $1.30$  to  $1.37 \text{ \AA}$  and  $1.81$  to  $2.60 \text{ \AA}$ ) from  $\text{Y} \rightarrow \text{Mo}$ , respectively. The latter increasing trend could be understood by the electronegativity difference between the transition metal ( $\text{Y} \rightarrow \text{Mo}$ ) and carbon, which are strongly correlated with the structural properties.<sup>57,58</sup>  $\text{YC}_2$  has the highest electronegativity difference ( $1.33$  on the Pauling scale), while  $\text{MoC}_2$  possesses the lowest ( $0.39$  on the Pauling scale), the angles of M–C–M ( $\angle \theta_{\text{M-C-M}}$ ) gradually decrease, resulting in an increase in the  $d_{\text{C-C}}$  and

**Table 1** The lattice constants ( $a$  and  $b$ , in  $\text{\AA}$ ), C–C bond length (bond-I, in  $\text{\AA}$ ), M–C bond length (bond-II along the  $x$  axis and bond-III along the  $y$  axis, in  $\text{\AA}$ ), bond angle ( $\angle \theta_{\text{C-M-C}}$ ), thickness ( $h$ ,  $\text{\AA}$ ) and cohesive energy ( $E_{\text{coh}}$ , in eV per atom) of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers

System	$a$	$b$	Bond-I	Bond-II	Bond-III	$\angle \theta_{\text{C-M-C}}$	$h$	$E_{\text{coh}}$
$\text{YC}_2$	5.77	4.45	1.30	2.39	2.51	$138.14^\circ$	1.81	−7.40
$\text{ZrC}_2$	5.31	3.92	1.34	2.21	2.33	$128.23^\circ$	2.07	−7.99
$\text{NbC}_2$	4.96	3.54	1.34	2.08	2.26	$119.74^\circ$	2.26	−7.98
$\text{MoC}_2$	4.84	3.03	1.37	2.03	2.27	$119.28^\circ$	2.60	−7.48

thickness of 2D  $\text{MC}_2$  from  $\text{Y}$  to  $\text{Mo}$  (Fig. S3†). Note that the C–C distances of  $\text{C}_2$  dimers are in the range of  $1.30$ – $1.37 \text{ \AA}$ , which are shorter than that in the  $\text{Ti}_8\text{C}_{12}$  cage and MXenes with the C–C distances in the range of  $1.40$ – $3.35 \text{ \AA}$ ,<sup>59–61</sup> implying stronger C–C bonding in  $\text{C}_2$  dimers.

#### 3.2 Stabilities of the $\text{MC}_2$ ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers

Prior to exploring the physical properties and evaluating the probability of experimental synthesis of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers, we firstly verified their thermodynamic, dynamic, thermal, and mechanical stabilities and investigated the underlying mechanisms for their stabilities.

First, we examined the thermodynamic stability by calculating their cohesive energy ( $E_{\text{coh}}$ ), which is defined as  $E_{\text{coh}} = (E_{\text{MC}_2} - nE_{\text{M}} - mE_{\text{C}})/(n + m)$ , in which  $E_{\text{MC}_2}$  and  $E_{\text{M}}/E_{\text{C}}$  are the energies of the  $\text{MC}_2$  monolayer and a free M/C atom, respectively, and  $n/m$  is the number of M/C atoms in one unit cell. According to this definition, a more negative  $E_{\text{coh}}$  value indicates a better thermodynamic stability of the structure. The computed  $E_{\text{coh}}$  values for  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers are  $-7.40$ ,  $-7.99$ ,  $-7.98$ , and  $-7.48 \text{ eV}$  per atom, respectively, lower than that of the  $\text{TiC}_2$  monolayer ( $-6.59 \text{ eV}$ ),<sup>37</sup>  $\text{VC}_2$  monolayer ( $-7.15 \text{ eV}$ ),<sup>38</sup>  $\text{ScC}_2$  monolayer ( $-6.33 \text{ eV}$ ),<sup>42</sup> and the synthesized  $\text{Ti}_2\text{C}^{62}$  ( $6.18 \text{ eV}$  per atom) MXene, all of which are demonstrated to be structurally and thermodynamically stable according to the first principles calculations or experimentally. Thus, the four  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers have solid thermodynamic stability.

Second, the dynamic stability of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers was evaluated by calculating their phonon dispersions, which are shown in Fig. S4.† All of them are dynamically stable as confirmed by the absence of imaginary phonon modes in the entire Brillouin zone. In particular, the highest frequencies for the dynamically stable monolayers ( $40.25$ – $49.59 \text{ THz}$ ) are higher or comparable to those of the  $\text{ScC}_2/\text{ScN}_2$  monolayer ( $50/38 \text{ THz}$ ),<sup>42</sup>  $\text{VC}_2$  ( $\sim 43 \text{ THz}$ ),<sup>38</sup> and the recently proposed  $\text{TaC}_2$  monolayer ( $42 \text{ THz}$ ),<sup>40</sup> suggesting strong M–C bonding in these  $\text{MC}_2$  nanosheets.

Third, FPMD simulations were performed to assess their thermal stability at room temperature ( $300 \text{ K}$ ), and the structures after annealing at  $300 \text{ K}$  for  $5 \text{ ps}$  are presented in Fig. S5a–d.† Neither bond breakage nor structural distortion can be noted, and then we conclude that the  $\text{YC}_2$ ,  $\text{ZrC}_2$ ,  $\text{NbC}_2$  and  $\text{MoC}_2$  monolayers possess excellent thermal stabilities at room temperature.

Finally, we assessed the mechanical stability of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers by calculating their elastic constants using the finite distortion method.<sup>63</sup> Mechanically, a stable 2D structure should meet the Born–Huang criteria<sup>64,65</sup> given by  $C_{11}C_{22} - C_{12}^2 > 0$  and  $C_{66} > 0$ . The calculated values of elastic constants fully satisfy these criteria (shown in Table 2), demonstrating that the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers are also mechanically stable.

To gain insights into the bonding nature and stabilizing mechanism, we calculated the electron localization functions



**Table 2** The elastic constants  $C_{11}$  and  $C_{22}$  (in  $\text{N m}^{-1}$ ), in-plane Young's modulus  $Y_x$  and  $Y_y$  (in  $\text{N m}^{-1}$ ), and Poisson's ratio of the  $\text{TiC}_2$ ,  $\text{YC}_2$ ,  $\text{ZrC}_2$ ,  $\text{NbC}_2$ , and  $\text{MoC}_2$  sheets

System	$C_{11}$	$C_{12}$	$C_{22}$	$C_{66}$	$Y_x$	$Y_y$	$\nu_x$	$\nu_y$
$\text{YC}_2$	79.33	22.17	32.21	16.51	64.07	26.01	0.69	0.28
$\text{ZrC}_2$	107.71	34.95	49.15	27.00	82.86	37.81	0.71	0.32
$\text{NbC}_2$	158.97	40.90	55.50	42.85	128.82	44.98	0.74	0.26
$\text{MoC}_2$	180.44	43.76	82.01	47.97	157.09	71.40	0.53	0.24
$\text{TiC}_2$ (ref. 37)	140.58	25.10	70.52	16.19	131.17	66.04	0.59	0.21

(ELFs) of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers. The ELF is an effective tool for characterizing chemical bonding and can reflect the electron localization in the system.<sup>66</sup> Generally, the ELF value near zero (blue) denotes a low electron density area, whereas the ELF values of 1.0 (red) and 0.5 (green) represent the perfect localization and the free electron-gas, respectively. As shown in Fig. S6,† in the ELF maps of the (001) and (010) slices we can see that the region between M and C atoms in all the  $\text{MC}_2$  monolayers is in the green color corresponding to an ELF of around 0.5, indicating fully delocalized electron distribution, which well shared and delocalized electrons make robust connection between the M and C atoms, and the Bader charge analysis revealed that the each M ( $M = \text{Y, Zr, Nb, and Mo}$ ) atom transfers 1.85, 1.81, 1.73, and 1.15  $e^-$  per atom to the  $\text{C}_2$  dimer, respectively, similar to the value of 1.80/1.50  $e^-$  for  $\text{TiN}_2/\text{C}_2$ ,<sup>37</sup> 1.74/1.71  $e^-$  for  $\text{ScC}_2/\text{N}_2$ ,<sup>42</sup> and 1.85  $e^-$  for  $\text{YN}_2$  (ref. 67) monolayers, indicating ionic interactions between M and C atom. While, the  $\text{C}_2$  dimer exhibits strong covalent bond characteristics, the results are in agreement with previous studies that the formation of the  $\text{C}_2$  dimer plays an important role in stabilizing metal 2D structures. As a consequence, the coexistence of ionic and covalent bonding is mainly responsible for the structural stability.

### 3.3 Mechanical and electronic properties of the $\text{MC}_2$ ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers

Having confirmed the stability of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers, the mechanical properties, including Young's

modulus  $Y(\theta)$  and Poisson's ratio  $\nu(\theta)$ , were investigated. The angle-dependent in-plane  $Y(\theta)$  and  $\nu(\theta)$  were estimated by using the following equation:<sup>68</sup>

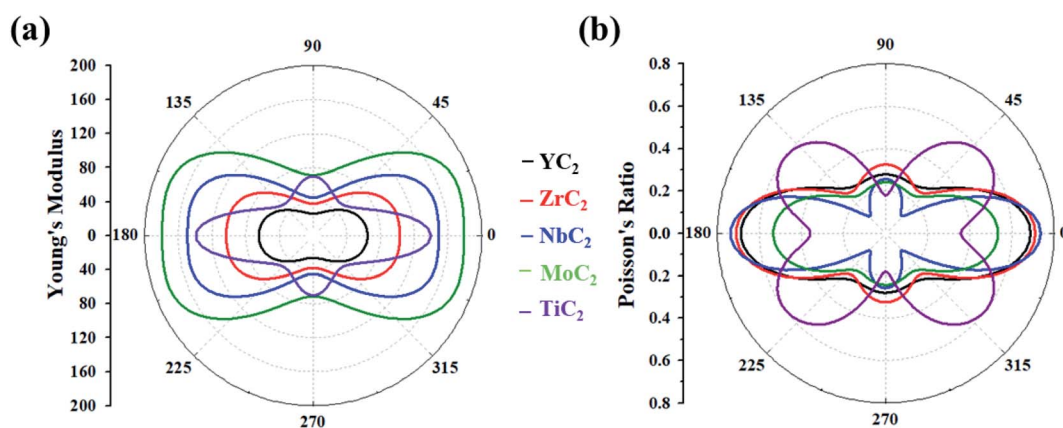
$$Y(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}\sin^4\theta + A\sin^2\theta\cos^2\theta + C_{22}\cos^4\theta} \quad (1)$$

$$\nu(\theta) = \frac{C_{12}\sin^4\theta - B\sin^2\theta\cos^2\theta + C_{12}\cos^4\theta}{C_{11}\sin^4\theta + A\sin^2\theta\cos^2\theta + C_{22}\cos^4\theta} \quad (2)$$

where  $A = (C_{11}C_{22} - C_{12}^2)/C_{66} - 2C_{12}$  and  $B = C_{11} + C_{12} - (C_{11}C_{22} - C_{12}^2)/C_{66}$ .

Based on the above equations, we plotted  $Y(\theta)$  and  $\nu(\theta)$  with the variation of angle  $\theta$  (Fig. 2). The  $Y(\theta)$  of  $\text{Y/Zr/Nb/MoC}_2$  monolayers decreases from a maximum value of 64.07/82.86/128.82/157.09  $\text{N m}^{-1}$  along the  $x$  direction to a minimum value of 26.01/37.81/44.98/71.40  $\text{N m}^{-1}$  along the  $y$  direction, reflecting their high mechanical anisotropy. However, the  $Y(\theta)$  of the  $\text{TiC}_2$  monolayer decreases from a maximum value of 131.17  $\text{N m}^{-1}$  in the  $x$  direction to a minimum value of 55  $\text{N m}^{-1}$  at about  $\theta = 46^\circ$ , which is consistent with a previous report.<sup>37</sup> Compared with other well-known 2D materials, strikingly, our calculated  $Y$  along  $x$  and  $y$  directions of these  $\text{C}_2$ -containing monolayers are comparable to the value of  $\text{MoS}_2$  (122  $\text{N m}^{-1}$ ),<sup>69</sup> silicene (61.7  $\text{N m}^{-1}$ ) and germanene (44  $\text{N m}^{-1}$ ),<sup>70</sup> but smaller than that of graphene (341.60  $\text{N m}^{-1}$ )<sup>71</sup> and hexagonal h-BN (271  $\text{N m}^{-1}$ ),<sup>72</sup> implying high flexibility for these monolayers. The modest mechanical properties are beneficial for the charge-discharge process of rechargeable ion batteries.

To analyze the electronic properties of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers, the atom-projected electronic band structure and partial density of states (PDOS) were carefully investigated (as shown in Fig. 3 and S7†). The results showed that all considered monolayers exhibit metallic character, as indicated by the partially occupied bands crossing the Fermi level in the Brillouin zone. The orbital analysis suggested that the bands near the Fermi level are dominated by the  $M_d$  orbitals, while the  $C_p$  orbitals make minor contribution by hybridizing with the  $M-d$  states, which is in line with the electrons transferred from M to C atoms based on the Bader charge analysis, as shown in Fig. S6.† The metallic nature of  $\text{MC}_2$  ( $M =$



**Fig. 2** (a) Young's modulus and (b) Poisson's ratio of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, Mo}$  and  $\text{Ti}$ ) monolayers as a function of the in-plane angle  $\theta$ , and  $\theta = 0^\circ$  corresponds to the  $x$ -axis.



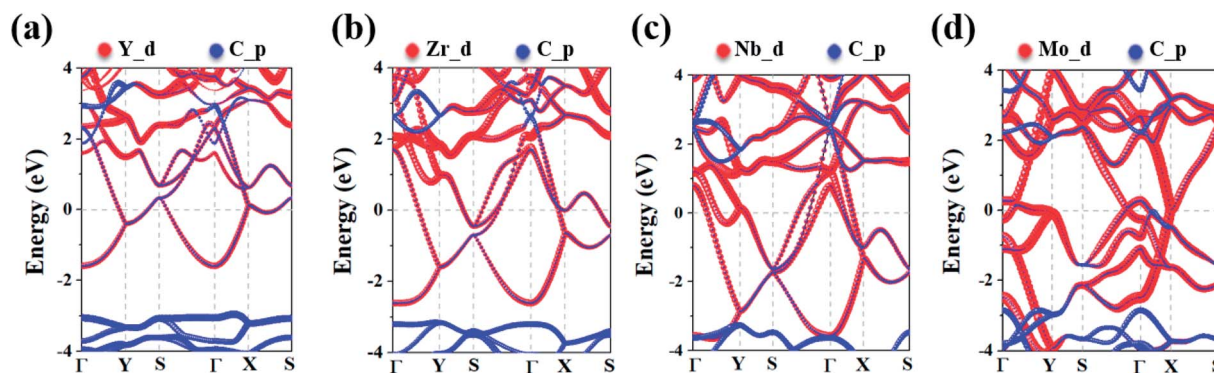


Fig. 3 The electronic band structures of the (a)  $\text{YC}_2$ , (b)  $\text{ZrC}_2$ , (c)  $\text{NbC}_2$ , and (d)  $\text{MoC}_2$  monolayers. The red and blue curves denote the d orbitals of the metal atoms and the p orbitals of C atoms, respectively. The Fermi energy is denoted by a dashed line at 0 eV.

Y, Zr, Nb, and Mo) monolayers indicates the advantage in electrical conductivity, which is highly desirable for high performance of electrode materials.

### 3.4 Na adsorption and diffusion on the $\text{MC}_2$ ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers

The development of sodium ion batteries (SIBs) is often hindered by the limited choice of anode materials. The modest mechanical properties and metallic feature of the examined  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers facilitate our investigation on their potential application as SIB anode materials.

The adsorption behavior between metal atoms and 2D materials closely correlates with the anode performance. Thus, we firstly examined the energy-preferred adsorption sites for a single Na atom on the surface of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers with a  $2 \times 2 \times 1$  supercell. Four high symmetry adsorption sites were considered, namely  $A_1$  (where Na sits over the midpoint of the bottom C-C bond),  $A_2$  (where Na sits over the midpoint of the top C-C bond),  $A_3$  (where Na sits over the M atom and interacts with four top C atoms) and  $A_4$  (where Na sits over the M atom and interacts with two top C atoms) sites, as

shown in Fig. 1a. After full relaxation, the energetically most favorable adsorption sites for Na on  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers were identified by calculating their adsorption energy ( $E_{\text{ads}}$ ), which is defined as:

$$E_{\text{ads}} = E_{\text{tot}} - E_{\text{MC}_2} - E_{\text{Na}} \quad (3)$$

where  $E_{\text{tot}}$  and  $E_{\text{MC}_2}$  are the energies of the  $\text{MC}_2$  supercell with and without a single Na atom, respectively, and  $E_{\text{Na}}$  represents the energy of an isolated Na atom. According to this definition, a more negative adsorption energy indicates a more favorable exothermic reaction between the  $\text{MC}_2$  monolayer and Na atom.

Almost all the investigated  $\text{MC}_2$  monolayers can effectively adsorb Na atoms, as indicated by the negative  $E_{\text{ads}}$  values (Fig. 4). Except for the  $\text{YC}_2$  monolayer, on which the most stable adsorption site of Na is the  $A_3$  site ( $E_{\text{ads}} = -1.55$  eV), the Na's energy-favorable site on the other three  $\text{MC}_2$  ( $M = \text{Zr, Nb, and Mo}$ ) monolayers is  $A_1$  with an  $E_{\text{ads}}$  of  $-1.67$ ,  $-2.45$  and  $-2.95$  eV, respectively, in agreement with the preferred adsorption site on  $\text{TiC}_2$  ( $A_1$ ),<sup>37</sup>  $\text{VC}_2$  ( $A_1$ ),<sup>38</sup> and  $\text{ScC}_2$  ( $A_3$ ).<sup>42</sup> In addition, the  $A_1$  ( $A_3$  and  $A_4$ ) site is the Na's second favorable adsorption site on the  $\text{YC}_2$  ( $\text{ZrC}_2/\text{NbC}_2$  and  $\text{MoC}_2$ ) monolayer. The difference of the most preferred Na adsorption site is due to the shorter Na-C bond lengths ( $d_{\text{Na-C}}$ ) formed between Na and C at the  $A_3$  ( $A_1$ ) site than those at the  $A_1$  ( $A_3$ ) site on  $\text{YC}_2$  ( $\text{ZrC}_2$ ,  $\text{NbC}_2$ , and  $\text{MoC}_2$ ): 2.51 vs. 3.54/3.70 Å (2.53 vs. 2.61, 2.59 vs. 2.62, and 2.78 vs. 2.81 Å). Among the four examined monolayers, Na has the strongest/weakest interaction with the  $\text{MoC}_2/\text{YC}_2$  monolayer, which can be understood by the gradually increasing distance between the adsorbed Na and the  $\text{MC}_2$  monolayer (from 1.49 Å on  $\text{MoC}_2$  to 1.64 Å on  $\text{YC}_2$ , as shown in Fig. 5).

Fig. 5 presents the fully optimized structures for the Na-adsorbed  $\text{YC}_2$  monolayer at the site  $A_3$  and  $\text{MC}_2$  ( $M = \text{Zr, Nb, and Mo}$ ) monolayers at the site  $A_1$ , respectively. For Na-adsorbed Y/Zr/Nb/MoC<sub>2</sub> monolayers, the Na-C bond length is 2.51/2.53/2.59/2.78 Å, and the adsorption height ( $h$ ), i.e., the vertical distance between the top-layer carbon and Na atom is 1.64/1.58/1.54/1.49 Å. Obviously, the  $\text{MC}_2$  monolayer with a larger atomic number (smaller atomic radii) from Y → Mo has a lower adsorption height ( $h$ ); however, the Na-C bond length

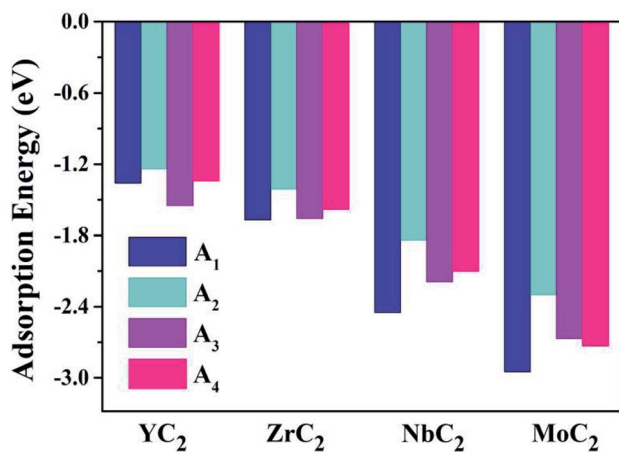


Fig. 4 The adsorption energies of a single Na atom on the ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayer at the four examined adsorption sites  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$ .



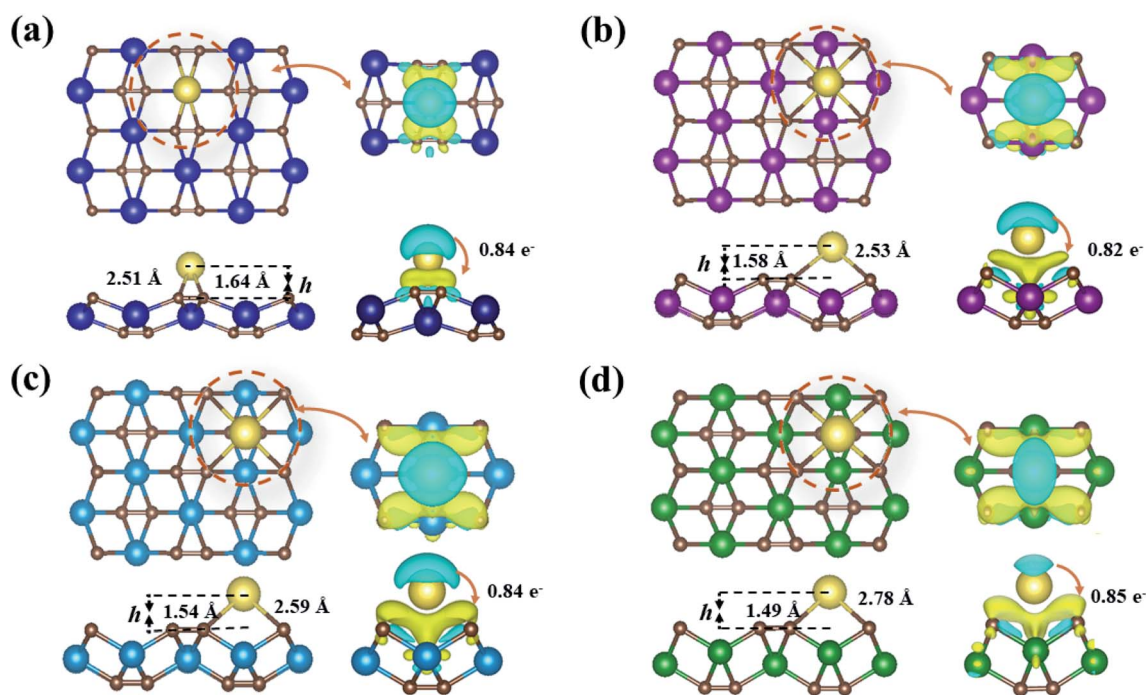


Fig. 5 Top and side views of the most stable Na-adsorbed configurations of  $\text{YC}_2$  (a),  $\text{ZrC}_2$  (b),  $\text{NbC}_2$  (c), and  $\text{MoC}_2$  (d) monolayers; right plane corresponds to the charge density difference. The isosurface level is set to  $0.002 \text{ e} \text{ \AA}^{-3}$ . Blue and yellow regions indicate electron depletion and accumulation, respectively.

and adsorption energy ( $E_{\text{ads}}$ ) are inversely proportional to the atomic radii.

To better understand the physical mechanism of the adsorption process, we investigated the charge transfer process between a single Na atom adsorbed on the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers by using the charge density difference using the following formula,

$$\Delta\rho = \rho_{\text{tot}} - \rho_{\text{MC}_2} - \rho_{\text{Na}} \quad (4)$$

where  $\rho_{\text{tot}}$  and  $\rho_{\text{MC}_2}$  denote the total electron densities of the relaxed  $\text{MC}_2$  monolayer with and without Na, respectively, and  $\rho_{\text{Na}}$  is the total electron density of an isolated Na atom. Fig. 5 right panel presents charge density difference plots for Na adsorbed  $\text{YC}_2$  at site  $A_3$  and  $\text{Zr/Nb/MoC}_2$  at site  $A_1$ , in which the electron accumulation (yellow) is located between the Na atom and  $\text{MC}_2$  monolayer, while the electron depletion (blue) is around the Na atoms, suggesting that the Na donates electrons and the  $\text{MC}_2$  monolayer accepts electrons, which originates from the smaller electronegativity of Na than that of C and metal atoms  $M$  ( $M = \text{Y, Zr, Nb, and Mo}$ ). The Bader charge analysis showed that the electrons transferred from Na to the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers are 0.84, 0.82, 0.84, and 0.85  $e^-$ , respectively. It can also be observed from the PDOS of Na-adsorbed  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) shown in Fig. S8† that hybridization exists between the Na atom and the C atom of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayer. At the same time, the adsorption of Na only slightly influences the electronic structure of the pristine  $\text{MC}_2$  monolayer, and the metallic features are maintained after the adsorption of Na according to

Fig. S8,† which is rather beneficial to their application as anode materials.

Metal mobility was another significant factor in the design and selection of effective anode materials, which are directly linked to the charge-discharge rates of rechargeable batteries. Thus, we further investigated the diffusion of Na on the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers (Fig. 6). For the  $\text{YC}_2$  monolayer (Fig. 6b), since  $A_3$  is the energetically most favorable site among the four adsorption sites ( $A_1, A_2, A_3,$  and  $A_4$ ), three representative possible diffusion pathways were considered: path-I ( $A_3-A_1-A_3$ ), where Na migrates from an  $A_3$  to another  $A_3$  by crossing an  $A_1$  site, marked by red arrows; path-II ( $A_3-A_4-A_3$ ), where Na migrates from an  $A_3$  to another  $A_3$  by crossing an  $A_4$  site, marked by blue arrows; path-III ( $A_3-A_2-A_3$ ), where Na migrates from an  $A_3$  to another  $A_3$  by crossing an  $A_2$  site, marked by black arrows. For the  $\text{Zr/Nb/MoC}_2$  monolayers (Fig. 6d, f and h), similarly, there are three diffusion pathways with both starting and ending sites at  $A_1$ : path-I ( $A_1-A_3-A_1$ ), path-II ( $A_1-A_2-A_1$ ), and path-III ( $A_1-A_4-A_1$ ), marked by red, blue and black arrows, respectively.

The energy profiles for Na diffusion over  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers along the examined diffusion pathways are illustrated in Fig. 6a, c, e and g. Obviously, Na diffusing along path-I has the lowest diffusion barrier ( $E_d$ ) on the  $\text{YC}_2$  ( $E_d = 0.21 \text{ eV}$ ),  $\text{ZrC}_2$  ( $E_d = 0.04 \text{ eV}$ ), and  $\text{NbC}_2$  ( $E_d = 0.20 \text{ eV}$ ) monolayers, while on the  $\text{MoC}_2$  monolayer, path-III has the smallest diffusion barrier of 0.22 eV. Actually, the energy-favored diffusion route is Na migration from the most energy-preferred site to another crossing the second energy-preferred site on the four



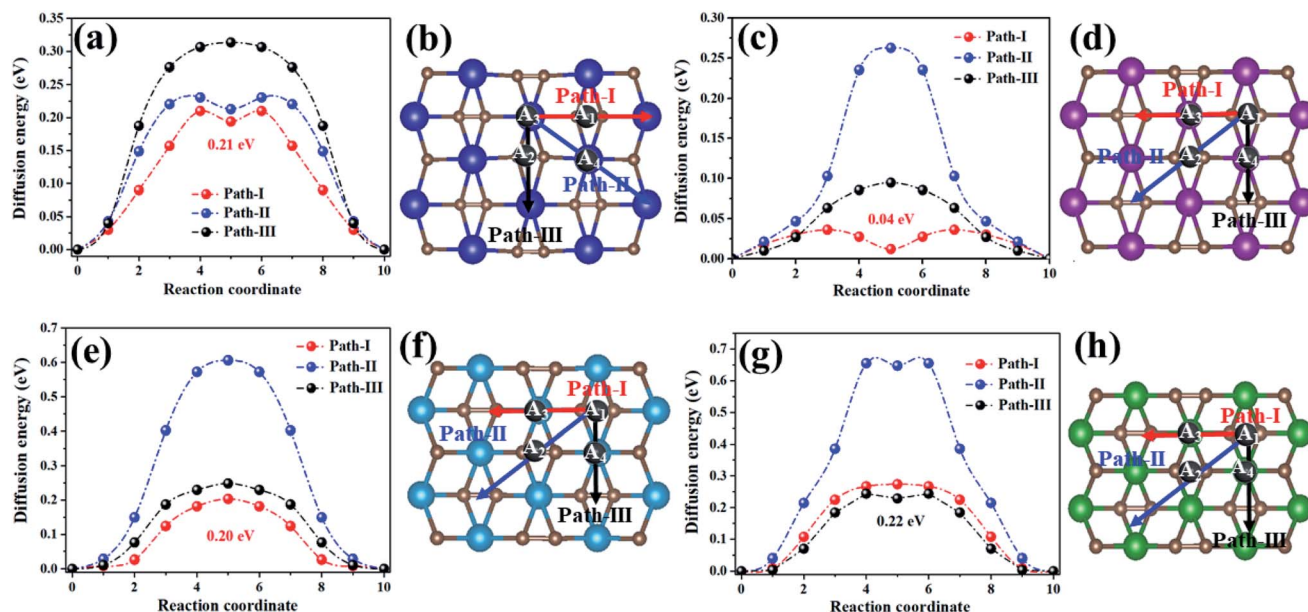


Fig. 6 The energy profile (left plane) and diffusion pathways (right plane) of Na diffusing on the  $YC_2$  (a and b),  $ZrC_2$  (c and d),  $NbC_2$  (e and f), and  $MoC_2$  (g and h) monolayers.

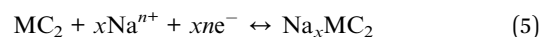
monolayers. Since the second lowest adsorption site on  $MoC_2$  is  $A_4$ , the Na diffusion path with the smallest barrier is path-III instead of path-I on the other three monolayers. The corresponding diffusion lengths of Na along the minimum energy pathways on the four  $MC_2$  monolayers are given in Fig. S9,† and the diffusion length of Na on  $MC_2$  monotonically increases with the lattice constant from the  $MoC_2$  to the  $YC_2$  monolayer. Note that the Na diffusion barriers on the four  $MC_2$  monolayers are all lower than that on borophene (0.32 eV),<sup>73</sup>  $Ti_3C_4$  (0.35)<sup>74</sup> and  $MoS_2$  (0.28 eV),<sup>75</sup> and the lowest  $E_d$  value of 0.04 eV on the  $ZrC_2$  monolayer is comparable with the  $E_d$  on  $ScC_2$  (0.05 eV)<sup>42</sup> and  $Ti_3C_2$  (0.096),<sup>76</sup> as shown in Table 3, indicating their excellent charge-discharge rate. Compared with the reported  $TiC_2$

monolayer as a promising anode for LIBs,<sup>37</sup> the Na diffusing along path-I has the lowest diffusion barrier on  $TiC_2$  ( $E_d = 0.19$  eV, Fig. S10†), and the  $E_d$  is comparable with the values on Y/Nb/ $MoC_2$  monolayers (0.20–0.22 eV), but higher than that on the  $ZrC_2$  monolayer (0.04 eV). Thus, as for SIB anode materials, compared to the  $TiC_2$  monolayer,  $ZrC_2$  distinguishes itself among the four examined  $MC_2$  ( $M = Y, Zr, Nb,$  and  $Mo$ ) monolayers, since it has the lowest Na diffusion barrier and high Na capacity comparable to that of  $TiC_2$ . Overall, from the perspective of Na diffusion behavior, anode materials with low energy barriers and short diffusion pathway lengths are suitable for SIBs.

### 3.5 Theoretical storage capacity and open-circuit voltage

2D materials as anode materials display a lot of attractive properties; besides mechanical flexibility, excellent electrical conductivity, and lower diffusion energies, they also have the ability to adsorb multilayer Na atoms and exhibit high capacity.<sup>77,78</sup> Inspired by these properties, we expect that the predicted  $MC_2$  ( $M = Y, Zr, Nb,$  and  $Mo$ ) monolayers can be used as anodes for SIBs with high storage capacity. Here, the two important descriptors, namely storage capacity ( $C$ ) and average open-circuit voltage (OCV), were calculated to determine the performance of the SIBs based on the charge-discharge mechanism.

The OCV can be evaluated from the following common half-cell reaction of the charge/discharge process:



when the volume and entropy effects during the sodiation process were neglected, the open-circuit voltage (OCV) can be derived from the average adsorption energy ( $E_{ave}$ ) as:

Table 3 Summary of the theoretical specific capacity (in  $mA\ h\ g^{-1}$ ) and diffusion barriers (in eV) of some widely investigated promising electrode materials for SIBs

	Theoretical specific capacity	Diffusion barrier	References
$YC_2$	478	0.21	This work
$ZrC_2$	699	0.04	This work
$NbC_2$	687	0.20	This work
$MoC_2$	675	0.22	This work
$TiC_2$	727	0.19	This work
$Ti_3C_2$	352	0.096	78
$Ti_3C_4$	560	0.35	74
$ScC_2$	777	0.05	42
$Sc_2C$	362	0.012	81
$Nb_2C$	271	0.015	33
$Mo_2C$	132	0.015	34
$MoC$	284.2	0.09	82
$MoS_2$	146	0.28	75
Phosphorene	315.52	0.30	80
$Na_2Mn_3O_7$	166.1	0.16	7





$$\text{OCV} = -E_{\text{ave}}/xne \quad (6a)$$

$$E_{\text{ave}} = (E_{\text{Na}_x\text{MC}_2} - E_{\text{MC}_2} - xE_{\text{Na-bulk}})/x \quad (6b)$$

where  $E_{\text{MC}_2}$ ,  $E_{\text{Na}_x\text{MC}_2}$ , and  $E_{\text{Na-bulk}}$  are the energy of the pristine  $\text{MC}_2$  monolayer, the total energy of Na adsorbed  $\text{MC}_2$ , and the energy per Na atom in the sodium bcc bulk, respectively,  $n$  is the number of valence electrons ( $n = 1$  for Na), and  $x$  is the chemical content of sodium atoms; ideally, the anode material can keep adsorbing Na atoms if  $E_{\text{ave}}$  is smaller than 0 eV per atom. The corresponding maximum capacity were calculated by using the following equation:

$$C = x_{\text{max}} \times F/M_{\text{MC}_2} \quad (7)$$

where  $x_{\text{max}}$  is the highest concentration of Na in  $\text{Na}_x\text{MC}_2$ ,  $F$  is the Faraday constant ( $26\,801 \text{ mA h mol}^{-1}$ ), and  $M_{\text{MC}_2}$  is the molar weight of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ).

Then the maximum storage capacity of Na atoms on  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers was evaluated by adding Na atoms to the surface gradually. As mentioned above, the most stable adsorption sites for Na on the four monolayers have been determined: the first layer of Na interaction at the  $A_3$  site for  $\text{YC}_2$  and the  $A_1$  site for  $\text{Zr/Nb/MoC}_2$ , respectively; when the adsorption positions of the first layer are completely occupied, the subsequently added Na atoms form a second and a third adsorption layer. In addition, for the different sodium concentrations on the  $\text{MC}_2$  monolayer, the most stable configurations for each concentration, we considered by calculating their formation energy ( $E_f$ ) of  $\text{Na}_x\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ )

compounds with respect to the  $\text{MC}_2$  monolayer and Na bulk phase as the references (Fig. S11<sup>†</sup>).<sup>79</sup>

Here, based on the  $\text{MC}_2$  monolayer, taking the process of successive adsorption of Na atoms on the  $\text{NbC}_2$  monolayer as an example, adding a Na atom at site  $A_1$  on one surface of  $\text{NbC}_2$  results in a low-limit chemical formula  $\text{Na}_x\text{NbC}_2$  ( $x = 0.125$ , Fig. 5c). Our computations showed that Na atoms tend to bond to both surfaces of the  $\text{NbC}_2$  monolayer when occupying the  $A_1$  site (Fig. S12–S14<sup>†</sup>). When the  $A_1$  sites of both surfaces were all occupied, Na atoms start to occupy the  $A_3$  sites in the second layer (Fig. S15<sup>†</sup>). Thus, the several possible configurations with both surfaces exposed to Na atoms were carefully considered for  $\text{Na}_x\text{NbC}_2$  systems with higher  $x$  values ( $x = 0.25, 0.375, 0.5, 1, 2, 3$ ), and the most stable configurations for each concentration are shown in Fig. 7a–f. The same approach was used to construct  $\text{Na}_x\text{YC}_2$ ,  $\text{Na}_x\text{ZrC}_2$ , and  $\text{Na}_x\text{MoC}_2$  systems.

The average adsorption energy decreases with the increase of Na concentration ( $x$ ), indicating the decreased thermodynamic stability of  $\text{Na}_x\text{MC}_2$  (Fig. 7g), which can be attributed to the repulsive interaction between Na atoms, thus making more adsorption more difficult. For the  $\text{Zr/Nb/MoC}_2$  monolayer, the first Na-adsorption layer is formed by placing Na at the most favorable sites ( $A_1$ ) on both sides with an  $E_{\text{ave}}$  of  $-0.41/-0.77/-0.65$  eV (the composite is  $\text{NaZrC}_2/\text{NaNbC}_2/\text{NaMoC}_2$ ), suggesting the feasibility of adsorbing the second Na layer. The  $E_{\text{ave}}$  of the second Na layer with Na adsorbing at site  $A_3$  ( $A_4$  for  $\text{MoC}_2$ ) is  $-0.27/-0.32/-0.28$  eV and the corresponding configurations are  $\text{Na}_2\text{ZrC}_2$ ,  $\text{Na}_2\text{NbC}_2$ , and  $\text{Na}_2\text{MoC}_2$ . When adding the third Na-layer on both sides with site  $A_4$  ( $A_3$  for  $\text{MoC}_2$ ), the  $E_{\text{ave}}$  is  $-0.14/-0.25/-0.24$  eV and the composites are  $\text{Na}_3\text{ZrC}_2$ ,

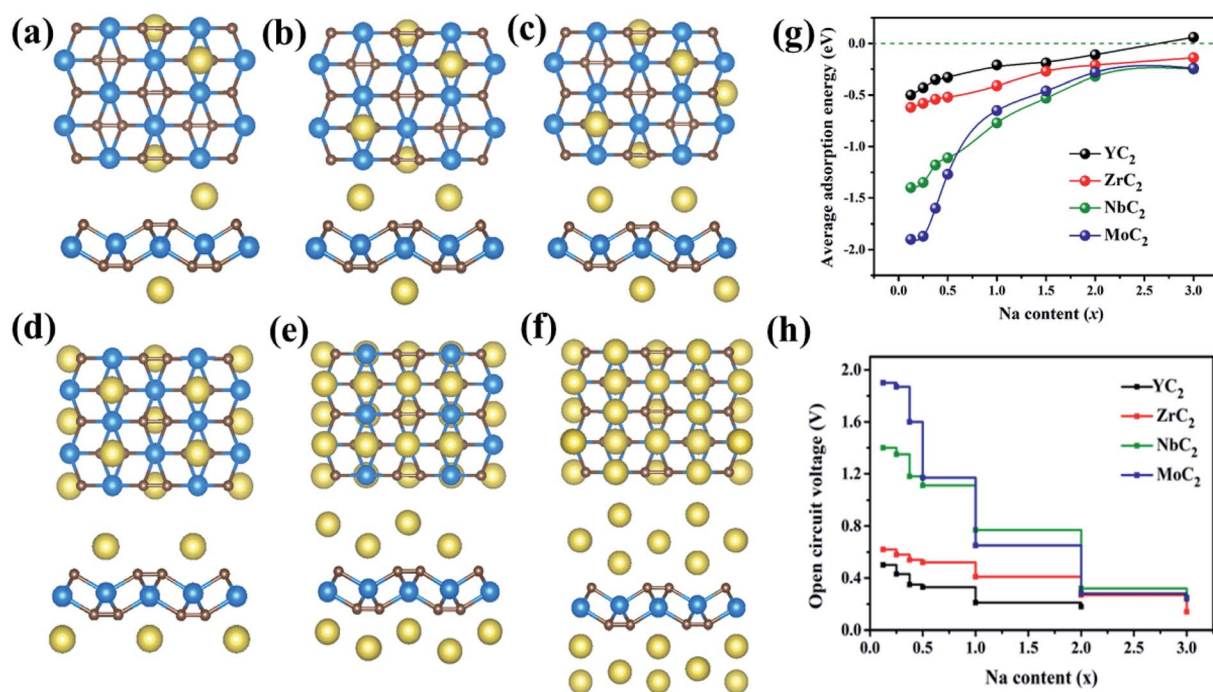


Fig. 7 Top and side views of the optimized structures of  $\text{Na}_{0.25}\text{NbC}_2$  (a),  $\text{Na}_{0.375}\text{NbC}_2$  (b),  $\text{Na}_{0.5}\text{NbC}_2$  (c),  $\text{NaNbC}_2$  (d),  $\text{Na}_2\text{NbC}_2$  (e), and  $\text{Na}_3\text{NbC}_2$  (f). The average adsorption energy (g) and open circuit voltage profile (h) of  $\text{Na}_x\text{YC}_2$ ,  $\text{Na}_x\text{ZrC}_2$ ,  $\text{Na}_x\text{NbC}_2$ , and  $\text{Na}_x\text{MoC}_2$  as a function of Na concentration.



$\text{Na}_3\text{ZrC}_2$ , and  $\text{Na}_3\text{MoC}_2$ . However, for the  $\text{YC}_2$  monolayer, in the first Na-layer Na atoms are adsorbed at the most favorable sites ( $A_3$ ) on both sides, and the  $E_{\text{ave}}$  is  $-0.21$  eV (the chemical formula is  $\text{NaYC}_2$ ). The  $E_{\text{ave}}$  of the second layer with Na atoms locating at site  $A_1$  is  $-0.11$  eV and the corresponding configuration is  $\text{Na}_2\text{YC}_2$ . The third Na-layer with Na atom adsorption at site  $A_4$  on both sides has an  $E_{\text{ave}}$  of  $0.06$  eV, which implies that only the two adsorption layers of Na atoms are stable on the  $\text{YC}_2$  monolayer. Thus, we can conclude that the three (two) layers of Na atoms can be stably adsorbed on the Zr/Nb/MoC<sub>2</sub> ( $\text{YC}_2$ ) monolayer.

Based on the above results, we estimated the maximum capacity ( $C$ ) and open-circuit voltage (OCV) of Na atoms adsorbed on the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers with the chemical stoichiometry of  $\text{Na}_2\text{YC}_2$ ,  $\text{Na}_3\text{ZrC}_2$ ,  $\text{Na}_3\text{NbC}_2$ , and  $\text{Na}_3\text{MoC}_2$  (Fig. 7h). The corresponding values of maximum capacity ( $C$ ) for SIBs are 478, 699, 687, and 675  $\text{mA h g}^{-1}$ , respectively. The  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers have much larger theoretical specific capacity in comparison to other electrode materials for SIBs, such as  $\text{Ti}_3\text{C}_2$  ( $352 \text{ mA h g}^{-1}$ ),<sup>76</sup> phosphorene ( $315.52 \text{ mA h g}^{-1}$ ),<sup>80</sup>  $\text{Sc}_2\text{C}$  ( $362 \text{ mA h g}^{-1}$ ),<sup>81</sup>  $\text{Nb}_2\text{C}$  ( $271 \text{ mA h g}^{-1}$ ),<sup>33</sup>  $\text{MoS}_2$  ( $146 \text{ mA h g}^{-1}$ ),<sup>75</sup>  $\text{MoC}$  ( $248.2 \text{ mA h g}^{-1}$ )<sup>82</sup> and Na-based layered materials ( $\text{Na}_2\text{Mn}_3\text{O}_7$ ,  $166.1 \text{ mA h g}^{-1}$ ),<sup>7</sup> as shown in Table 3. We also estimated the Na capacity on the  $\text{TiC}_2$  monolayer and found that the  $\text{TiC}_2$  monolayer can adsorb two Na layers with the final formula of  $\text{Na}_2\text{TiC}_2$ , and the corresponding maximum specific capacity was then determined to be  $727.29 \text{ mA h g}^{-1}$ , higher than that of the Y/Zr/Nb/MoC<sub>2</sub> monolayer. Thus, as for SIB anode materials, compared to the  $\text{TiC}_2$  monolayer,  $\text{ZrC}_2$  distinguishes itself among the four examined  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers, since it has the lowest Na diffusion barrier and high Na capacity comparable to that of  $\text{TiC}_2$ .

In addition, the OCV values are 0.11, 0.18, 0.25 and 0.24 V, which can avoid the dendrite formation of Na metal during the charge–discharge process due to satisfying the requirement of 0.1–1.0 eV for SIB anode materials.<sup>83</sup> At the same time, the values are rather low and comparable to or slighter larger than that of 2D materials  $\text{Mo}_2\text{C}$  (0.166 V),<sup>34</sup>  $\text{Ti}_3\text{C}_2$  (0.137 V),<sup>78</sup> and  $\text{NiC}_3$  (0.17 V).<sup>84</sup> The OCV values are low for Na atoms to be adsorbed on  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) nanosheets, which are beneficial for increasing and operating voltage and safety in practical applications.

Then, we examined the geometries of the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers upon Na adsorption to evaluate the expansion in volume. The changes of the lattice constant and volume for the host sheets with interacted Na atoms are listed in Table S1.† Compared with the bare sheets, the expansions of the lattice and volume for the maximum Na concentrations are less than 8% and 10%, respectively, comparable to or much smaller than the lattice changes of the  $\text{FeSe}$  monolayer (5.50%)<sup>71</sup> and the volume expansion of graphite (10%)<sup>85</sup> and Na-based bulk electrode material  $\text{NaTiF}_4$  (13%),<sup>7</sup> implying good cycling stability.

Finally, we explored the stability of the examined four  $\text{C}_2$ -containing  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers under high concentration Na adsorption, by carrying out the FPMD

stimulations of  $\text{Na}_2\text{YC}_2$ ,  $\text{Na}_3\text{ZrC}_2$ ,  $\text{Na}_3\text{NbC}_2$ , and  $\text{Na}_3\text{MoC}_2$  monolayers for 5 ps at 300 and 500 K, respectively. No bond breakage or atomic structure reconstruction was observed, indicating that the 2D  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) materials are still stable under the maximum coverage of sodium. Overall, we conclude that the good structural stability of  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) sheets endows them with great potential as high-performance anode materials for SIBs.

## 4. Conclusions

In summary, based on first-principles calculations, we proposed four  $\text{C}_2$ -containing monolayers ( $\text{MC}_2$ ,  $M = \text{Y, Zr, Nb, and Mo}$ ) and systematically investigated the structural stability, mechanical and electronic properties, as well as the performance as anode materials for SIBs. Our results show that the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers possess high cohesive energy and good dynamic, thermal and mechanical stability, and have metallic properties with excellent electronic conductivities. When used as battery electrodes for adsorbing Na atoms, the  $\text{YC}_2$  and Zr/Nb/MoC<sub>2</sub> monolayers can adsorb two and three layers of Na atoms with the final formula of  $\text{Na}_2\text{YC}_2$  and  $\text{Na}_3\text{ZrC}_2/\text{Na}_3\text{NbC}_2/\text{Na}_3\text{MoC}_2$ , respectively, and the corresponding maximum specific capacities (open circuit-voltage) were calculated to be 478 (0.11) and 699 (0.18)/687 (0.25)/675 (0.24)  $\text{mA h g}^{-1}$  (V), respectively. Taking advantage of containing  $\text{C}_2$  dimers, the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers show superior stability and have high Na capacity due to the higher content of C. In addition, Na atoms show fast diffusion on the  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers with low diffusion barriers (0.21, 0.04, 0.20 and 0.22, respectively), indicating excellent rate capability. In view of the superior properties, such as good electronic conductivity, fast Na diffusion, low OCV, and high theoretical Na storage capacity,  $\text{MC}_2$  ( $M = \text{Y, Zr, Nb, and Mo}$ ) monolayers become promising anode materials for SIBs.

## Conflicts of interest

There are no conflicts of interest to declare.

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