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## Atomic insight into the effects of precursor clusters on monolayer WSe<sub>2</sub>†

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Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have been attracting much attention due to their rich physical and chemical properties. At the end of the chemical vapor deposition growth of 2D TMDCs, the adsorption of excess precursor clusters onto the sample is unavoidable, which will have significant effects on the properties of TMDCs. This is a concern to the academic community. However, the structures of the supported precursor clusters and their effects on the properties of the prepared 2D TMDCs are still poorly understood. Herein, taking monolayer WSe<sub>2</sub> as the prototype, we investigated the structure and electronic properties of Se<sub>N</sub>, W<sub>N</sub> (N = 1–8), and W<sub>8–N</sub>Se<sub>N</sub> (N = 1–7) clusters adsorbed on monolayer WSe<sub>2</sub> to gain atomic insight into the precursor cluster adsorption. In contrast to W clusters that tightly bind to the WSe<sub>2</sub> surface, Se clusters except for Se<sub>1</sub> and Se<sub>2</sub> are weakly adsorbed onto WSe<sub>2</sub>. The interaction between W<sub>8–N</sub>Se<sub>N</sub> (N = 1–7) clusters and the WSe<sub>2</sub> monolayer decreases with the increase in the Se/W ratio and eventually becomes van der Waals interaction for W<sub>1</sub>Se<sub>7</sub>. According to the phase diagram, increasing the Se/W ratio by changing the experimental conditions will increase the ratio of Se<sub>N</sub> and W<sub>1</sub>Se<sub>7</sub> clusters in the precursor, which can be removed by proper annealing after growth. W clusters induce lots of defect energy levels in the band gap region, while the adsorption of W<sub>1</sub>Se<sub>7</sub> and Se<sub>N</sub> clusters (N = 3–6, 8) promotes the spatial separation of photo generated carriers at the interface, which is important for optoelectronic applications. Our results indicate that by controlling the Se/W ratio, the interaction between the precursor clusters and WSe<sub>2</sub> as well as the electronic properties of the prepared WSe<sub>2</sub> monolayer can be effectively tuned, which is significant for the high-quality growth and applications of WSe<sub>2</sub>.

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## Introduction

Two-dimensional (2D) layered transition metal dichalcogenides (TMDCs) belong to a large family that exhibit rich properties.<sup>1–5</sup> Compared to zero-gap graphenes, semiconducting TMDCs with proper bandgaps have attracted much attention.<sup>6–10</sup> Moreover, the band gap of these TMDCs is tunable *via* the number of layers and strain.<sup>11–15</sup> Monolayer WSe<sub>2</sub>, a member of TMDCs, exhibits a typical sandwich structure, Se–W–Se, where the W atomic layer is surrounded by two Se atomic layers and can be mechanically exfoliated from the bulk WSe<sub>2</sub>.<sup>16–18</sup> When the layer thickness of WSe<sub>2</sub> is reduced to monolayer, an indirect-to-direct band gap transition is observed.<sup>19,20</sup> WSe<sub>2</sub> has large exciton binding energies,<sup>21–23</sup> large carrier mobility,<sup>24–26</sup> and large absorption coefficients in the range of infrared to visible region,<sup>27–29</sup> which are promising in the field of photonics, optoelectronics, and photo-detectors. In addition, WSe<sub>2</sub> has excellent catalytic performance.<sup>30–33</sup>

Surface-supported clusters have been extensively studied, as the interaction between clusters and substrates plays an important role in the performance of catalysts and the growth of 2D

materials.<sup>34–43</sup> For example, Au cluster depositions on a TiO<sub>2</sub> surface can effectively catalyze CO oxidation.<sup>34,35</sup> TiC-supported Ni clusters could capture and activate methane at room temperature.<sup>38</sup> Chen *et al.* studied 134 bare and compound clusters anchored on 2D N vacancy W<sub>2</sub>N<sub>3</sub> (NV-W<sub>2</sub>N<sub>3</sub>) by high-throughput screening and proposed that VNiCu cluster-anchored NV-W<sub>2</sub>N<sub>3</sub> shows the best performance for electrocatalytic nitrogen reduction reactions.<sup>42</sup> Theoretical calculations show that the interaction between phosphorene nanoflakes and substrates around 0.35 eV per P atom is moderate to maintain the 2D feature of the phosphorene nanoflake.<sup>36</sup> The cesium iodide cluster prefers to form on monolayer graphenes, while 2D CsI forms only on bilayer graphenes.<sup>39</sup> In addition, a multilayer reduced graphene oxide (rGO)-supported Co<sub>4</sub>W<sub>18</sub> cluster shows excellent catalytic performance for Li<sub>2</sub>S deposition and oxidation and better for Li–S batteries.<sup>40</sup> Zhang *et al.* theoretically investigated the structure and electronic properties of Li<sub>2</sub>S<sub>n</sub> cluster adsorption on various 2D materials and revealed that a suitable interaction between the Li<sub>2</sub>S<sub>n</sub> cluster and anchor materials can enhance the performance of Li–S batteries.<sup>44</sup> The post-synthesis strategies by incorporating excess Mo into MoTe<sub>2</sub> and MoSe<sub>2</sub> can modify the phase structure and electronic properties.<sup>45</sup>

The high-quality synthesis of WSe<sub>2</sub> is a prerequisite for its application. Chemical vapor deposition is the most common method for synthesizing WSe<sub>2</sub>.<sup>46–48</sup> The selenium/tungsten (Se/W) ratio plays an essential role in the growth of monolayer WSe<sub>2</sub> and determines the type of precursor clusters. For example, Yue *et al.* proposed a high Se/W ratio, and an elevated substrate temperature is better for the growth of monolayer WSe<sub>2</sub>.<sup>49</sup> Li *et al.* realized the precise control of heteroepitaxy direction by manipulating the metal/chalcogenide ratio.<sup>50</sup> The theoretical calculations showed that at a high Se/W ratio, W<sub>1</sub>Se<sub>3</sub> clusters are the dominant species in the growth process, and the diffusion barrier of W<sub>1</sub>Se<sub>3</sub> clusters of only 0.4 eV promotes the growth along the in-plane direction.<sup>50</sup> In contrast, in a low Se/W ratio atmosphere, the components of W<sub>1</sub>Se<sub>x</sub> ( $x = 1–3$ ) coexist, and W<sub>1</sub>Se<sub>1</sub> clusters have a large diffusion barrier of about 1.2 eV, which can act as a nucleation site favorable for the growth along the out-of-plane direction.<sup>50</sup>

At the end of the chemical vapor deposition growth of 2D TMDCs, the adsorption of excess precursor clusters on the sample is unavoidable. As discussed above, these precursor clusters will have significant effects on the properties of TMDCs. However, the structures of the supported precursor clusters and their interaction with the 2D TMDCs as well as the effects on the properties of the prepared 2D TMDCs are still poorly understood.

In this work, we systematically investigated the structures of WSe<sub>2</sub>-supported possible precursor clusters including Se<sub>N</sub>, W<sub>N</sub> ( $N = 1–8$ ) and W<sub>8–N</sub>Se<sub>N</sub> ( $N = 1–7$ ) as well as their influence on the electronic properties of WSe<sub>2</sub> monolayer using first-principles calculations. The interaction between precursor clusters and the WSe<sub>2</sub> monolayer strongly depends on the Se/W ratio. By tuning the Se/W ratio, WSe<sub>2</sub> with weakly adsorbed precursor clusters can be obtained, and the precursor clusters are

expected to be removed by proper annealing. Interestingly, weakly adsorbed precursor clusters (W<sub>1</sub>Se<sub>7</sub> and Se<sub>N</sub> clusters ( $N = 3–6, 8$ )) will promote the spatial separation of photo generated carriers at the interface, which is important for optoelectronic applications. W clusters will tightly bind to the WSe<sub>2</sub> surface and induce lots of defect energy levels in the band gap region. Our results provide an atomic insight into the precursor cluster adsorption on the WSe<sub>2</sub> monolayer, which is significant for the high-quality growth and applications of WSe<sub>2</sub>.

## Computational methods

Following previous works, the ground-state structure of bare W<sub>N</sub> or Se<sub>N</sub> ( $N = 1–8$ ) clusters in vacuum was constructed manually. The possible structure of W<sub>8–N</sub>Se<sub>N</sub> ( $N = 1–7$ ) clusters was searched using a self-developed comprehensive genetic algorithm (CGA) code implemented in the DMol<sup>3</sup> program,<sup>51,52</sup> which has been proved to be a reliable and powerful tool for cluster structure search.<sup>52</sup> The W<sub>8–N</sub>Se<sub>N</sub> ( $N = 1–7$ ) clusters were optimized using the double numerical basis including d-polarization function (DND) and the Perdew, Burke and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).<sup>53</sup> There are no symmetry constraints in the structure optimization. The number of maximum iterations of each search is set to 3000, and 16 members are retained in the population.

Vienna *Ab initio* Simulation Package (VASP)<sup>54</sup> can handle the problem of cluster adsorption on the surface well and give results that are in good agreement with the experiments. For example, by investigating the differences in the structure and stability of carbon clusters of adjacent sizes using DFT calculations with the VASP code, the branched C<sub>21</sub>-3C clusters were proposed to have special stability on the Ru/Rh surface, revealing the true structure of the experimentally observed dominant clusters.<sup>55,56</sup> By investigating boron clusters on the Cu(111) surface using DFT calculations with the VASP, Liu and co-workers predicted the growth mechanism of borophene on a metal surface,<sup>57</sup> which was confirmed by later experiments.<sup>58,59</sup> Recently, combining experiments and VASP theoretical calculations, Zhou and co-workers investigated the growth mechanism of 67 types of transition metal chalcogenides (TMCs) and transition metal phosphorous chalcogenides (TMPCs) on a silicon substrate.<sup>60</sup> The calculations regarding the chemical transition between different phases of TMCs well matched the experimental observation. Therefore, for the study of W<sub>8–N</sub>Se<sub>N</sub> ( $N = 0–8$ ) clusters on the WS<sub>2</sub> monolayer layer, we adopted the VASP code.

The searched W<sub>8–N</sub>Se<sub>N</sub> ( $N = 1–7$ ) cluster structure is then further optimized using the VASP code. The structure and electronic properties of the bare W<sub>N</sub> or Se<sub>N</sub> ( $N = 1–8$ ) cluster and the composite W<sub>8–N</sub>Se<sub>N</sub> ( $N = 1–7$ ) cluster adsorption on the monolayer WSe<sub>2</sub> were studied by spin-polarized density functional theory (DFT) calculations implemented in the VASP. The GGA-PBE was used to tackle the exchange and correlation

functional. The electron-ion interactions were described by the projector augmented wave (PAW) potentials.<sup>61</sup> The Grimme scheme DFT-D3 with a Becke–Johnson damping approach was used to describe the van der Waals (vdW) interactions between the cluster and the substrate.<sup>62,63</sup> A vacuum space larger than 20 Å along the z-direction was set to avoid the interactions between the periodic replicas. The energy cutoff of the plane wave basis set was 500 eV. The Monkhorst–Pack *k*-point mesh with a separation of 0.02 Å<sup>-1</sup> was used to sample the Brillouin zones.<sup>64</sup> All atoms were relaxed and the lattice was fixed. The total energy convergence criterion was 10<sup>-5</sup> eV and the force convergence criterion was 0.01 eV Å<sup>-1</sup>. The diffusion barrier of a single W or Se atom on the monolayer WSe<sub>2</sub> surface was simulated by the climbing-image nudged elastic band (CI-NEB) method.<sup>65,66</sup> Four images were used to simulate the diffusion path. The charge transfer between the cluster and the monolayer WSe<sub>2</sub> surface was obtained by Bader charge analysis.<sup>67</sup> The simulated scanning tunneling microscopic (STM) images were obtained using the Tersoff–Hamann approximation.<sup>68</sup> The distance from the surface was kept constant, and the details are listed in Table S1.†

## Results and discussion

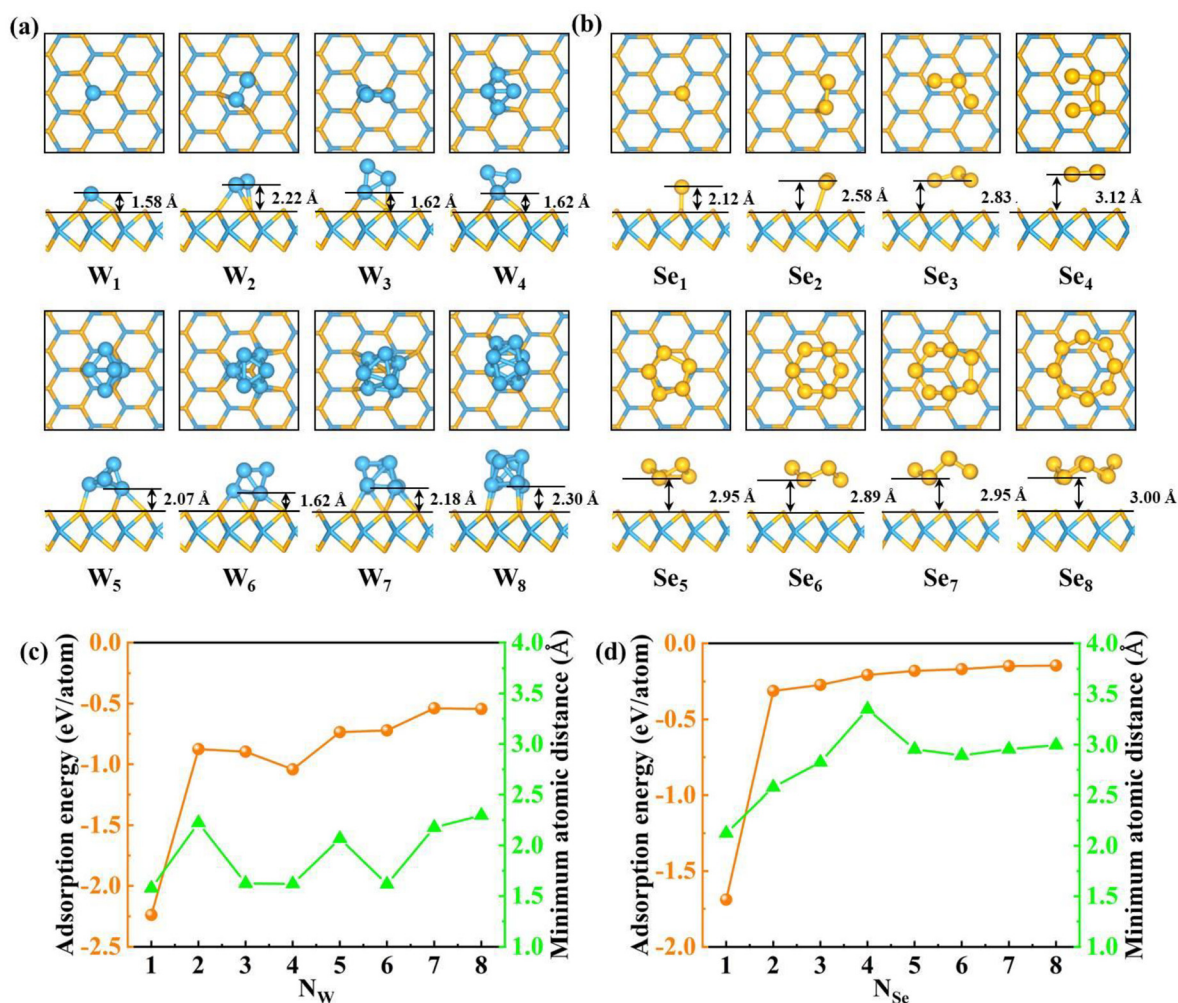
Before investigating the structures of WSe<sub>2</sub>-supported W<sub>N</sub>, Se<sub>N</sub> (*N* = 1–8) and W<sub>8–N</sub>Se<sub>N</sub> (*N* = 1–7) clusters, the primitive cell of monolayer WSe<sub>2</sub> is fully relaxed. The calculated equilibrium lattice constant of monolayer WSe<sub>2</sub> is 3.316 Å, which is in good agreement with the previous theoretical results.<sup>69–72</sup> We then transformed the primitive cell of WSe<sub>2</sub> into the orthogonal unit cell and created a (5 × 3) supercell, as shown in Fig. S1.† The lattice constants of the (5 × 3) supercell of WSe<sub>2</sub> are 16.58 Å and 17.229 Å along the *x*- and *y*-directions, respectively. Such a dimension of the supercell is expected to sufficiently avoid the interactions between periodic replicas.

We first studied the adsorption of a single W atom on the perfect WSe<sub>2</sub> surface. Here, we consider three adsorption sites, including the top of the W atom (T<sub>W</sub>), the top of the Se atom (T<sub>Se</sub>) and the hollow (H) site, as shown in Fig. S1.† By comparing the total energy of the three adsorption sites, the most stable adsorption site of the single W atom on the monolayer WSe<sub>2</sub> surface was obtained, *i.e.* the W atom prefers to adsorb on the T<sub>W</sub> site of the monolayer WSe<sub>2</sub> surface, as shown in Fig. S2a† and Fig. 1a. Our results agree well with the previous study that the W atom prefers the T<sub>W</sub> site of the WSe<sub>2</sub> surface, which verifies the accuracy of our work.<sup>73</sup> In addition, we considered the possible configurations that the W single atom was buried within the WSe<sub>2</sub> layer, as shown in Fig. S2d and e.† The W atom buried within the WSe<sub>2</sub> layer can significantly reduce the energy and the configuration of the W atom embedded at the T<sub>W</sub> site has the lowest energy, which is in agreement with the result reported by Zheng *et al.*<sup>74</sup> This phenomenon is very interesting and additional energy must be needed to trigger this process. In this paper, we will not consider the burial of

W atoms, leaving the discussion of the formation mechanism in our next work.

We then investigated the possible adsorption configuration of W<sub>N</sub> (*N* = 2–8) clusters on monolayer WSe<sub>2</sub>. For each size, several different structures are constructed to find out the most stable one, as shown in Fig. S3–S9 in the ESI.† After geometry optimization, the most stable structures for W<sub>N</sub> (*N* = 1–8) are shown in Fig. 1a. For the W<sub>2</sub> cluster on the WSe<sub>2</sub> monolayer, the most stable configuration is that one W atom is set on the T<sub>Se</sub> site of the WSe<sub>2</sub> surface and the other W atom is set on the hollow site and binds with two Se atoms. For the W<sub>3</sub> cluster, after structure optimization, the linear W<sub>3</sub> cluster is reconstructed into the triangle W<sub>3</sub> cluster, which is the most stable configuration of W<sub>3</sub> cluster adsorption on the monolayer WSe<sub>2</sub> surface. Two W atoms of the W<sub>3</sub> cluster bind with Se atoms on the surface with one W atom at the T<sub>W</sub> site and the other W atom at the T<sub>Se</sub> site. For W<sub>4</sub> on WSe<sub>2</sub>, the most stable configuration is a tetrahedral W<sub>4</sub> cluster with two W atoms at the T<sub>W</sub> site binding with Se atoms on the surface. The result indicates that the linear configuration is not favorable for the W<sub>4</sub> cluster on the WSe<sub>2</sub> surface. Therefore, we ignore linear clusters for larger W clusters. The stable W<sub>5</sub> cluster is a pentahedral with two W atoms chemically binding with Se atoms on the surface. The W<sub>6</sub> cluster prefers a triangular antiprism structure with three W atoms binding with Se atoms. For W<sub>7</sub> and W<sub>8</sub> clusters on the surface, four W atoms bind with Se atoms on the surface.

The ground state structure of bare W<sub>N</sub> (*N* = 1–8) clusters in vacuum has been widely studied theoretically, which is also optimized in this work, as shown in Fig. S10.†<sup>75,76</sup> The calculated bond length of the W<sub>2</sub> cluster is 1.860 Å, which is in agreement with the previous study, 1.835 Å.<sup>76</sup> The structure of the free-standing W<sub>3</sub> cluster is equilateral triangle with a bond length of 2.235 Å. For the size larger than 3, all the structures of the free-standing W cluster show 3D geometries. For example, the W<sub>4</sub> cluster is a tetrahedron, the W<sub>5</sub> cluster is a distorted trigonal bipyramid, and the W<sub>7</sub> cluster is a distorted pentagonal bipyramid. Compared with Fig. 1a and Fig. S10,† we can see that the W<sub>N</sub> (*N* = 4–8) cluster is preferred to form 3D configuration irrespective of whether in vacuum or on substrate, which indicates that the W atom on the substrate showed consistent behavior with that in vacuum. However, the most stable configuration is slightly different from that in vacuum. For example, for the W<sub>2</sub> cluster, the bond length of the W–W bond is 1.940 Å, slightly longer than that in vacuum by about 0.08 Å. For the W<sub>3</sub> cluster, the shape of the W<sub>3</sub> cluster on the WSe<sub>2</sub> surface is distorted from equilateral triangle to irregular triangle with bond lengths of 2.134 Å, 2.414 Å and 2.317 Å, respectively. The bond lengths of the W–W bond in the W<sub>4</sub> cluster are stretched from 2.540 Å to 2.839 Å. The minimum atomic distance between the W<sub>N</sub> (*N* = 1–8) cluster and the substrate is also marked in Fig. 1a. The single W atom has the smallest relative minimum atomic distance, 1.58 Å. The W<sub>8</sub> cluster has the largest relative minimum atomic distance, 2.30 Å. The relative minimum atomic distance between W<sub>N</sub> (*N* = 2–7) clusters and the substrate is in the range of



**Fig. 1** Top and side views of (a)  $W_N$  ( $N = 1-8$ ) and (b)  $Se_N$  ( $N = 1-8$ ) cluster adsorption on the monolayer  $WSe_2$  surface. The blue and orange spheres indicate W and Se atoms, respectively. For the sake of clarity, the substrate is shown as a stick. The adsorption energy of (c)  $W_N$  ( $N = 1-8$ ) and (d)  $Se_N$  ( $N = 1-8$ ) clusters on the substrate (yellow line) and the minimum atomic distance between clusters and the substrate (green line).

1.58 Å–2.30 Å. To evaluate the possibility of cluster formation on the  $WSe_2$  surface, the formation energy is defined as follows:

$$E_f = (E_{\text{total}} - E_{\text{sub}} - N \times E_X) / N,$$

where  $E_{\text{total}}$  and  $E_{\text{sub}}$  are the total energies of the absorbed system and bare monolayer  $WSe_2$  substrate, respectively.  $E_X$  is the energy per atom in bulk W or Se. The subscript X represents element W or Se. N is the number of atoms in the  $W_N$  or  $Se_N$  cluster.

The formation energy of  $W_N$  clusters in vacuum and on substrate is plotted in Fig. S11.† As the size increases, the formation energy gradually decreases. For supported  $W_N$  ( $N = 1-8$ ) clusters, the formation energy has a similar trend as in vacuum, but always lower in energy, indicating that the  $WSe_2$  monolayer can stabilize  $W_N$  ( $N = 1-8$ ) clusters. Larger W clusters have lower formation energies than those of smaller W clusters. Therefore, we investigated the energy barrier of single W atom diffusion on the  $WSe_2$  surface to form large W clusters,

as shown in Fig. S12.† The initial state (IS) is set as two W atoms adsorbed on the two separate  $T_W$  sites. In addition, the final state (FS) is a  $W_2$  cluster. As shown in Fig. S12,† the  $W_2$  cluster adsorption configuration is more stable than the configuration of the two separate W atoms. The calculated energy barrier of W atom diffusion on the  $WSe_2$  surface is 0.62 eV, and the small atom diffusion barrier indicates that the W atom is easy to diffuse, which implies that *via* W atom diffusion into the  $WSe_2$  surface, growing large W cluster is more feasible. The corresponding transition state (TS) is shown in Fig. S12c,† where a W atom is moved from the  $T_W$  site to the nearby  $T_{Se}$  site.

We then calculated the adsorption energy of the  $W_N$  clusters on the monolayer  $WSe_2$  surface. The adsorption energy is defined as follows:

$$E_{\text{ads}} = (E_{\text{total}} - E_{\text{sub}} - E_{X_N}) / N$$

where  $E_{X_N}$  is the energy of the  $X_N$  cluster, X is W or Se. The adsorption energy of  $W_N$  ( $N = 1-8$ ) clusters on the  $WSe_2$  mono-

layer is shown in Fig. 1c. From this, we can see that the adsorption energy of  $W_N$  ( $N = 1-8$ ) clusters on the  $WSe_2$  surface is below zero, indicating that the surface favors the adsorption of  $W_N$  ( $N = 1-8$ ) clusters. Among them, the single W atom has the largest adsorption energy,  $-2.24$  eV per atom. In general, the adsorption energy gradually decreases with the increase in size, and the minimum atomic distance increases with the size of the cluster. It can be expected that the inter-cluster atomic interaction is stronger than the cluster-substrate interaction as the size increases.

Furthermore, the projected band structures of monolayer  $WSe_2$  with  $W_N$  ( $N = 1-8$ ) clusters on the surface were calculated (Fig. S13<sup>†</sup>). Compared to the pristine  $WSe_2$  monolayer,  $W_N$  clusters induce many impurity states in the gap region. The Fermi level is close to the CBM, indicating that W clusters transfer electrons to the  $WSe_2$  monolayer and make the monolayer n-doped. In addition, the  $W_1$ ,  $W_5$  and  $W_8$  clusters will induce spin polarization (as shown in Fig. S13a, e and h<sup>†</sup>).

Next, we begin to investigate the structure of  $Se_N$  ( $N = 1-8$ ) cluster adsorption on the  $WSe_2$  surface. For single Se atoms, we consider five configurations, as shown in Fig. S14a-e.<sup>†</sup> The most favorable adsorption site is the  $T_{Se}$  site (Fig. 1b), which is consistent with the previous results.<sup>77</sup> In contrast with the W atom, the configuration with the Se atom embedded in the  $WSe_2$  layer is very high in energy.

For  $Se_N$  ( $N = 2-8$ ) clusters on monolayer  $WSe_2$ , several different structures are constructed for each size to find out the most stable one, as shown in Fig. S15-S21 in the ESI.<sup>†</sup> After geometry optimization, the most stable structures for  $Se_N$  ( $N = 1-8$ ) are shown in Fig. 1b. For the  $Se_2$  cluster on the  $WSe_2$  monolayer, the most stable configuration is a Se dimer with one Se atom chemically bonded with one Se atom on the surface. When  $N > 2$ , no chemical bond appears at the  $Se_N$  cluster/ $WSe_2$  interface. For  $Se_5$ ,  $Se_6$ ,  $Se_7$  and  $Se_8$ , five-, six-, seven- and eight-membered rings are the most stable configurations.

The Se vapor is predominantly  $Se_N$  ( $N < 8$ ) cluster, as indicated by the mass spectra.<sup>78</sup> Subsequently, the structure of the free-standing  $Se_3$  to  $Se_8$  clusters was theoretically calculated.<sup>79,80</sup> We reproduced the previously predicted structure of free-standing  $Se_N$  ( $N = 3-8$ ), as shown in Fig. S22.<sup>†</sup> The structure of free-standing  $Se_3$  and  $Se_4$  clusters is an open triangular structure and an open planar tetragonal structure, respectively. From  $Se_5$  to  $Se_8$  clusters, the structure is buckled pentagon, hexagon, heptagon and octagon ring, respectively. Compared with the structure of the  $Se_2$  cluster in vacuum, the bond length of the Se-Se bond in the  $Se_2$  cluster on the substrate is extended from  $2.194$  Å to  $2.230$  Å. For the  $Se_3$  cluster, which is not bonded to the  $WSe_2$  surface, the length of the Se-Se bond in the  $Se_3$  cluster changed from two equal bond lengths of  $2.228$  Å to two unequal bond lengths of  $2.292$  Å and  $2.251$  Å, respectively, and the bond angle changed from  $116.658^\circ$  to  $112.481^\circ$ . Similar to the  $Se_3$  cluster, the  $Se_4$  cluster is not bonded to the substrate. The Se-Se bond in the  $Se_4$  cluster can be divided into two types, namely, two equivalent short Se-Se bonds ( $2.187$  Å) and one longer Se-Se bond

( $2.785$  Å). After adsorption on the  $WSe_2$  surface, the bond length of the short bond increased to  $2.191$  Å, and the longer bond length decreased to  $2.682$  Å. For the  $Se_5$  cluster, the length of the Se-Se bond slightly increased from  $2.300$  Å to  $2.302$  Å,  $2.390$  Å to  $2.400$  Å, and  $2.387$  Å to  $2.391$  Å, respectively. For the  $Se_6$  cluster, the length of the Se-Se bond increased from  $3.364$  Å to  $3.370$  Å. For the  $Se_7$  and  $Se_8$  clusters, the length of the Se-Se bond changed by less than  $0.005$  Å. The single Se atom has the smallest minimum atomic distance,  $2.12$  Å. This is followed by the  $Se_2$  cluster,  $2.58$  Å. The  $Se_4$  cluster has the largest minimum atomic distance,  $3.35$  Å.

The formation energy of  $Se_N$  ( $N = 1-8$ ) clusters in vacuum is shown in Fig. S23.<sup>†</sup> It can be seen that as the cluster size increases, and the formation energy gradually decreases. The  $Se_8$  cluster has the lowest formation energy of  $0.26$  eV per atom. The formation energy of  $Se_N$  ( $N = 1-8$ ) clusters on the monolayer  $WSe_2$  surface has a similar trend with  $Se_N$  ( $N = 1-8$ ) clusters in vacuum, but it is always lower than that in vacuum, indicating that  $Se_N$  ( $N = 1-8$ ) clusters prefer to be deposited on the monolayer  $WSe_2$  surface. Based on the formation energy of  $Se_N$  ( $N = 1-8$ ) clusters on the  $WSe_2$  surface, we can conclude that large-sized clusters are easily formed on the  $WSe_2$  surface. Therefore, the barrier of Se atom diffusion on the  $WSe_2$  surface to form large clusters was investigated, as shown in Fig. S24.<sup>†</sup> The initial state is two Se atoms on separate  $T_{Se}$  sites and the final state is set at the  $Se_2$  cluster adsorption on the  $WSe_2$  surface. On the  $WSe_2$  monolayer, the  $Se_2$  cluster is more stable than the two separate Se atoms and the energy barrier of Se atom diffusion is  $1.02$  eV. The high barrier indicates that it is difficult to form large Se clusters by the diffusion of single Se atoms on the surface and that the direct deposition of the vapor large Se clusters on the surface is practical.

The adsorption energy of  $Se_N$  ( $N = 1-8$ ) clusters on the  $WSe_2$  monolayer is shown in Fig. 1d, from which we can see that the single Se atom has the largest adsorption energy ( $-1.69$  eV per atom). The adsorption energy of  $Se_2$  to  $Se_8$  clusters is in the range of  $-0.14$  to  $-0.31$  eV per atom. Compared to  $W_N$  ( $N = 1-8$ ) clusters,  $Se_N$  ( $N = 1-8$ ) clusters have weaker interaction with the substrate. The minimum atomic distance between the  $Se_N$  ( $N = 1-8$ ) cluster and the substrate increases with the increase in cluster size, and is always greater than that between the  $W_N$  ( $N = 1-8$ ) cluster and the substrate. Especially, the interaction between  $Se_N$  ( $N = 3-8$ ) clusters and the  $WSe_2$  monolayer is weak vdW interaction, indicating their ease of removal under proper annealing.

To check the effect of  $Se_N$  ( $N = 1-8$ ) cluster adsorption on the electronic properties of  $WSe_2$ , the projected band structures are plotted (shown in Fig. S25<sup>†</sup>). In general, few defects are induced in the band gap region, which is in sharp contrast with the case of W clusters. According to the location of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbits of the  $Se_N$  clusters,  $Se_N$  clusters ( $N = 3-6, 8$ ) would promote the spatial separation of photo generated carriers at the interface. The high efficiency charge separation is a key factor affecting the photocatalytic performance of semiconductors.<sup>81-87</sup> For example, charge sep-

aration greatly improves the efficiency of CO<sub>2</sub> photo-reduction and hydrogen evolution reactions.<sup>81,87</sup> Therefore, the Se<sub>N</sub> ( $N = 3-6, 8$ ) cluster deposition on the WSe<sub>2</sub> surface provided an atomic level strategy to promote charge separation, which is important for optoelectronic applications.

For convenient experimental observation of the clusters, the scanning tunneling microscopic (STM) images of W<sub>N</sub> and Se<sub>N</sub> ( $N = 1-8$ ) clusters are simulated and shown in Fig. 2. In general, the adsorbed W<sub>N</sub> clusters appear as a big bright point in the STM image, and the larger the cluster, the larger the bright point. For Se<sub>N</sub> clusters, they also appear as bright points and the patterns in STM images are more recognizable. For example, the Se<sub>2</sub> cluster shows as a bone-like pattern and the Se<sub>8</sub> cluster appears as an eight-membered ring.

To further illustrate the cluster-substrate interaction, the charge density difference and the corresponding Bader charge transfer between the clusters and the WSe<sub>2</sub> monolayer are plotted, as shown in Fig. 3. The results show that W<sub>N</sub> ( $N = 1-8$ ) clusters transfer electrons to the WSe<sub>2</sub> monolayer, resulting in n-type doping of the monolayer WSe<sub>2</sub>. Se<sub>N</sub> ( $N = 1-4$ ) clusters

gain electrons from the WSe<sub>2</sub> layer, while Se<sub>5</sub> slightly transfers electrons to the WSe<sub>2</sub> layer. For Se<sub>6</sub>, S<sub>7</sub> and Se<sub>8</sub> clusters, there is almost no electron transfer between clusters and the WSe<sub>2</sub> layer. The less charge transfer between Se<sub>N</sub> clusters and the WSe<sub>2</sub> layer again confirms the weak interaction at the interface which is in sharp contrast to W<sub>N</sub> clusters.

In experiments, the selenium/tungsten (Se/W) ratio has a strong influence on the growing monolayer WSe<sub>2</sub>.<sup>50,88,89</sup> Using the self-developed CGA software,<sup>52</sup> several low-energy W<sub>8-N</sub>Se<sub>N</sub> ( $N = 1-7$ ) binary clusters in vacuum were determined (shown in Fig. S26-S32†). The detailed discussion about the ground state (GS) structures of free-standing W<sub>8-N</sub>Se<sub>N</sub> ( $N = 1-7$ ) binary clusters can be found in the ESI.† Subsequently, these searched W<sub>8-N</sub>Se<sub>N</sub> ( $N = 1-7$ ) binary clusters were put on the WSe<sub>2</sub> monolayer (shown in Fig. S33-S39†) to investigate supported W<sub>8-N</sub>Se<sub>N</sub> ( $N = 1-7$ ) binary clusters. The most stable structures of the WSe<sub>2</sub>-supported W<sub>8-N</sub>Se<sub>N</sub> ( $N = 1-7$ ) binary clusters are shown in Fig. 4a. In comparison, the WSe<sub>2</sub> substrate has a great influence on the geometry of the compound clusters. For example, compared to the free-standing GS W<sub>7</sub>Se<sub>1</sub>

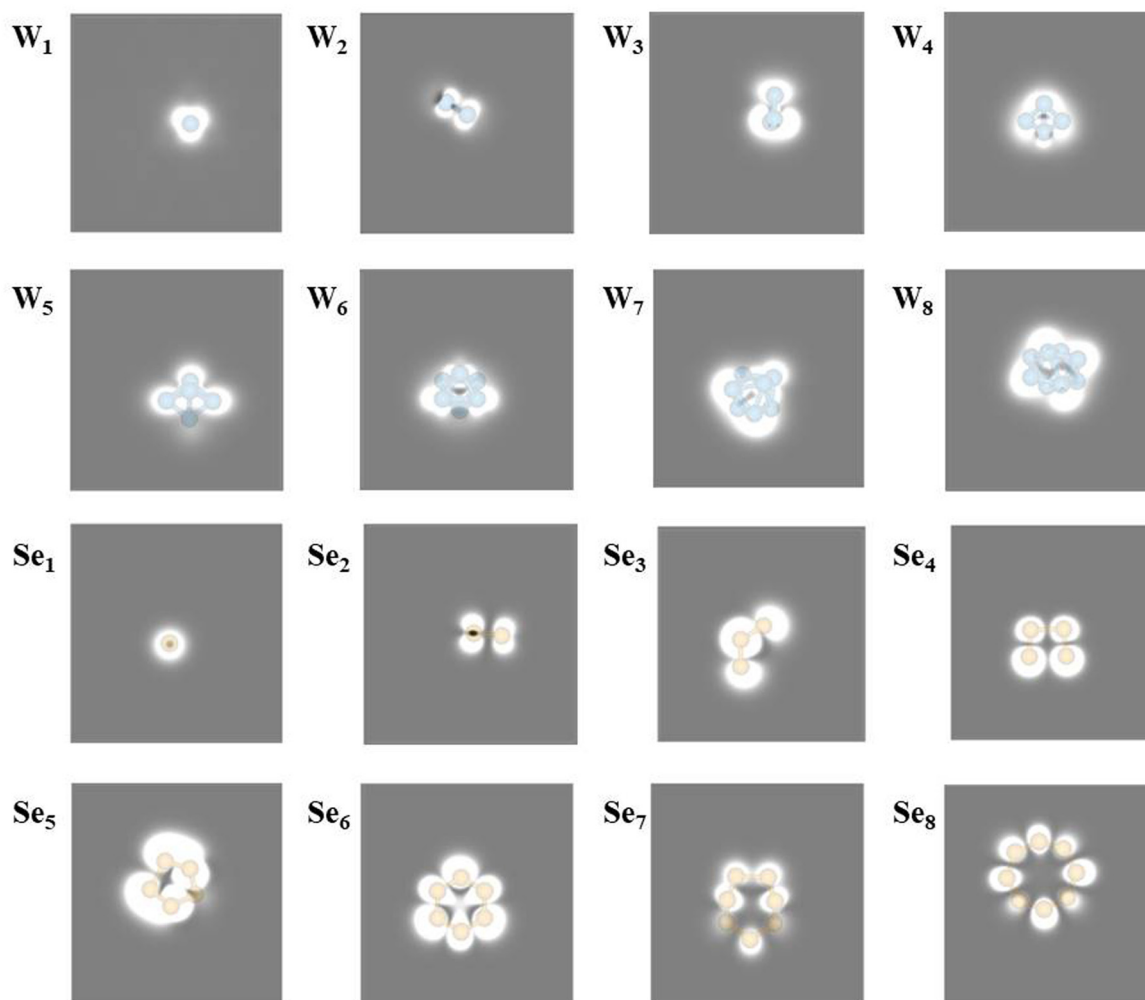
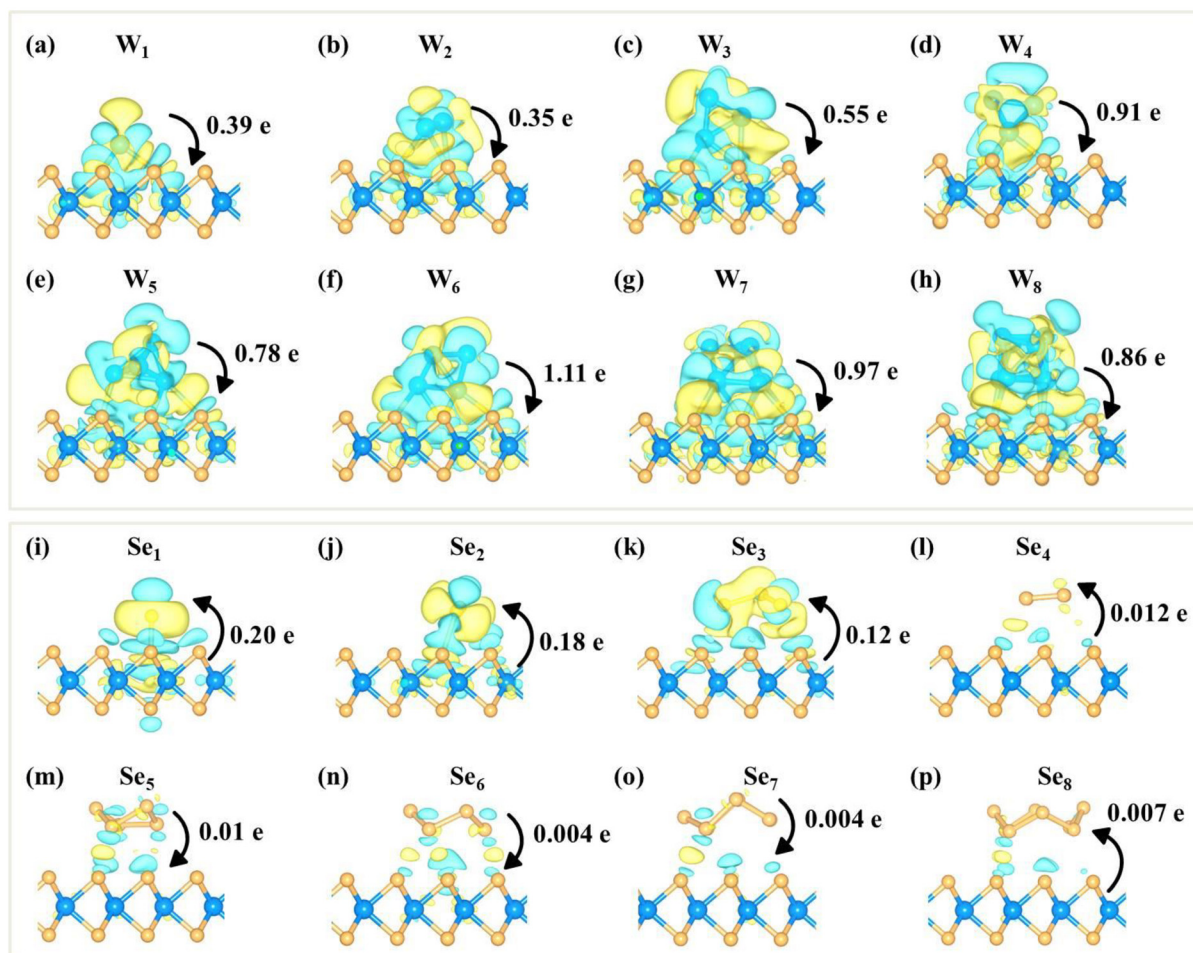


Fig. 2 Simulated STM of W<sub>N</sub> ( $N = 1-8$ ) and Se<sub>N</sub> ( $N = 1-8$ ) cluster adsorption on the WSe<sub>2</sub> surface at  $-0.6$  V bias, respectively.



**Fig. 3** Charge density difference of (a–h)  $W_N$  ( $N = 1–8$ ) and (i–p)  $Se_N$  ( $N = 1–8$ ) clusters adsorbed on the  $WSe_2$  surface. The accumulation and depletion of charge density are represented in yellow and green colors. The value and direction of the Bader charge transfer are also marked. The isosurface value is  $0.0005 e \text{ Bohr}^{-3}$ .

cluster, the supported GS  $W_7Se_1$  cluster is distorted. The metastable  $W_1Se_7$  cluster in vacuum (Fig. S32b<sup>†</sup>) becomes the most stable one when adsorbed on the surface (Fig. 4a). When the Se/W ratio is less than 7, the  $W_{8-N}Se_N$  ( $N = 1–6$ ) clusters prefer to bond with the surface through W-Se chemical bonds. Therefore,  $W_{8-N}Se_N$  ( $N = 1–6$ ) clusters interact strongly with the  $WSe_2$  surface. As the Se/W ratio increases, the number of chemical bonds at the interface decreases. When the Se/W ratio reaches 7, the minimum atomic distance between the cluster and the  $WSe_2$  substrate increases from 1.64 Å to 3.02 Å and no chemical bonds exist at the interface. The  $W_1Se_7$  clusters prefer physical adsorption on the  $WSe_2$  surface. Therefore, by tuning the Se/W ratio, the interaction between  $W_{8-N}Se_N$  and the  $WSe_2$  layer can be effectively tuned.

The charge density difference and the corresponding Bader charge transfer between the  $W_{8-N}Se_N$  ( $N = 1–7$ ) cluster and the  $WSe_2$  surface are shown in Fig. 4 to reveal the interaction between the cluster and the substrate. When the number of Se atoms increases from 1 to 7, there is almost no electron transfer between the cluster and the substrate. The  $W_1Se_7$  cluster

transfers only 0.014 e to the substrate, again indicating the weak interaction between the  $W_1Se_7$  clusters and the substrate. The  $W_{8-N}Se_N$  ( $N = 1–4$ ) cluster donates electrons to the substrate, resulting in an n-type  $WSe_2$  monolayer, while the  $W_{8-N}Se_N$  ( $N = 5, 6$ ) cluster accepts electrons from the substrate resulting in a p-type  $WSe_2$  monolayer. For  $W_1Se_7$ , there is almost no charge transfer.

For  $W_N$  and  $Se_N$  ( $N = 1–8$ ) clusters,  $W_8$  and  $Se_8$  are the most stable on the  $WSe_2$  monolayer. To estimate the stability of binary  $W_{8-N}Se_N$  ( $N = 1–7$ ) clusters, we constructed the phase diagram of  $W_8$ ,  $Se_8$  and  $W_{8-N}Se_N$  ( $N = 1–7$ ) clusters on the substrate based on the chemical potential of W and Se atoms. The formation energy of  $W_{8-N}Se_N$  ( $N = 1–7$ ) clusters as a function of W chemical potential ( $\mu_W$ ) and Se chemical potential ( $\mu_{Se}$ ) is defined as follows:

$$E_f = E_{\text{total}} - E_{\text{sub}} - (8 - N) \times \mu_W - N \times \mu_{Se},$$

where  $E_{\text{total}}$  and  $E_{\text{sub}}$  are as defined above.  $N$  is the number of Se atoms in the  $W_{8-N}Se_N$  ( $N = 1–7$ ) cluster. In Fig. 5, nine stable phases are determined, marked by different colors. In

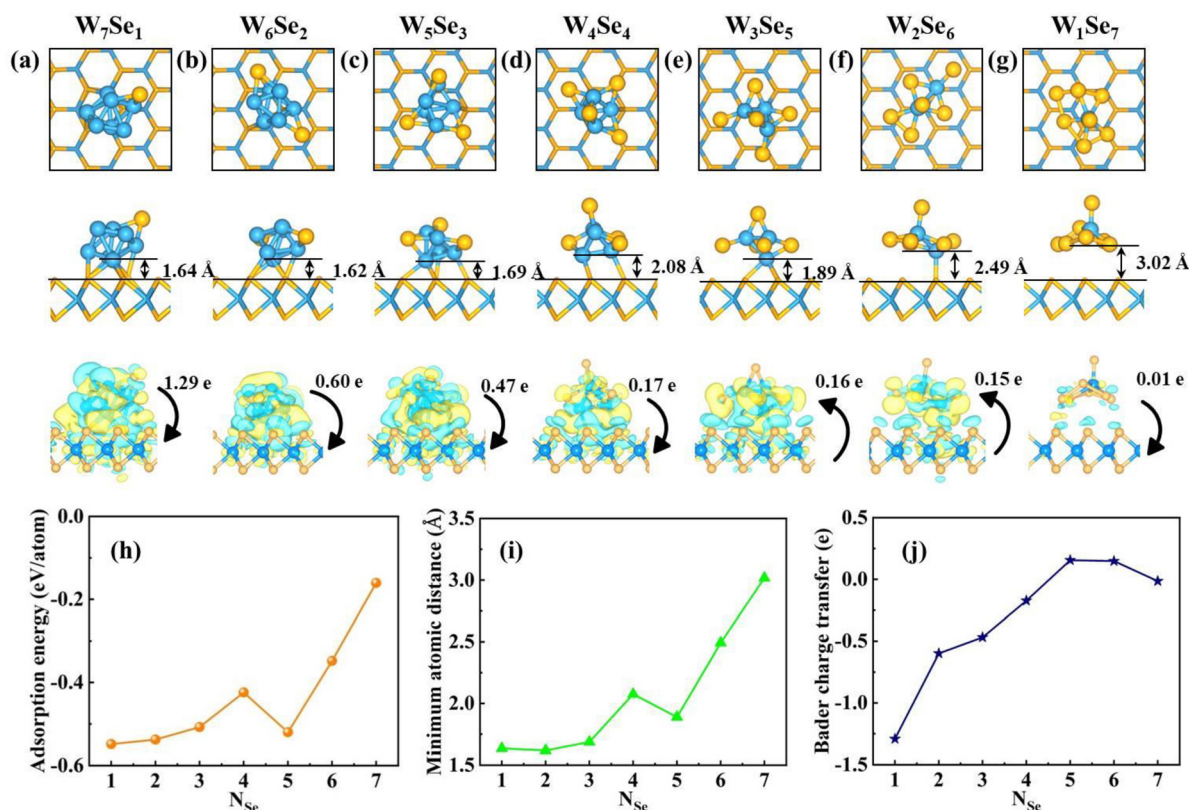


Fig. 4 Top and side views of (a–g)  $W_{8-N}Se_N$  ( $N = 1-7$ ) cluster adsorption on the monolayer  $WSe_2$  surface, the minimum atomic distance, charge density difference and corresponding Bader charge transfer. (h) Adsorption energy of  $W_{8-N}Se_N$  ( $N = 1-7$ ) cluster adsorption on the monolayer  $WSe_2$  surface. (i) Minimum atomic distance of  $W_{8-N}Se_N$  ( $N = 1-7$ ) cluster adsorption on the monolayer  $WSe_2$  surface. (j) Bader charge transfer of  $W_{8-N}Se_N$  ( $N = 1-7$ ) cluster adsorption on the monolayer  $WSe_2$  surface. The negative value of the Bader charge transfer indicates that the cluster loses electrons and the positive value of the Bader charge transfer indicates that the cluster gains electrons.

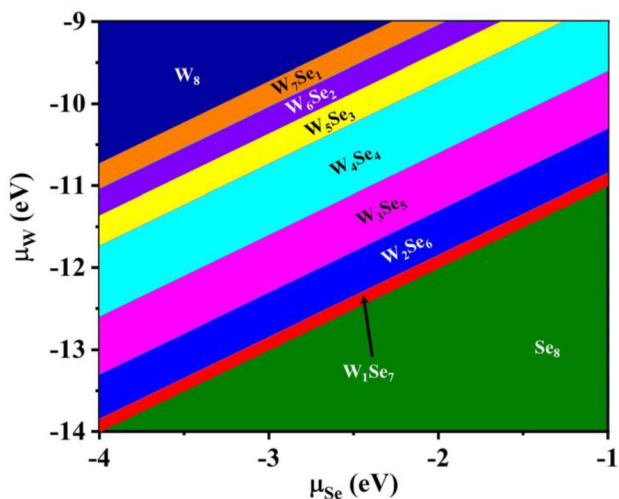


Fig. 5 Phase diagram of bare  $W_8$ ,  $Se_8$  and compound  $W_{8-N}Se_N$  ( $N = 1-8$ ) clusters adsorbed on the  $WSe_2$  surface.

experiments, by tuning  $\mu_{Se}$  and  $\mu_W$  in an appropriate range, the desired phase could be formed. For example, if  $\mu_{Se}$  is  $-1$  eV and  $\mu_W$  is in the range of  $-10$  to  $-9$  eV, the  $W_3Se_5$  cluster could

be formed on the  $WSe_2$  surface. The STM images of the  $W_{8-N}Se_N$  ( $N = 1-7$ ) cluster are also simulated, as shown in Fig. S40.† The simulated STM image is more complicated than the  $W_N$  and  $Se_N$  ( $N = 1-8$ ) clusters.

The projected band structures of the  $WSe_2$  monolayer with  $W_{8-N}Se_N$  ( $N = 1-8$ ) clusters on it are also examined, as shown in Fig. S41.† At a low Se/W ratio ( $N < 7$ ),  $W_{8-N}Se_N$  clusters will induce many impurity states in the gap region like  $W_N$  clusters. For the  $W_1Se_7$  cluster, the LUMO and HOMO of the  $W_1Se_7$  cluster are staggered with the valence band maximum (VBM) and conduction band minimum (CBM) of  $WSe_2$ , implying that the  $W_1Se_7$  cluster and  $WSe_2$  monolayer surface form a type-II band alignment, which will promote the spatial separation of photo generated carriers at the interface.

Briefly, among the  $W_N$ ,  $Se_N$  ( $N = 1-8$ ) and  $W_{8-N}Se_N$  ( $N = 1-7$ ) clusters,  $Se_N$  ( $N = 3-8$ ) and  $W_1Se_7$  clusters have low adsorption energy on the  $WSe_2$  surface, which are more easily removed from the surface to form clean monolayer  $WSe_2$ . In addition, cluster adsorption on the  $WSe_2$  surface is an effective tool to modify the electronic properties of  $WSe_2$ . The  $Se_N$  ( $N = 3-6, 8$ ) and  $W_1Se_7$  cluster adsorption could form a unique type-II band alignment.  $W_N$  ( $N = 1-8$ ) and  $W_{8-N}Se_N$  ( $N = 1-7$ ) clusters induced a large number of impurity states in the band gap

region of the pristine WSe<sub>2</sub> monolayer. In this work, the dynamic process of cluster transition from W<sub>7</sub>Se<sub>1</sub> to W<sub>1</sub>Se<sub>7</sub> and the specific temperature needed to remove Se<sub>N</sub> clusters by annealing were not considered. The effect of the presence of hydrogen on the structure was also not considered. There are also interesting and important issues to be discussed and they are left to be solved in our next work.

## Conclusions

In summary, the adsorption of possible precursor clusters W<sub>N</sub> and Se<sub>N</sub> (N = 1–8) as well as W<sub>8–N</sub>Se<sub>N</sub> (N = 1–7) on monolayer WSe<sub>2</sub> was carefully investigated using first-principles calculations. The GS structures for these clusters in vacuum and on the WSe<sub>2</sub> layer were well studied. The interaction between W<sub>N</sub> clusters and the WSe<sub>2</sub> layer is very strong, so that it is hard to remove W<sub>N</sub> clusters. In contrast, the interaction between Se<sub>N</sub> clusters and the WSe<sub>2</sub> layer is weak vdW interaction except for single Se atoms and Se dimers. The interaction between W<sub>8–N</sub>Se<sub>N</sub> and the WSe<sub>2</sub> layer depends on the Se/W ratio. A high Se/W ratio (N = 7) results in weak interaction at the interface, while low Se/W (N < 7) results in W–Se chemical bonds at the interface. The stability of W<sub>N</sub> and Se<sub>N</sub> (N = 1–8) as well as W<sub>8–N</sub>Se<sub>N</sub> (N = 1–7) on monolayer WSe<sub>2</sub> is related to the chemical potential of W and Se and the phase diagram is plotted. Increasing the Se/W ratio by changing the experimental conditions would increase the ratio of Se<sub>N</sub> and W<sub>1</sub>Se<sub>7</sub> clusters in the precursor clusters, which can be removed by proper annealing. Moreover, W<sub>N</sub> clusters induce many defect states in the band gap region. Se<sub>N</sub> (N = 3–6, 8) and W<sub>1</sub>Se<sub>7</sub> clusters will promote the spatial separation of photo generated carriers at the interface, due to the alignment of HOMO and LUMO of the clusters with the VBM and CBM of the WSe<sub>2</sub> monolayer. This spatial separation is important for optoelectronic applications. Our results provide an atomic insight into the precursor clusters adsorbed on the WSe<sub>2</sub> monolayer. We suggest that the interaction between the precursor clusters and the WSe<sub>2</sub> monolayer as well as the electronic properties of the prepared WSe<sub>2</sub> monolayer can be tuned by controlling the Se/W ratio, which is significant for the high-quality growth and applications of WSe<sub>2</sub>.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

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