A rational computational study of surface defect-mediated stabilization of low-dimensional Pt nanostructures on TiN(100)‡

Young Joo Tak,‡ Woosun Jang,‡ Norina A. Richter and Aloysius Soon*

Platinum is known as a catalyst with exceptional reactivity for many important reactions, e.g. the oxygen reduction reaction. To reduce the high cost of pure platinum catalysts, platinum on a carbon support is widely used in industrial fuel cell applications. However, these Pt/C systems suffer from poor stability. As a cost-efficient and more durable alternative, Pt single-atom catalysts on a TiN support have recently been suggested, and it has been shown that the single-atom catalysts are stable when anchored at a nitrogen vacancy site on the TiN surface in a nitrogen-lean environment. To further explore the perspective of Pt/TiN catalytic systems, we provide insights into the stability and morphology of Pt nanostructures at the TiN(100) surface, using a density-functional theory approach in combination with ab initio atomistic thermodynamics. Our results show that the formation of two-dimensional Pt nano-layers is preferred over the formation of three-dimensional Pt nano-clusters on the TiN substrate. Similar to the single-atom catalysts, nano-layers of Pt can be stabilized on the TiN(100) surface by surface nitrogen vacancies under nitrogen-lean conditions. By analyzing the electronic metal–support interaction (EMSI) between the Pt nano-layer and the TiN surface with surface defects, we demonstrate that a strong EMSI between the surrounding Ti and Pt atoms is important for stabilizing the catalyst nano-layer at the TiN surface, and that N vacancies lead to stronger Pt–Ti interaction. This work provides a rational computational platform for the design of new generation high-performance Pt-based fuel cells.

I. Introduction

Among the different fuel cell technologies that have been developed, polymer electrolyte membrane fuel cells (PEM FCs) are preferred for mobile devices due to their low weight, low operating temperatures, and low emission, where the benign waste product is hydrogen as a fuel is water. However, the commercialization of these PEM FCs has been challenging due to their low durability and high cost. In order to overcome these challenges, having a deeper understanding of the role of the nanocatalyst and its support in PEM FCs is pivotal to the design of new generation high-performance PEM FCs.

Nanocatalyst supports are used to maximize the surface area and corrosion resistivity of the nanocatalyst system, as well as to increase its catalytic performance. To overcome durability issues, there has been a high demand for Pt-nanocatalyst supports that fulfill these criteria even under harsh, corrosive, and oxidizing PEM FC operating conditions. Amongst the class of metallic ceramics, titanium-based compounds (e.g. TiN, TiC, and TiB2) are known for their high resistance to corrosion and many possess good electrical conductivity, making them suitable candidates as highly durable functional supports that meet the high demands of such Pt-based PEM FCs.

Besides their durability, it has been recently demonstrated that novel supports like TiN and TiC can also considerably enhance the catalytic properties of a metal catalyst due to strong electronic metal–support interactions (EMSI), even if the metal catalyst is present in minute amounts. These reports further corroborate the superiority of these Ti-based supports for PEM FC applications; however a detailed atomistic picture of these new nanocatalyst systems is still lacking. Given that a detailed nanoscale structure of catalyst–support is fundamental to understanding the mechanisms of chemical reactions, a microscopic description of the catalyst–support interface structure is highly desirable.

In view of this, recently, first-principles electronic structure calculations (based on density-functional theory) have been performed for single-atom Pt/TiN nanocatalyst systems and have shown that Pt atoms indeed interact strongly with the TiN support, especially when anchored at the surface N vacancy sites on TiN(100). These single-atom Pt/TiN nanocatalysts are...
predicted to be thermodynamically stable under N-lean conditions and are also speculated to mitigate CO poisoning problems in these Pt-based PEM FCs.16

However, in a realistic PEM FC environment, it is rather unlikely to only find these novel single-atom Pt nanocatalyst centers. Depending on the Pt concentration and specific operating conditions, one might speculate that Pt nano-layers or nanoclusters could also well form on the surface of the support.17–20 For instance, on a Au substrate, the formation of Pt nano-layers has been observed in an experiment and investigated using density-functional theory by Lee and co-workers.19,20

As a basis for optimizing these Pt/TiN catalysts for PEM FC applications, it is essential to know the stability and local morphology of the surface structure of these nanocatalysts. Thus, in this work, we address these aspects using density-functional theory (DFT) calculations coupled with ab initio atomistic thermodynamics. We calculate the thermodynamic stability of various possible two- and three-dimensional Pt nanostructures on TiN(100), and identify those that bind most strongly, depending on their immediate chemical environment. To understand why certain TiN-supported nanostructures of Pt are more stable than others, we analyze the density-of-states, Bader charges, and the corresponding changes in the electron-density distribution upon Pt adsorption. We also demonstrate how surface defects on TiN(100) account for the experimentally observed electronic metal–support interaction (EMSI) between the Pt nano-layer and the TiN surface with surface defects, providing a rational computational platform for the design of the next generation high-performance Pt-based PEM FCs.

II. Computational methodology and approach

All DFT calculations have been performed using the Vienna Ab initio Simulations Package (VASP).21–23 We employ the projector augmented-wave (PAW) method and the Perdew, Burke and Ernzerhof (PBE) exchange–correlation functional for our calculations.23–25 We use a kinetic energy cutoff of 500 eV for all structures and a Methfessel–Paxton smearing of width below 0.1 eV to determine the occupation of each orbital. In this work, total energies are converged to within $1.0 \times 10^{-5}$ eV. We use asymmetric slabs, where the surface structures are adsorbed on one side of the slab. Therefore, we use the dipole correction for all our calculations. A $k$-point mesh size in the Brillouin zone of $8 \times 8 \times 8$, $18 \times 18 \times 18$, $12 \times 12 \times 8$, and $4 \times 4 \times 1$ is employed for Pt bulk, TiN bulk, Ti bulk, and all Pt/TiN(100) surface slab structures, respectively, where we have used the primitive unit cells for the bulk structures and a $p(3 \times 3)$ TiN(100) surface cell. In this study, we consider various structures of Pt layers on the TiN(100) surface. Fig. 1 shows the top-view of different surface coverages of Pt from 0.11 to 1 monolayer (ML), and various two- and three-dimensional nanostructures of Pt (Fig. 1c).

Our surface slab models of the TiN(100) surface as a substrate material for the catalyst consist of four atomic layers with a vacuum distance of 18 Å between repeating layers. To address the different surface coverages of Pt, different numbers of Pt atoms on TiN(100) in a $p(3 \times 3)$ surface cell are used, ranging from a single Pt atom to a 1.33 ML Pt adlayer, which corresponds to 12 Pt atoms in the $p(3 \times 3)$ supercell (as shown in Fig. 1a). We also calculate a full monolayer (ML) of Pt atoms (i.e. 9 Pt atoms) adsorbed on different sites of the TiN surface (Fig. 1b). In addition, different Pt surface structures with heights of one to three Pt atomic layers (i.e. up to 4 ML which corresponds to 36 Pt atoms on TiN) are determined. Thus, after including the consideration of possible surface vacancies of Ti and N (up to three vacancies) on TiN(100), in total, we start from an initial set of more than 100 surface nanostructures of varying Pt surface coverages (from 0.11 to 4 ML) and relax the atomic positions of all Pt atoms on the TiN surface and of the atoms in the two upper layers of the TiN slabs. After geometry
relaxation, 71 optimized Pt/TiN nanostructures are found and then accounted for in the results of this paper. Details of the atomic structures of these Pt/TiN nanostructures can be found in the ESI.†

To understand the thermodynamic stability of the TiN-supported Pt adatoms and adlayers, we adopt the average binding energy per Pt atom $E_b^p$ as a function of chemical potential of nitrogen, $\mu_N$, for each system,$^{15}$

$$E_b^p = \frac{E_{tot} - E_{slab}}{(n\mu_p + m\mu_N + l\mu_T)} \frac{1}{n},$$  
(1)

where $E_{tot}$ and $E_{slab}$ are the total energies of the system with the adsorbed structure and the clean slab without vacancies, respectively. $\mu_p$, $\mu_N$, and $\mu_T$ are the atomic chemical potential of Pt, N, and Ti, respectively. $n$, $m$, and $l$ are the number of Pt atoms adsorbed on the TiN surface, the number of nitrogen surface vacancies, and the number of titanium surface vacancies, respectively.$^{15}$ We assume that the chemical potential of Pt, $\mu_p$, is that of a Pt atom in bulk Pt. A negative value for $E_b^p$ will suggest that the system with the Pt nanostructure is thermodynamically stable with respect to bulk-like Pt clustering.

In analogy, we calculate the formation energy for surface N or Ti vacancies at TiN(100) according to

$$E_f^b = E_{tot,V} - E_{slab} + \mu_A,$$  
(2)

where $E_{tot,V}$ is the total energy of the TiN(100) surface with one vacancy of atom type A (either N or Ti) and $\mu_A$ is the chemical potential of the removed atom.

We consider N-lean and N-rich conditions for mimicking environments where either nitride decomposition or nitrogen condensation takes place. Under N-lean conditions, where the nitride tends to decompose into metal and nitrogen gas, the atomic chemical potentials are given by $\mu_T$ = $E_{T1}^{bulk}$ and $\mu_N$ = $E_{N}^{bulk} - E_{T1}^{bulk}$. Under N-rich conditions, $N_2$ tends to condensate on the surface. In this environment, the atomic chemical potential of N and Ti can be expressed as $\mu_N$ = $E_{N}^{bulk} - \frac{1}{2}E_{N_2}$ and $\mu_T$ = $E_{Ti}^{bulk} - \frac{1}{2}E_{N_2}$. Here, $E_{T1}^{bulk}$, $E_{N}^{bulk}$, and $E_{N_2}$ denote the total energies of bulk TiN, bulk Ti, and the $N_2$ molecule, respectively.$^{15}$

Partial density-of-states, Bader charge analysis$^{26}$ and evaluation of the electronic charge difference densities are performed using the optimized atomic structures for the single Pt atom on TiN(100), and for a nano-layer of Pt on TiN(100) with N vacancies. These Pt/TiN surface nanostructures exhibit the lowest average Pt binding energies $E_b^p$ among the various adatom/ adlayer structures that we determined.

III. Results and discussion

First, we calculate the bulk properties of TiN and Pt. For bulk TiN, we obtain a PBE lattice constant of 4.25 Å, which is in good agreement with the experimental value of 4.24 Å (ref. 27) and PBE values of 4.23–4.26 Å reported in earlier studies.$^{15,28-21}$ We determine its bulk modulus as 278 GPa, which is also in good agreement with the theoretical value of 280 GPa in the literature$^{22}$ and the experimental value of 288 GPa.$^{24}$ For bulk Pt, the calculated lattice constant is 3.98 Å, and its bulk modulus is 242 GPa, which agrees well with the published theoretical (4.00 Å for lattice constant$^{24}$ and 250 GPa for bulk modulus$^{25}$) and experimental results (3.92 Å [ref. 34] and 277 GPa [ref. 36] for the corresponding values of the lattice constant and the bulk modulus of Pt).

Next, we consider the average binding energy of Pt nanostructures in the 71 optimized Pt/TiN nanostructures described above. Fig. 2a shows the average binding energy per Pt atom for the various Pt/TiN models considered on the pristine, defect-free TiN(100) surface for various Pt surface coverages. All binding energy values have been calculated using eqn (1), where $m = 0$ and $l = 0$. Our results show that all calculated Pt binding energies on pristine TiN(100) are positive (i.e. thermodynamically unstable to bulk-like Pt clustering) and decrease with increasing Pt surface coverage. This indicates that the dominant Pt–Pt cohesive interaction weakens the binding of Pt atoms to the pristine TiN surface. The Pt nano-layer shown in Fig. 1a on the very left side (12 Pt atoms on TiN(100) in the p(3 x 3) supercell) shows the lowest, but still positive average binding energy of 0.17 eV. From this, we conclude that Pt is unlikely to form stable nanostructures on the clean pristine TiN(100) surface, regardless of its morphology or coverage.

In retrospect, under realistic experimental conditions, the TiN(100) surface is prone to having surface defects, in particular, surface N defects.$^{32}$ When considering the surface vacancy formation energies for N and Ti surface defects at the TiN(100) surface (Fig. 2b), we see that surface N vacancies are present in thermodynamic equilibrium under N-lean conditions. Surface vacancy concentration ($x_v$) is determined by dividing the number of surface vacancies by the number of possible surface vacancy sites. Surface mono-vacancies ($x_v$ = 0.11) have the lowest formation energy and this is in agreement with the recent theoretical study by Lee and co-workers.$^{32}$ Under the considered conditions in this work, both the surface Ti and N vacancy formation energies are repulsive in nature, i.e. they increase considerably with increasing surface vacancy concentration, $x_v$. For example, the surface N vacancy formation energy under N-lean conditions increases from $-0.65$ eV at $x_v = 0.11$ to $-0.22$ eV at $x_v = 0.33$, albeit still energetically favourable.

Next, to investigate the effect of surface defects on the average binding energy of Pt, we select the Pt/TiN nanostructures with the lowest average Pt binding energy (compare Fig. 2a) and calculate its average binding energy again when adsorbed on TiN(100) with surface N or Ti vacancies (Fig. 2c) at varying concentrations of surface defects ($x_v = 0.11$, 0.22, and 0.33). From our calculations, we found that the Pt/TiN nanostructures are now thermodynamically stable on TiN(100) with surface N vacancies, particularly under N-lean conditions. In other words, surface vacancies play a key role in stabilizing these Pt nanostructures which would otherwise prefer bulk-like Pt clustering at the surface of TiN. This defect-mediated stabilization is inline with our previous work on single Pt atom adsorption on defective TiN(100).$^{15}$ One interesting observation is that under N-lean conditions, the surface N vacancy formation energy increases with increasing $x_v$ (Fig. 2b), while the average Pt binding energy presents an opposite trend (i.e. decreases with increasing $x_v$).
Note also that while the Pt nano-layer is bound to the TiN surface with surface N vacancies (with average Pt binding energies of 0.04 to 0.30 eV depending on N vacancy concentrations), the average binding energy of a Pt single atom catalyst anchored at the surface N vacancy is still more favourable (1.11 eV). This shows that the Pt–Pt interaction in the Pt nano-layer could destabilize the adsorption of Pt at this surface.

To study the average adlayer–substrate (i.e. Pt–TiN) distance for these Pt/TiN nanostructures, we perform a pair distribution function calculation (see Fig. 3), considering only the vertical distance between the Pt adatoms in the nanostructures and the outermost atoms of TiN(100). Our statistical data show that the mode distance value is 2.37 Å, and we can divide the collected statistics into three sections: below a vertical distance of 4.80 Å, these Pt atoms are confined to the first Pt atomic-layer (as shown in the white area in Fig. 3), and between 4.80 and 6.25 Å, these Pt atoms belong to the second atomic layer (as shown in light gray in Fig. 3), and lastly those above 6.25 Å then reside in the third atomic layer of Pt. In comparison, for Pt nano-clusters adsorbed on an Al₂O₃ support, an average distance of about 1.97–2.10 Å was reported by Kochubei and co-workers. 

We next consider the average Pt binding energy of these Pt/TiN nanostructures as a function of the distance between Pt atoms, d_{Pt–Pt}. Since we are interested in the effect of Pt–Pt interactions, we exclude the previously studied single-atom Pt/TiN nanostructures from the 71 surface structures. The average Pt binding energy as a function of d_{Pt–Pt} on pristine, defect-free TiN(100) is shown in Fig. 4a. Here we find that the average Pt binding energy decreases, as d_{Pt–Pt} approaches that in bulk Pt (2.83 Å). Furthermore, from Fig. 4a, we find that the d_{Pt–Pt} values for the various Pt/TiN nanostructures converge to that in bulk Pt with increasing Pt surface coverage, hinting that bulk-like Pt clustering may indeed occur for high surface coverages of Pt, lowering the over binding energy of Pt but not enough to stabilize these nanostructures on pristine TiN(100).

Again, considering only the most stable Pt/TiN nano-layer (i.e. with 12 Pt atoms in the p(3 × 3) surface supercell and corresponding to a Pt surface coverage of 1.33 ML) with varying surface N and Ti vacancy concentrations (with \(x_v = 0.11–0.33\)), we plot the average Pt binding energy as a function of d_{Pt–Pt} in...
Fig. 4b and c, respectively. Details of the atomic structures of these vacancy-containing Pt/TiN nanosystems can be found in the ESL.† The \(d_{\text{Pt-Pt}}\) in the Pt/TiN nano-layer with surface N or Ti vacancies are found to be smaller than that in bulk Pt, but they are all very close to the equilibrium bulk interatomic distance. This can be explained by the confinement due to the interaction between the Pt nano-layer and the surface vacancies at the TiN(100) surface. The surface vacancies act as anchoring sites for the Pt nano-layer and due to this strong anchoring effect, the lateral \(d_{\text{Pt-Pt}}\) is decreased with respect to the bulk interatomic distance. For the Pt nano-layer on TiN(100) with surface N vacancies, the bulk-like \(d_{\text{Pt-Pt}}\) of the Pt atoms has a stabilizing effect on the overall Pt/TiN nanosystem. However, this criterion alone does not lead to a stable Pt/TiN nanosystem.

Fig. 5 Partial density-of-states and top-views of the Pt/TiN nanostructures with the corresponding Bader charge analysis (insets) for (a) Pt single-atom anchored at a surface N vacancy site, (b) Pt nano-layer on TiN(100) with one surface N vacancy \(x_v = 0.11\), (c) Pt nano-layer on TiN(100) with two surface N vacancies \(x_v = 0.22\), and (d) the Pt nano-layer on TiN(100) with three surface N vacancies \(x_v = 0.33\). The Bader charge for each atom is noted in units of electronic charge and the values are color-coded from positive (in red) to negative (in blue). Gray filled circles denote the positions of surface N vacancies below the Pt adatoms. The Fermi energy is indicated by the vertical dashed line at 0 eV.
By comparing the systems with surface N and Ti vacancies, it is obvious that the surface morphology of the TiN support has a strong impact on the stability of the adsorbed Pt atoms. Comparing N-lean with N-rich conditions in Fig. 4b, we also note that unfavorable ambient conditions can strongly destabilize the Pt/TiN nanosystem.

After corroborating the calculated thermodynamics of these Pt/TiN nanosystems with the measured atomic distances, we now turn to the electronic structure of these systems to investigate the electro-chemical origins of these defect-mediated stabilization of Pt nanostructures on TiN(100) with surface defects. To analyze the electronic structure of the most stable Pt/TiN nanosystems that we have found, we first calculate their electronic density-of-states (DOS) and perform a Bader charge analysis for the atoms in these Pt/TiN nanosystems. In Fig. 5a, the DOS projected on both the Pt 5d and Ti 3d states is shown for the Pt/TiN single-atom nanosystem.\(^{15}\) We compare this to that for the most stable Pt nano-layer on TiN(100) with the \(x_n\) values of 0.11, 0.22, and 0.33 (Fig. 5b–d, respectively). Here, we compare the renormalized Pt 5d states for these four different Pt/TiN nanosystems with that of Pt bulk (shaded in gray) and clean Pt(100) (shaded in orange). For the system with the lowest binding energy per Pt atom, the single-atom catalyst, the Pt 5d state is lowest in energy with respect to the Fermi level (shown by a dashed vertical line).

For the Pt nano-layer adsorbed on the N-deficient TiN surface, the Pt 5d electronic states are more delocalized as compared to that for the Pt single-atom. For increasing the concentration of surface N vacancies, the effective overlap between the Pt 5d states and the Ti 3d states of the neighbouring Ti surface atoms becomes more pronounced. We have shown above that the average Pt binding energy decreases with increasing surface vacancy concentration (cf. Fig. 2b). This corroborates well with our calculated DOS results, and comparing to our calculated Bader charges, we also observe that the number of negatively charged Pt atoms is increased as the surface vacancy concentration increases (Fig. 5, inset). From experiments, a modulation of the charge state of Pt is believed to lead to an improvement in the catalytic properties of the metal catalyst, as demonstrated in the recent work by Hu and co-workers.\(^{9}\) These negatively charged Pt atoms in the nano-layer can be expected to show higher catalytic reactivity for the oxygen reduction reaction, since electrons could be transferred from the catalyst system to the reactants. Our results seem to suggest that a reorganization of electronic charges has taken place between the Pt nanostructure and the underlying TiN support, strongly suggesting a significant EMSI that could then explain an improved catalytic performance as observed in recent experiments.\(^{9,10,12}\)

To further verify this defect-mediated EMSI effect, we calculate the difference in electronic charge density for these Pt/TiN nanosystems and plot them in Fig. 6. We adopt the following definition for the charge density difference, \(\Delta \rho\), as \(\Delta \rho = \rho^{\text{WS}} - \rho^{\text{PT}} - \rho^{\text{TiN}},\) where \(\rho^{\text{WS}}, \rho^{\text{PT}}\), and \(\rho^{\text{TiN}}\) are the charge densities of the TiN support with the adsorbed Pt system, the Pt catalyst without support, and the TiN surface with vacancies, respectively.

For the calculation of the latter two quantities, the atomic positions are fixed according to the respective Pt/TiN system. Upon anchoring a Pt single-atom at the surface N vacancy site, a decrease (in cyan) of electron density on both the Pt atom and the nearest-neighbour surface Ti atoms occurs, and we see a ring-shaped charge density accumulation (in yellow) between Pt and surface Ti atoms (as shown in Fig. 6a). This EMSI effect effectively locks the Pt atom to the TiN(100) surface, rendering it stable to bulk-like Pt clustering. The electronic charge density redistribution that leads to the bonding between the Pt atoms and surface Ti atoms is also clearly visible for the Pt nano-layer on TiN(100) with surface N vacancies (Fig. 6b–d). However, given that there are more than one Pt atoms in the nano-layer, this charge accumulation is not as pronounced as that for the single-atom Pt/TiN.

From our electronic structure analysis, it is clear that upon forming these single-layered Pt nanostructures on TiN(100) with surface N vacancies, they are largely stabilized/anchored at the surface defect sites via chemical bonds and weakly charging the Pt nano-layer in the process. We have thus provided the electro-chemical origin to this defect-mediated stabilization process in low-dimensional Pt nanostructures on TiN(100), providing direct evidence to the proposed EMSI by recent experiments.

![Fig. 6 Side-views and top-views (insets) of the electronic charge density difference for (a) a Pt single-atom adsorbed at the surface N vacancy site of TiN(100), (b) Pt nano-layer on TiN(100) with one surface N vacancy, (c) Pt nano-layer on TiN(100) with two surface N vacancies, and (d) Pt nano-layer on TiN(100) with three surface N vacancies. The isosurface level used is 0.025 e Å\(^{-3}\) for (a) and 0.010 e Å\(^{-3}\) for (b–d). The electronic charge depletion is indicated in cyan, while the charge accumulation is shown in yellow.](image-url)
IV. Conclusions

Using first-principles DFT calculations, various Pt nanostructures have been investigated on TiN(100) with surface vacancies. We found that none of the Pt nanostructures are stable when formed on the pristine, defect-free TiN(100) surface. However, accounting also for the presence of surface defects, our results clearly show that in analogy with the Pt single atom considered in earlier studies, Pt nano-layers are likely to form and anchor at the TiN(100) support with surface N vacancies, especially under N-lean conditions. The formation of a Pt nano-layer on the TiN support with surface Ti vacancies is energetically unfavorable. With increasing concentration of surface N vacancies at TiN(100), the average Pt binding energy of the Pt nano-layer on the TiN support becomes more favourable, and these energetics are easily rationalized and are in accord with the calculated electronic structures of these Pt/TiN nanosystems, providing direct evidence for the proposed EMSI by recent experiments.

Acknowledgements

This work was supported by the Global Frontier R & D Program (2013M3A6B1078881) on Center for Hybrid Interface Materials (HIM) funded by the Ministry of Science, ICT & Future Planning. Computational resources have been provided by the Korea Institute of Science and Technology Information (KISTI) supercomputing center through the strategic support program for the supercomputing application research (KSC-2014-C3-006). We also thank C.E. Kim for his contribution to the distance distribution analysis in this work.

References

Supplementary Materials for:

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(Dated: February 4, 2015)
FIG. 1. Side- and top-view of the atomic structures of Pt nanostructures on pristine TiN(100) in a $p(3 \times 3)$ surface cell. These structures are labelled from 001 to 050 and the suffix “s” and “t” are used to differentiate the side- and top-views of a particular structure, accordingly. Here, the yellow, blue, and white spheres denote the Pt, N, and Ti atoms, respectively.
FIG. 2. Top-view of the atomic structures of the possible arrangements of surface nitrogen vacancies on TiN(100) in a $p(3 \times 3)$ surface cell. The structures labelled 001 contains one surface nitrogen vacancy, while 002 to 006 contain two surface nitrogen vacancies, and 007 to 016 three surface nitrogen vacancies, respectively. Here, the blue and white spheres denote the N and Ti atoms.
FIG. 3. Top-view of the atomic structures of the possible arrangements of surface titanium vacancies on TiN(100) in a $p(3 \times 3)$ surface cell. The structures labelled 017 contains one surface titanium vacancy, while 018 to 022 contain two surface titanium vacancies, and 023 to 032 three surface titanium vacancies, respectively. Here, the blue and white spheres denote the N and Ti atoms.