

Computation details

In the current work, all density-functional theory (DFT) calculations were performed in the DMOL3 code.²³ The Perdew Wang²⁴ (PW91) version of generalized gradient approximation (GGA) was employed as exchange correlation function. The tolerances of geometry optimization were set as the difference of the total energy within 10^{-5} hartree, maximum force within 0.002 hartree/Å and maximum displacement in 0.005 Å. The Gaussian smearing of electron density was applied with the energy range of 0.005 hartree.

TiC_{1.0} and TiN_{1.0} are face centered cubic (fcc) structures belong to Fm-3m space group. First, the crystal which contains 4 metal Ti atoms and 4 non-metal C/N atoms was made. The metal atom sit at (0, 0, 0) and the non-metal atom sit at (0.5, 0.5, 0.5). The lattice constants for TiC_{1.0} and TiN_{1.0} are 4.33 and 4.25, respectively. Second, a 2×2×2 supercell was constructed consists of 32 Ti atoms and 32 C/N atoms (see Figure A). The models for different stoichiometry of TiC_x and TiN_x we adopt from Hugosson's work²² are shown in Figure 1. The corresponding values of *x* of the substoichiometric TiC_x and TiN_x were 0.50, 0.625, 0.75, 0.875 and 1.0. The formation energies (*E*_{form}) of TiC_x and TiN_x with different stoichiometries were shown in Table A.

Figure B shows the crystal structures the {100} and {111} surfaces. It can be seen that the {100} planes contain both Ti and C(N) atoms in each slab, but the polar {111} planes contain alternating arrangement of Ti and C(N) layers and is Ti terminated at both the ends. The minimum slab thickness for TiC_x and TiN_x is 7 atom

layers for {100} surfaces, and 9 for {111} surfaces. The surfaces calculated in the work are fully relaxed for all layers. To model the {100} and {111} surfaces, we used the supercell approach with a vacuum of 15 Å between the slabs.

The surface energy of {100} and {111}, σ , can be given by

$$\sigma = (E_{tot} - N_{Ti}\mu_{Ti} - N_{C/N}\mu_{C/N})/2A \quad (1)$$

Here, E_{tot} is the total energy of the slab, and μ_{Ti} and $\mu_{C/N}$ are the chemical potentials of each Ti and C(N) atom, respectively. In addition, N_{Ti} and $N_{C/N}$ are the numbers of the corresponding atoms in the slabs. The total chemical potential of the elemental Ti and C(N) is in equilibrium with that of bulk $TiC_{1.0}$ and $TiN_{1.0}$:

$\mu_{TiC(N)_{1.0}}(\text{bulk}) = \mu_{Ti} + \mu_{C/N}$. Accordingly, Eq. (1) becomes

$$\sigma = (E_{tot} - N_{Ti}\mu_{TiC(N)_{1.0}}(\text{bulk}) + (N_{Ti} - N_{C/N})\mu_{C/N})/2A \quad (2)$$

The elemental C(N) chemical potential was used to replace the corresponding bulk chemical potential which is -1.66×10^{-16} J/atom and -2.38×10^{-16} J/atom, respectively.

The Brillouin-zone integrations were set within $6 \times 6 \times 6$ k-point mesh for the bulk and $6 \times 6 \times 1$ k-point mesh for the slab. None spin polarization was used for both bulk and surface calculations.

FIGURE CAPTIONS

Figure A. The crystal structures of single crystal and supercell of $\text{TiC}_{1.0}$ ($\text{TiN}_{1.0}$).

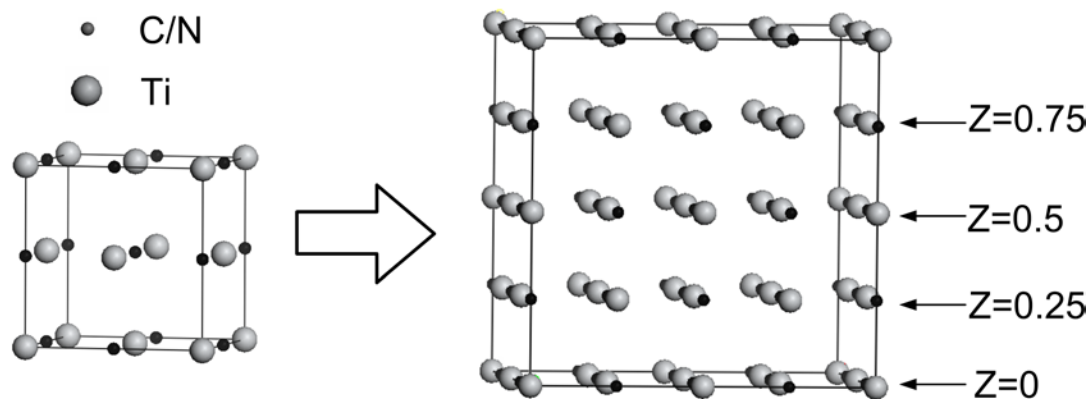


Figure B. Crystal structures of $\{100\}$ and $\{111\}$ surfaces with a vacuum of 15 Å between the slabs.

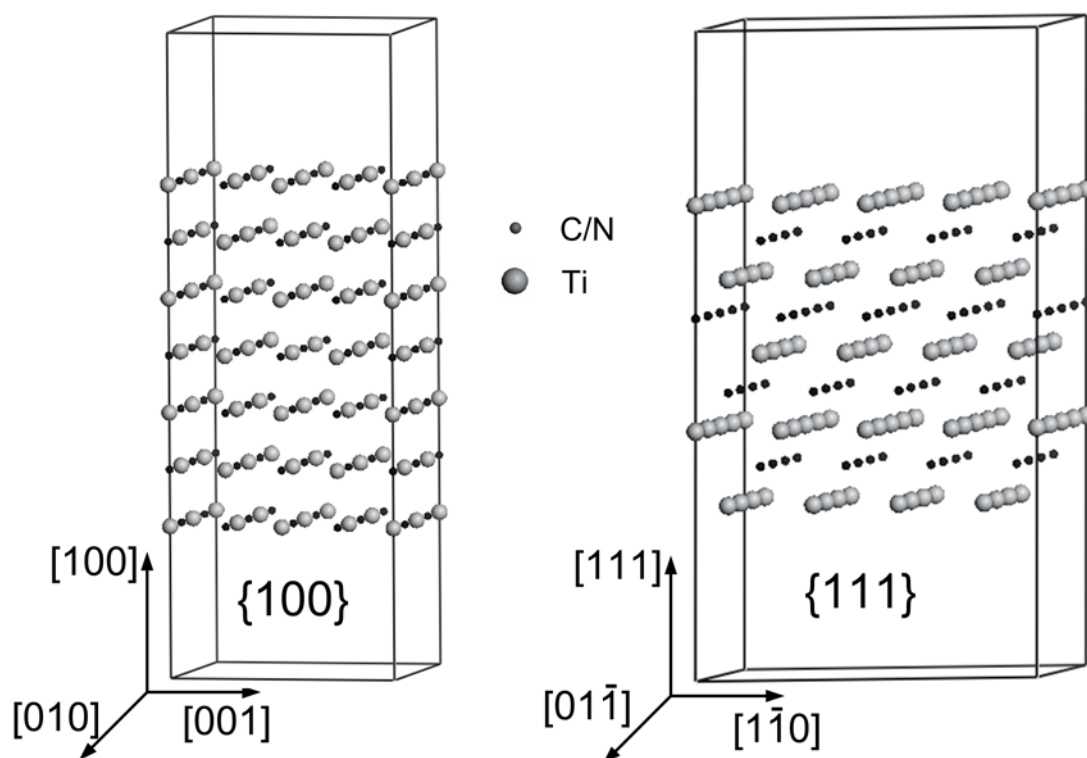


Table A. The formation energies (E_{form}) of TiC_x and TiN_x with different stoichiometry x .

x	0.5	0.625	0.75	0.875	1.0
$E_{\text{form}}(\text{J/atom})$					
TiC_x	-1.10×10^{-19}	-1.26×10^{-19}	-1.35×10^{-19}	-1.43×10^{-19}	-1.47×10^{-19}
TiN_x	-2.12×10^{-19}	-2.45×10^{-19}	-2.68×10^{-19}	-2.84×10^{-19}	-2.95×10^{-19}