Discovery of Stable Surfaces with Extreme Work Functions by High-Throughput Density Functional Theory and Machine Learning

Peter Schindler,* Evan R. Antoniuk, Gowoon Cheon, Yanbing Zhu, and Evan J. Reed

The work function is the key surface property that determines the energy required to extract an electron from the surface of a material. This property is crucial for thermionic energy conversion, band alignment in heterostructures, and electron emission devices. This work presents a high-throughput workflow using density functional theory (DFT) to calculate the work function and cleavage energy of 33,631 slabs (58,332 work functions) that are created from 3,716 bulk materials. The number of calculated surface properties surpasses the previously largest database by a factor of ≈27. Several surfaces with an ultra-low (<2 eV) and ultra-high (>7 eV) work function are identified. Specifically, the (100)-Ba-O surface of BaMoO₃ and the (001)-F surface of Ag₂F have record-low (1.25 eV) and record-high (9.06 eV) steady-state work functions. Based on this database a physics-based approach to featurize surfaces is utilized to predict the work function. The random forest model achieves a test mean absolute error (MAE) of 0.09 eV, comparable to the accuracy of DFT. This surrogate model enables rapid predictions of the work function (≈10² faster than DFT) across a vast chemical space and facilitates the discovery of material surfaces with extreme work functions for energy conversion and electronic device applications.

1. Introduction

The work function is a fundamental surface parameter of a material that determines how much energy is required to extract an electron to a field-free region outside the surface; lower work functions facilitate electron emission. Work functions play a key role in technologies that require precise control of contact barriers such as printed and organic electronics.[1–3] Materials with low work functions are crucial for electron emission devices (THz sources[4,5] and fluorescent light bulbs[6]), electron sources for scientific instruments,[7,8] and high-brightness photocathodes.[9] Especially for thermionic energy converters (TECs),[10–12] discovery of thermally stable, ultra-low work function materials (less than 1.5 eV) would allow thermionic conversion of heat (>1500 °C) directly to electricity with efficiencies exceeding 30% (typical thermionic and thermoelectric converters have efficiencies around 10%). Materials with high work functions play a key role in engineering the electron tunneling barrier in electronics (for example in dynamic RAM applications[13] and for contacts in modern 2D-based transistors[14]), as well as selective contacts in solar cells.[15] The most commonly used materials for low work function applications that are chemically and thermally stable are compounds like lanthanum hexaboride[16,17] and...
thoriated tungsten\cite{18-21} with a work function around 2.5 eV. For thermionic converters, extremely low work functions are required, which are achieved by sub-monolayer coatings of alkali metals (most commonly cesium) on metal surfaces. The resulting work functions are much lower than the work function of either metal or coating individually. This effect is due to the partial transfer of electron charge from the adsorbate to the substrate and the resulting formation of surface dipoles that lower the vacuum energy level near the surface.\cite{22} Perovskite oxides containing transition metals have also shown promise for low work function applications down to 1.6 eV\cite{23} Alkaline vanadates (e.g., SrVO$_3$) have also shown promise in thermionic emission devices.\cite{24} Coatings using cesium or barium combined with oxygen are well known to achieve $\approx 1$ eV work functions in photocathode applications, for instance on III-V semiconductors or silver.\cite{25-27} The anti-fluorite X$_2$O$_3$ family (where X is an alkali metal) is known to exhibit work functions down to 1.2 eV.\cite{28-30} Ruthenium oxide with a work function of 6.1 eV has been developed that is able to estimate the work function fairly accurately for metals and alkaline-metal-coated surfaces.\cite{67} This phenomenological equation is a function of the atomic radius and the number of atomic sites per unit cell area. However, it relies on a single parameter (loosely related to the number of electrons that an atom can donate to the surface) that is not clearly defined for more complex surfaces and takes on nonphysical values in the case of alkaline coatings. In recent work, Hashimoto et al.\cite{68} attempted to screen for low and high work function materials using a Bayesian optimization approach. However, they assume the work function to be approximated solely as a bulk property neglecting any surface contributions during screening. For the highest and lowest “bulk work function” material candidates the actual surface contributions have then been included which rendered most of their top candidate materials to exhibit average work functions between 3 and 6 eV. Unsurprisingly, among their top candidate materials, they have found that the (110) surface of elemental Cesium has a low work function of 2.0 eV and that the (111) surface of KEuO$_2$ has a relatively high work function of 8.4 eV. The approximated bulk work function of some of the screened work function candidates differs as much as 7 eV from the actual work function when including the surface contributions. This clearly shows that, while for simple structures (such as elemental metals) the work function can theoretically be predicted from bulk properties alone,\cite{69} it is important to consider surface contributions to quantitatively predict the work.
function of a material. The surface termination, atom adsorption (most commonly oxygen and hydrogen), contamination, and reconstructions can affect the surface dipole and hence the effective work function. While a crystal graph convolutional neural network has been used successfully to predict the cleavage energies of intermetallic slabs, there have been no reports on featureizing slabs to predict the work function (except for the MXene 2D-material class).

In this paper, we use high-throughput DFT to calculate 58,332 surface work functions and 33,631 cleavage energies based on 3,716 bulk crystal structures (up to ternary compounds with a bandgap less than 0.1 eV). The created database gives insight into work function trends observed across a large chemical space. Based on the database we develop a machine learning model with a low test mean absolute error (MAE) of 0.09 eV, which is more than six times lower than the baseline (i.e., predicting every surface to have the database-average work function) and about four to five times better than state-of-the-art benchmarking machine learning models (automatminer and Coulomb matrix). The database and machine learning model enable us to identify several promising, stable material surfaces with extremely low (<2 eV) and extremely high (>7 eV) work functions. Further, the work function model established in this work enabled the discovery of new ultra-bright photocathode materials reported in Refs. [72, 73].

2. Materials Selection and High-Throughput Workflow

The workflow of the work function database’s creation is illustrated in Figure 1. A total of 3,716 crystal structures were queried from the Materials Project (on 2/2/2023) using the REST framework.[56,74] Up to ternary materials with ten or fewer atoms in the conventional unit cell were considered that have an energy above the hull of less than 20 meV/atom, are metallic ($E_{gap} < 0.1$ eV), and are tagged as experimental (i.e., there exists at least one ICSD entry that reports the corresponding material as experimentally synthesized). Materials with an element present that is radioactive, a noble gas, or from the actinide group were excluded. Further, materials that have experimental tags that indicate high-pressure or low-temperature conditions, as well as low-dimensional materials were excluded. The frequency with which each chemical species appears in the database (bulk compounds) is plotted as a heat map on the periodic table in Figure S3 (Supporting Information).

From this set of materials, surfaces up to a Miller index of 1 were generated using Pymatgen’s surface module.[59,75,76] Each surface Miller index generally has more than one unique surface termination. The Pymatgen surface module has a built-in option to generate slabs with different terminations determined by possible shifts in the c-direction. We have developed an alternate algorithm to ensure that we generate all possible unique terminations based on the local environment of surface atoms, as summarized in the dashed block in Figure 1 and described in more detail in the Supporting Information.

According to the determined total number of unique terminations we generate slabs that contain the appropriate number of atomic layers to expose each unique termination. Further, we minimize the number of slabs required for the DFT calculations by having two distinct terminations on either side of the slab, whenever possible. The initial slab thickness is minimized while still ensuring that after all necessary subtractions the final slab is at least 10 Å thick. Following this procedure, we created 37,163 slabs and 17,998 reoriented bulk structures of which 36,962 and 17,993 converged, respectively during self-consistent field calculations with a total computational time of around 440,000 core hours. The converged calculations after duplicate removal (described in the machine learning model training section) returned

Figure 1. Workflow of the creation of the surface property database and surrogate machine learning model. The illustration includes the steps for material selection, high-throughput DFT calculations, surface slab creation, and supervised machine learning predictions. The dashed block details the procedure of determining the unique terminations of all surfaces up to a Miller index of 1.
3. Results and Discussion

3.1. Analysis of Surface Database

First, we analyze the surface property database created by high-throughput DFT (33,631 slabs based on 3,716 bulk crystals) in terms of its distribution and trends in the studied chemical space. A contour plot of the database distribution of DFT-calculated work functions versus surface energies is shown in Figure 2a for ionically unrelaxed slabs. The calculated cleavage energy is exactly equal to the surface energy in the case of symmetric slabs that exhibit either a mirror or glide plane parallel to the surface or a twofold rotation axis normal to the surface. For slabs lacking this symmetry, $2 \cdot E_{\text{cleavage}}$ is used as an upper bound to the surface energy. The work function distribution of ionically unrelaxed surfaces is plotted in Figure 2b and shows a near-Gaussian distribution with an extended tail toward higher work functions. The average of the entire distribution is at 3.92 eV with a standard deviation of 0.86 eV, ranging from a minimum to a maximum cleavage energy of 1.17 to 396.3 meV Å$^{-2}$, respectively.

The observation that the distribution in work functions is near-Gaussian could indicate that the chemical space we chose was diverse enough to evenly sample work functions across possible values. The extended tail at the high work function end

| Number | Average | St.Dev. | Min. | Max. |
|--------|---------|---------|------|------|
| Elemental | 261 | 3.72 | 0.84 | 2.30 | 5.70 |
| Binary | 14,623 | 4.00 | 0.91 | 1.43 | 10.54 |
| Ternary | 43,448 | 3.89 | 0.84 | 1.17 | 11.07 |
| All | 58,332 | 3.92 | 0.86 | 1.17 | 11.07 |

maximum cleavage energy of 1.0/0.3 to 396.3/397.3 meV Å$^{-2}$, respectively.

The observation that the distribution in work functions is near-Gaussian could indicate that the chemical space we chose was diverse enough to evenly sample work functions across possible values. The extended tail at the high work function end

| Sym. | Number | Average | St.Dev. | Min. | Max. |
|------|--------|---------|---------|------|------|
| Elemental | Yes | 206 | 81.5 | 57.0 | 240.7 |
| Elemental | No | 30 | 42.4 | 25.1 | 5.7 |
| Binary | Yes | 3,596 | 88.7 | 50.2 | 396.3 |
| Binary | No | 5,819 | 109.0 | 58.1 | 397.3 |
| Ternary | Yes | 2,229 | 87.3 | 37.0 | 296.4 |
| Ternary | No | 21,751 | 102.0 | 41.8 | 388.5 |
| All | Yes | 6,031 | 88.0 | 46.0 | 1.0 |
| All | No | 27,600 | 103.4 | 45.8 | 0.3 |

Table 1. Detailed work function distribution metrics for elemental, binary, and ternary compounds for unrelaxed slabs. All values in eV.

Table 2. Detailed cleavage energy distribution metrics for elemental, binary, and ternary compounds for unrelaxed symmetric and asymmetric slabs. All values in meV Å$^{-2}$. 

...
appears to be an artifact coming from ionically unrelaxed surfaces where a small, electronegative atom (e.g., oxygen or hydrogen) is cleaved at a large, unphysical distance (as discussed in the next section and corroborated by Figure S10, Supporting Information). This might also be the case for the low work function tail but appears to be less pronounced. This artifact can be mitigated by ionically relaxing the surface slabs (see next section) and we expect this to result in an overall slightly narrower distribution. Interestingly, the work function distributions of binary and ternary compounds have similar averages and standard deviations. This may be explained by the observation that the work function is primarily determined by the chemical species present in the topmost layer at the surface (as discussed in the next paragraph), and will largely not depend on the total number of chemical species present in the entire unit cell. Moreover, the average work function of the database is lower than the average work function for the JARVIS database and C2DB (4.91 and 5.43 eV, respectively, cf. Table S1, Supporting Information) while the standard deviations are somewhat similar (1.22 and 1.08 eV, respectively). The minimum/maximum work functions decrease/increase going from unary to binary to ternary materials. We hypothesize that this is partly an effect of the increasing amount of data points in each of the respective classes, but also due to multi-component alloys exhibiting more complex chemistries that may give rise to more pronounced extremes. The average cleavage energy of all asymmetric slabs (103.4 meVÅ$^{-1}$) is higher than the average for all symmetric slabs (88.0 meVÅ$^{-1}$). This is expected because this database is calculated for unrelaxed slabs and cleaving asymmetric slabs may lead to dangling atoms in nonphysical positions too far/close to the other surface atoms.

Trends in the work function based on which chemical species are present at the surface are shown in Figure 3. The fraction of surfaces with a low work function (<2.5 eV, i.e., roughly 1.5 times the standard deviation below average) is especially high for surfaces with alkali or alkaline metals present in the topmost atomic layer. Conversely, the fraction of surfaces with a high work function (>5.5 eV, i.e., roughly 1.5 times the standard deviation above average) is especially high for surfaces with halogens, carbon, nitrogen, sulfur, selenium, or oxygen present in the topmost atomic layer (cf. Figure 3a). Surfaces with hydrogen present exhibit more of both low and high work functions than average, likely due to complex chemistries. The total number of surfaces (rather than fractions) is shown in Figure S4 (Supporting Information). Overall, 48.8% (29.5%) of surfaces that exhibit a work function below 2.0 (2.5) eV contain either alkali or alkaline metals in the topmost atomic layer. Conversely, 54.1% (38.0%) of surfaces that exhibit a work function above 6.0 (5.5) eV contain either carbon, oxygen, or halogens in the topmost atomic layer.

The average work function is plotted as a heat map based on the chemical species present in the topmost two atomic layers. The trends observed in Figure 3a are also seen in the average work function trend in Figure 3b. However, one can also observe trends based on combinations of chemical species in the topmost and second atomic layers. For example, the work function average is high for surfaces where halogens are present in the first or second layer. In contrast, the work function average is low for surfaces with alkali or alkaline metals present in the first layer and sulfur or selenium present in the second layer – however, the work function average is high for the reversed layers (i.e., sulfur/selenium in the topmost layer). Further trends are plotted in Figures S5 (Supporting Information) (bar chart of average work function as a function of the chemical species present at the topmost layer) and Figure S6 (Supporting Information) (heat maps showing percentage and the total number of low and high work function surfaces as a function of chemical species present in the top two layers).

The trends described generally agree with the chemical intuition that surfaces terminated with electropositive atoms from the alkali or alkaline groups give a low work function, whereas electronegative atoms from the non-metal groups cause increased
work functions. However, it is worth noting that while ≈ 15% of surfaces that have an alkali/alkaline metal present in the topmost atomic layer have work functions below 2.5 eV, still ≈ 85% have work functions above 2.5 eV (of which ≈ 7% even have a work function above 5.5 eV), contrary to chemical intuition. This shows that for complex chemistries (e.g., hydrogen-containing compounds) basic chemical intuition is insufficient to predict the work function.

3.2. Surfaces with Extreme Work Functions

Material surfaces found on the tail ends of the work function distribution in Figure 2 are of interest for energy conversion and electronic device applications. However, the calculated ab-initio work functions are based on surfaces without considering ionic relaxations. Hence, to screen for viable ultra-low and ultra-high work function candidates, we carry out ionic relaxation calculations for unrelaxed slabs that have a cleavage energy less than 200 meV Å⁻² and either surface with a work function that is lower than 2 eV or higher than 7 eV. From 340 slabs on the extreme ends of the distribution, 284 slabs converged during ionic relaxation to a force less than 0.05 eV Å⁻¹. Atoms within the top 3 Å of the topmost atom were allowed to relax while the coordinates of the remaining atoms in the slab were fixed. The cleavage energy is generally reduced through ionic relaxation (cf. Figure S12, Supporting Information). As expected, the work functions for materials on the low-end shift toward lower values (mean signed deviation =+0.20 eV). The work functions for materials on the high-end shift toward lower values (mean signed deviation =−0.62 eV).

Hence, this effect is much more pronounced for the high work function tail-end, as can be observed in Figure S10 (Supporting Information). This effect is also more pronounced for non-symmetric slabs compared to symmetric ones. However, even after ionic relaxation, many material candidates retain record-low and -high work functions.

Ionically relaxed surfaces with the lowest (<2 eV) and highest (>7 eV) work functions are listed in Table 3. Surfaces created from structurally equivalent materials (but with distinct atom-type occupations) are grouped into material families using a notation of chemical formulas with placeholders accompanied by a list of possible elements present for each placeholder. The compound that resulted in the lowest/highest work function is listed alongside its work function value and cleavage energy for each family. The Miller indices and the atom termination of the surfaces yielding extreme work functions are specified. Polar surfaces have been excluded and the symmetry of the non-polar slabs is indicated in the rightmost column. A slab that indicates “n” (no) in the “Sym.” (symmetry) column refers to slabs that require off-stoichiometric slabs to ensure that the top and bottom surfaces are equivalent. All listed slabs are non-polar regardless of the symmetry tag (i.e., for each listed candidate with the “n” tag there exists an off-stoichiometric slab that is symmetric). For slabs that state “y” (yes) in the symmetry column, the cleavage energy is equal to the surface energy, otherwise 2 · Eclavage is an upper bound to the surface energy.

Among the discovered low work function candidate surfaces the most common terminations are Ba, Sr, and Cs, in agreement with chemical intuition and previous literature reports (e.g., cesium oxide). The lowest work function after ionic relaxation was calculated for the (100)-Ba-O termination of BaMoO3 at 1.25 eV with a cleavage energy of 67.2 meV Å⁻². This is the lowest steady-state work function computationally predicted in literature for a metallic surface without requiring any (alkaline) monolayer coating, in agreement with a previous computational study by Ma et al. that focused on screening through perovskite oxides. The identification of BaMoO3, as a promising candidate with a low work function validates our screening methodology. However, it should be noted that experimental studies of this material in polycrystalline form exhibited a thermionically measured work function of ≈ 2.6 eV. This discrepancy has been attributed to patch field effects caused by nanoscale features decorating individual surface facets.

The identification of BaMoO3 as a promising candidate with a low work function candidate surfaces identified in the previous version of the database (and why we exclude it) refer to the Supporting Information. A full list of low and high work function surfaces, further analyses can be carried out in future research to assess viability for device applications, such as assessing stability in air/moisture and surface reconstructions.

3.3. Machine Learning Model for Work Function Predictions

The large database created by high-throughput DFT calculations forms the basis for a surrogate machine learning model that enables the prediction of the work function at a fraction of the computational cost. As a first step, we assess common models from
Table 3. Surfaces with ultra-low and ultra-high work functions sorted by spacegroup (sg). Surfaces stemming from structurally equivalent materials (but occupied with different chemical species) are grouped into families described by chemical formulas containing placeholder letters A and B. For each family, the compound that resulted in the lowest/highest work function is listed alongside its work function value and cleavage energy. The Miller indices and the atom termination of the surfaces yielding extremum work functions are specified. Work functions are given in eV and cleavage energies in meV Å⁻². The cleavage energy is equal to the surface energy for slabs that state y(es) in the right-most column (i.e., the bottom and top surfaces of these slabs are equivalent while the slab maintains stoichiometry), otherwise, \( 2 \cdot E_{\text{cleavage}} \) is an upper bound for the surface energy.

| sg  | Material Family | Comp. with min/max ϕ | Miller planes - Termination | ϕ [eV] | \( E_{\text{cleavage}} \) [meV Å⁻²] | Sym. |
|-----|-----------------|-----------------------|----------------------------|--------|-------------------------------|------|
| Low ϕ surfaces | | | | | | |
| 2 | CsHg | (11)-Hg | 1.79 | 8.9 | y |
| 63 | BaA | A=Sn,Si | BaSi | (110)-Ba-A, (010)-Ba-A | 1.69 | 16.0 | y |
| 123 | BaMgA₂₃ | A=Si,Ge | BaMg₂Si₃ | (001)-Ba | 1.71 | 72.0 | n |
| 129 | BaMgA | A=Ge,Si | BaMgSi | (001)-Ba | 1.65 | 15.7 | y |
| 139 | Ba₂B₂A | A=Ag,Zn,Cu,Pd, B=Ge,Sn,As, Sb | BaPd₂Sb₂ | (101)-Ba, (101)-Ag, (001)-Ba | 1.73 | 51.9 | n |
| 164 | BaSi₂ | (100)-Ba, (100)-Si | SrFe₂O | (100)-Sr | 1.58 | 67.0 | n |
| 193 | Cs₂O | (110)-Cs, (101)-Cs | Cs₂ScCl₃ | (100)-Sc, (100)-Cs-Cl | 1.42 | 5.5 | y |
| 221 | BaAO₃ | A=Nb,Mo | BaMoO₃ | (100)-Ba-O | 1.25 | 67.2 | n |
| High ϕ surfaces | | | | | | |
| 2 | CuAuF₅ | (011)-F, (011)-Cu-F, (100)-Au, (101)-F, (101)-F, (110)-Au, (110)-F, (110)-Au, (111)-F, (111)-F, (111)-F | 7.78 | 11.4 | y |
| 12 | CuAF₆ | A=Mo, Sn | CuSnF₆ | (101)-F, (101)-Cu, (100)-F, (111)-F, (111)-F, (111)-Cu | 8.00 | 32.3 | y |
| 14 | AF₂ | A=Cu,Ag | CuAgO₂ | (001)-O, (01-1)-O | 8.19 | 81.4 | n |
| 15 | AgO | (010)-O | Ag₂ | (011)-Ag, (011)-Ag, (01-1)-F, (001)-F, (011)-A, (01-1)-F, (011)-A, (110)-F, (110)-F, (110)-F, (110)-F, (11-1)-F | 7.01 | 22.2 | y |
| 127 | KCuF₃ | (110)-Cu-F | PbO₂ | (101)-O-Pb, (101)-O, (111)-O-Pb-O | 7.20 | 61.4 | y |
| 162 | As₂PbO₄ | (001)-O | As₂PbO₄ | (001)-F | 8.13 | 48.9 | n |
| 164 | As₂F | A=Ag,F | As₂F | (001)-F | 9.06 | 64.2 | n |
| 176 | ACI₃ | A=Eu,Ce | EuCl₃ | (100)-A-Cl, (101)-Cl, (110)-A-Cl, (111)-Cl | 7.10 | 3.5 | y |

the materials science machine learning community as a benchmark. For that, we employ the automatminer testing suite,\(^8\) and a conventional Coulomb matrix (trained with a random forest model).\(^9\) For automatminer we use the “express” setting and compare using the bulk unit cell and the topmost five atomic layers of the surface slabs as inputs. As a baseline model, we predict the work function to be the average work function regardless of the surface. The automatminer model performs only marginally better than the baseline model when bulk structures are used as input. When the surface slabs are used as inputs the performance increases and is comparable to the performance of the Coulomb matrix. The MAEs are shown for the training and test sets in Figure 4a (cf. Figure S9, Supporting Information for RMSEs). The baseline MAE is 0.60 eV and the DFT accuracy is indicated in the green-shaded area between 0.022 and 0.1 eV, corresponding to the convergence error (see Experimental Section) and the error between PBE-calculated and experimental work functions\(^7\) respectively.

It is not surprising that the model performance is poor when the bulk structure is used as an input as the database contains multiple surfaces of different work functions for any given bulk structure. While the performance of the benchmarking models...
improves when the surface slab is used as the input instead, the MAEs are still large, and significant overfitting is observed. This is likely due to the fact, that the models cannot distinguish between the top and bottom of the input slab (which in general are not symmetric) and the database consists of all unique terminations. In general, if one termination (located at the top surface) is labeled with the calculated work function, the same termination may exist in another input structure at the bottom surface (whereas the calculated work function always refers to the top surface). Hence, the shortcomings of the automated benchmarking models do not come from the machine learning models used but rather from the implementation of the featurization of surface slabs.

We developed a custom featurization of the surface slabs by considering physically motivated features of the topmost three surface layers. Atoms are regarded to belong to the same layer if their z-coordinate lies within a tolerance of 0.4 Å (see the effect of tolerance value on model performance in Figure S7, Supporting Information). The considered atomic features are electronegativity $\chi$, inverse atomic radius $1/r$, first ionization energy $E_{\text{ion}}$, and Mendeleev number $n_{\text{mend}}$. Given that each layer may contain more than one atom type, we consider the minimum, maximum, and average of each of these atomic features. This gives a total of 36 elemental features for the topmost three layers. Additionally, we add structural features: The packing fraction for each layer (number of atoms per unit cell area) $A_{\text{pack}}^{-1}$ and the distances between atomic layers 1 and 2, $d_{1-2}$, and between layers 1 and 3, $d_{1-3}$. Angle-based features are calculated by considering the angles between the surface normal vector and the vectors spanned between atoms in the topmost layer and their respective nearest neighbors. After all angles are calculated we consider the minimum and maximum values as two features, $\theta_{\text{min}}$ and $\theta_{\text{max}}$. Out of this total 43 features, the most significant features are selected with (backward) recursive feature elimination (RFE) using a random forest model, as plotted in Figure 4b. The top eight features largely account for the model performance: $\langle \chi_1 \rangle$, $\langle E_{\text{ion},1} \rangle$, $\langle E_{\text{ion},2} \rangle$, $\langle n_{\text{mend},1} \rangle$, $d_{1-1}$, $A_{\text{pack}}^{-1}$, $\min(\chi_j)$, and $\min(1/r_j)$. For the final model, we use the best 15 features, which are the eight features mentioned above and $\theta_{\text{min}}$, $\theta_{\text{max}}$, $d_{1-2}$, $<1/r_1>$, $\min(E_{\text{ion},2})$, $\max(\chi_j)$, and $\min(n_{\text{mend},1})$. SHAP (SHapley Additive exPlanations) were used to further assess the feature importance (cf. Figure S13, Supporting Information), which largely agrees with the RFE-based feature selection. The top six most predictive features stem from the top-most atomic layer ($\min(\chi_j)$, $\langle \chi_1 \rangle$, $\langle E_{\text{ion},1} \rangle$, $\langle n_{\text{mend},1} \rangle$, $\langle E_{\text{ion},2} \rangle$, $A_{\text{pack}}^{-1}$, and $\min(1/r_j)$).

It is worth noting that the majority of features we selected were physics-motivated or based on correlations observed in literature. The work function has been shown to linearly correlate with electronegativity for elemental crystals and binary compounds, and inversely correlate with the atomic radius. Another work has proposed a phenomenological equation for the work function that depends on the atomic radius and the number of atomic sites per unit cell area at the surface. We chose the ionization energy as a feature based on physical intuition that low ionization energies lead to easy electron extraction. Lastly, the Mendeleev number has been shown to be a descriptive feature for many material property predictions. Interestingly, the most predictive features (top eight) are features from the topmost layer (including the layer distance $d_{1-1}$ except for $\langle E_{\text{ion},2} \rangle$). This is in agreement with the fact that clear trends are observed considering only the topmost surface (cf. Figure 3a). The final 15 features contain only two features that relate to the third atomic layer: $\langle E_{\text{ion},3} \rangle$ and $d_{1-3}$. Also, we note that we tried adding further elemental features without a clear physics-based motivation.
Using this featurization approach (with 15 features) outperforms all benchmarking models (automatminer, in comparison, uses 200 features) even when a linear regression model is chosen, as seen in Figure 4a. This performance improvement is due to the superior implementation of how we featurize our slabs rather than the machine learning model itself. When a non-linear learning model is used (neural network or random forest model) the MAEs are significantly reduced. Our best model using random forests has a test-MAE of 0.09 eV, comparable to the accuracy of DFT while being roughly 10⁵ times faster. Using this approach facilitates the probing of a vast chemical space for novel material surfaces with exceptionally low or high work functions.

5. Experimental Section

First Principles Calculations: The total energies of the slab and bulk, as well as the work functions were calculated by gradient-corrected DFT using the PBE exchange-correlation functional. Self-consistent, periodic, total energy calculations were performed using Quantum Espresso (v.7.1) with finite-temperature Gaussian smearing (σ = 0.1 eV). A dipole correction was applied in the

4. Conclusion

In summary, we demonstrate a workflow to create a work function and cleavage energy database from high-throughput DFT calculations that enables us to gain insight into chemical trends of the work function and surface stability. The database reveals 34 ultra-low and 56 ultra-high work function surfaces many of which have low surface energies. The low surface energy candidates are expected to be the stable surface termination and orientation of the corresponding stable bulk material and are hence promising candidates for experimental verification. To our knowledge, we identify the lowest and highest computationally predicted work functions in literature (1.25 and 9.06 eV, respectively) for steady-state metallic surfaces without requiring any monolayer coatings. Further, we establish a surrogate machine learning model for rapid work function predictions. Our model has a test-MAE of 0.09 eV, comparable to the accuracy of DFT while being ∼10⁵ times faster. Using this approach facilitates the probing of a vast chemical space for novel material surfaces with exceptionally low or high work functions.

It is recommended to also use them during inference. This is

sensible because relaxed slabs are not convenient ML model inputs that require prior DFT calculations. Model predictions on sparse monolayer coatings of electropositive atoms are not expected to be faithful as they were not present in the training set (cf. Figure S14, Supporting Information showing the DFT-calculated and ML-predicted work functions of Cs on W-(110) as a function of Cs coverage). Lastly, the ML model can reasonably well predict the work function of commonly known elemental surface reconstructions (MAE of 0.28 eV) despite them not being part of the training set (cf. Figure S15, Supporting Information). However, this may not generally be expected for more complex surface reconstructions of binary and ternary alloys.

The prediction of the work function using this model is roughly 10⁵ times faster than DFT while having an MAE comparable to the accuracy of DFT. The database is available open-source (see data availability section). The machine learning model is available at Zenodo (https://doi.org/10.5281/zenodo.10449567). This enables other researchers to use this model for work function predictions and help experimentalists in their materials/synthesis choice.
c-direction. The work function, \( \phi \), was determined by the difference between the electrostatic energy in the vacuum region, \( E_{\text{vac}} \), and the Fermi energy, \( E_F \). The PBE exchange-correlation functional had previously been shown to give reliable work functions for elemental crystals in agreement with experimental values with a slight systematic underestimation. The errors with respect to experiment had been reported to be below 0.3 eV for elemental crystals\(^{[87]}\) and 0.15 eV for elemental metals\(^{[89]}\). It was also worth noting that work functions measured experimentally could significantly vary based on the technique and specimen (single- vs. polycrystalline) used.\(^{[78]}\) Moreover, comparing the work function calculated for a diverse chemical set of 2D materials with a zero bandgap (taken from the C2DB\(^{[62]}\)) shows a good agreement between HSE and PBE-calculated work functions. The MAE between HSE- and PBE-calculated values across the entire C2DB dataset was 0.27 eV (cf. Figure S16, Supporting Information). The DFT calculation inputs for Quantum Espresso are automatically generated with the atomic simulation environment (ASE)\(^{[90]}\). Python packages and submitted into a high-performance computing queueing system (SLURM) using job arrays.

To estimate the convergence accuracy of the DFT-calculated work functions \( \approx 1 \) % of the database (randomly selected) was rerun with stricter convergence parameters (energy cutoff of 850 eV and Brillouin zone sampling with a grid spacing of \( \leq 0.02 \ \text{Å}^{-1} \)). The resulting MAE and RMSE of the work function were 22 and 30 meV, respectively.

The cleavage energies had been calculated via total energy calculations of the stoichiometric slab, \( E_{\text{slab}} \), and the respective bulk, \( E_{\text{bulk}} \), with the same unit cell orientation as the slab. This reorientation ensures more efficient convergence with slab thickness due to \( k \)-point matching of the two calculations.\(^{[91]}\) The cleavage energy is defined as

\[
E_{\text{cleavage}} = \frac{E_{\text{slab}} - n_{\text{bulk}} \cdot E_{\text{bulk}}}{2 - A_{\text{slab}}} = \frac{\gamma_{\text{top}} + \gamma_{\text{bottom}}}{2}
\]  

(1)

where \( n_{\text{bulk}} \) is the number of bulk unit cells contained in the slab and \( A_{\text{slab}} \) is the surface area of the slab. The surface energies are denoted as \( \gamma_{\text{top}} \) and \( \gamma_{\text{bottom}} \) for the top and bottom surface of the slab, respectively. Using this definition, the cleavage energy is equal to the surface energy, \( E_{\text{cleavage}} = \gamma \), for the case of symmetric slabs (i.e., there exists a mirror or glide plane parallel to the surface, or a twofold rotation axis normal to the surface). For non-symmetric slabs, the upper bound for both surface energies is \( 2 \cdot E_{\text{cleavage}} > \gamma_{\text{top, bottom}} \). This workflow had also been used to calculate adhesive properties in electrolyte interfaces for solid-state battery applications.\(^{[89]}\)

For the slabs that exhibit extreme work functions, ionic relaxation calculations of the topmost surface. atoms (atoms within 3 Å of the surface were relaxed, the remaining atoms fixed) of the 1 \times 1 slab were converged to a force less than 0.05 eVÅ\(^{-1}\). Only the surface of interest was ionically relaxed while the opposite side remained fixed.

Machine Learning Model Training: The dataset was randomly split into training and test sets (90/10 split) and the hyperparameters were optimized with a grid-search implementing tenfold cross-validation on the training set. Multivariate linear regression, random forest, and neural network models were set up with the scikit-learn package in Python. The custom featureization procedure was laid out in the results and discussion section. Surfaces that had identical features to any other surface in the dataset (and a difference in work function between the two surfaces of \( < 0.1 \) eV) were removed as duplicates from the dataset before training. For benchmarking purposes, the automatminer testing suite\(^{[80]}\) (200 features) and a conventional Coulomb matrix (topmost five surface atoms as input, matrix sorted by \( L_2 \)-norm of columns — the flattened matrix yields 25 features that were used in a random forest model) was used.\(^{[91]}\) For automatminer, the "express" setting and for comparison the bulk unit cell and the topmost five atomic layers of the surface slab were used as inputs. As a baseline model, the work function was predicted to be the average work function regardless of the surface.

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

Acknowledgements
P.S. gratefully acknowledged the start-up funds from Northeastern University, Department of Mechanical and Industrial Engineering. This work was completed in part using the Discovery cluster, supported by Northeastern University’s Research Computing team. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Author and Professor E. J. R. passed away in March 2022. E. J. R. contributed great guidance toward the project. The authors are incredibly grateful for his contributions.

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
P. S. performed writing – original draft (lead); review and editing (equal); software (lead); methodology (lead); visualization (lead); investigation (lead); data curation (lead); conceptualization (supporting); supervision (equal); resources (lead). E. R. A. performed review and editing (equal); methodology (supporting); conceptualization (supporting). G. C. performed review and editing (equal); conceptualization (supporting). Y. Z. performed review and editing (equal); conceptualization (supporting). E. J. R. performed conceptualization (lead); review and editing (equal); supervision (equal).

Data Availability Statement
The data that support the findings of this study are openly available in zenodo at https://doi.org/10.5281/zenodo.10381505, reference number 10381505.

Keywords
ab initio, band alignment, electron emission, high throughput, machine learning, thermionic energy conversion, work function

Received: February 5, 2024
Revised: March 3, 2024
Published online: March 20, 2024

\[ \text{[1]} \] Y. Zhou, C. Fuentes-Hernandez, J. Shim, J. Meyer, A. J. Giordano, H. Li, P. Winget, T. Papadopoulos, H. Cheun, J. Kim, M. Fenoll, A. Dindar, W. Haske, E. Najafabadi, T. M. Khan, H. Sojoudi, S. Barlow, S. Graham, J.-L. Brédas, S. R. Marder, A. Kahn, B. Kippenlen, Science 2012, 336, 327 LP.

\[ \text{[2]} \] L. Lindell, A. Burquel, F. L. E. Jakobsson, V. Lemaur, M. Berggren, R. Lazzaroni, J. Cornil, W. R. Salaneck, X. Crispin, Chem. Mater. 2006, 18, 4246.

\[ \text{[3]} \] A. L. Dadlani, P. Schindler, M. Logar, S. P. Walch, F. B. Prinz, J. Phys. Chem. C 2014, 118, 24827.
