Understanding Chemical versus Electrostatic Shifts in X-ray Photoelectron Spectra of Organic Self-Assembled Monolayers

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Supporting Information

ABSTRACT: The focus of the present article is on understanding the insight that X-ray photoelectron spectroscopy (XPS) measurements can provide when studying self-assembled monolayers. Comparing density functional theory calculations to experimental data on deliberately chosen model systems, we show that both the chemical environment and electrostatic effects arising from a superposition of molecular dipoles influence the measured core-level binding energies to a significant degree. The crucial role of the often overlooked electrostatic effects in polar self-assembled monolayers (SAMs) is unambiguously demonstrated by changing the dipole density through varying the SAM coverage. As a consequence of this effect, care has to be taken when extracting chemical information from the XP spectra of ordered organic adsorbate layers. Our results, furthermore, imply that XPS is a powerful tool for probing local variations in the electrostatic energy in nanoscopic systems, especially in SAMs.

1. INTRODUCTION

A convenient way of tuning the properties of a given substrate is by covering it with covalently bonded self-assembled monolayers (SAMs). Such interface modifiers have been applied in numerous ways, e.g., for controlling the wettability of surfaces,4−6 for providing protection from corrosion,7,8 for enabling adhesion of biological cells,9 as sensors,10,11 for nanopatterning,12−14 and in organic electronics. In the latter context, they were applied for modifying electrode−semiconductor interface15−32 and dielectric−semiconductor33,34 interfaces. SAMs were also used as active layers in organic transistors.25−34

Of crucial importance for electronic applications are changes of the substrate work function induced through SAMs bearing polar terminal groups31−33 or polar units embedded into the molecular backbones.32,34 Embedded dipolar groups also directly impact the electronic states within the SAMs and their alignment relative to the Fermi level.35,36

A common approach for characterizing the properties of such SAMs is X-ray photoelectron spectroscopy (XPS).37,38 By means of chemical shifts (i.e., shifts in the core-level binding energies induced by the immediate chemical environment of an atom), it is possible to verify the chemical integrity of the SAM, to understand details of its composition, and to explore its homogeneity.39 Recently, in addition to chemical shifts, a variety of factors affecting the XPS peak positions have been mentioned.40−43 For ionic crystals it is known that the Madelung energy needs to be taken into account to correctly describe shifts in binding energies.44,45 A related effect of particular interest in the present case is that for SAMs containing dipolar elements within the molecular backbones binding-energy shifts can be associated with changes of the local electrostatic energy due to potential shifts caused by the dipoles.32,34 Indeed, collective electrostatic effects arising from the superposition of the fields of periodically assembled dipoles have been discussed extensively in the context of the valence electronic structure of organic adsorbate layers.46−48 They are also crucial for understanding adsorbate-induced work-function changes,29,46−50 and more recently, their exploitation as a tool for designing monolayers with highly complex electronic properties has been suggested.35 As XPS is very sensitive to such effects it provides a highly valuable tool for characterizing the local electrostatic energy in complex adsorbate structures. However, for such a task it is absolutely crucial to understand how collective electrostatic effects and chemical shifts interact to give rise to the finally measured XPS signals.

Consequently, the purpose of the present paper is to obtain a coherent understanding of the interplay between these two effects. This is achieved by performing density functional theory (DFT) calculations on carefully selected model SAMs and comparing the results to high-resolution XPS (HRXPS) measurements.32,51 In this way we show that both chemical and collective electrostatic effects have to be taken into account to fully interpret XP spectra. The presented results imply that when chemically identical entities are incorporated into complex adsorbate layers their XPS signature can serve as an efficient probe for variations in the local energy landscape.

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2. INVESTIGATED SYSTEMS

The interplay between chemical and electrostatic shifts for core-level energies is relevant far beyond the field of self-assembled monolayers and applies to all systems in which assemblies of polar elements occur. Still, their discussion is most straightforward for extended and typically very well-ordered chemically bonded SAMs, where complications such as core-hole screening effects become less relevant (vide infra). Thus, we chose two SAMs, whose properties and chemical integrity are very well characterized. They belong to the most established type of SAMs, namely substituted alkyl thiolates on Au(111), and therefore serve as prototypical model systems for the present study. They comprise a partially fluorinated alkyl thiolate and a similarly long alkyl thiolate containing a polar ester group embedded into the aliphatic backbone. Their structures and the used surface unit cells are shown in Figures 1 and 2, respectively. Their full experimental characterization is contained in the above-mentioned references.

Both layers are bonded to Au(111) surfaces. The choice of the partially fluorinated alkyl thiolate (hereafter referred to as F8H11SH consistent with ref 51) is motivated by the presence of five chemically different carbon species that can be identified in high-resolution XP spectra. This makes this SAM an ideal candidate for studying chemical shifts and for benchmarking the applied methodology. The alkyl thiolate (hereafter referred to as C10ECS consistent with ref 32) contains a polar ester group and is an example of a system for which electrostatic shifts in the XP spectra have been suggested. An important aspect of C10ECS, in which it conceptually differs from F8H11SH, is that the alkyl chains above and below the ester group (blue and red in Figure 1a) are chemically identical; i.e., there are two chemically equivalent segments of the chains, which are separated by a dipole. In both refs 32 and 51 several chain lengths, degrees of fluorination, and different ester positions have been investigated; we chose the present systems because they are of comparable lengths. Moreover, the CS segment above the ester in C10ECS is short enough that in experiments an appreciable signal from the bottom chain can...
still be detected (with similar intensities for the C5 and C10 segments for a photon energy of 580 eV), while it is long enough to be well ordered.32

The F8H11SH SAMs on Au(111) have been shown to grow in a commensurate p(2 × 2) arrangement with one molecule in the unit cell.33 This structure is also chosen in the present study (cf. Figure 2). In passing, we note that also a c(7 × 7) cell containing 17 molecules and noncommensurate structures have been reported.52–53 These are not considered here. For the ester containing alkyl thiolates we used a (3 × 2√3) unit cell containing four nonequivalent molecules in a herringbone arrangement52 in analogy to a structure commonly reported for nonsubstituted alkyl thiolates.57–62 The above choice of unit cells results in a molecular footprint, A, of 29.70 Å2 for F8H11SH and 22.27 Å2 for C10EC5. Note that the reduced packing density for the F8H11SH SAM is a consequence of the larger size of the fluorine atoms compared to the hydrogens. Accordingly, a chiral arrangement of the CF2 groups is favored,51 while for all alkyl segments a coplanar, all-trans conformation is obtained.

For the reduced-coverage calculations of F8H11SH a 4 × 4 supercell was chosen, and all molecules but one were removed, yielding A = 475.2 Å2. This corresponds to a nominal coverage Θ = 1/16. In the C10EC5 case, the unit cell was doubled in the longer direction and quadrupled in the shorter one, and again all molecules but one were removed. Nominally, this yields Θ = 1/32 (note that here the primitive unit cell contained four molecules), but as the packing density in the full coverage is only 712.8 Å2. In this context it is important to note that we kept the molecules fixed at the adsorption geometries of Θ = 1, in order to isolate the effect of diluting the dipoles from the massive changes of the molecular orientation occurring at low coverages, where alkyl thiolates are known to lie flat on the Au substrate.37

3. THEORETICAL METHODS

3.1. Computational Details. We performed slab-type band-structure calculations based on density functional theory using the Vienna ab initio simulation package (VASP v5.3.2)53–66 and employing the Perdew–Burke–Ernzerhof (PBE) functional67,68 in conjunction with the projector augmented-wave method (details on the potentials are specified in the Supporting Information).69–70 Long-range van der Waals interactions were accounted for using the vdW86d model71 in the implementation of Al-Saidi et al.72 The used cutoff energy for the plane-wave basis set was 400 eV, and the total energy was converged to 10−6 eV. Γ-centered k-point meshes with 8 × 8 × 1 and 4 × 4 × 1 k-points were used for F8H11SH and C10EC5 SAMs at full coverage (bearing in mind the different sizes of the respective surface unit cells). When increasing the unit-cell size, the k-point mesh was scaled accordingly.

In all simulations the surfaces were represented by slabs consisting of five layers of Au to model the Au(111) surface with the SAM adsorbed on only one side of the slab. To avoid spurious surface relaxations, the Au lattice constant was determined by applying the same methodology as used for calculating the surfaces. It was found to be 4.141 Å, which is very close to measured (4.079 Å3) and calculated values (4.154 Å3) reported in the literature. The geometry optimizations were started with thiolates placed at fcc hollow sites of the Au(111) surface; periodic replicas of the slab were decoupled by a vacuum gap of ca. 30 Å and a self-consistently determined dipolar layer.73 In the simulations, the two topmost layers of the Au slab were allowed to relax, while the other three layers were fixed at the bulk geometry. The geometry was optimized until the maximum residual force per atom was smaller than 10−2 eV Å−1.

The geometry update was performed via the GADGET tool, which (i) enables the use of internal coordinates for describing the adsorbate layer and (ii) provides advanced algorithms69 for the initial guess of the Hesse matrix, where in the present work Fischer’s model77 was applied. To sample the very rich configurational space of the highly flexible midchain ester-functionalized alkyl thiolates, we did a preoptimization using molecular dynamics (for details see the Supporting Information).

3.2. Calculating XPS Core-Level Shifts. Relative XPS core-level shifts were calculated within the initial-state approach, which in VASP relies on a recalculation of the Kohn–Sham eigenvalues of the core states subsequent to the self-consistent determination of the charge density associated with the valence electrons.78 Relative shifts of these energies are often found to reproduce very well the experimentally obtained results.79–81.29 In passing, we note that we compared the results obtained using this approach to full-potential calculations employing the FHI-aims code,82 which yielded quantitatively consistent core-level shifts (for details see the Supporting Information).

For the present systems, where we are primarily interested in core-level excitations of atoms relatively far away from the metal surface, the initial-state approach is preferable over the a priori more sophisticated final state approaches.83–90 In the latter, screening effects especially by the metal are considered explicitly in the quantum-mechanical simulations. This is particularly important for atoms very close to the metal surface, i.e., the sulfur atoms91 and the first few carbons. It would, however, result in serious artifacts in the present case: Final-state approaches rely on calculating the energy for a situation with one or one-half of an electron (employing Slater’s transition state theory92) excited from the core into the valence region. In our systems, the unoccupied valence region is represented by states in the metal right above Ec. This means that any carbon core-level excitation is associated with a charge transfer from an atom within the SAM into the metal substrate (i.e., over an appreciable distance especially for carbon atoms near the surface of the SAM). This gives rise to a sizable dipole moment, which would not pose a significant problem if the excitation happened only in individual molecules (as in the experiments). Because of the periodic boundary conditions, one, however, deals with an excitation-induced large dipole in every unit cell, resulting in an artificial potential gradient and in a shift of the core-level energies due to collective electrostatic effects (vide supra). Hence, for including screening effects via the final-state approach, one would need to converge the size of the unit cell until the excitation-induced dipoles are dilute enough such that the described artifacts become significantly smaller than the shifts in core-level energies that one intends to describe. This would require intractably large unit cells.

As in the here-applied initial-state approach the screening of the core hole by the highly polarizable metal substrate is not directly considered in the calculations of the core-level energies,93,94 it needs to be accounted for by an electrostatic image charge model.95,96 There the core-level energies including screening are expressed (in atomic units) as
$$\varepsilon_{\text{C1s,screened}} = \varepsilon_{\text{C1s}} + \frac{1}{4\varepsilon(z - z_0)}$$  \hspace{1cm} (1)$$

Here, $\varepsilon$ is the dielectric constant of the SAM. We chose $\varepsilon = 2.26$ for both systems for the full coverage case.32 This approach neglects that the SAMs are of only finite thickness, which is expected to have a negligible effect on the results. Also direct screening effects within the dielectric SAM are not accounted for. For the low coverage calculations $\varepsilon = 1.0$ was used, since these calculations represent essentially isolated molecules on the substrate. The constant $z_0$ is the position of the image plane. It was set to 0.9 Å above the average $z$-position of the top Au layer.97,98 $z$ is the position of the atom whose core level is excited. The screening shifts core-level energies to less negative values (smaller binding energies) and affects the atoms closest to the substrate most. As the molecules we investigated consist of rather long alkyl chains, the overall impact of screening on the XP spectra is comparatively small, since the atoms in the SAM far away from the substrate, for which screening is least relevant, contribute most strongly to the experimental signals. To compare the results of the calculations directly to the experiments, we simulated XP spectra by associating each C 1s core level with a Gaussian peak99 centered at $E_{\text{C1s,screened}}$ and subsequently summing over the contributions of all atoms weighted by an exponential attenuation function to account for the finite escape depth of the photoelectrons:100

$$w_i(d) = \frac{w_0}{\lambda} \exp\left(-\frac{d}{\lambda}\right)$$  \hspace{1cm} (2)$$

The individual weights $w_i(d)$ depend on $d$, the vertical distance between atom $i$ and the topmost layer of atoms in the SAM, and the damping factor, $\lambda$. $w_0$ is a scaling constant, which does not affect the shape of the spectra. $\lambda$ is given by100

$$\lambda = 0.3E_{\text{kin}}\varepsilon^0$$  \hspace{1cm} (3)$$

where $E_{\text{kin}}$ is the kinetic energy of the escaping electron, which is determined by the energy of the incident photon (in our case 580 eV) minus the binding energy of the electron (calculated C 1s energy). The empirical attenuation factor $\beta$ was chosen such that experimental relative peak heights were reproduced by our calculations. We used $\beta = 0.638$ for ester SAMs and $\beta = 0.55$ for partially fluorinated SAMs, where the smaller value in the latter case accounts for the stronger damping due to the significantly increased electron density in the fluorinated SAM.

4. RESULTS AND DISCUSSION

4.1. XP Spectrum of the Partially Fluorinated SAM (F8H11SH): Dominance of Chemical Shifts. The calculated core-level energies are shown together with the simulated and measured XP spectra for densely packed F8H11SH SAMs in Figure 3. It is well established that calculated core-level energies are better suited to reproduce core-level shifts rather than absolute binding energies.85,79–81 Therefore, while the core-level energies in the left panel of Figure 3 are reported as calculated, the simulated spectrum in the right panel of Figure 3 is stretched by a factor of 1.15 and shifted by 20.1 eV to align them with the experimental curve. This is analogous to the strategy commonly applied when comparing calculated energies of Kohn–Sham orbitals with experimentally measured binding energies in the valence region.101 In this context it needs to be stressed that while this procedure improves the quantitative agreement between the measured and simulated curves, it is by no means necessary for reproducing the experimentally observed trends in our calculations.

For understanding the details of the calculated as well as measured XP spectra, it is useful to identify groups of carbon atoms with chemically different environments along the chain. In ref 51 five chemically distinct carbon species have been assigned to various features of the high-resolution XP spectra (cf. Figure 3): (1) the terminal carbon atom bonded to three fluorine atoms giving rise to the peak at the most negative binding energy (violet curve); (2) the carbon atoms in the fluorinated segment having two fluorinated carbon atoms as nearest neighbors and associated with the highest intensity feature in the spectrum (green curve); (3) the other terminal carbon atom in the fluorinated segment adjacent to the hydrocarbon segment visible as an asymmetry of the line shape of the main peak (yellow curve); (4) the terminal carbon atom of the hydrocarbon segment, adjacent to the fluorinated segment (dark blue); and (5) the carbons in the other CH$_2$ groups with only CH$_2$ carbons and sulfur (see below) as neighbors causing the peak at least negative binding energies (red curve). These assignments are fully confirmed by a comparison between the simulated and measured spectra and by tracing back the features in the simulated XP spectrum to the core levels of individual carbon atoms in the left panel of Figure 3. The simulations also clearly reveal a slightly shifted binding energy of the very first carbon atom due to the bonding to the sulfur atom. Moreover, we observe increasingly less negative core-level binding energies for the CH$_2$ carbon atoms upon approaching the metal surface, which is a consequence of the increasing screening. The latter two effects are not resolved in the experiments due to the close values of the binding energies for the respective carbon atoms as well as the progressively strong attenuation of the photoelectron signal for the atoms far from the surface. Overall, the excellent agreement...
between theory and experiment for the F8H11SH SAM confirms that the used methodology is capable of reliably describing chemical shifts in photoemission for self-assembled monolayers.

4.2. XP Spectrum of the Alkyl Thiolate SAM Containing an Embedded Ester Group (C10ECS): Significance of Electrostatic Shifts. As can be clearly seen in Figure 4, also for the C10ECS SAM the main features of the measured XP spectra, namely the relative peak positions and the relative peak intensities, are very well reproduced in the simulations. The peak associated with the carbonyl carbon (marked yellow in Figure 4) at the most negative binding energy is clearly resolved in the experiments. This is a consequence of the modified chemical environment of that particular carbon atom that is bonded to two oxygen atoms. Right next to it we find the peak associated with the ether C (marked green in Figure 4), which is still significantly chemically shifted with respect to the emission from the carbon atoms in the aliphatic chain segments, albeit to a lesser degree than for the carboxylic C atom. As in the F8H11SH case, we find that the peak associated with the first carbon directly bound to the sulfur docking group is slightly shifted to more negative binding energies in the calculations. The feature due to the terminal CH3 carbon is not resolved as a separate peak in the simulated and measured XP spectra as the associated shift is much smaller than for the CF3 carbon in the F8H11SH example.

While all these differences in core-level energies can be understood as a consequence of different chemical environments, this is not the case for the shift between the two most prominent peaks of the spectrum located around −285 eV. They can be unambiguously assigned to the CH2 groups in the bottom and top segments of the molecule (below and above the ester group). These two segments are chemically equivalent, but still the associated average C 1s core-level energies differ by as much as 0.86 eV. In passing, we note that this difference is not caused by different degrees of screening of the core holes in the upper and lower segments, as can be gauged by experiments on nonsubstituted alkyl thiolate SAMs\textsuperscript{102} and also from a simulation in which a difference of 0.71 eV is still present when this screening is switched off. Thus, there must be another origin for that shift in core-level energies. As already suggested by Cabarcos et al.,\textsuperscript{32} this has to be related to the regular arrangement of the ester dipoles. Although the dipole moments originating from the polar ester groups are strongly inclined relative to the surface normal,\textsuperscript{32} their components perpendicular to the substrate are still sizable. This can be shown by calculating the dipole moments per molecule perpendicular to the film surface in hypothetical free-standing SAMs arranged in the geometry the molecules adopt on the surface (but after replacing the polar thiol group by a hydrogen to isolate the polar contribution of the ester). The obtained perpendicular dipole moments per molecule then amount to 0.51 D at full and to 0.76 D at 1/32 coverage. The smaller value at full coverage is the consequence of well-known depolarization effects. The horizontal components of the dipoles are compensated by a polarization of the metal (cf. mirror charges).

The individual electric fields originating from the ester dipole perpendicular to the substrate add up and cause a sharp drop in the electrostatic energy.\textsuperscript{47} The drop is very strongly localized, as contrary to the situation of isolated dipoles, electric fields decay rapidly in densely packed SAMs.\textsuperscript{46} As also the core levels are strongly localized at individual carbon atoms, their energies directly follow the dipole-induced change of the electrostatic energy. This results in very different binding energies of the core levels of the upper and lower alkyl segments relative to the Fermi level of the metal and, consequently, in strongly different kinetic energies of the photoelectrons. This is illustrated schematically in Figure 5. In that sense, the core-level energies serve as very sensitive probes of the local electrostatic energy within the SAM.

Since this shift in the electrostatic potential arises from the collective superposition of the fields of the 2D arranged dipoles, it is (i) directly proportional to the dipole density and (ii) expected to diminish for individual dipoles, where instead of the highly localized\textsuperscript{40} step in the electrostatic energy a much smaller and smeared out shift in the binding energy of the core levels due to the electric field of an individual dipole is to be expected.\textsuperscript{47} This provides an efficient handle for testing the above hypothesis that such electrostatic effects indeed impact measured core-level energies: Upon reducing the coverage of the SAM (with - in this computer-experiment - maintained geometry and dipole orientation, vide supra), XPS core-level shifts induced by collective electrostatic effects should decrease and for very low coverages essentially disappear. In contrast, chemically induced shifts ought to persist.

4.3. XP Spectra at Reduced Coverage: Turning Off Collective Electrostatic Effects. In the following, we discuss core-level energies at strongly reduced coverages (cf. section 2) for the C10ECS and F8H11SH systems. The evolution of the spectra for gradually reducing the coverage can be found in the Supporting Information. A conceptually related situation, at least as far as the impact of the ester dipoles is concerned,
would be a homogeneously mixed SAM consisting of a minority of C10EC5 molecules embedded into alkyl thiolates.

Figure 6a compares the core-level energies of C10EC5 molecules in full and low coverage SAMs. The most important result of this comparison is that for the low coverage SAM the shift between the core-level energies of the upper and lower alkyl segments has essentially disappeared. As a consequence, in the simulated XP spectra the main peak is no longer the superposition of two clearly resolved maxima but is rather dominated by a single feature. This very much supports the above hypothesis that the shift in the full-coverage SAM is of purely electrostatic origin. Consistent with this scenario, the carbonyl carbon and the ether carbon core-level energies are still shifted with respect to the rest of the chain, as the origin of that shift is mostly “chemical” in nature.

What still remains to be explained is why the positions of all C 1s core levels are shifted to smaller binding energies in the low-coverage SAMs. This can again be traced back to collective electrostatic effects (or rather the lack thereof) in the low-coverage situation: One must not forget that also at the metal/SAM interface a significant dipole is present (i) due to the thiolate group and (ii) as a consequence of bonding-induced charge rearrangements. This second ordered dipole layer causes a potential drop at the metal/SAM interface at full coverage. At low coverage that step-like change in the electrostatic energy diminishes and is replaced by the much weaker potential energy modification due to an individual dipole. Noteworthy, the rigid shift of the C 1s core levels in the bottom segment far from the dipoles between the two different coverages allows a determination of an upper limit for the shift in the electrostatic energy due to the thiolates (including the bonding to the metal), which for the present configuration of the chains amounts to 1.25 eV. The reason for this value representing only an upper limit is that it is affected also by differences in the core-hole screening (cf. section 3.2). When neglecting screening effects, the shift is reduced to 0.94 eV.

The above “electrostatic” view is fully corroborated by the electron electrostatic energy within the SAM at full and low coverages, which is shown in Figure 7. There one clearly sees the significantly higher electrostatic energy around the isolated molecule (right) compared to the densely packed monolayer (left). What is also clearly resolved is that the top and bottom segments of the C10EC5 molecule at low coverage experience a very similar electrostatic environment, while there is a significant shift in energy between the regions around the top and bottom segments at full coverage; i.e., the polar ester groups induce a potential energy step at high coverages, while the potential modifications associated with the ester group are comparably local for the isolated molecule.

When comparing the F8H11SH high- and low-coverage SAMs a picture evolves that is consistent with the above considerations (see Figure 6b): There is a rigid shift of all C 1s core-level energies to lower binding energies in the low-coverage case. Again, the reason is that the step in the
electrostatic energy due to the thiolates diminishes at low coverages. The effect is somewhat smaller for the F8H11SH SAM (only 1.0 eV compared to 1.25 eV for the C10EC5 SAM). This is a consequence of (i) the lower density of docking groups in the fluorinated section of the SAM; i.e., also in F8H11SH electrostatic shifts do play a role, but they are very small compared to the chemical shifts and therefore typically not accounted for when interpreting the experiments. When reducing the coverage, these electrostatic shifts again disappear explaining the smaller net shift to lower binding energies in the fluorinated section of the SAM.

5. CONCLUSIONS

The considerations in this paper show that shifts in the core-level binding energies measured for thin organic films by X-ray photoelectron spectroscopy are not only determined by the chemical environment of the atoms of interest. Additionally, variations in the electrostatic energy caused by collective electrostatic effects (albeit often overlooked) play an equivalently important role. This is shown by a comparison between experimental and theoretical XP spectra combined with an in-depth analysis of the local electrostatic situation in two prototypical thiolate-bonded self-assembled monolayers. As a consequence, great care has to be taken when exclusively associating experimentally observed changes in core-level binding energies with chemical changes occurring in an adsorbate layer. Peak shifts of several tenths of an electronvolt or more can be caused either by interfacial charge rearrangements (here due to the bonding of the thiolates) or by polar groups incorporated into the studied molecules. As a consequence, when using chemically identical species in different spatial regions of an adsorbate (i.e., when ruling out chemical shifts), XPS can become a powerful tool for probing local variations in the electrostatic energy, making it a highly promising technique for studying nanoscopic electronic devices even beyond its well-recognized capabilities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12387.

Further details of the computational methodology, additional data of test calculations performed with soft PAW potentials and core-level energies of intermediate coverage SAMs for both F8H11SH and C10EC5; comparison of experimental and simulated spectra without stretching the energy scale of the latter (PDF)

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Notes

The authors declare no competing financial interest.

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