Reproducible flaws unveil electrostatic aspects of semiconductor electrochemistry

Predicting or manipulating charge-transfer at semiconductor interfaces, from molecular electronics to energy conversion, relies on knowledge generated from a kinetic analysis of the electrode process, as provided by cyclic voltammetry. Scientists and engineers encountering non-ideal shapes and positions in voltammograms are inclined to reject these as flaws. Here we show that non-idealities of redox probes confined at silicon electrodes, namely full width at half maximum <90.6 mV and anti-thermodynamic inverted peak positions, can be reproduced and are not flawed data. These are the manifestation of electrostatic interactions between dynamic molecular charges and the semiconductor’s space-charge barrier. We highlight the interplay between dynamic charges and semiconductor by developing a model to decouple effects on barrier from changes to activities of surface-bound molecules. These findings have immediate general implications for a correct kinetic analysis of charge-transfer at semiconductors as well as aiding the study of electrostatics on chemical reactivity.

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n 1876 Ferdinand Braun presented to a Natural Society meeting the first deviations from Ohm’s law he had observed in crystals of galena, a natural form of lead sulfide. In the following century his discovery revolutionized our civilization. From galena to silicon, materials that can turn from conductors to insulators are at the basis of all our digitized technology. Understanding the full spectrum of factors at play, when charges are transferred across a semiconductor interface is crucial; it underpins the design of devices whose function span from converting light into electricity, to sensing their environment, to converting in depletion and thereby it requires illumination to carry a current (see Supplementary Fig. 1). This is the conceptual equivalent of the reverse bias in a solid junction, where the current is mainly carried by holes flowing under the barrier (Fig. 2b). The ferrocene-confined probes exhibit broad voltammetry waves (black symbols in Fig. 2a), with the observed full width at half maximum (fwhm hereafter) being on average 142 ± 6 mV.

The ideal fwhm from the Langmuir isotherm of a nernstian process is 90.6 mV (model 1, Supplementary Note 1), and theoretical models exist to relate the non-ideal behavior of a voltammetric peak to the balance between attractive and repulsive interactions experienced by a strongly-adsorbed molecule. The increase over the ideal fwhm’s is often observed in the literature and can be attributed to a predominance of repulsive interactions between the electroactive species. The apparent kinetics is fast (k∞ = 200 s⁻¹, see Supplementary Fig. 2 and Supplementary Note 1 (finite kinetics limit) for details on the calculations of charge-transfer rates) and a quantitative model that takes into account these interactions can be implemented by assuming a nernstian behavior (i.e., very fast electrode kinetics) and Frumkin isotherm, as reported by Laviron in his seminal works (model 2, Supplementary Note 2)17, 18. The simulated curves are shown in Fig. 2a as a solid black line. Only the Frumkin parameter G was adjusted in the model; changes to G account for an imbalance in the electrostatic push/pull, forcing the voltammetric wave to broaden or narrow when the activities of the reduced and oxidized species do not follow their surface concentrations. A predominance of repulsive forces in S-2 samples leads to negative G values of −0.93 ± 0.10 in average. This is expected due to the high density of ferrocenes (Γ = 2.89 ± 0.24 × 10⁻¹⁰ mol cm⁻², ca. 65% of a full monolayer) and in fact similar observations.
(i.e., large fwhm’s and negative G values) are observed for S-2 samples of a similar coverage prepared on substrates of different conductivity type and level (Supplementary Fig. 3). It is therefore apparent from the broad shape of the voltammograms in Fig. 2a (black traces) that detecting evidence of an electrostatic effect by the space-charge would first require limiting the extent of in-plane ferrocene—ferrocene repulsions and/or decreasing the dielectric screening between the space-charge and the ferrocene (Supplementary Note 3). By means of shortening the click reaction time of azide 2 on samples of S-1 to a few seconds, the ferrocene coverage can be lowered to 5.9 × 10^{-11} mol cm^{-2} (ca. 13% of a full monolayer), however, this has no significant impact on the attraction/repulsion balance (Supplementary Fig. 4) and fwhm’s remain above the ideal 90.6 mV.

Very surprisingly, the experimental fwhm’s drops reproducibly below the ideal value when the monolayer coverage is being lost by deliberately introducing an oxidative damage (Fig. 2a, blue symbols). Applying a large anodic bias to samples of S-2 results in the partial loss of the monolayer, with the density of ferrocenes dropping below 1.7 × 10^{-10} mol cm^{-2} (i.e., ca. 35% of a full monolayer) and fwhm’s unexpectedly dropping to 75–55 mV (Fig. 2a, blue traces, and Supplementary Fig. 5). The experimental voltammograms in Fig. 2a are fitted to yield a G value of +0.52 (solid blue line, model 2), which is diagnostic of attractive forces dominating on the surface tethers. Several lines of evidence relate this remarkable increase in Frumkin G to a space-charge effect. Firstly, to the best of our knowledge this has never been observed on a metallic electrode. Secondly, we discarded that these interactions could involve ionized silicon dioxide (SiO₂); the effect is pH-independent and narrow waves are observed at both pH values of 0.5 and 6.0 (Supplementary Fig. 5). At these values of pH, and neglecting for simplicity fields effects30, the chemical equilibrium between ionizable surface groups should lead to either positive (SiOH₂⁺) or negative (SiO⁻) surface groups, respectively31. Furthermore, a deliberate oxidative damage to samples of S-2 prepared on highly doped electrodes led to no noticeable effects on G (Supplementary Fig. 6) and thereby it is unlikely that, besides the space-charge of a lowly doped substrate, other obvious sources of electrostatic interactions, such as anions from the electrolyte27, are contributing toward such a large increase in the self-interaction parameter. AFM images and XPS narrow scans of the Si 2p region in Fig. 3 show the increase in SiO₂ presence and the evolution of surface topography upon the deliberate anodic damaging of S-2 samples. Voltammograms appear as insets to the AFM micrographs to illustrate that as soon as the high-energy XPS emissions from silicon oxides (Si⁺–Si⁴⁺, SiO₂Si 2p peak area ratio of 0.05) become measurable in Fig. 3e, the voltammetric traces narrow below 90.6 mV. The parallel between the spectroscopic appearance of oxides and topographical changes (Fig. 3a–c) is also noteworthy. Figure 3a shows an AFM image taken for an as-prepared S-2 sample. The surface roughness is extremely low which is an indication of the high quality of the surface samples (ca. 0.2 nm peak-to-valley roughness measured by AFM on individual terraces, details in Fig. 3, or a ca. 0.3 nm overall roughness determined independently by X-ray reflectometry, Supplementary Note 4)32–34. The width of the individual surface terraces amounts to ca. 70–100 nm, with the height of the steps being ca. 0.5 nm, which is only slightly higher than a single atomic step between the adjacent lattice planes (0.3 nm). The (111) terraces are also remarkably smooth, with an Rq value of 0.08 ± 0.02 nm (Rₘ, mean 0.15 nm), however a number of small protrusions can be observed (ca. 200 protrusions µm⁻²), which are on average 0.4 nm in height and 5 nm in radius. An extensive anodic treatment (Fig. 3c, f, SiO₂Si 2p of ca. 0.1) leads to a rougher surface (Rq of 0.11 ± 0.01 nm (Rₘ, .023 nm), Supplementary Figs. 7 and 8) and the number

*Fig. 2* Reproducible electrochemical flaws. a Representative background-subtracted voltammograms (100 mV s⁻¹, 1.0 M HClO₄) for S-2 samples on n-type Si(111). Simulated traces (solid black line) for as-prepared samples (symbols) indicate repulsive forces dominate the electrostatic balance of the monolayer system. Applying a potential step of 0.3 V for 140 s shift the balance in favor of attractive interactions (blue line and symbols). Averaged values from cathodic and anodic peaks of experimental fwhm’s and refined Frumkin G values appear as labels in figure. b Distortion of the semiconductor side of the barrier for a photoanode due to the presence of an electrochemically induced dipole layer of surface charges. The depiction of the photodiode used for the simulations indicates downward flip of the bands due to the positive ferriicenium units and the changes to the photogenerated anodic current. c Inverted voltammograms for S-2 samples (25 mV s⁻¹, n-type). E_p,c is 15 mV higher than E_a,c. The hydrosilylation reaction time (S-1) is 10 min.
and size of protrusions increases (ca. 900 protrusions μm⁻², 0.5 nm in height and 8 nm in radius). However, if the anodic treatment is milder (SiOₓ:Si 2p of ca. 0.05), just to suffice in narrowing peaks below 90.6 mV (inset to Fig. 3b), there are no measurable changes to surface Rₚ and Rₓ×Rₚ,c (Fig. 3b; Supplementary Fig. 7) but only an increase to the number of nanometer-sizes protrusions (ca. 300 protrusions μm⁻², Fig. 3b; Supplementary Fig. 7). It has been suggested by Allongue and co-workers that the number of these rounded features is possibly related to silica islands that can be measured by AFM even when the XPS SiOₓ emission is below the detection limit (Fig. 3a).

**Inversion of peak potentials.** As for the current-potential data shown in Fig. 2a, the near-surface barrier of the electrode can be transiently lifted by illumination in the visible. Even a strong illumination will only minimize without nulling the semiconductor barrier, hence illumination—which is required to get a current output—may not totally compromise the semiconductor’s ability to sense or exert electrostatic interactions on nearby molecules. Figure 2b shows the conventional energy-band representation that describes a plausible overall effect of an externally applied electric field and a dipole layer of surface charges on the semiconductor barrier. The convention is to draw energy-level diagrams such that the energy of the system is lowered as electrons fall down toward the source of positive potential (i.e., drawn at the bottom of the diagram). The experimental observation of voltammetric fwhm’s below 90.6 mV and a refined positive G indicates the presence of attractive forces on the positive ferricenium tethers, which can be conceptualized as electrons redistributing over the semiconductor side of the barrier. We should therefore analyze this hypothesis against its most obvious consequence. According to the convention on energy-level diagrams, the higher the semiconductor side is raised above the top of the barrier (i.e., increasing reduction rates). At the same time, this distortion of the bands, induced by the presence of the dipole layer of surface charges, should lift the opposition current carried by holes (i.e., decreasing oxidation rates). The direct consequence would be a very intriguing inversion of peak positions (Supplementary Note 5), with the potential for the cathodic peak shifting anodic of the anodic maxima (Eₓ,p,c > Eₓ,p,a)²⁷. The narrowing of the peaks below 90.6 mV and the inversion of the peak potentials are therefore the anticipated manifestation of the same electrostatic process. Interestingly, only narrow but not inverted peak potentials are observed consistently. In our lowly doped n-type system, S-2 samples systematically showed inverted peak potentials (5–55 mV, Fig. 2c; Supplementary Fig. 9) only if the hydrosilylation reaction time to prepare S-1 samples was lowered from 2 h to either 10 or 2 min (Supplementary Figs. 9–11). Notably, short times for the passivation step also lead to the inversion and narrow waves, and with no requirements of an oxidative pretreatment, but the phenomena is however short-lived and does not allow for systematic changes in the voltage sweep rate and hence rigorous data modeling (Supplementary Fig. 9c). We speculate that a low coverage of diyne molecules after a short 2 or 10 min reaction suffices to reduce the dielectric screening of the carboxaneous film (Supplementary Fig. 12)³⁰, thereby allowing for inversion, but on the other hand the poor passivation leads to the growth of SiOₓ which masks the inversion by reducing the electron transfer kinetics (vide infra). It is in fact very plausible that the manifestation of peak potential inversion is
standing of the inversion effect, where decreases in response to an increase in the surface concentration can yield quantitative information on the parameters for the diode element can be determined in the across the space-charge (model 3, Supplementary Note 6).

Parameters describing diode effects for the potential and currents either 100 s$^{-1}$ or 1 s$^{-1}$ (a, b). Frumkin $G$ was +0.5 and $\theta$ is adjusted from 0.04 in the anodic segment to 1.95 in the cathodic one. This increase in $\theta$ reflects the ca. 50-fold drop in the (photo)hole opposition current ($I_{\text{ph}}$, model 3), and it manifests as inverted peak potentials (Fig. 4a). For the same $G$ value and the same change in $\theta$ but under a slower kinetics, for instance with $k_{\text{et}}$ dropping to 1.0 s$^{-1}$, the peak order would revert to an apparent normal situation (i.e., $E_{\text{pp}} > E_{\text{pc}}$, Fig. 4b). The apparent $k_{\text{et}}$ for the narrow blue trace in Fig. 2a is ca. 80 s$^{-1}$ (see also Supplementary Fig. 2), but upon more extensive oxidative damage of the sample (Fig. 3c, f; Supplementary Fig. 2), this value declines further towards the irreversible region ($k_{\text{et}} = 17 s^{-1}$). At this point both experimental data and simulations (Supplementary Figs. 2, 14 and 15) indicate that the electrostatic pull between the space-charge and surface-bound molecules, which leads to narrow waves and inversion, is completely masked by kinetics. As a consequence of the positive charges on the surface tethers, bands in the semiconductor are distorted downward (Fig. 2b). Using the model 3 (Supplementary Note 6, finite kinetics limit), we have accounted for the inverted peak potentials in n-type S-2 samples and rationalized this as an electrostatics-induced decrease in the anodic photocurrent in the reverse scan (Fig. 2c; Supplementary Figs. 9 and 13).

Electrostatic effects on diode and kinetic analysis. If our reasoning is correct, and electrostatics is indeed a major factor at play, it is thereby easy to see that a similar inversion effect ($E_{\text{pp}} > E_{\text{pc}}$) would also hold for p-silicon photocathodes (Fig. 5a, $I_1$ here increases in the reverse scan, vide infra). The technical problem here is that the chemical system (i.e., S-2) we are using to sense the electrostatics of the solid/liquid interface has a relatively anodic formal potential, and it would therefore fall in the accumulation regime of a p-type electrode. To get around this problem we prepared control S-2 samples on thin films (ca. 4 $\mu$m) of amorphous silicon (a-Si hereafter) that are grown on highly doped p-type substrates. The a-Si electrodes used in this study are near-intrinsic photodconductors, but the nature of the p-type back-contact forces the interface to act, to some degree, as a photocathode (Supplementary Fig. 16). Figure 5b and Supplementary Figs. 17 and 18 show cyclic voltammograms for S-2 samples on a-Si. It is apparent that on the a-Si surface the redox tether experiences analogous attractive electrostatic forces as observed for the n-type Si(111) samples. The interactions between charged ferricenium cations and the semiconductor side of the barrier (Fig. 5a) consistently leads to narrow waves and inverted peak potentials, but unlike the crystalline Si(111) system, the effect is already apparent in as-prepared samples (Fig. 5b, black trace), it does not require a short anodic pulse (Fig. 2a) and it is long-lived (Supplementary Fig. 18). A rigorous explanation on these aspects—as why the manifestation of electrostatics is more pronounced and more robust in rough amorphous samples (Supplementary Fig. 19)—is beyond the scope of this work, but at this stage it is possible to speculate on a relationship between disorder in the film and kinetics factors. The electrochemical non-idealities (i.e., narrow and inverted waves) in a-Si samples are sustained over a prolonged analysis; hence, it is possible to apply model 3 (Supplementary Note 6) to its full extent. At voltage sweep rates of about 100 mV s$^{-1}$ we can observe a drift from the inverted region (Fig. 5b, black traces, and Fig. 6) to a normal region, where the shift caused by redox kinetics masks the...
electrostatic effect (Fig. 5b, blue and red traces). In Fig. 6, we have tentatively marked two regions relative to the scan rate (R as short hand for reversible and NR for non-reversible, Supplementary Note 7) and it is clear that the reverse peak suffers the strongest influences of both diode and kinetics. In the a-Si system the photodiode element is expected to point towards the electrolyte in inversion of the current peak on the potential. An increase in the voltage sweep rate, \( \nu \), leads to a decrease of the effective rate constant \( k_{\text{red}} \), and therefore to an enhancement of the reaction rate constant \( k_{\text{red}} \) at the anodic potentials, leading to a decrease in the effective rate constant \( k_{\text{red}} \), and therefore to an enhancement of the reaction rate constant \( k_{\text{red}} \) at the anodic potentials, leading to a decrease in the effective rate constant \( k_{\text{red}} \), and therefore to an enhancement of the reaction rate constant \( k_{\text{red}} \) at the anodic potentials, leading to a decrease in the effective rate constant \( k_{\text{red}} \), and therefore to an enhancement of the reaction rate constant \( k_{\text{red}} \).

Model 3 combines the effects of diode (through photocurrent and reverse saturation current) plus finite kinetics for the charge-transfer reaction at the monolayer side (through the corresponding rate constant and charge-transfer coefficient in the B–V formalism), and presence of interactions (through the Frumkin interaction parameters). The model appears therefore to be rather complex, but nonetheless the manifestation of the electrostatic effect remains simple to diagnose in terms of narrow and inverted waves. The parameters used to refine theoretical curves (Fig. 5b, solid lines) against experimental data (symbols) are given in Table 1. From the data in Table 1 it can be concluded that for small potential sweep rates (e.g., 20 mV s\(^{-1}\)), there is no significant perturbation caused by the redox kinetics on the electrostatic of the system. As a consequence of the electrostatics experienced by the space-charge of the electrode the photocurrent value for the reverse scan is one order of magnitude greater that in forward scan.

**Table 1 Interaction parameters obtained from current-potential curves in Fig. 5b**

| Scan rate (mV s\(^{-1}\)) | Direct scan | Reverse scan |
|---------------------------|-------------|--------------|
| \( Q_{0} \) | \( G \) | \( s \) | \( y \) | \( Q_{0} \) | \( G \) | \( s \) | \( y \) |
| 20          | 6.9         | 1.0         | 0.15       | 0.2   | 6.1 | 1.0 | -0.9       | 0.2   |
| 100         | 7.5         | 1.0         | -0.2       | 0.2   | 6.5 | 0.9 | -0.8       | 0.2   |
| 500         | 6.7         | 1.2         | -0.7       | 0.1   | 6.7 | 0.8 | -0.6       | 0.2   |

Refined parameters are \( k_{\text{red}} = 80 \mu \text{A} \, \text{s}^{-1} \), \( \alpha = 0.5 \), \( I_{0} = 10^{-5} \mu \text{A} \), \( I_{0} \) (direct scan) = 10 \mu \text{A} \, \text{L} \) (reverse scan) = 100 \mu \text{A} \, \text{L} \) and \( Q_{0} \) is in \( \mu \text{C} \) and defined as the product \( FAF_{T} \). The interaction parameters can be calculated as \( a_{+} = (y-G)/2 \), \( a_{-} = (G+y)/2 \), \( a_{+} = -(y-y)/2 \).
Discussion

This study highlights the previously overlooked importance of the electrostatic interactions between a molecular layer and excess charges in the space-charge of a semiconductor electrode. We show how these interactions do manifest at a Si(111)/liquid interface and under what circumstances they dominate dynamic currents to and from a surface tether. We demonstrate that electrochemical non-idealities cannot be overlooked and discarded as flaws (fwhm’s < 90.6 mV and inverted peak potentials, $E_{\text{peak \, anodic}} < E_{\text{peak \, cathodic}}$). A model is developed to account for these observations based on the relative weight of diode currents, the balance between static attractions and repulsions, and kinetic factors for the electron transfer reaction. It expands on previous work devoted to account for molecular charges on the potential profile at metallic electrodes, showing that the inclusion of dynamic changes to the local energy of bound molecules (i.e., changes to activation free energy of the reaction linked to the presence of intermolecular interactions as described by Frumkin isotherm) and dynamic changes to space-charge effects (i.e., changes to diode parameters) are crucial for a suitable description of semiconductor electrodes. It has immediate implications for the study of electrode kinetics at semiconductors and photoconductors since the electrostatics of the space-charge on surface-tethered molecules can either be prevented or enhanced at will by modifying, for instance, the dielectric of the surrounding environment, here exemplified by changes to the surface coverage of the organic monolayer upon electrochemical cleavage. The cautionary note is that the established kinetic models based on the analysis of peak positions in current-potential traces must either be revised to take into account electrostatics, or the experimentalist must take precautions to limit this type of effects.

The models described are also intended to guide the development of the experimental platforms for the study of how charged groups or externally applied electric fields can influence chemical bonding and reactivity, an area that is beginning to attract significant interest in chemical catalysis. This electrostatic aspect of chemistry has been long suggested by theoreticians, with models developed and refined by Shaik and others starting from 1981, but until recently this has remained mainly a theoretical exercise. Some progress has been made on insulators, where Kanan and co-workers have demonstrated the effect of static electricity on carbene reactions and epoxide rearrangements at insulators/electrolyte interfaces using elegant surface chemistry on insulating Al2O3 films. The use of an electrical insulator (Al2O3) blocks the flow of faradaic currents, and, at least in part, it removes complications from redox side reactions. There are however two caveats with insulators. Firstly, insulators can indeed gain excess surface charge, but in a material that by its very nature does not conduct electricity it is hard to define, control and measure these effects systematically. These tasks can also be further complicated by surface ionization and adventitious adsorption reactions. Secondly, and most importantly, the use of an insulator compromises a priori the exploration of electrostatic effects over chemical processes that involve a mixed sequence of redox and non-redox steps, or the possible use of redox switches together with external electric fields to control plasmonic resonances. A key example of the former case, still awaiting an experimental scrutiny, is cytochrome P450. Intriguing theoretical predictions by Shaik suggest an external oriented field could be used to promote both the non-redox gating as well as the two reduction steps in the cycle of P450; overall increasing at will the enzyme's efficiency. The experimental insights reported in this paper will help to decouple the electrostatic from the dynamic electrochemical process; most importantly allowing one to detect the presence of residual static charges while redox currents are allowed to flow.

Electrode preparation. Silicon samples were mechanically cut into ~1 cm² pieces, cleaned under a stream of nitrogen gas, rinsed several times with small portions of dichloromethane and water, cleaned in hot Piranha solution for 20 min (100 °C), a 3:1 (v/v) mixture of concentrated sulfuric acid to 30% hydrogen peroxide), rinsed thoroughly with water and immediately etched with an argon-saturated 40% aqueous ammonium fluoride solution for 10–12 min under an argon atmosphere. The etching bath was added with a small amount (ca. 5 ml) of ammonium fluoride. The freshly etched samples were washed sequentially with water and dichloromethane and blown dry in argon before the dropping of a small deoxygenated solution of diyne 1 (ca. 50 μl) on the wafer. The liquid sample was contacted with a quartz slide to limit evaporation, rapidly transferred to an air-tight and light-proof reaction chamber, and kept under positive argon pressure. A collimated LED source (λ = 365 nm, nominal power output >190 mW, Thorlabs part M365L2) was focused over the sample at a distance of ca. 10 cm. After illumination for a 2 h period (unless stated otherwise, see Supplementary Figs. 9, 10 and 12) the acetylene-functionalized samples (S-1, Fig. 1) were removed from the reaction chamber, rinsed several times with dichloromethane and rinsed in a sealed vial under dichloromethane at 4 °C for 8 h. The acetylene-terminated samples (S-1) were then rinsed several times with small amounts of 2-propanol and transferred to a reaction tube containing (i) the ferrocene molecule (2, 0.5 mM, 2-propanol/water, 1:1), copper(II) sulfate pentahydrate (0.001 M relative to 2) and sodium ascorbate (ca. 100 mol % relative to 2). Unless stated otherwise (see Supplementary Fig. 4), the click copper-catalyzed alkyne–azide cycloaddition reaction (CuAAC in short hand) was carried out in the dark, at room temperature under air and stopped by removing the ferrocene-functionalized samples (S-2) from the tube after a reaction time of 30 min. Samples (S-2) were dissolved sequentially with copious amounts of 2H2O, dichloromethane, 0.5M aqueous hydrochloric acid, water, 2-propanol, dichloromethane, and blown dry under nitrogen before being analyzed.
We note that in this work the schematics on band-diagrams and diode elements electroactive molecules, space-charge diode effects and fast or \( R \) \( \lambda \) incidence and momentum transfer (Supplementary Note 1 and 2, respectively). Model 2 using Bruker published works17, 18, 55, 60, 61 and were written and performed in MATLAB showed non-idealities that were explained by comparison of the data against 14.0. Model 1 Note 1)61. This model describes the voltammetric responses for electroactive sur-

Electrochemical characterization. Electrochemical experiments were performed in a single-compartment, three-electrode PtFE cell with the modified silicon surface (S-2) as the working electrode, a platinum mesh as the counter and a silver/silver chloride in saturated potassium chloride as the reference electrode. All potentials are reported vs. the reference electrode. Aqueous solutions for electrochemical experiments contained 1.0 M of either NaClO4 or HCIO4 (with a pH of 6.0 and 0.5, respectively). The surface coverage, \( \Gamma \), expressed in mol cm\(^{-2}\), was calculated from the faradaic charge taken as the background-subtracted integrated current from the anodic scan of the voltammograms. Unless specified otherwise, all electrochemical experiments were performed in air at room temperature (22 ± 2 °C) under the illumination provided by a collimated 625 nm LED source (nominal power output > 770 mW, Thorlabs part M625L3, coupled to a SM1P25-A collim-

Simulation methods. The experimental cyclic voltammograms of S-2 samples showed non-idealities that were explained by comparison of the data against simulated current-potential responses. Three simulation models were used in this work. Model 1 is described only briefly below in greater detail in Supplementary Note 2, Supplementary Notes 1, 2 and 6. The models for simulations 1 and 2 were based on published works17, 18, 55, 60, 61 and were written and performed in MATLAB®. Model 3 accounts for finite kinetics and for the presence of attractive and repulsive electrostatic forces on space-charge diode and it was programmed in Mathcad14, 10, MDS®—The Landolt-Börnstein model for a single charge-transfer (Supplementary Note 1)61. This model describes the voltammetric responses for electroactive surface adsorbed molecules on metallic electrodes when either fast or finite kinetics (Supplementary Note 1 and 2, respectively). Model 2—The interaction model for a single charge-transfer (Supplementary Note 2). The model includes parameters describing interactions between the adsorbed molecules, which are reflected in changes to \( f \) and \( \phi \) vs. \( n \) is varied. \( \phi \) is varied between 4.30 and 2.45, and \( f \) is varied between 2.78 and 2.26, \( s \) is the standard deviation, and \( n \) is the number of measurements. \( R \) is between 5 and 10. \n
Space topography was imaged with a Bruker x-ray reflectometry. Specular X-ray reflectometry was measured under ambient conditions at the solid—air interface using a Panalytical X'Pert Pro X-ray reflectometer. The X-ray beam was focused and collimated using a Gobel mirror and a 0.1 mm wide pre-sample slit. Specular reflection (angle of incidence = angle of reflection) was collected at glancing angles with an incident angle range of 0.05° to 5.00° using a step size of 0.01°. The counting time for each step was 7 s. The data were reduced by normalizing the raw data so that the critical edge was unity and was presented as reflectivity (= reflected intensity/incident intensity) vs. momentum transfer (Q) which is equal to \( 4 \pi \) \( \sin \theta \)/\( \lambda \), where \( \theta \) is the angle of incidence and \( \lambda \) is the X-ray wavelength (1.54 Å). Structural parameters for the monolayer were refined in MOTOFFIT reflectometry analysis software64. The surface topography data were analyzed using a Nanoscope software by measuring the average root mean square, \( \phi \) below, and in more detail in the Supple-

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