Electrocatalytic hydrogen evolution at full atomic utilization over ITO-supported sub-nano Pt\textsubscript{n} clusters: High, size-dependent activity controlled by fluxional Pt hydride species

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Abstract:
A combination of density functional theory (DFT) and experiments with atomically size-selected Pt\textsubscript{n} clusters deposited on indium-tin oxide (ITO) electrodes was used to examine the effects of applied potential and Pt\textsubscript{n} size on the electrocatalytic activity of Pt\textsubscript{n} (n = 1, 4, 7, 8) for the hydrogen evolution reaction (HER). Activity is found to be negligible for isolated Pt atoms on ITO, increasing rapidly with Pt\textsubscript{n} size, such that Pt\textsubscript{7}/ITO and Pt\textsubscript{8}/ITO have roughly double the activity per Pt atom compared atoms in the surface layer of polycrystalline Pt. Both DFT and experiment find that hydrogen under-potential deposition (H\textsubscript{upd}) results in Pt\textsubscript{n}/ITO (n = 4, 7, 8) adsorbing \textasciitilde2 H atoms/Pt atom at the HER threshold potential, equal to ca. double the H\textsubscript{upd} observed for bulk Pt or Pt nanoparticles. The cluster catalysts under electrocatalytic conditions are hence best described as a Pt hydride compound, significantly departing from a metallic Pt cluster. The exception is Pt\textsubscript{1}/ITO, where H adsorption at the HER threshold potential is energetically unfavorable. Theory combines global optimization with grand canonical approaches for the influence of potential, uncovering that several metastable structures contribute to HER, changing with the applied potential. It is hence critical to include reactions of the ensemble of energetically accessible Pt\textsubscript{n}H\textsubscript{x}/ITO structures to correctly predict the activity vs. Pt\textsubscript{n} size and applied potential. For the
small clusters, spillover of H\textsubscript{ads} from the clusters to the ITO support is significant, resulting in a competing channel for loss of H\textsubscript{ads}, particularly at slow potential scan rates.

I. Introduction:

The hydrogen evolution reaction (HER) is a major process for energy conversion and storage, motivating considerable interest in improving the cost-effectiveness of electrolyzers.\textsuperscript{1–5} To lower the high cost of the electrocatalysts, which are currently made of expensive metals like platinum\textsuperscript{4,6} and iridium\textsuperscript{7}, the precious metal concentration must be decreased. Dispersing the metals on supports as single atoms or sub-nanometer clusters can help lower the metal content by ensuring that every metal atom is accessible throughout the catalytic process. Due to their unique topologies and electronic properties, which are crucial to understanding their chemisorption properties, small nanoclusters are also interesting from a fundamental perspective. There may be substantial adsorbate-induced reconstructions for such a small cluster, altering the geometry and electronic structure of the active sites during the reaction \textsuperscript{8–10}, maybe for the better. There is also the possibility for adsorbate- or potential-induced sintering or cluster disintegration, modifying the catalyst properties and possibly reducing the catalyst lifetime\textsuperscript{11}. These small clusters can also exhibit fluxionality, which denotes their capacity to not only reorganize under reaction conditions but also to access not just a single but a collection of low-free energy structures\textsuperscript{12}.

To maximize insights regarding the activity of sub-nano clusters it is important that the electrocatalysts be atomically monodisperse, and theory must follow the ensemble of dynamically coupled isomers, rather than focusing on just a static global minimum structure. For example, Sun et al. reported that the most stable isomer of Cu\textsubscript{4}O\textsubscript{3} was inactive for alkane oxidative dehydrogenation, however, barrierless isomerization to metastable isomers with low barrier facilitated its catalytic activity\textsuperscript{13}. Pt\textsubscript{13} can populate low-energy metastable structures under hydrogen pressure, which play a major role in its catalytic reactivity\textsuperscript{14}. Pure and alloyed Pt clusters supported on Al\textsubscript{2}O\textsubscript{3} were also extensively studied theoretically and experimentally\textsuperscript{15–17}, showing that at temperatures typical for catalysis, the cluster geometry changes frequently. For the catalysis of CO oxidation, Ghosh et al.\textsuperscript{18} investigated Au clusters deposited on CeO\textsubscript{2} (111) with O vacancies. They discovered that, in this case, cluster fluxionality promotes the reaction. In the presence of CO, Au\textsubscript{2} on ceria dissociates, whereas Au\textsubscript{3} survives. Reorganization of supported clusters under electrochemical potential and adsorbates of oxygen reduction reaction was also recently reported\textsuperscript{8,10}.\textsuperscript{8,10}
While small, electrode-supported Pt clusters allow reactant access to all the Pt atoms, it is unclear how cluster size affects reactivity of the atoms. The hydrogen adsorption energy is a key reactivity descriptor for HER, and extended Pt surfaces, such as Pt(111), have H binding energies slightly more negative, but close to the theoretical optimum ($\Delta G_{\text{ads}} \approx 0 \text{eV}$)$^{19}$. The Pt atoms in small Pt clusters have lower Pt-Pt coordination, and have H adsorption energies at low coverage which are more negative (i.e. more stable) than those for extended surfaces$^{20}$, and on this basis would appear to be poor candidates for HER catalysts. This low H coverage picture is, however, insufficient because high H coverages can adsorb on such small Pt clusters under HER conditions$^{21,22}$. Sun et al. have used DFT calculations to study the Pt$_{13}$ cluster under high coverage of hydrogen (Pt$_{13}$H$_{26}$)$^{14}$. They showed that the most stable structure presents a compact cuboctahedra structure and a H adsorption energy at least 0.2 eV stronger (more negative) than Pt (111): it would, therefore, not be a good catalyst for HER. Metastable isomers of Pt$_{13}$H$_{26}$ can provide optimal H adsorption energies that would give high HER activity, but they are too energetically unstable and do not have significant populations at room temperature. As a result, Pt$_{13}$H$_{26}$ was predicted to be a poor HER catalyst. In contrast, here we show by a combination of experiments and simulations, that smaller supported cluster sizes (n=4, 7, 8) have high HER activity.

The development of single atom and cluster-based catalysts, where cluster size-dependent activity was observed, has received a lot of attention over the past few decades. Indeed, recent advances in experimental techniques made it possible to prepare and observe catalysts consisting of atomically dispersed species$^{23}$. It has been reported that highly dispersed Pt atoms and clusters on transition metal oxide layers have a higher catalytic activity toward the HER compared to bulk Pt and commercial Pt nanoparticles$^{24-26}$. In addition, size effects of sub-nano cluster catalysts are also of fundamental interest, as adding or removing a single atom can cause large, non-monotonic variations of the clusters’ electronic and chemical properties, with contrasted impact for different reactions. An excellent perspective paper by Vajda and coworkers$^{27,28}$ reviewed size- and composition-dependent cluster catalysis and electrocatalysis, and the Vajda group has reported several cluster electrochemistry studies with strong size effects$^{28,29}$. Heiz, Arenz, and coworkers$^{30,31}$ provided an experimental framework addressing electrocatalytic processes that are mediated by size-selected Pt clusters and nanoparticles, with a particular focus on the oxygen reduction reaction (ORR) and potential-induced sintering. In this regard, von Weber et al. showed
non-monotonic order-of-magnitude variations in the activity of Pt$_n$ (n = 1 – 14) deposited on indium tin oxide (ITO) electrodes for ethanol electro-oxidation$^{32}$ and showed that the activity correlated with Pt electronic properties probed by X-ray photoelectron spectroscopy (XPS), but the same Pt$_n$/ITO electrodes showed a monotonic size effect on the branching between water and H$_2$O$_2$ products in the oxygen reduction reaction (ORR)$^{33}$. Sun and coworkers$^{23}$ produced ensembles of single Pt atoms using atomic layer deposition (ALD) and investigated how size affected the HER. Other research teams have examined the catalysis of single Pt atom ensembles in a variety of settings, including the HER on Pt-doped MoS$_2$ substrates$^{34}$ and CO oxidation on FeO$_x$ substrates$^{35}$.

Here, we present a comprehensive study of the effects of Pt cluster size on the HER activity for atomically size-selected Pt atoms and clusters deposited on ITO electrodes. ITO is a transparent conducting oxide prepared by doping In$_2$O$_3$ with Sn (~5%)$^{9,36,37}$, and is common in both electrochemical and photoelectrochemical investigations. To understand how size affects the HER mechanism, the experiments used mass-selected cluster ion deposition in ultra-high vacuum to prepare atomically monodisperse electrodes, and density functional theory (DFT) was used along with the grand canonical basin hopping method (GCBH) to explore the structural diversity of small Pt-clusters deposited on ITO under electrochemical conditions. We explored the effects of cluster restructuring and multiple accessible adsorption isomers on the catalytic surface and HER activity.

**II. Results and Discussion:**

**A. Potential Energy Surface exploration under the electrochemical reaction condition.**

In this section, we explore the structures of Pt$_1$H$_x$, Pt$_4$H$_x$, Pt$_7$H$_x$, and Pt$_8$H$_x$ clusters supported on ITO at a potential of E = 0V vs. SHE and pH = 1 using the GCBH method (Theoretical SI-3). For this free energy surface (FES) exploration, we use the following mutations in our GCBH method:

A. The cluster can move randomly over the ITO surface to find its most stable adsorption site.

B. The cluster shape can change randomly by a move of one Pt atom to find the most stable cluster shape.

C. The H coverage is mutated grand canonically to find the most stable H coverage across the different clusters. The changing H coverage under the electrochemical reaction condition can also modify the cluster shape and the adsorption site.

D. The hydroxyl groups on the ITO surface can move around and transfer to the cluster.
Using the above four mutations together, we generated 2343, 2894, and 3222 unique structures for Pt$_4$H$_x$, Pt$_7$H$_x$, and Pt$_8$H$_x$, respectively. The FES for the clusters with varying hydrogen coverages is given in the Fig. S7. The global minimum for the Pt$_1$ structure was taken from our previous work.$^9$ The optimum global minimum H coverage and structures for the different cluster sizes at U = 0V vs. SHE and pH = 1 are given in Fig. 1 (a,b,c,d). For comparison, Fig. 1e provides the Pt$_8$/ITO structure found via GCBH with no H coverage (E = 0 V vs SHE), showing how the Pt cluster core structure changes due to the high H coverage under electrochemical conditions. We find that, independent of the cluster size, the Pt atoms tend to stay in close interaction with the surface Sn atoms on the ITO surface. This result is consistent with our previous work, in which Pt$_1$, Pt$_2$, and Pt$_3$ all preferred interacting with the Sn. The nearby hydroxyls and O atoms also help anchor the clusters, stabilizing them and restricting them from diffusing across the support.$^9$

Except for Pt$_1$, all other cluster sizes were observed to have high optimum hydrogen coverage at E = 0 (vs SHE) and pH = 1, averaging at ~2 H/Pt atom. As the potential goes negative, the optimum hydrogen coverage increases, as shown in Fig. 2(e) focusing on the window from +0.025 to -0.1 V to -0.1 V vs. SHE, i.e., at potentials above and below the HER onset potential (see SI for details about the choice of the potential window). In the case of Pt$_1$, we observe that in the potential range from 0 to -0.1 V vs. SHE, the most stable structure was Pt$_1$H$_0$/ITO, i.e., there is zero H adsorption in the UPD and HER region. Only after the potential reaches an overpotential of -0.3 V does the Pt$_1$H$_2$/ITO structure become the most stable one (Fig. S9). On the other hand, all the other cluster sizes (4, 7, and 8) show a very high hydrogen coverage in the potential range from 0.025 to -0.1 eV. The high overall H content (~2H/Pt) shows that the initially metallic Pt cluster transforms in
electroreduction conditions to Pt hydride species. Pt di-hydride species are known for ligated Pt molecular complexes, and poly-hydrides have been seen in gas phase clusters via photoelectron spectroscopy supplemented with theory. Pt hydride species have also been computationally proposed in the case of small $\text{Pt}_n$ clusters ($n=8,13$) on alumina exposed to a gas phase of hydrogen, and hence are not specific to electroreduction conditions. Bulk Pt, in the form of nanoparticles for example, does not form a hydride under normal catalytic or electrocatalytic conditions becoming covered by just a monolayer of H, i.e. a 1:1 H:Pt ratio for Pt surface atoms, hence giving a smaller H/Pt ratio. The bulk hydride species $\text{PtH}$ is only formed at high pressure ($>20 \text{ GPa}$).

To accommodate such high hydrogen coverage, our calculations show that the clusters tend to form open structures with an average Pt-Pt coordination number (CN) of 2.5, 2.57, and 3 for $\text{Pt}_4\text{H}_7$, $\text{Pt}_7\text{H}_{12}$, and $\text{Pt}_8\text{H}_{16}$, respectively ($r_{\text{cutoff}}$ for Pt-Pt distance is taken as 2.87 Å). These CNs are low compared to the CNs for bulk Pt surfaces (e.g. CN = 9 for Pt(111)) and for $\text{Pt}_8\text{H}_{16}$ compared to that of the bare supported $\text{Pt}_8$ cluster (4.9). The avg. bond lengths of first-neighbor Pt-Pt pairs and Pt-H pairs are given in Table 1. All Pt-Pt distances are compressed compared with bulk Pt. Both the avg. Pt-H and Pt-Pt bond length increases as we increase the Pt cluster size. We also compare the avg. Pt-Pt distance of the $\text{Pt}_n\text{H}_x$/ITO systems with Pt$_3$/ITO from our previous work and Pt$_8$/ITO (global minimum structure from GCBH of Pt$_8$ cluster on ITO, (Fig 1(e)), showing that with H coverage, the avg. Pt-Pt bond distance increases. This result agrees well with previous work by Itoi et al. and Sun et al., where they observed the contraction of the Pt-Pt bond for nanoparticles below 1 nm and Pt-Pt bond expansion upon H$_2$ adsorption. It is important

<table>
<thead>
<tr>
<th>System</th>
<th>Avg. Pt-H (Å)</th>
<th>Avg Pt-Pt (Å)</th>
</tr>
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<tbody>
<tr>
<td>$\text{Pt}_4\text{H}_7$/ITO</td>
<td>1.65</td>
<td>2.71</td>
</tr>
<tr>
<td>$\text{Pt}<em>7\text{H}</em>{12}$/ITO</td>
<td>1.66</td>
<td>2.75</td>
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<tr>
<td>$\text{Pt}<em>8\text{H}</em>{16}$/ITO</td>
<td>1.68</td>
<td>2.76</td>
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<tr>
<td>Pt$_3$/ITO$^{34}$</td>
<td>-</td>
<td>2.62</td>
</tr>
<tr>
<td>Pt$_8$/ITO</td>
<td>-</td>
<td>2.66</td>
</tr>
<tr>
<td>Pt bulk</td>
<td>-</td>
<td>2.81</td>
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*Table 1: Avg. Pt-H and Avg. Pt-Pt bond lengths for different systems*
to note that the Pt$_n$ clusters are not static but adapt their shape and support interaction in response to the hydrogen coverage, itself determined by the electrochemical potential value, as can be seen in Fig 1 for the example of Pt$_8$.

Figure 2: CVs obtained for (a) 0.03 ML Pt$_1$/ITO, (b) 0.03 ML Pt$_4$/ITO, (c) 0.03 ML Pt$_7$/ITO, (d) 0.03 ML Pt$_8$/ITO, from left to right, in Ar-saturated 0.1 M HClO$_4$ at a scan rate of 0.1 V s$^{-1}$. For each cluster electrode, the first and second CV cycles are shown as gray and colored solid curves, overlapping closely except for Pt$_1$. The dashed curves show the second CV for Pt-free ITO recorded under the identical conditions. The error bars represent the standard deviations of repeated measurements. (e) H atom coverages on the global minima for Pt$_1$, Pt$_4$, Pt$_7$, and Pt$_8$ on ITO(111) at varying potentials, indicate by the numbers in the data points. (f) Negative sweep of the voltammograms for 0.03 ML Pt$_n$/ITO (n = 1, 4, 7, 8) after subtracting the capacitive background current from ITO, $i_c$. The subtracted currents were integrated to calculate the total charge transferred in the H$_{upd}$ potential region, assumed to extend to -0.036 V. For example, the integration area for Pt$_7$/ITO is shaded gray. (g) Bars give the size-dependent numbers of H atoms per Pt atom adsorbed in the UPD region, estimated from the integrated H$_{upd}$ currents from (g). Error bars represent standard deviations of repeated measurements. The black dots represent the H atom coverage per Pt atom determined from GCBH and DFT at the potential $E = -0.05 V$ vs SHE.
Figure 2 (a-d) shows the first and second cyclic voltammetry (CV) data for each 0.03 monolayer (ML) Pt<sub>n</sub>/ITO electrode in the potential range between −0.196 and 0.514 V vs. SHE, showing the absolute currents. Except for Pt<sub>1</sub>, the first and second CVs are essentially superimposable, i.e., the voltammetric responses are already essentially in steady state during first CV cycle. The dashed curves show the currents observed in the second CV for Pt-free ITO, primarily due to non-faradaic (capacitive) contributions. Note that because all Pt<sub>n</sub>/ITO samples had the same 0.434 ng of Pt present, the relative activities are directly proportional to the measured currents.

Figure 2(f) shows the faradaic current responses of the 0.03 ML Pt<sub>n</sub>/ITO electrodes in the potential range near the thermodynamic HER threshold (gray vertical line), obtained by subtracting the ITO background current from the voltammograms in Fig. 2. At potentials negative of the threshold, the Pt<sub>n</sub>/ITO electrodes catalyze HER, with activities increasing rapidly with cluster size, and negligible activity for Pt<sub>1</sub>/ITO. These background-subtracted currents are reported as mass activities, i.e., currents normalized to the Pt mass, as discussed in the SI.

In addition to HER, for n = 4, 7, 8, the experiments also find large reduction currents at potentials positive of the HER threshold, in the H underpotential deposition (H<sub>upd</sub>) region, where protons adsorb, building up H<sub>ads</sub> coverage. The currents are proportional to the scan rate, which is characteristic of an electrode-adsorbed species involved in the reaction<sup>8</sup> (see Figs. S4 and S5). For reference Fig. S4 shows CVs for polycrystalline Pt (Pt<sub>poly</sub>) taken using the same cell and electrolyte, showing the expected H<sub>upd</sub> structure in the potential range between ~0.3 and 0 V vs. SHE. We rule out the possibility of other reduction reactions contributing to the currents in the H<sub>upd</sub> region, as no further reduction signals appeared even when the potential was cycled over the potential range up to 1.2 V (see Fig. S3 top). We also measured ORR in electrolyte that was not Ar-purged (Fig. S3 bottom), showing that the potential dependence of the ORR current is quite different from the currents observed for Ar-purged electrolyte, extending well positive of the H<sub>upd</sub> region. Thus, we conclude that the currents in the H<sub>upd</sub> region for Ar-purged electrolyte are not significantly contaminated by ORR currents.

Since the H<sub>upd</sub> feature in acidic media represents the one-electron Volmer reaction (H<sup>+</sup> + e<sup>−</sup> → H<sub>ads</sub>), integration of the H<sub>upd</sub> current allows quantification of the number of H atoms adsorbed on each Pt<sub>n</sub> cluster in the H<sub>upd</sub> potential range, as summarized in Fig. 2(g) with details in Table S1. Except for Pt<sub>1</sub>, the Pt<sub>n</sub> clusters were found to adsorb well over 1 H atom/Pt atom in the H<sub>upd</sub> potential range, i.e., substantially more H/Pt than is observed for bulk Pt and most Pt-based
electrocatalysts. The measured high $H_{\text{upd}}$ coverage is consistent, however, with the large number of adsorbed H atoms predicted by theory at the same potential (~2H per Pt) discussed above. Furthermore, the onset potential for $H_{\text{upd}}$ on Pt$_n$/ITO electrodes (~0.45 V vs. SHE) was found to be substantially higher than that for Pt$_{\text{poly}}$ (~0.3 V vs. SHE, Fig. S3), consistent with the theoretical finding that the H adsorption energy on small Pt clusters is higher than on bulk Pt at low coverages.

**B. Ensemble of structures for HER via thermodynamic analysis.**

![Formation energies of the cluster(eV)](image)

Figure 3: Formation energies of the ensemble of low energy structures for Pt$_7$H$_x$/ITO from each hydrogen coverage value evaluated using the surface charging method. Electrochemical condition: $E = 0$ V vs SHE, $pH = 1$.

To model the HER activity of the clusters under electrochemical conditions, we first need to determine the ensemble of cluster structures that would be energetically accessible to perform HER in the relevant potential range and not only the global minimum, as previously shown on fig. 1. To determine this ensemble of structures, we have exploited first-principles thermodynamics to calculate the formation energy of the various Pt$_n$H$_x$ isomers, using Pt bulk as a reference and the surface charging method to express the potential dependence.
We consider the ensemble of structures within 0.3 eV in free energy of formation from the global minima (GM) for the various cluster sizes. These not only include the metastable structures (MS) with the same hydrogen coverage as the GM but also include structures from other hydrogen coverages neighboring the minima. Fig. 3 presents the ensemble of structures for Pt$_7$H$_x$/ITO at E = 0 V vs SHE, pH = 1. As previously mentioned, Pt$_7$H$_{12}$ is the GM, but there is still a significant

Figure 4: HER current plot from the Butler Volmer type kinetic modeling for Pt$_7$H$_x$/ITO; (a) network of various elementary reactions on Pt$_7$H$_x$/ITO where energetically accessible structures of the Pt$_7$H$_x$ cluster are connected by curved arrows representing 2-step Volmer-Heyrovsky reactions, and pairs of straight arrows representing 3-step Volmer-Tafel reactions. The HER currents for the reactions in (a) are given in the potential range (b) -0.10 – -0.05 V vs SHE and (c) -0.05 – 0 V vs SHE (d) Total simulated HER currents obtained by combining all the currents from various reaction channels for Pt$_n$/ITO (n = 1, 4, 7, 8), considering all accessible (i.e., GM+MS) structures are shown by solid lines. Currents calculated considering only GM structures are shown as dashed lines. (e) Raw experimental voltammograms for 0.03 ML Pt$_n$/ITO (n = 1, 4, 7, 8) in an Ar-saturated 0.1 M HClO$_4$ solution at a scan rate of 0.1 V s$^{-1}$. The capacitive current from ITO has not been subtracted, and only the negative-going sweeps are shown. The error bars represent the standard deviations of repeated measurements. (f) Tafel plots of 0.03 ML Pt$_n$/ITO (n = 1, 4, 7, 8) obtained from (a). Tafel slopes are indicated for n = 4, 7, 8.

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Boltzmann probability (at $T = 294K$) that other structures are populated under reaction conditions and participate in the HER reaction network. The ensembles of low energy structures for the other cluster sizes $\text{Pt}_1\text{H}_x$, $\text{Pt}_4\text{H}_x$, and $\text{Pt}_8\text{H}_x$ are provided in the SI. Note that in the low energy ensemble, the $\text{Pt}_n$ core structures and their adsorption geometries on the ITO support are unaffected by the (slightly) varying H coverages, i.e., the clusters are fluxional only in the sense that hydrogen numbers and adsorption sites are quite variable. This comment is valid only for the limited ranges of hydrogen coverages predicted to be present near the HER threshold potential. As shown in Fig. 1 for $\text{Pt}_8$, the cluster structure is quite different for that at zero H coverage.

**C. Hydrogen evolution reaction: Microkinetic Analysis and Role of Metastable states.**

A factor that is important to consider is the fluxionality of the $\text{Pt}_n\text{H}_x$/ITO structures and the ensembles of reaction channels that contribute to the HER activity. These effects are illustrated in Fig. 4a-c for the case of $\text{Pt}_7\text{H}_x$/ITO, which is the most fluxional of the cluster sizes studied, judging by the number of accessible isomers. We first construct a network of reaction paths that contribute to HER (Fig. 4a) involving all the accessible isomers with different H coverages. The hydrogen coverages and isomers are indicated by numbers within in the circles. For example $12_n$ indicates the $n^{th}$ isomer of $\text{Pt}_7\text{H}_{12}$ with higher $n$ indicating higher energy isomers. Figs. 4b and 4c shows contributions from each path to the HER currents, simulated using a Butler-Volmer-type formulation as explained in the SI. The analogous networks and simulations for the other cluster sizes are given in the SI.

To build reaction networks, we need to consider the ensemble of structures, such as those for $\text{Pt}_7\text{H}_x$/ITO from Fig 3. In acidic electrochemical conditions, HER can proceed via two different catalytic cycles: the Volmer-Tafel reaction, where two protons adsorb on the catalyst, neutralize, and combine to form H$_2$:

Volmer step $\text{H}^+_\text{(aq)} + e^- \rightarrow \text{H}_{\text{ad}}$

Tafel step $\text{H}_{\text{ad}} + \text{H}_{\text{ad}} \rightarrow \text{H}_2, \text{gas}$

and the Volmer-Heyrovsky reaction, where just one proton adsorbs, reacting with a second proton impinging from solution to form H$_2$.

Volmer step $\text{H}^+_\text{(aq)} + e^- \rightarrow \text{H}_{\text{ad}}$

Heyrovsky step $\text{H}^+_\text{(aq)} + \text{H}_{\text{ad}} + e^- \rightarrow \text{H}_2, \text{gas}$
The reaction network for Pt\textsubscript{7}H\textsubscript{x}/ITO is illustrated in Fig. 4(a). The hydrogen coverages and isomers are shown in the circles. For example, 12\textsubscript{n} indicates the \textit{n}th isomer (higher \textit{n} = higher energy) of Pt\textsubscript{7}H\textsubscript{12}. 2-step Volmer-Heyrovsky catalytic cycles (e.g., 11H \rightarrow 12H\textsubscript{1} \rightarrow 11H) are represented in Fig. 4a by single curved arrows, which pairs of straight arrows represent 3-step Volmer-Tafel reactions (e.g., 11H \rightarrow 12H\textsubscript{1} \rightarrow 13H\textsubscript{1} \rightarrow 11H). The arrow colors differentiate between various possible reactions in the reaction network.

To evaluate the HER activity contribution, we calculated HER currents for all the reactions from the reaction network and plotted them as a function of potential in Fig. 4(b,c) for two different potential ranges. The kinetic formulation used here for simulating HER activities is directly adapted from the work of Zhang et al\textsuperscript{44} and is explained thoroughly in the SI. At low negative potential (range [-0.05, 0] V vs. SHE) the HER current mainly involves structures with 12, 13, and 14 H coverage, and both the Volmer-Tafel and Volmer-Heyrovsky reaction mechanisms come into play (Fig. 4(c)). As we move toward more negative potentials in Fig. 4(b), the dominant contributions to the HER current shift to 14, 15, and 16 H coverage. This is directly related to the fact that as we move toward negative potential, the optimum hydrogen coverage on the cluster increases (Fig. 2e).

To compare the HER activity for the different cluster sizes, we combine the individual currents from the different reaction pathways (e.g., Fig. 4(b,c) and SI) for each cluster size to give the total theoretical currents for that cluster size, which are shown in Fig. 4(d). The experimental voltammograms are shown in Fig. 4(e), where only the cathodic current responses are shown, and the ITO capacitive current has not been subtracted. For reference, the currents for blank, Pt-free ITO is also shown.

Both simulations and experiments show that the HER activity is strongly dependent on the cluster size, with negligible activity for Pt\textsubscript{1}/ITO and increasing activity with size in the order 0 \approx Pt\textsubscript{1} \ll Pt\textsubscript{4} \ll Pt\textsubscript{7} \ll Pt\textsubscript{8}. Because the Pt\textsubscript{n}/ITO samples contained identical amounts of Pt (0.434 ng), ng), the differences in currents show that the activity \textit{per} Pt atom increases with cluster size. The low activity for Pt\textsubscript{1}/ITO is theoretically found to result from the H adsorption step from Pt\textsubscript{1}H\textsubscript{0}/ITO \rightarrow Pt\textsubscript{1}H\textsubscript{1}/ITO being energetically unfavorable, with an overpotential of -0.3V vs. SHE. This also explains why Pt\textsubscript{1}/ITO shows no H\textsubscript{upd} current (Fig. 1). The observed low activity of single Pt atoms on ITO contrasts with other results in the literature for Pt1 on nitrogen-doped graphene.
nanosheets\textsuperscript{25} or WO\textsubscript{x}\textsuperscript{26} support. One explanation of the difference could be a distinct influence of the support, or that the single Pt atom sinter into larger catalytically active clusters.

The sharp increase in HER activity with increasing cluster size raises the question of what particle size would be optimum. One point is certain, that as the clusters become larger, eventually they will adopt more compact structures with higher Pt-Pt coordination, and with an increasing fraction of the Pt no longer in the surface layer. The Pt atoms in the core would no longer be catalytically accessible, which would result in activity/Pt loss. Therefore, the HER activity will be high till these clusters remain very open where every Pt atoms is catalytically utilized.

The theoretical HER currents shown as solid lines in Fig. 3d include the contributions from all the structures present in the energetically accessible ensembles of structures for each cluster size. Fig. 3d also shows theoretical voltammograms evaluated considering only the GM structures (dashed lines), to emphasize the importance of including contributions from the metastable structures. Note that if only GM structures are included, the predicted HER activity has an incorrect dependence on cluster size (Pt\textsubscript{1} < Pt\textsubscript{7} < Pt\textsubscript{4} < Pt\textsubscript{8}) versus experiment because the metastable structures make a strong contribution to the Pt\textsubscript{7}H\textsubscript{x}/ITO HER current, increasing it by upto \(\sim 60\%\).

To probe this issue further, we evaluated the normalized activity contributions at varying potentials, as shown in Fig. 5(a). Consider the potential \(E = -0.01\text{V vs. SHE}\); at this potential, the dominant reactions are shown in Fig. 5(b). The dominant contribution (36\%) is the Volmer-Tafel

![Diagram](image)

**Figure 5:** (a) Normalized activity contribution from various elementary reactions vs the potential. (b) The contribution from various reactions at -0.01V vs SHE (marked as the blue dashed line on (a)).
reaction between structures $12H_1, 13H_1$ and $14H_1$, which all are global minima for the respective hydrogen coverages. There is a 30% contribution from another Volmer-Tafel reaction involving the metastable structure $12_2$ and the GM structures for 13 and 14 H coverages. There are also significant contributions from Volmer-Heyrovsky reactions involving metastable structures, including $13_2 \rightarrow 14 \rightarrow 13_2$ (R5), $12_1 \rightarrow 13 \rightarrow 12_1$ (R2), and $12_3 \rightarrow 13_2 \rightarrow 12_3$ (R4), representing a total of 31.2% to the HER current. Clearly, it is essential to include the ensemble of accessible structures in calculating activity for sub-nano cluster catalysts.

Another intriguing finding is that for Pt$4H_x$/ITO, adding the metastable structures reduces the overall HER current, in contrast to the Pt$7H_x$/ITO system. This can happen when some of the thermally populated metastable structures are catalytically inactive but reduce the populations of the catalytically active structures. In this case, the GM isomers are considerably more catalytically active than some of the energetically accessible metastable isomers, so that populating metastable isomers reduces the total activity. Again, this demonstrates the importance of considering the full ensemble of accessible isomers.

Our results also show that Volmer-Tafel reactions are dominant over Volmer-Heyrovsky reactions in the case of Pt$7H_x$/ITO. For Pt$8H_x$/ITO, the HER current comes solely from the Volmer-Tafel reaction between 16, 17, and 18 H-coverages in the potential range above -0.05V vs. SHE (Fig S10). For Pt$4H_x$/ITO, however, there are significant contributions from both Volmer-Tafel and Volmer-Heyrovsky reactions, with Volmer-Tafel dominating (Fig S9). Therefore, the Volmer-Tafel mechanism appear to be dominant (or exclusive) for Pt$4$, Pt$7$ and Pt$8$. In addition, in each case a Volmer step was found to be the rate determining step at a potential -0.15 V vs SHE.

From the experimental viewpoint, the Tafel plots shown in Fig. 4(f), show that the Pt$4H_x$/ITO ($n = 4, 7, \text{and } 8$) catalysts all show similar Tafel slopes of 130-160 mV dec$^{-1}$. From the experimental viewpoint, the Tafel plots shown in Fig. 4(f), show that the Pt$6H_x$/ITO ($n = 4, 7, \text{and } 8$) catalysts all show similar Tafel slopes of 130-160 mV dec$^{-1}$. These values are fully compatible with a Volmer rate-determining step involving one electron transfer.$^{45}$ The theoretical Tafel slopes are also given in Fig. S13, which predicts a similar trend of the slope as Pt$4 \approx$ Pt$7 >$ Pt$8$. However, because small, supported clusters have very different properties than bulk Pt or Pt nanoparticles, specifically in the amount of adsorbed H and adsorption energies, it is not obvious that the Tafel plots can be interpreted in a manner analogous to macroscopic Pt surfaces.
D. Size-dependent stability analysis of the clusters in electrochemical conditions.

We have evaluated the relative thermodynamic stability of the 4 different cluster sizes at 3 different potentials (0, -0.05, -0.1 V vs. SHE) given in Fig. 6(a), to qualitatively explore whether the larger clusters might disintegrate or sinter under electrochemical conditions. The hydrogen coverages at different potentials from Fig. 2(f) were mapped to evaluate the formation energy per Pt atom. The positive formation energy (details on how the formation energy is evaluated is given in SI) here that clusters are slightly less stable than bulk platinum, as expected, and a less positive value indicates a more stable structure. For each cluster size, the formation energy per Pt atom is almost independent of the applied potential, but the stability increases with cluster size (smaller the formation energy the more stable the cluster), suggesting that larger clusters should not disintegrate into smaller clusters under the HER conditions of our study. To study the effect of hydrogen coverage on stability, we also compare the formation energy/Pt atom of Pt₈Hₓ/ITO (~0.7eV) and Pt₈/ITO (0.89eV). The decrease in formation energy is directly related to the increased number of adsorbed H, which stabilize the cluster by ~0.2 eV. Therefore, the hydride clusters formed in electroreduction conditions are more stable than bare clusters, and thus should have reduced tendency to sinter.

Figure 6: (a) Formation energies per Pt atom (Eₚt/Pt atom) for the supported PtₙHₓ clusters as a function of the particle size w.r.t Pt bulk. Chronoamperometry of 0.03 ML Ptₙ/ITO (n = 1, 4, 7, 8) and blank ITO electrodes in an Ar-saturated 0.1 M HClO₄ solution at applied potentials of (b) –0.116 and (c) 0.004 V vs. SHE. The error bars represent the standard deviations of repeated measurements.
Experimentally, we probed the stability of the Pt\textsubscript{n}/ITO catalysts by chronoamperometry. As shown in Fig. 6(b), the Pt\textsubscript{n}/ITO catalysts gave slowly declining currents, but remained active after 300 s at −0.116 V, and the size-dependent magnitude of the HER current (Pt\textsubscript{8} > Pt\textsubscript{7} > Pt\textsubscript{4} > Pt\textsubscript{1}) was consistent with the HER activity order observed in the voltammograms in Fig. 4 (e). The decrease may relate to cluster degradation of some sort; however, we note that small clusters at low loadings are extremely sensitive to poisoning by contaminants in the electrolyte\textsuperscript{32}.

The amperograms in Fig. 6(c) were obtained at a potential of 0.004 V, which is slightly positive of the thermodynamic HER threshold, but because the H\textsubscript{2} pressure is essentially zero, some HER may occur, in addition to hydrogen underpotential deposition. Note that for ITO and Pt\textsubscript{1}/ITO, there were no significant currents apart from the initial double-layer-charging peak. For the cluster/ITO electrodes, small but significant currents were observed, persisting long after the initial capacitive charging current decayed. This could be due to HER driven by the negligible H\textsubscript{2} product pressure, but as discussed below there is also evidence for some non-electrochemical process that removes adsorbed H atoms from the Pt clusters, which would free sites for additional proton adsorption.

If there is, indeed, such a non-electrochemical H removal process, we might expect that little or no H desorption signal (i.e., H\textsubscript{ads} → H\textsuperscript{+} + e\textsuperscript{−}) would be observed during scans to positive potentials, and that is the case for slow potential scan speeds, as shown in Fig. 2(a-d). As shown in Figs. S4 and S5, however, significant H desorption signals were observed for high scan rates, implying that this non-electrochemical H removal process is slow, allowing significant H coverage to remain adsorbed on the few-second time scale.

Our experiment provides no direct insight into the nature of this non-electrochemical H\textsubscript{ads} removal process, however, we might expect that H spillover to the ITO support would be more significant for sub-nano Pt\textsubscript{n} clusters compared to larger Pt nanoparticles. Indeed, on some sub-nano Pt-based catalytic systems, spillover of adsorbed species has been found to be quite efficient, due to the short pathways from Pt to oxide supports.\textsuperscript{26,46–49} The fate of H spilled over to the oxide support is unclear, but possibilities include incorporation into the oxide lattice or recombinative desorption as H\textsubscript{2}.

E. Mass activity comparison with other Pt-based HER catalysts
The sharp increase in HER activity with increasing cluster size raises the question of what particle size would be optimum, and how the activity of the Pt\textsubscript{n}/ITO compares to other HER catalysts. Because our samples have a precisely known amount of Pt deposited (0.434 ng), it is straightforward to convert the background-subtracted HER currents (Fig. 1g) to mass activities, i.e., currents per milligram of Pt deposited. Figure 7 compares the mass activities at a potential of -0.086 V vs. SHE, corresponding to an overpotential $\eta = 0.05$ V, for our 0.03 ML Pt\textsubscript{n}/ITO electrodes and polycrystalline Pt (Pt\textsubscript{poly}). For Pt\textsubscript{poly} a true mass activity cannot be calculated, and the “mass activity” reported in the figure is a “top layer mass activity”, i.e., the measured current normalized to the mass of just the top monolayer of the wetted Pt\textsubscript{poly} electrode area, which was estimated using the electrochemically active surface area measured in the same cell and under the same conditions as the Pt\textsubscript{n}/ITO measurements (see Fig. S4a for the Pt\textsubscript{poly} CVs). This top layer mass activity represents an upper limit on the actual Pt\textsubscript{poly} mass activity, but it allows the mass activity of the clusters to be compared to the activity of the exposed surface atoms of a standard Pt electrode.

As noted, Pt\textsubscript{1}/ITO is the least active Pt\textsubscript{n}/ITO electrode, with a mass activity of just $0.06 \pm 0.04$ A mg\textsubscript{Pt}\textsuperscript{-1}. For Pt\textsubscript{4}, Pt\textsubscript{7}, and Pt\textsubscript{8} on ITO, the mass activities are $0.38 \pm 0.10$ A mg\textsubscript{Pt}\textsuperscript{-1}, $0.88 \pm 0.26$ A mg\textsubscript{Pt}\textsuperscript{-1}, and $0.96 \pm 0.26$ A mg\textsubscript{Pt}\textsuperscript{-1}, respectively. The Pt\textsubscript{poly} top layer mass activity was $\sim 0.5$ A mg\textsubscript{Pt}\textsuperscript{-1}. Thus, activity per Pt atom of Pt\textsubscript{4}/ITO was already nearly as high as the activity per surface atom for Pt\textsubscript{poly}, and the activities per atom of the Pt\textsubscript{7} and Pt\textsubscript{8}/ITO electrodes were substantially greater.

**III. Conclusion:**

We demonstrated that the HER activity of small ITO-supported Pt clusters is strongly cluster-size dependent, with Pt\textsubscript{1}/ITO being inactive, and the activity per Pt mass significantly rising from Pt\textsubscript{4}/ITO to Pt\textsubscript{8}/ITO, with Pt\textsubscript{7}/ITO and Pt\textsubscript{8}/ITO having activity per Pt atom roughly double the activity per surface atom for Pt\textsubscript{poly} under the same conditions. Additionally, the clusters present...
H\textsubscript{upd} currents \textit{per} Pt atom roughly twice as large as those reported for bulk Pt or large Pt nanoparticles, equating to adsorption of \~2 H atoms per Pt atom. The large H\textsubscript{upd} currents are consistent with the DFT results, which found open, low Pt-Pt coordination Pt\textsubscript{n}H\textsubscript{x}/ITO structures under electrochemical conditions, with x \~ 2n. The cluster catalysts under electrocatalytic conditions are hence best described as a Pt hydride compound, significantly departing from a metallic Pt cluster.

The use of global optimization techniques and first-principles thermodynamics to predict structural ensembles, factoring in the changing numbers of adsorbates at various electrochemical potentials was also proven to be effective in predicting the observed currents using microkinetic models based on Butler-Volmer-type equations. Low-energy metastable isomers were shown to contribute significantly to the experimentally observed HER activities, sometimes increasing but sometimes decreasing the activity, pointing out the importance of considering the accessible isomer ensembles when simulating properties of sub-nano supported cluster catalysts. On the formed open Pt hydride clusters under potential, HER can occur on a very flat free energy surface.

We analyzed the mechanisms that account for the HER currents for varying cluster sizes and showed that Volmer-Tafel mechanisms combining two proton reductive adsorptions and a non-electrochemical H\textsubscript{2} desorption step dominate. We are also able to better understand the stability of the clusters under reaction conditions with the use of computational thermodynamic analysis and chronoamperometry measurements. This study demonstrates that clusters are stabilized by the H overlayer and only show a small increase of stability with cluster size, in the range n=4-8. The clusters are further anchored to the support by the hydroxyls and oxygen on the ITO surface, which should tend to limit the clusters' ability to diffuse across the surface, thereby decreasing the likelihood that they may sinter.

Small Pt clusters on ITO bind hydrogen strongly, which at first sight can be considered as very unfavorable for HER. However, as shown in this paper, they transform under potential to a hydride compound (PtH\textsubscript{2})\textsubscript{n}, which, in the case of large enough clusters (n=7,8), provide multiple sites with optimal binding energy for H and hence high HER activity. These clusters, exposing all Pt atoms, have high mass activity for HER.

The finding that it is crucial to include the ensembles of accessible metastable structures under reaction conditions to predict catalytic activity correctly is expected to apply to many other types of electrocatalysts where a local rearrangement would produce a slightly less stable but much more
reactive site. Such metastability-induced surface reactivity may be important to not only catalysis but also film growth and surface reactions.

IV. Computational and Experimental Methods

1. Computational Details:

1.1 Model: We have modelled 5% doped ITO (111) as our ITO substrate model, in link with our experiments, as it has been previously reported to provide an optimum tin doping level for the highest carrier density\(^5\), we found that all Sn atoms prefer to locate in the surface layer. For a four-layer slab, with unit cell dimension in the surface plane of 14.65 x 14.65 Å, 8 Sn (5% atom) atoms are present, 4 in the top and 4 in the bottom layer. 3 Sn atoms replace the In atoms in 5 coordinated sites, and 1 Sn atom replaces the In in the 6 coordinated site. The unit dimension in the surface plane for ITO is 14.65 x 14.65 x 60 Å. From our previous study, the surface has 4 H\(_2\)O molecules \textit{per} cell; two are dissociatively adsorbed, and the other two are adsorbed intact. For full details of the surface structure and water interaction with the surface, we refer the reader to our previous work\(^9\). To explore possible adsorption sites and shapes of the Pt\(_n\) (n = 1, 4, 7, 8) clusters, we used the Grand Canonical Basin Hopping (GCBH) global optimization method. The motivation to use basin hopping for our studies was from Sun \textit{et al}\(^{41}\) \textit{and} our previous work\(^9\). The full details of the GCBH method are provided in the SI.

1.2 Total Energy Calculations: All calculations were carried out within the density functional theory framework using the Vienna ab-initio simulation package (VASP)\(^{51,52}\). The electron-ion interactions are treated using the projector augmented wave (PAW) method\(^{53}\). We use the Perdew–Burke–Ernzerhof (PBE) functional to treat the exchange-correlation interactions\(^{54}\). The Gaussian smearing method with a smearing of 0.01eV is used to improve K-point convergence. The valence electronic states are expanded in plane-wave basis sets with an energy cutoff of 500 eV. The Brillouin-zone (BZ) integration is sampled by adopting the Monkhorst–Pack (MP) k-point grids of 5x5x1 for all the surfaces. During the geometry relaxations of the surface, only the outer atoms were allowed to relax. The cell parameters and inner atoms (in a 2 Å thick middle layer) were fixed to those determined for bulk ITO. Inversion symmetry was kept in all calculations to nullify the dipole moment. Structures were relaxed until the force on each atom was less than 0.01 eV/Å\(^{-1}\). Accounting for solvation effects was achieved by exploiting the implicit solvation model implemented by Hennig and co-workers under the name VASPso\(^{55-57}\). The electrochemical potential was modified using a
surface-charging method based on the linearized Poisson–Boltzmann (PB) equation implemented in the VASP solv.$^{56,58}$ This equation allows us to include an idealized electrolyte distribution in the electronic structure computations. This electrolyte distribution also balances the surface charge without correction terms, in contrast to a surface-charging model relying on a homogeneous background charge.$^{59}$ The cavity surface tension was set at 0.00, and the electrolyte concentration within the linearized PB equation was set as 1.0 M. The vacuum for surface charging calculations have been set to 60 Å.

2. Experimental

2.1 Sample electrode preparation: ITO-supported Pt$_n$ cluster working electrodes (Pt$_n$/ITO; $n = 1, 4, 7, 8$) were prepared using a home-built cluster beam deposition/surface analysis instrument described previously.$^{32,33,60,61}$ This instrument consists of a cluster source, a mass-selecting ion beamline, and an ultrahigh vacuum (UHV) end station for cluster deposition and analysis (see the SI for details). The ITO substrates used were 12 mm $\times$ 8 mm $\times$ 1.1 mm. Each ITO substrate was sonicated in 18.2 MΩ cm deionized water and in 95% ethanol, and was cleaned after introduction into the UHV system by Ar$^+$ sputtering and annealing in the presence of O$_2$. This cleaning protocol has been found to leave undetectably low contaminant levels. Pt$_n^+$ clusters were generated by means of laser vaporization, mass filtered to select the desired cluster size, and deposited on the ITO surface at a kinetic energy of $\sim$1 eV/atom and substrate temperature of 300 K. Detailed cleaning and deposition conditions are discussed in the SI. Note that all the electrodes have precisely the same total amount of Pt present (0.434 ng), deposited in the form of different size clusters. This amount of Pt corresponds to 3% of a close-packed monolayer over the 2 mm diameter cluster spot, therefore we refer to the Pt loading as 0.03 ML coverage.

2.2 Electrochemical measurements: CV and chronoamperometry were performed using a bench-top electrochemical measurement system, composed of a three-compartment electrochemical cell with working and Pt counter electrode compartments separated by a glass frit, with the Ag/AgCl leak-free reference electrode housed in the counter electrode compartment, but isolated by its leakless membrane (see Fig. S1). This design minimizes contamination of the working electrode by species produced at the counter electrode or diffusing from the reference electrode. Details are in the SI. After preparation of a size-selected Pt$_n$/ITO working electrode, it was transferred out of the UHV system, and mated to the electrochemical cell, with the 2 mm cluster spot centered in the 4 mm cell opening. A 0.1 M HClO$_4$ electrolyte solution was
injected into the cell compartments, each of which was purged with Ar, bubbled through the electrolyte prior to, and flowed through the cell headspaces during the electrochemical measurements.

The CV measurements were done first (see Fig. S2 for the potential wave sequence applied), followed by the chronoamperometry. All data were recorded at room temperature, which was typically ~21 °C. To facilitate comparison with the computational results, the potentials vs. Ag/AgCl were converted to potentials vs. the standard hydrogen electrode (SHE) (see SI). In these bench-top measurements, the Pt$_n$/ITO electrodes were briefly exposed to air during transfer from the UHV instrument to the bench-top cell, however, results presented below show no evidence of any oxygen reduction or other chemistry associated with adsorbed oxygen.

One question is whether sub-nano Pt clusters are stable with respect to sintering or dissolution under HER conditions. The best evidence in this regard is the observation of substantial effects of the deposited cluster size, and the fact that the size effects are stable in repeated CV cycling. As noted, all the Pt$_n$/ITO electrodes have the same amount of Pt present (1.35 × 10$^{12}$ Pt atoms = 0.434 ng), differing only in the cluster size deposited. Thus, if sintering or other processes (dissolution/re-precipitation) significantly degraded the initial size selection, the cluster size dependence would be unstable. Dissolution would result in loss of activity and sintering or dissolution/reprecipitation would change the size distribution, and therefore cause the size effects to disappear over time. Thus, from the stability of the size effects and activity, we can conclude that the clusters are stable, at least on the time scale examined. This conclusion is consistent with the relatively strong Pt-ITO bonding observed in the DFT calculations.

V. Conflicts of interest

There are no conflicts to declare.

VI. Acknowledgements

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VII. References:


Global Minima + Metastable states $\Rightarrow$ Total Current

$E$ (V vs. SHE)

$i - i_c$ (μA)

High $H_{\text{upd}}$

Pt$_1$

Pt$_4$

Pt$_7$

Pt$_8$

Pt$_{\text{Hx/ITO}}$

H coverage