Restructuring and Hydrogen Evolution on Pt Nanoparticle†

Guang-Feng Wei and Zhi-Pan Liu*

The restructuring of nanoparticles at the in situ condition is a common but complex phenomenon in nanoscience. Here, we present the first systematic survey on the structure dynamics and its catalytic consequence for hydrogen evolution reaction (HER) on Pt nanoparticles, as represented by a magic number Pt44 octahedron (~1 nm size). Using a first principles calculation based global structure search method, we stepwise follow the significant nanoparticle restructuring under HER conditions as driven by thermodynamics to expose (100) facets, and reveal the consequent large activity enhancement due to the marked increase of the concentration of the active site, being identified to be apex atoms. The enhanced kinetics is thus a "byproduct" of the thermodynamical restructuring. Based on the results, the best Pt catalyst for HER is predicted to be ultrasmall Pt particles without core atoms, a size below ~20 atoms.

Introduction

Nanoparticles are common forms or carriers of heterogeneous catalysts1–3 and also of wide application in many other fields, e.g. as biomedical drug delivery agents4 and for energy conversion and storage devices.5 Special physicochemical properties emerged at the nanoscale adding a new complexity in understanding and optimizing reactions on nanoparticles. Compared to chunky crystalline materials, nanoparticles are more flexible in morphology and under reaction conditions, the reshaped nanocatalyst may exhibit a completely different activity, either poisoned or promoted after a so-called induction period.6–9 Despite the vast amount of research on nanoparticle synthesis and morphology control, major gaps in our knowledge still exist, especially with regard to our molecular level understanding on the in situ dynamic restructuring of nanoparticles: this is reflected in our inability to predict whether such restructuring is beneficial or detrimental to catalyst activity. Controlling the nanostructure dynamics for the desirable property, e.g. catalytic activity, is paramount for rational catalyst design and is a general goal in nanomaterial applications.10–11

Pt is a unique metal with high catalytic performance for a wide range of reactions, and it is perhaps the most efficient HER catalyst in electro- and photocatalytic water splitting.12–13 It has been constantly pursued in research to reduce the Pt usage by identifying the optimum particle size for activity. On model single crystalline surfaces, it was however found that HER is only weakly dependent on the crystal facet: the ridged Pt(110) is about two times more active than the (111) and (100) terraces.14–17 On going to the nanoscale, there is no consensus on the particle size effect.18–21 The presence of the particle-support interaction further complexes the understanding of the particle size effect on activity.22 A very recent study by Schweinberger et al. using size-selected Pt nanoparticles supported on Cds nanorods shows that the particle of a critical particle size ~46 atoms (1 nm) can achieve the maximum H2 production, whilst the mass activity is the highest when the particle size shrinks down to the subnanoscale with only 8 atoms (Pt8).23 To date, there is much uncertainty on the physical origin of the HER activity on small nanoparticles. The nature of the active site and the dynamic structural evolution are two key issues that need to be resolved first.

Here we present the first quantum mechanics simulation on the structure dynamics of Pt nanoparticles during HER and quantify its catalytic consequence. The Pt nanoparticle considered in this work is represented by a Pt cluster of ~1 nm diameter, Pt44, which is identified as a magic number size with Oh symmetry. Significant restructuring-induced promotion is revealed on the Pt44 nanoparticle at the HER condition, and theory further predicts that such a promotional effect due to restructuring is prominent only for nanoparticles below ~1.8 nm. In general, the restructuring as driven by the exothermicity of the adsorption of reaction intermediates may or may not increase the active site concentration that depends on the nature of the reaction and also the particle size.
As both nanoparticle restructuring and catalytic reactions are rare events with high barriers, it presents a challenge to computer simulation since the long simulation times of molecular dynamics, or even the use of enhanced sampling techniques, may not be able to capture the desired reaction patterns. For example, in HER on Pt(111), the barrier of H–H coupling to form H2 can be as high as 0.92 eV at the working conditions. The approach we adopt here is to use the first principles density functional theory (DFT) based stochastic surface walking (SSW) global optimization method,\textsuperscript{20–27} SSW-DFT, to explore the Pt nanoparticle morphology at the HER condition. The recently-developed SSW method is able to visit the minima on PES by following likely pathways, and therefore is a powerful tool for both structure prediction and pathway search.\textsuperscript{25} Using the new technique, we are able to stepwise follow the particle restructuring in a H2 atmosphere and determine the HER activity.

Calculation methods

DFT calculation

All SSW calculations and the reaction modelling were performed in combination with the DFT calculations as implemented in the SIESTA package\textsuperscript{28–29} with Troullier–Martins norm conserving pseudopotentials.\textsuperscript{30} The exchange–correlation functional utilized was at the generalized gradient approximation level, known as GGA-PBE.\textsuperscript{31} The optimized double-ζ plus polarization (DZP) basis set with extra diffuse function was employed for metal. The orbital-confining cut-off was determined from an energy shift of 0.010 eV. The energy cut-off for the real space grid used to represent the density was set at 150 Ry. The Quasi-Newton I-BFGS method is used for geometry relaxation until the maximal force on each degree of freedom is less than 0.01 eV Å\textsuperscript{–1}. To correct the zero-point energy for the reaction barrier, the vibrational frequency calculations were performed \textit{via} the finite-difference approach. Transition states (TSs) of the catalytic reaction were searched using the Constrained-Broyden-based TS-searching methods.\textsuperscript{32, 33}

For all the Pt clusters from Pt\textsubscript{12} to Pt\textsubscript{46} (see Fig. S1†), at least four lowest-lying isomers obtained from the SSW-DFT/SIESTA search were further checked using the spin-polarized plane wave calculations with ultrasoft pseudo-potentials\textsuperscript{34} or projected augmented wave\textsuperscript{35, 36} pseudo-potentials, as implemented in VASP.\textsuperscript{37} The plane-wave kinetic energy cut-off of 400 eV was used and the exchange–correlation functional utilized was at the generalized gradient approximation level, GGA-PW91 (ref. 38) and GGA-PBE.\textsuperscript{39} Although small Pt clusters in the gas phase are generally spin polarized, the energy contribution of spin polarization is diminished for clusters above 39 atoms (< 0.03 eV).

SSW calculation

In all SSW simulation, the key parameters utilized are the same with those utilized previously for exploring the PES of carbon and boron clusters,\textsuperscript{25–27} i.e. the Gaussian width being 0.6 Å, the number of Gaussian potential being 10.

To identify the global minimum structure of Pt\textsubscript{x} (x = 12 to 46) (see Fig. S1†), we set the temperature utilized in Metropolis Monte Carlo as being 3000–5000 K. The higher temperature is used to verify the obtained global minimum structure. In the SSW search, we performed four to ten parallel runs and up to 300 minima are collected at the first stage, from which the most stable configuration is obtained. Next, we verified the result from the most stable configuration of the first stage and collected another 300 minima. This process was repeated until no more further stable configurations were identified at the stage of verification.

For the grand canonical Monte Carlo (GCMC) simulation for Pt\textsubscript{44}H\textsubscript{2} system, the basic procedure of the SSW simulation at each fixed H concentration was the same as that described above for pure Pt clusters. In the GCMC simulation, the major difference was that every 300 SSW steps, we evaluated the chemical potential of adsorbed H atom with respect to that of H in the gas phase \(\Delta G_{44}\) (see below in eqn (2)) based on the current most stable configuration. According to the value \(\Delta G_{44} < 0\), we were able decide to accept or refuse the current most stable configuration. To speed up the structure search for reaching the \(\Delta G_{44} = 0\) equilibrium, the newly-arrived H atoms will be always added to the vacant surface sites, e.g. vacant bridge site; the removal of H atoms will always choose the atop H atoms or subsurface H atoms, if present, which are calculated to have the poorest adsorption energy.

The exothermicity of restructuring under HER condition

In HER, the nanoparticle is in the H\textsubscript{2} atmosphere and an equilibrium of H chemical potential needs to be achieved at the steady state. The exothermicity of the H adsorption on the bare nanoparticle provides the driving force of the restructuring. This is measured by \(\Delta G\) per Pt atom with reference to Pt\textsubscript{44} octahedron and H\textsubscript{2} gas (the standard condition is utilized here), as shown in eqn (1).

\[
\Delta G = \left[ G(\text{Pt}_{44}\text{H}_{x}) - G(\text{Pt}_{44}) - x/2G(\text{H}_{2}) \right]/44
\] (1)

Here \(G(\text{Pt}_{44}\text{H}_{x})\) and \(G(\text{Pt}_{44})\) can be computed from DFT directly by including the zero point energy (ZPE) correction, and \(G(\text{H}_{2})\) is the free energy of the gas phase H\textsubscript{2} that can be obtained from standard thermodynamics data.\textsuperscript{39}

Results and discussion

Pt\textsubscript{44} octahedron

In this work, we utilize Pt\textsubscript{44} as the model catalyst for investigating the HER on ~1 nm Pt nanoparticles. Pt\textsubscript{44} is predicted to a magic number size based on the unbiased SSW-DFT global structure search (see ESI discussion and Fig. S1†), which was also suggested previously\textsuperscript{40} by comparing with other putative high symmetry structures of Pt\textsubscript{44}. From the SSW trajectories 4788 minima of Pt\textsubscript{44} were collected and the GM of Pt\textsubscript{44} is found to be a \(O_{h}\) symmetry octahedron with bulk-like face-centered cubic (fcc) packing, exposing only \{111\} facets and containing six core atoms and 38 shell atoms, see Fig. 1. It should be mentioned that Pt\textsubscript{44} is the smallest octahedron of Pt...
nanoparticle with high stability, which exhibits a remarkable structure similarity to the bulk Pt crystal: the average Pt–Pt distances of Pt$_{44}$ is 2.74 Å, being only 2.7% shorter than that in Pt bulk. This affords Pt$_{44}$ to be a good model for understanding nanoparticle behaviour under reaction conditions.

From all the minima of Pt$_{44}$ collected from SSW trajectories, we have constructed the configurational spectrum of Pt$_{44}$ in Fig. 1 to provide insights into the PES of Pt nanoparticle in general. The structures of typical less stable minima are also shown. In general, the conformation of the Pt nanoparticle is discrete at the energy window 0–0.5 eV above GM and becomes continuous-like above 0.5 eV. Most of the low lying structures have a common core–shell feature as the GM with 6 core atoms and 38 shell atoms. The continuous energy spectrum appears just 0.5 eV above GM, indicating that the Pt nanoparticle is highly mobile and the reconstruction of the shell is kinetically allowed even at ambient conditions.

**Structure evolution under HER condition**

To simulate the structure evolution dynamics at the HER conditions, we consider the Pt$_{44}$/H$_2$ system as a grand canonical ensemble where the chemical potential of the adsorbed H atoms will eventually reach equilibrium with that in the gas phase, i.e. $\Delta G_H \rightarrow 0$. $\Delta G_H$ can be calculated as follows,

$$\Delta G_H = \Delta E_{\text{DFT}} + \text{ZPE} - 1/2G(\text{H}_2) \tag{2}$$

where $\Delta E_{\text{DFT}}$ and ZPE are the differential adsorption energy and the zero point energy of the newly-arrived H atom on particle; and $G(\text{H}_2)$ is the free energy of H$_2$ in the gas phase at the standard state. The grand canonical Monte Carlo (GCMC) simulations based on SSW/DFT global structure search (GCMC/SSW-DFT) are thus performed to investigate the structure evolution. This is obtained by adding/subtracting H atoms into/from the system, Pt$_{44}$H$_n$, every few hundred (>300) SSW steps of structure search at a fixed H concentration. In fact, at the initial stage of simulation, the addition of H atoms is always energetically preferable as new vacant sites emerge continuously due to the surface reconstruction where newly-arrived H atoms can adsorb. The simulation reaches equilibrium at the stage of Pt$_{44}$H$_{80}$, when $\Delta G_H$ of newly-arrived H atoms become positive. From the trajectories of GCMC simulation, we selected representative structures at several Pt$_{44}$H$_n$ stages, as shown in Fig. 2, and they are described as follows.

Pt$_{44}$H$_{50}$

Our GCMC/SSW-DFT simulation starts from a Pt$_{44}$H$_{50}$ octahedron, when {111} facets are fully occupied by H atoms (>1 monolayer, ML) and $\Delta G_H$ starts to exhibit an appreciable decrease due to the switch of the adsorption site for H atom. The simulation shows that the particle leaves the octahedron shape immediately after only 3 SSW steps. The initial reconstruction starts by the collective migration of the vertex Pt atoms of the octahedron, thereby exposing {100} facets (see ESI animation-1†). This is simply because {100} facet is able to adsorb more H atoms than {111} and thus is thermodynamically preferred. In the restructuring, the surface atoms including H diffuse around to find the energetically favorable position and as a result, {100} facets emerge by breaking large {111} facets into small {111} microfacets (Fig. 2b). The surface becomes rough. For Pt$_{44}$H$_{80}$, additional SSW runs were performed to understand the restructuring dynamics (see ESI animation-2†). After a long simulation of 2021 SSW steps, Pt$_{44}$H$_{80}$ becomes significantly different from the initial octahedron, possessing 11 {111} and 6 {100} facets (Fig. 2b), although the core–shell structure still remains: Pt$_{44}$H$_{80}$ has 7 core atoms and 37 shell atoms.
Pt_{44}H_{61–80}

With the increase of H coverage, the small \{100\} microfacets start to merge with each other to yield large \{100\} facets, and simultaneously the area of \{111\} facets shrinks. The polyhedron shapes start to reappear as the stable forms and \(\Delta G_{\text{H}}\) gradually approaches to zero. The identified GM of Pt_{44}H_{80} is found to be a C_{2h} tetradecahedron of fcc packing, with 8 \{111\} facets, 6 \{100\} facets and 18 apex Pt atoms (five or six coordinated Pt atoms shared by at least three facets). \(\Delta G_{\text{H}}\) at Pt_{44}H_{80} is \(-0.07\) eV.

The GCMC/SSW-DFT simulation conveys two important messages for the HER-driven nanoparticle restructuring: (i) adsorbed H atoms are always more stable on the surface even when the equilibrium coverage is above 2 ML. Importantly, the subsurface H atoms inside the Pt nanoparticle is found to be unstable (see ESI Fig. S2†) since the stronger Pt–Pt bond is energetically preferred compared to the Pt–H bond in forming the particle core. This implies a high stability of Pt nanoparticles under HER conditions. (ii) The restructuring is driven to maximally expose \{100\} while the core–shell structure of Pt nanoparticles is always kept to minimize the total energy. Only \{100\} and \{111\} facets are present at the GM of Pt_{44}H_{80}. Overall, the core Pt atoms increase from 6 to 8 and the shell Pt atoms decrease from 38 to 36 (the surface density drops) after the restructuring, which is consistent with the typical surface reconstruction observed in surface science studies.41

HER activity

We are now at the position to investigate the HER on the Pt_{44}H_{80} polyhedron. We have considered all the likely reaction patterns for the hydrogen evolution via the coupling of two adsorbed H atoms, H + H \rightarrow H_2, the so-called Tafel mechanism in electrocatalytic HER that is preferable at high H coverage conditions (see our recent work on HER kinetics on surfaces44 where the electrochemical potential and solvation effect have been considered; here we follow the main conclusions obtained there).

Fig. 3a shows that the calculated free energy barriers (\(\Delta G_{\text{a}}\)) of H–H coupling on Pt_{44}H_{80} span from 0.47 to 1.07 eV depending on the local sites. Unexpectedly, \(\Delta G_{\text{a}}\) at the apex sites are 0.47–0.71 eV, which is much lower than that on the \{111\}, edge and \{100\} sites, 0.88, 0.88 and 1.07 eV, respectively. We also noticed that the calculated \(\Delta G_{\text{a}}\) of the H–H coupling on the \{111\} facets of Pt_{44}H_{80} (F1) is in fact similar to that on the extended Pt{111} (–0.9 eV). The optimized structures of the transition state (TS) are also similar in two cases (see ESI Fig. S3†). Similarly, \(\Delta G_{\text{a}}\) at the apex sites of the unreconstructed Pt_{44}H_{48} octahedron (AO) is also in the \(\Delta G_{\text{a}}\) range of the apex sites on Pt_{44}H_{80}. These results indicate that the HER activity can be assessed largely by the local geometry of the Pt site.

By identifying the critical role of apex sites and the local reactivity in HER, we can discuss their implication to HER catalysis. In Fig. 4, we first estimated the HER activity of Pt particles on differently sized as-synthesized nanoparticles at the equilibrium shape in solution, i.e. no restructuring due to H\(_2\) (data taken from experiment and our recent study).42,43 We then
count the apex, \{111\} and \{100\} and edge sites of the particles and sum the overall HER rate (specific activity of HER, SA, mol cm\(^{-2}\) s\(^{-1}\)) on all the sites based on microkinetics, as shown in eqn (3).

\[
SA = 0.5 \times S^{-1} N_A^{-1} \times \sum_{site} (k_B T/h) \exp(-\Delta G_a/RT) \theta_{site}
\]  

(3)

where \(k_B\) is Boltzmann’s constant and \(h\) is Planck’s constant \((k_B T/h = 6.25 \times 10^{-12}\) at 298.15 K from classic TS theory); \(\Delta G_a\) is the estimated free energy barrier statistically averaged according to the data in Fig. 3a, i.e. 0.48 eV for apex sites, 0.88 eV for terrace sites, and 0.89 eV for edge sites; \(\theta_{site}\) is the number of the active sites on the nanoparticles; \(S\) is the surface area. Here we assume the same HER activity at the same type of site based on the fact of local reactivity of HER identified above. The calculated HER rate on the nanoparticle is thus plotted in Fig. 4 black curve, showing the maximum activity around \(-1.8\) nm when the highest concentration of the apex site (per unit surface area) is reached. It should be mentioned that the HER activity estimated in the black curve agrees reasonably with the kinetic data reported in experiment and validates largely the local reactivity of HER identi- 

Conclusions

New DFT-based global optimization theoretical methods allow the observation of the dynamic catalyst structure evolution and the quantification of the activity change of Pt nanoparticles for HER. Unexpectedly, we found that the HER occurs preferentially on Pt low-coordinated apex Pt sites, which totally dominates the activity for Pt nanoparticles. The restructuring of nanoparticles can promote HER, but appreciably only below a certain size threshold, \(\sim 2\) nm, where the apex sites dynamically created can reach the maximum concentration. The subnano Pt clusters without core atoms are predicted to have the highest HER activity.

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Notes and references

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