



Short Communication

Quantum nutcracker for near-room-temperature H₂ dissociation

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Solid surfaces are well known to mediate the dissociation of molecules via electronic interactions (heterogeneous catalysis). In particular, H₂ dissociation on metal surfaces has been widely studied for several decades because it is an important step in hydrogenation reactions. The efficiency of the process depends on both the electronic properties of the metal surface and the surface microstructures [1]. Enhanced efficiency and reduced cost are usually achieved by using nanoparticles, which have increased the surface-to-volume ratio and low-coordination atoms [2]. Another approach is to optimize the local electronic states of the metal surface by doping [3], alloying with other elements [4], or by taking advantage of strong interactions between metal nanoparticles and the supporting substrate [5]. These methods often work together to tailor the adsorption properties on surfaces and show major efficiency enhancement.

Here, we introduce an alternative paradigm for the catalytic dissociation of molecules using H₂ as an example. By employing density-functional-theory (DFT) calculations, we design a “quantum nutcracker” that is predicted to be active for H₂ dissociation at near-room temperature. The quantum nutcracker is composed of two inert components (two nutcracker jaws) that are weakly bonded by van der Waals (vdW) interactions: transition-metal phthalocyanine (TMPc) molecules physisorbed on a metal surface. TMPc molecules show low activity to dissociate H₂. For fundamental science purposes, we investigated the Au(1 1 1) surface because Au is the most inert transition metal for H₂ dissociation [6] (clusters of gold show catalytic activity because of quantum-size effect). We also investigated the Cu(1 1 1) surface, which is also inert at room temperature, while Cu is of course very inexpensive [7].

DFT calculations demonstrate that the quantum cracking process comprises three stages as illustrated in Fig. 1a: H₂ molecules migrate on the surface and enter the channel between the nutcracker jaws, where catalytic H₂ splitting occurs by a cooperative quantum action of the two jaws, followed by the atomic H leaving the jaws.

For the first stage, a dynamic entry barrier caused by up-and-down vibrations of TMPc molecules indicates that H₂ molecules enter the space between TMPc molecules and the metal substrate when the TMPc molecule is at or near its highest excursion from the surface. Our quantum molecular dynamics (QMD) calculations show that this process is mediated by a dynamic energy barrier (0.64 eV for MnPc/Au and 0.80 eV for MnPc/Cu) caused by large up-and-down vibrations of the MnPc molecules, which can be overcome at room temperature (Figs. S1–S6 online).

For the second stage, when an H₂ molecule enters the TMPc/metal interface, it is trapped in-between the jaws of the quantum nutcracker, which we define as the initial state (IS) in the H₂ bond-splitting process. Apparently, without the nutcracker structure, the six TMPc molecules, containing a V, Cr, Mn, Fe, Co, or Ni ion in the center, bind rather weakly with hydrogen molecule (Fig. S7 online). In the nutcracker jaws, the reaction pathway and the evolution of the relative potential energy are presented in Fig. 1b for the four typical systems: MnPc/Au, FePc/Au, NiPc/Au, and MnPc/Cu (other systems shown in Fig. S8a (online) and bond length shown in Fig. S8b (online)). We also show the evolution of the nutcracker system schematically in Fig. 1b. After an H₂ molecule enters into the interface, the TMPc presses the H₂ molecule down towards the Au(1 1 1) surface like a “nutcracker”. As a result of the ensuing quantum interactions, the H₂ molecule breaks up and the dissociated H atoms adsorb at hollow sites of the metal surface (the final state (FS)). For all combinations, the H₂ molecule splitting at the interface is exothermic. The rate-limiting barriers are also shown

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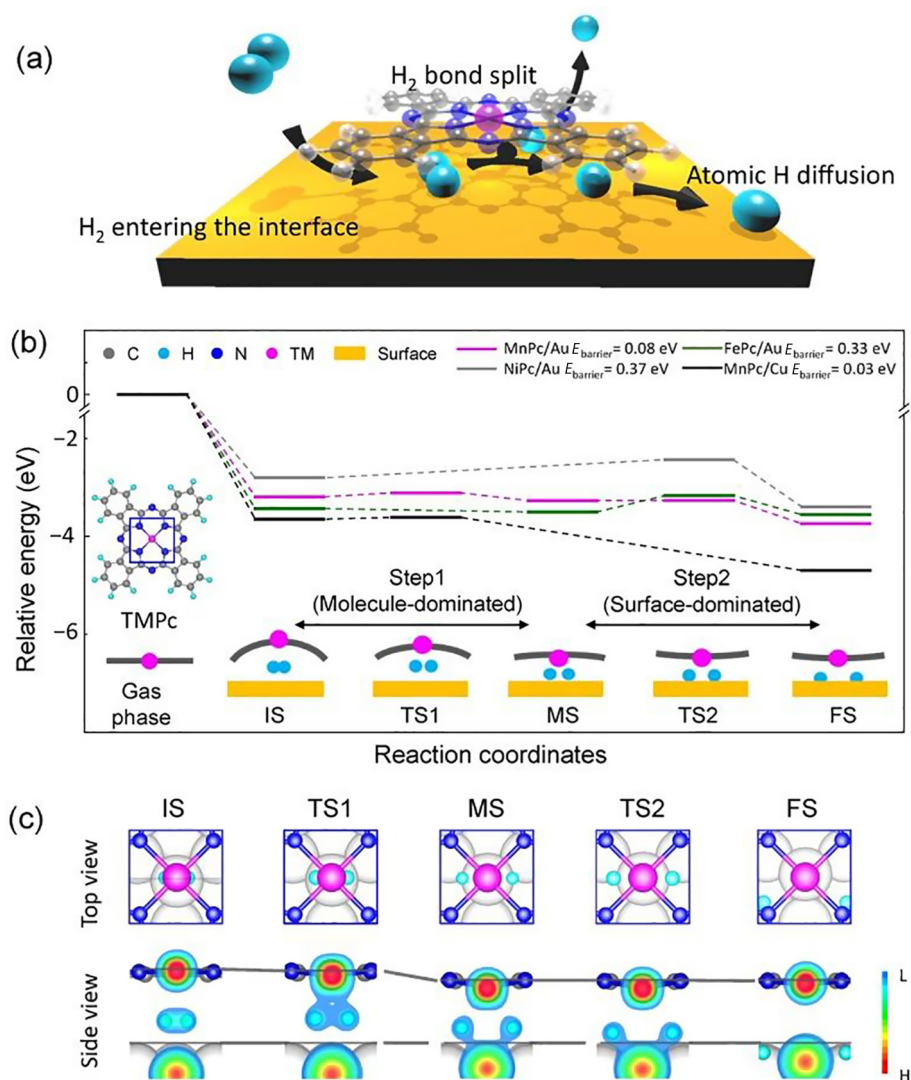


Fig. 1. (Color online) Reaction process of H₂ dissociation at TMPC/metal interface. (a) Schematic diagram of a quantum nutcracker. A quantum nutcracker consists of two inert components as two jaws. The cracking process is divided into the following stages: H₂ entering the interface, dissociation of H₂, and the dissociated H atoms leaving the interface. (b) Potential energy landscape and a schematic side view of the H₂ splitting process. The reference state is set to the gas phase of a H₂, a TMPC molecule and a clean metal surface. (c) Top view of zoom-in structures at different stages of the reaction process in MnPc/Au systems (upper panel). The side views (lower panel) are the corresponding slices (as indicated by the black line in the top view of IS) of electron density across the Mn ion and the Au atom underneath. The black dashed lines in the side view indicate that the two jaws (Mn ions and Au atoms) are getting closer as the H₂ molecule is cracked. The isosurface is 0.09 e/Bohr³. The zoom-in shows that the central Mn atom is the active site.

in Fig. 1b. All the TMPC/metal interfaces act as nutcrackers for H₂ dissociation, while MnPc/Au has the best performance with the least rate-limiting barrier (0.08 eV). It is notable that, although the reaction barrier of MnPc/Cu (0.03 eV) is lower than the barrier of MnPc/Au in the second stage, the overall performance of the MnPc/Cu interface might be compromised due to an increased H₂ entry barrier (0.80 eV, compared to 0.64 eV for MnPc/Au) into the MnPc/Cu interface.

We plot the slices of electron density across the transition metal ion and the surface atom under it for a typical MnPc/Au system in Fig. 1c (others shown in Fig. S9 online). The slices of electron density of different states demonstrate that an H₂ molecule interacts first with the MnPc molecule from IS to MS (metastable state), which can be regarded as a molecule-dominated process, and then interacts with the Au(111) surface from MS to FS, which is a surface-dominated process. The variation of the electron density and the electron density difference in the H₂ bond-splitting process (shown in Supplemental Movies 1 and 2 online) also indicate that, an electron density rearrangement happens between H₂ and Mn in

Step1 and between H₂ and Au in Step2. Compared to IS, the electron accumulation disappears in MS, indicating that the H₂ molecule splits into two isolated H atoms. From MS to FS, the individual H atoms leave the MnPc molecule and adsorb on the Au(111) surface.

The VPc/Au and CrPc/Au systems exhibit the same behavior as the MnPc/Au system as described above: a two-step reaction process in which Step1 is molecule-dominated and corresponds to the rate-limiting step, i.e., the energy barrier has an early transition-state character. The FePc/Au system exhibits a unique behavior: Step1 is barrierless. The CoPc/Au and NiPc/Au systems exhibit a third kind of behavior: Step1 is skipped altogether (no MS state exists) and a single energy barrier with late transition-state character exists between IS and FS, corresponding to what is labeled Step2 in the other systems. Finally, for the MnPc/Cu system, Step2 is skipped and the feature of transition state is similar to the TS1 in the MnPc/Au system.

We analyze the reaction pathway and the slices of electron density, and find that the trend can be understood according to the

universality principle in heterogeneous catalysis, namely the Brønsted-Evans-Polanyi relation [8]. At IS and TS1, the total energy relative to the gas phase for the CrPc system is higher than MnPc by ~ 1.2 and 1.4 eV, respectively. In addition, the difference in binding strength is illustrated by the electron density overlap between H_2 and transition-metal ions for TS1 in Fig. S9 (online), indicating a weaker interaction between H_2 and TMPc in CrPc/Au than that in MnPc/Au. Therefore, the H_2 dissociation barrier for CrPc/Au is larger than that for MnPc/Au in TS1. As for FePc, the total energy relative to the gas phase is around 0.2 eV lower than that for MnPc at both IS and MS in Fig. 1b, and the electron density overlap between H_2 and transition-metal ions also illustrates stronger interactions between H_2 and TMPc in both IS and MS for FePc/Au than that for MnPc/Au system. This stronger interaction between H_2 and FePc in MS results in a larger barrier for FePc/Au than that for MnPc/Au in TS2. As for NiPc, the slice of electron density does not show obvious interaction between the Ni ion and H_2 , resulting in a single-barrier process with the highest H_2 dissociation barrier. For MnPc/Cu, the slices of charge density at different states indicate a similar mechanism as MnPc/Au except that the Cu substrate is more engaged than Au in the reaction because its d orbitals are closer to the Fermi energy, making the interaction between Cu and H_2 stronger than that between Au and H_2 at IS and MS states. Therefore, MnPc/metal has an optimal interaction strength between the two jaws and H_2 , whereas VPC, CrPc and NiPc are too weak, and FePc and CoPc are too strong.

Electronic structure calculations clearly reveal how the optimal interaction strength between the electron orbitals of the transition-metal ion and the H_2 molecule makes MnPc/Au the best H_2 dissociation catalyst among all TMPcs in the Au-based quantum nutcracker systems. The projected density of states (PDOS) of CrPc/Au, MnPc/Au and FePc/Au in Fig. S10 (online) indicate that the cooperative interaction contributed by the TM ion d_{xz} and Au d_{xz} orbitals facilitates the H_2 splitting. Moreover, the d orbital rearrangement during the reaction process plays a significant role in the H-H bond breaking. The cooperative quantum nutcracker system increases the activity in terms of out-of-plane d_{z^2} and d_{xz}/d_{yz} rearrangement in the TMPc molecule. At IS in Fig. S10 (online), the major peaks at the Fermi level for CrPc/Au and MnPc/Au are d_{z^2} and d_{xz} orbitals, respectively. At TS1, compared to CrPc/Au, H-H is more stabilized in MnPc/Au as indicated by the d_{xz} orbital's larger shift toward lower energy. The PDOS also shows the origin of strong binding between H_2 and FePc at IS: the degenerate d_{xz}/d_{yz} orbitals split completely and d_{xz} strongly hybridizes with the H_2 antibonding state whereas the d_{z^2} orbital is almost absent. As a result, there is no activation barrier from IS to MS. In conclusion, the d orbital rearrangement of TMPc molecules determines the catalytic activity of the quantum nutcracker.

For the final stage, QMD simulations indicate that the dissociated H atoms on the Au(1 1 1) surface can leave the MnPc/Au interface at room temperature (binding energy for a H atom at the interface is 0.11 eV lower than on Au(1 1 1) surface. QMD result of the variation of H_2 bond length is in Fig. S11 online). Overall, the combination of TMPc and metal can be regarded as a quantum nutcracker for H_2 dissociation. Evidently, Step1 is the rate-limiting step in the H_2 splitting process and the pertinent barrier (83 meV) is much lower than the barrier of H_2 dissociation on a pure Au(1 1 1) surface. The significantly lowered barrier indicates that, once an H_2 molecule enters the MnPc/Au interface, the splitting can easily happen at room temperature. We note, however, that the overall rate-limiting step for the H_2 dissociation process is the entry of an H_2 molecule into the MnPc/Au interface as discussed above.

Finally, we checked the possible poisoning of the quantum nutcracker by considering H atoms adsorbed on MnPc. Indirect exper-

imental evidence indicates that H_2 molecules do split in the presence of manganese-phthalocyanine (MnPc) molecules adsorbed on Au(1 1 1), and the dissociated hydrogen atom stays on top of the MnPc molecule [9,10]. We found that the nutcracker catalytic systems remain active. The H_2 splitting barrier increases from 83 to 419 meV in the case of MnPc/Au and from 30 to 103 meV in the case of the MnPc/Cu systems (Fig. S11 online).

In summary, a quantum-nutcracker consisting of two inert components is proposed for near-room-temperature H_2 dissociation. In the quantum nutcracker, TMPc molecules bond to a noble-metal surface by vdW interactions. The quantum nutcracker can be an active H_2 dissociation catalyst. The entire dissociation process has been described by DFT calculations and QMD simulations: H_2 molecules adsorb and diffuse on the surface, then enter at the TMPc/metal interface where they dissociate by the nutcracker action, and, finally, dissociated H atoms diffuse away from the interface. The H_2 dissociation reaction can happen at or near room temperature. We report the most detailed analysis of results for the TMPc/Au systems. DFT calculations reveal that cooperation between the d orbitals of TMPc and Au(1 1 1) plays an important role. Various $3d$ TMPc molecules on Au(1 1 1) have been tested. All the $3d$ TMPc are active, while MnPc shows the best performance in the nutcracker systems. The d orbital rearrangement determines the catalytic activity of the quantum nutcracker by rendering different interaction strengths between the metal ion of TMPc and H_2 molecule. The Au(1 1 1) surface can be replaced by a less expensive Cu(1 1 1) substrate with similar performance. We checked possible poisoning of the nutcracker by H atoms adsorbing on the TMPc molecules and found that the catalyst remains active, especially for the case of Cu substrate. Our design of the quantum nutcracker shows promise for developing inexpensive, high-performance heterogeneous catalysts by using the flexibility of vdW-bonded systems.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scib.2018.11.005>.

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