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Hydrogen-triggered metal filament rupture in Cu-based Resistance Switches

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Abstract

Cation based resistance switches have been considered as promising candidates for memory cells and other novel devices. So far, the most accepted switching processes of such devices are based on the formation/rupture of metallic filaments between two electrodes. Although many recent studies have identified the existence of H₂O (and resulting -OH groups) in such devices, their effects on the switching process are still unclear. In the present work, by taking Cu/Ta₂O₅/Pt device as an example, we have theoretically revealed that H ions may dissociate from -OH groups and accumulate onto the Cu filament in amorphous Ta₂O₅. After that, the adsorbed H ions will induce a series of changes, such as the elongation of the adjacent Cu-Cu bonds, the weakening of the Cu-Cu bonds, the increase of charge on Cu cations, and the enhancement of diffusivities of Cu cations, all of which eventually lead to the rupture of the Cu filament. Interestingly, our proposed “H-triggered metal filament rupture” model is similar to the

widely studied “hydrogen embrittlement phenomenon”. The crucial point of this model is the high catalytic activity of Cu towards the splitting of -OH group. Consequently, it is expected that this model could be applicable to other Cu-cation based resistance switches.

Keywords: Resistance switch; First-principles simulation; Rupture of metal filament; Hydrogen Embrittlement.

1. Introduction

In recent years, resistance switches have been considered to be one of the most promising candidates as the next generation memory cells and neuromorphic devices, mainly due to their low power consumption, high read/write speed, size scalability and other advantages.^[1-4] Resistance switches are composed of sandwich structure (electrode/insulator/electrode), in particular, the devices with the amorphous metal oxides (such as TaO_x^[5], NbO_x^[6], HfO_x^[7], AlO_x^[8]) as the insulator layer show excellent performance. The resistive switching processes of such devices are mainly due to the diffusion of active ions (such as metal cations, oxygen anions or positive charged oxygen vacancies) in the insulator layer under the electric field and/or Joule heating effects, which results in the formation (low resistance state, SET) or rupture (high resistance state, RESET) of conductive filaments (CF) between two electrodes.^[8-10]

However, so far, resistance switches have never been widely realized commercially. One of the main reasons for this is the lack of the full understanding on their switching mechanism. Although many experimental works have been carried out to understand the switching processes, it is still difficult to observe the diffusion of ions (especially H ions) in resistance switches since the switching processes occur at the nanosecond level. Therefore, at present, the switching processes (especially the rupture process of as-formed CF) are still unclear, which has become the key factor restricting the development of resistance switches.^[11,12]

Among all the metal-oxide based resistance switches, amorphous TaO_x (a-TaO_x) based devices are considered to be the most promising. This is mainly due to its advantages of fast switching speed, long service life and low operating voltage. In particular, the Cu/Ta₂O₅/Pt resistance switch has been widely studied. The generally accepted switching mechanism of such device is as follows: when applying the electric field with different polarities, the Cu cations generated at the interface of Cu/Ta₂O₅ will migrate in Ta₂O₅ under different directions, accompanied by the formation and rupture of the Cu filaments between two electrodes, so that the device can realize resistive switching. Tsuruoka et al. experimentally revealed that the rupture of Cu filament is mainly due to Joule-heating effect,^[13] Wang et al. showed that the rupture of Cu filament is mainly caused by the diffusion of Cu cations on the surface of Cu filament,^[14] Pan's and Liu's research groups proposed that the growth direction of the metal filament depends on the diffusion rate of Cu cations in the insulator layer.^[15,16] Our previous theoretical studies confirmed the ionization of Cu at the Cu/Ta₂O₅ interface,^[17] the moisture effect on the diffusion of Cu cations in Ta₂O₅,^[18] the diffusion behavior of Ta/O in a-TaO_x,^[19] and proposed the atomic structure of Cu filament.^[20]

However, so far, the studies on the switching mechanism of Cu/Ta₂O₅/Pt device mainly focuses on the behavior of Cu cations, while ignoring the role of other ions in the switching process. Experiments showed that a-Ta₂O₅ is nanoporous, and the water in the environment is easily adsorbed on its nanopore surface.^[5,21] In this regard, previous studies have revealed that the diffusion of Cu cations occurs along the nanopore structures in a-Ta₂O₅ adsorbing by water, so there will be water around the as-generated Cu filament. On the other hand, it is well known that the Cu surface could catalyze the water dissociation, and the as-generated protons could diffuse easily on the surface of the Cu.^[22] In addition, the interstitial hydrogen could also diffuse fast in the Cu.^[23] Huang et al. recently showed that the H₂ bubbles will be generated on the top surface of Cu electrode during the switching process of such device.^[24] Tsuruoka et al. experimentally revealed that H ions were generated via the electrochemical reaction of adsorbed water in such device.^[25] All the above results indicate the existence of H ions in such a device.

It is worth noting that if there are H in metal, the bonding strength between the metal atoms will become weak, accompanied by the decohesion of metal atoms, which eventually leads to the fracture of the metal. This is the so-called "hydrogen embrittlement (HE)" phenomenon which has been proposed in the industry field several decades ago and has been widely studied till now.^[26] Recently, Yin et al. further confirmed that the existence of H ions would lead to the rupture of pure metal nanowires easily;^[27] Zhang et al. revealed that the presence of H ions in Cu electrode could weaken the Cu-Cu bond and eventually results in the restructuring of Cu (100) surface.^[28]

Based on the discussions above, we believe that the RESET process of Cu/Ta₂O₅/Pt device (i.e., rupture of Cu filament) is most likely triggered by H ions. To confirm this point, in the present theoretical work, we have studied the behavior of H ions in such a device, and its effects on the rupture process of Cu filament. Finally, we propose a "H-triggered metal filament rupture" model to understand the RESET process of Cu/Ta₂O₅/Pt device, which could be applicable to other Cu-cation based resistance switches.

2. Calculation Methods

All calculations were performed using the Vienna *ab initio* simulation package (VASP).^[29] The projector augmented-wave (PAW)^[30] method and the generalized gradient approximation (GGA) in the PW91 form^[31] were adopted to describe the atomic core electrons and electron-electron interactions, respectively. Considering the large number of atoms in the systems (> 100 atoms), the geometries were fully optimized until the forces on each atom is less than 5 eV/pm. The Brillouin zone integration was sampled by $1 \times 1 \times 2$ and $2 \times 2 \times 4$ *k*-grids for geometry optimizations and electronic properties calculations, respectively. Molecular dynamics (MD) simulations were carried out at 1000 K using the NVT ensemble with a time step of 1.5 fs. The Nose-Hoover thermostat was used for temperature control.

3. Results and Discussion

To verify the crucial role of H ions during the rupture process of Cu filament in Cu/Ta₂O₅/Pt resistance switch, we first examined the effect of H ions on the stability of pure Cu nanowire. By taking Cu nanowire with the interlaced trigonal packing structure as an example (Figure 1a, left), we have considered the most probable adsorption sites for one H ion. It is found that the H ion prefers to locate on the top of Cu triangle site by forming three H-Cu bonds as shown in Figure 1b (left). It is noted that energy differences among all the considered H-adsorption sites are very slight (within 0.03 eV), which implies that the H ion may occupy the adsorption sites with nearly equal probabilities. For the second H ion, it tends to locate in the adjacent site of the first H ion as shown in Figure 1c (left), which means that the H ions prefer to accumulate together on the surface of Cu nanowire. In particular, the atomic structure of Cu nanowire undergoes the obvious deformation after the adsorption of second H ion. It is noted that the lengths of Cu-Cu bonds around the H ion adsorption-sites are elongated by about 3 and 9 pm in the cases of one H (1H)- and two H (2H)-doped Cu nanowire, respectively, as shown in Figure S1a. This means that the Cu-Cu bonds in this region are weakened, which may result in the instability (or rupture) of Cu nanowire.

To verify this point, MD simulations at 1000 K (the rupture temperature of Cu filament in Cu/Ta₂O₅/Pt device)^[13] were performed on pure, 1H- and 2H-doped Cu nanowires, respectively. As shown in Figure 1a (right), the pure Cu nanowire sustains its one-dimensional structure after 75 ps MD simulation, while both the 1H- and 2H-doped Cu nanowires have already been ruptured after the MD simulations as shown in Figure 1b and 1c. Specifically, the ruptures of 1H- and 2H-doped Cu nanowires occur at the simulation times of 36 and 19 ps, respectively. The calculated mean squared displacement (MSD) of Cu in pure, 1H- and 2H-doped Cu nanowires are shown in Figure 1d. It is found that, with the presence of H ion(s), Cu atoms tend to accumulate together to form the big clusters during the first 34 and 13 ps in the cases of 1H- and 2H-doped Cu nanowires, respectively. Interestingly, the diffusivities of Cu atoms in the nanowires could be obviously enhanced with the presence of H ion(s), especially in the case of 2H, which is due to the elongation of Cu-Cu bond and the weakening of Cu-Cu bond strength. After the next several ps, the

H-doped Cu nanowires will be ruptured. Based on the results above, we could conclude that the presence of H ions on Cu nanowire could weaken the Cu-Cu bond strengths and enhance the diffusivities of Cu, which eventually results in the rupture of Cu filament. After that, the Cu atoms in ruptured Cu filament tend to accumulate together to form the big sphere-shape cluster, which is due to the decrease of surface Gibbs free energies during this process. Interestingly, such H-triggered rupture of metal nanowire is similar to the hydrogen embrittlement (HE) phenomenon as has been proposed and widely studied in the metallurgical field.^[26,27] Even though the detailed process for HE is not necessarily clear so far, one mechanism that can be responsible for HE is H-enhanced decohesion mechanism (HEDE).^[32-34] The HEDE was proposed based on the weakening of the metal bonds and the decrease of cohesive strength in presence of H ions, which eventually results in the fracture of metal. Such HEDE mechanism is similar to our proposed H-induced metal filament rupture model. As mentioned in previous studies,^[13,20] the atomic structure of Cu filament in the amorphous Ta₂O₅ is similar to the pure Cu nanowire. Thus, the occurrence of HE-like phenomenon during the rupture process of Cu filament in Cu/Ta₂O₅/Pt resistance switch is not surprising.

We should note that the models based on the pure Cu nanowires employed above are very simple, and it is necessary to verify the H-triggered Cu filament rupture process by considering the real chemical environment in Cu/Ta₂O₅/Pt device. It has been theoretically and experimentally suggested that the Cu cations prefer to diffuse along the a-Ta₂O₅ nanopore surfaces covered by water, and thus the as-formed Cu filament in a-Ta₂O₅ is actually surrounded by the -OH groups.^[5] However, it is questionable whether this physical model is the final state or only the intermediate. It is well known that Cu has the ability to catalyze the cleavage of O-H bond, and the as-formed H ion could easily diffusion on the Cu.^[22,23] This gives us the hint that the -OH groups around the Cu filament could split up, and the resulting H ions would diffuse around the Cu filament. It is noted that, during the switching processes, the formation/rupture of Cu filament in a-Ta₂O₅ mainly occurs within the thinnest part (composed by only several atoms). Accordingly, we have previously constructed the atomic structures of Cu filaments with

various diameters in a-Ta₂O₅ (Ta₃₂O₈₀Cu_x, with *x* values from 6 to 12) via the MD simulations,^[20] which could well explain the experimental phenomenon.^[35]

In this context, by taking the a-Ta₂O₅ with the thinnest Cu nanowire (a-Ta₃₂O₈₀Cu₆, in Figure 2a) as an example, we first examined the preferable location of one single H ion in a-Ta₃₂O₈₀Cu₆. The lattice parameters for a-Ta₃₂O₈₀Cu₆ are as follows: *a* = 15.86, *b* = 16.30, *c* = 8.40, *alpha* = 87.08, *beta* = 91.41, *gamma* = 123.86. In doing so, the most probable H-doping sites have been considered, including all the O sites and on the Cu filament. Note that the Ta sites were not considered since most of them have been saturated by O atoms. By taking the most stable structures as the reference energies, the corresponding relative energies for all the considered structures and the most stable adsorption structures for 1H and 2H on Cu filament are shown in Figure 2a and 2b, respectively. It is expected that the H ion prefers to adsorb on the Cu filament, but not the formation of -OH group, which means that the migration of H in -OH group to the surface of Cu filament is thermodynamically feasible process. To further confirm this point, we have calculated the energy barriers of such O-H splitting process in the a-Ta₃₂O₈₀Cu₆H system by using the Climbing Image Nudge Elastic Band Method (CI-NEB).^[36] To do this, the first 8 energetically most stable a-Ta₃₂O₈₀Cu₆H structures with the formation of H-Cu bonds were considered as the final structures, and their adjacent O-sites (forming H-O bonds) were considered as the initial structures. As shown in Figure 3, all the calculated energy barriers for the migration of H from O to Cu filament are lower than 0.36 eV, which are easily overcome even at room temperature. In contrast, the reversed H migration processes (from Cu nanowire to the adjacent O) have to overcome the high energy barriers ranging from 0.90 to 1.40 eV, which are hard to take place. The detailed 8 reaction pathways can be found in Figure S2 in the supporting information. In this regard, the -OH group on Cu filament is energetically unstable and prefers to split into -O and -H. In addition, we have considered the doping of the second H into the a-Ta₃₂O₈₀Cu₆H system, and the most probable H-doping sites have been considered (including all the O sites and on the Cu filament). The results revealed that the second H prefers to adsorb on the Cu filament adjacent the first H, which is consistent with the case in pure Cu nanowire as has been

mentioned above. To further verify this point, we have considered the adsorption of two H ions on the Cu filament with even long length in α -Ta₂O₅, which will be discussed later. Based on the results above, we could say that the as-formed Cu filament in Cu/Ta₂O₅/Pt device is actually covered by H ions, which prefer to accumulate together, and eventually result in the high H contents in certain part of Cu filament.

Next, let's consider the effects of H ion on the Cu-Cu bond strength and the Cu diffusivity in Cu filament. To do this, we first examined the most stable atomic structures of Cu nanowires in α -Ta₂O₅ with and without the presence of H ion(s). As shown in Figure S1b, the Cu-Cu bond lengths adjacent the H-site(s) become longer than those without the presence of H ion(s). The most obvious increases of Cu-Cu bond lengths are from the 2.42 Å (without H), to 2.54 and 2.59 Å (with the presence of 1H and 2H). Accordingly, the Cu-Cu bonds have been weakened after the doping of H ion(s), especially in the case of 2H-doped Cu nanowire. To further confirm this point, we have examined the effects of H ion(s) on the averaged Cu-Cu bond lengths of Cu filament in α -Ta₂O₅ during the MD simulations at 1000 K (with the time step 1.5 fs and total time 75 ps). As shown in Figure 4a, the values of averaged Cu-Cu bond lengths dramatically increased during the initial stage of MD simulation because of the high simulation temperature, and then become stable after about 40 ps. The corresponding values are about 2.48, 2.51 and 2.53 Å in the systems of α -Ta₃₂O₈₀Cu₆, α -Ta₃₂O₈₀Cu₆H and α -Ta₃₂O₈₀Cu₆H₂, respectively. All the above results revealed that the Cu-Cu bond length could lengthen with the presence of H ion(s), which results in the weakening of Cu-Cu bond strength.

Next, we have calculated the MSD of Cu cations in the above systems as shown in Figure 4b. To obtain the diffusion coefficients of Cu cations, according to He et al.'s study,^[37] the initial ballistic region in the MSD should be excluded with the cutoff value of $0.5a^2$, where a is the Cu-Cu distance (~ 2.40 Å). The last part of MSD also needs to be excluded in view of its relatively large statistic errors. To do this, the cutoff simulation times were selected to ensure the R^2 values in fitting the slopes of MSD are approximate to 1, i.e., 50 and 30 ps in the cases without and with the H ion(s) in our systems. As a result, the calculated diffusion coefficients for the Cu cations of Cu nanowires in α -Ta₂O₅ without, and with the

1H- and 2H-doped cases are 6.20×10^{-6} , 7.04×10^{-6} and 7.59×10^{-6} cm²/s at 1000 K, respectively, which confirms that the diffusion of Cu cations could be enhanced with the presence of H ion(s).

It is noted that only the temperature (or joule heating) effect is considered in the above simulations, while another important factor to affect the diffusion of Cu in the real device is the applied electric field. It is known that the diffusivities of cations under the electric field could be enhanced by the decrease of electrons on them. In this regard, we have calculated the Bader charges on each Cu in a-Ta₃₂O₈₀Cu₆, a-Ta₃₂O₈₀Cu₆H and a-Ta₃₂O₈₀Cu₆H₂ systems. As shown in Figure 5, the number of electrons on the Cu cation obviously decreases after its bonding with H ion. Accordingly, we could say that the presence of H ions in the Cu filament of Cu/a-Ta₂O₅/Pt device could not only weaken the Cu-Cu bond strength, but also increase the charges on the Cu, both of which could enhance the diffusivities of Cu cations.

However, we should note that the rupture process of Cu filament in Cu/a-Ta₂O₅/Pt with and without the presence of H ion(s) were not found in the above MD simulations, which is mostly due to the short lengths of Cu filaments in the above model systems. To overcome this, a-Ta₃₂O₈₀Cu₆ structure was repeated twice in its *c* direction to construct a larger model (a-Ta₆₄O₁₆₀Cu₁₂), followed by the structure optimization as shown in Figure 6a (left). In the 1H-doped case (a-Ta₆₄O₁₆₀Cu₁₂H), the most stable H adsorption site was directly taken from the a-Ta₃₂O₈₀Cu₆H system in view of their similar atomic structures (Figure 6b, left). On the other hand, in the case of 2H (a-Ta₆₄O₁₆₀Cu₁₂H₂), we have considered the most probable adsorption sites for the second H on the Cu nanowire of a-Ta₆₄O₁₆₀Cu₁₂H. The most stable adsorption structure is shown in Figure 6c (left), which further confirmed that the H ions prefer to accumulate on the Cu filament. Based on these models, the MD simulations at 1000K were carried out. As shown in Figure 6 (right), the Cu filament without H ions sustained its one-dimension structure after 75 ps MD simulation, while the Cu filaments in the 1H- and 2H-doped cases were ruptured after 30 and 6 ps MD simulations, respectively. The results further confirmed the occurrence of HE phenomenon during the rupture process of Cu filament in Cu/Ta₂O₅/Pt device.

Now, we would like to discuss the charge states of H ions in this work. For this purpose, the Bader charges were examined for H ion(s) located in various chemical environments (including Cu-site in pure Cu nanowire, Cu- or O-site in one Cu doped $a\text{-Ta}_{32}\text{O}_{80}$, Cu- or O-site in Cu nanowire doped $a\text{-Ta}_{32}\text{O}_{80}$ and $a\text{-Ta}_{64}\text{O}_{160}$). Obtained net Bader charge values were listed in Table S2. It is found that the net charges of respective H ions in H-Cu bonds are between -0.20 and -0.37 e (e: elementary charge), while the net charges of H ions bonded with O are between +0.54 and +0.72 e. Accordingly, the calculated Bader charges of H ions have large variation in the current systems. It is noted that the determination of the exact charge state of H ion may be not straightforward, because separation of continuous charge distribution into atomic charges has some ambiguity and we examined only Bader charges.

Next, we would like to comment on our simulation model. In the real device, the structure of Cu filament is formed by the assistance of defects and not a straight atomic chain. However, clarifying the structure of Cu filament experimentally is very difficult, and under the lack of experimental data on its atomic arrangement, the computational cost to explore its structure is beyond our available computational resources. Therefore, we adopted the $a\text{-Ta}_{64}\text{O}_{160}\text{Cu}_{12}\text{H}_x$ structures to examine the effect of H cations on the stability of Cu filament. This model is still very simple compared with the real situation in RRAM devices. However, since both the Cu-Cu bonding and effects of surrounding $a\text{-Ta}_2\text{O}_5$ are included, we expect that the essence of the phenomenon can be captured in this model. In addition, we have examined only the stoichiometric case, i.e., Ta_2O_5 , and the deviation from this composition (or the present of defects) may have considerable influence on the stability of Cu filament. However, simulations to get conclusive results on this issue will be very time consuming, thus we leave the confirmation using a more realistic model as a future task. On the other hand, in our model adopted in the present study, the chemical environment of each Ta or O in $a\text{-Ta}_2\text{O}_5$ is not identical because of the inherent structural properties of amorphous material. In this sense, we can say that the influences of defects on the stability of Cu filament have been considered in the present study in some extent. We also note that the $a\text{-Ta}_{32}\text{O}_{80}\text{Cu}_6$ structure used in the present work was the same as the one used in our previous study,^[20] the structural features of

which agree with the experimental result, and the Cu filament in this structure was stable during the MD simulation for 75 ps at 1000 K. Based on the above discussions, we expect that simulations based using our model structure can reflect the experimental phenomena well.

Finally, we would like to discuss the applicability of our proposed “H-triggered metal filament rupture” model to other resistance switches. Based on the above discussions, this model would be valid when the following conditions are satisfied simultaneously, (i) the formation of metal filament in the metal-oxide film; (ii) the high catalytic activity of metal filament towards O-H bond. The first condition could be satisfied in most of cation-based resistance switches, since the precipitation of metal and subsequent filament formation have been observed in the amorphous metal-oxide films in such resistance switches. On the other hand, not all the cation based resistance switches could satisfy the second condition. For example, it is well known that Ag, which has been widely used as the active metal electrode in cation based devices like Cu, exhibits poor catalytic activity towards O-H bond.^[22,38] Accordingly, we infer that the H-triggered metal filament rupture could most likely to take place during the RESET process in Cu-cation based resistance switches but may not in Ag-cation based ones.

4. Conclusions

In the present work, we have studied the water effect on the RESET processes of cation-based resistance switches. By taking Cu/Ta₂O₅/Pt device as an example, we revealed that Cu filament exhibits the high catalytic activity for splitting its adjacent -OH groups, accompanied by the adsorption and accumulation of H ions on the Cu filament. Such process is feasible in both kinetics and thermodynamics. Subsequently, adsorbed H ions will trigger the rupture of Cu filament because of the elongated Cu-Cu bond length, weakened Cu-Cu bond strength, increased charges on Cu cations, and enhanced diffusivities of Cu cations. Accordingly, we proposed a “H-triggered metal filament rupture” model to understand the RESET process of Cu/Ta₂O₅/Pt. It is noted that, except Cu/Ta₂O₅/Pt device, the existence of -OH groups

and the formation of metallic filaments have been verified in many other cation-based resistance switches with the insulator composed by amorphous oxides. Accordingly, it is expected that our proposed model could be applicable to other Cu-cation based resistance switches.

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Figure Captions

Figure 1. The atomic structures for the (a) pure, (b) 1H- and (c) 2H-doped Cu nanowires before and after the MD simulations at 1000K, and (d) the corresponding mean square displacements for Cu.

Figure 2. The relative energies and the corresponding most preferable sites for the doping of (a) one, and (b) two H ions in the most probable sites of a-Ta₃₂O₈₀Cu₆.

Figure 3. The energy barriers for the migration of one H ion from Cu sites to its adjacent O sites in a-Ta₃₂O₈₀Cu₆.

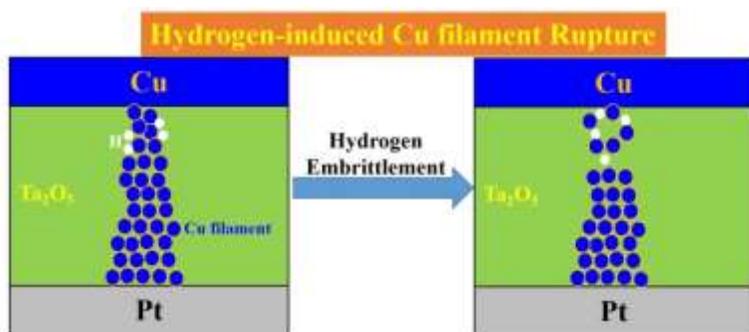
Figure 4. The averaged Cu-Cu bond lengths (a), and the mean square displacements (b) during the MD simulations at 1000 K for pure, 1H- and 2H-doped a-Ta₃₂O₈₀Cu₆.

Figure 5. The Bader charges on each Cu cations in pure, 1H- and 2H-doped a-Ta₃₂O₈₀Cu₆.

Figure 6. The atomic structures for (a) pure, (b) 1H- and (c) 2H-doped a-Ta₆₄O₁₆₀Cu₁₂ before and after MD simulations at 1000 K.

Cation based resistance switches have been considered as the promising candidates for memory cells and other novel devices. So far, the most accepted switching processes of such devices are based on the forming/rupture of metallic filaments between two electrodes. Although many recent studies have identified the existence of H₂O (and as-resulted -OH groups) in such devices, their effects on the switching process are still unclear.

In the present work, by taking Cu/Ta₂O₅/Pt device as an example, we have theoretically proposed that the H ions take the very important role during the rupture process of Cu filament in such device. Interestingly, our proposed “H-triggered metal filament rupture” model is similar to the widely studied “Hydrogen Embrittlement” phenomenon in the industry field, which serves as additional evidence supporting the credibility of such model. The crucial point of mechanism of this model is considered to be the high catalytic activity of Cu towards the splitting of -OH group. Consequently, it is expected that this model could be applicable to other Cu-cation based resistance switches.



Graphical Abstract

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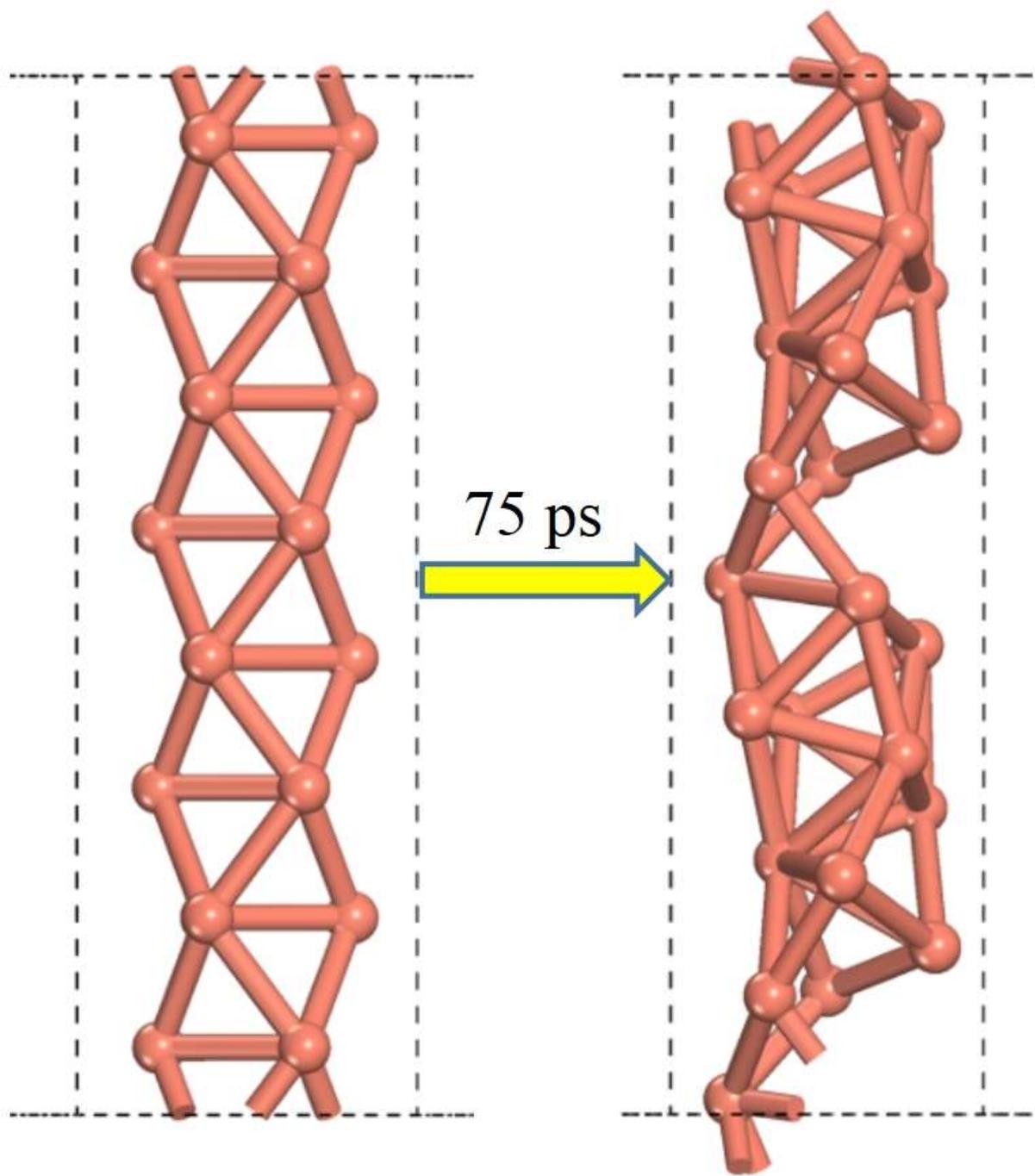


Figure 1a

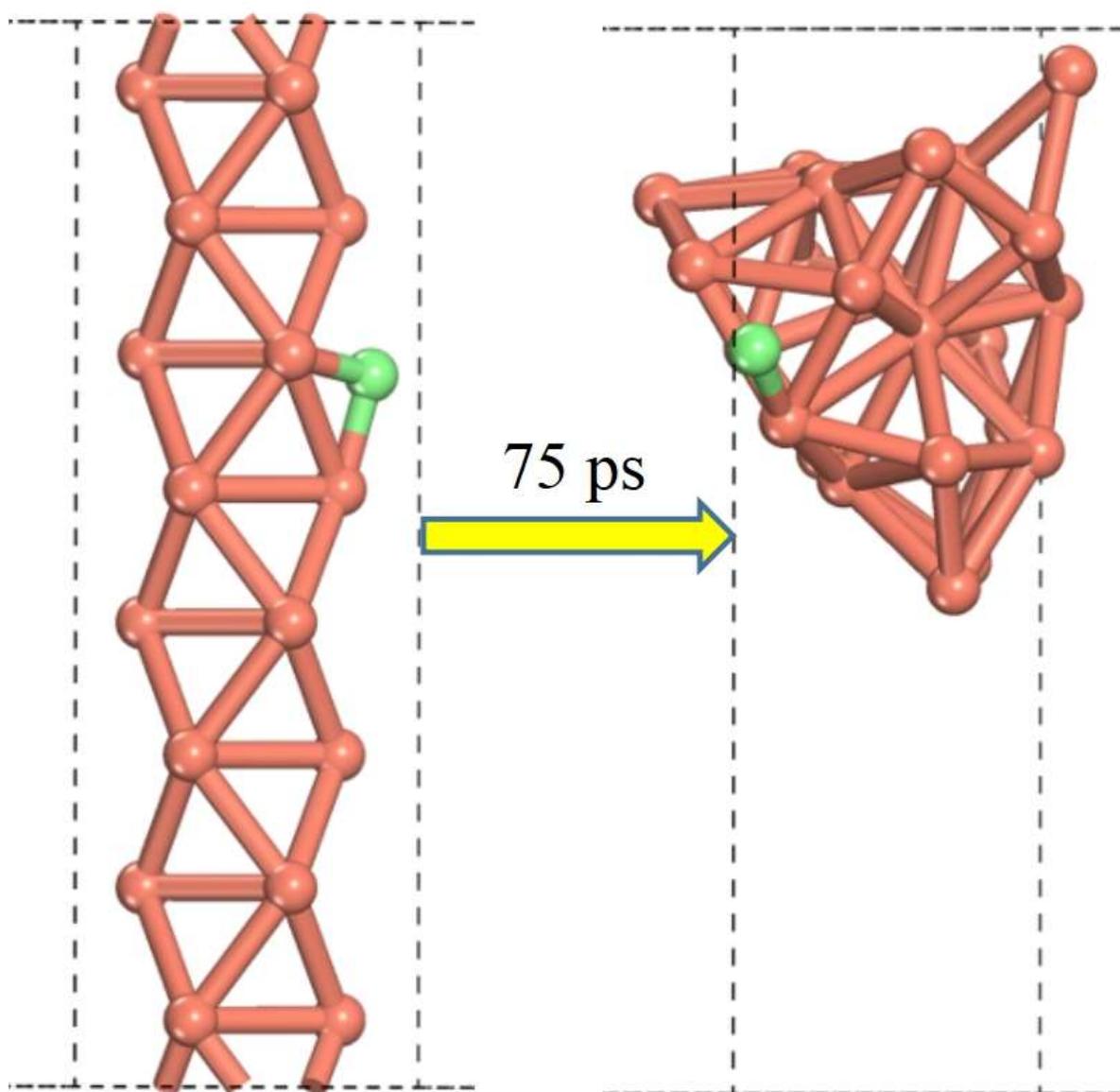


Figure 1b

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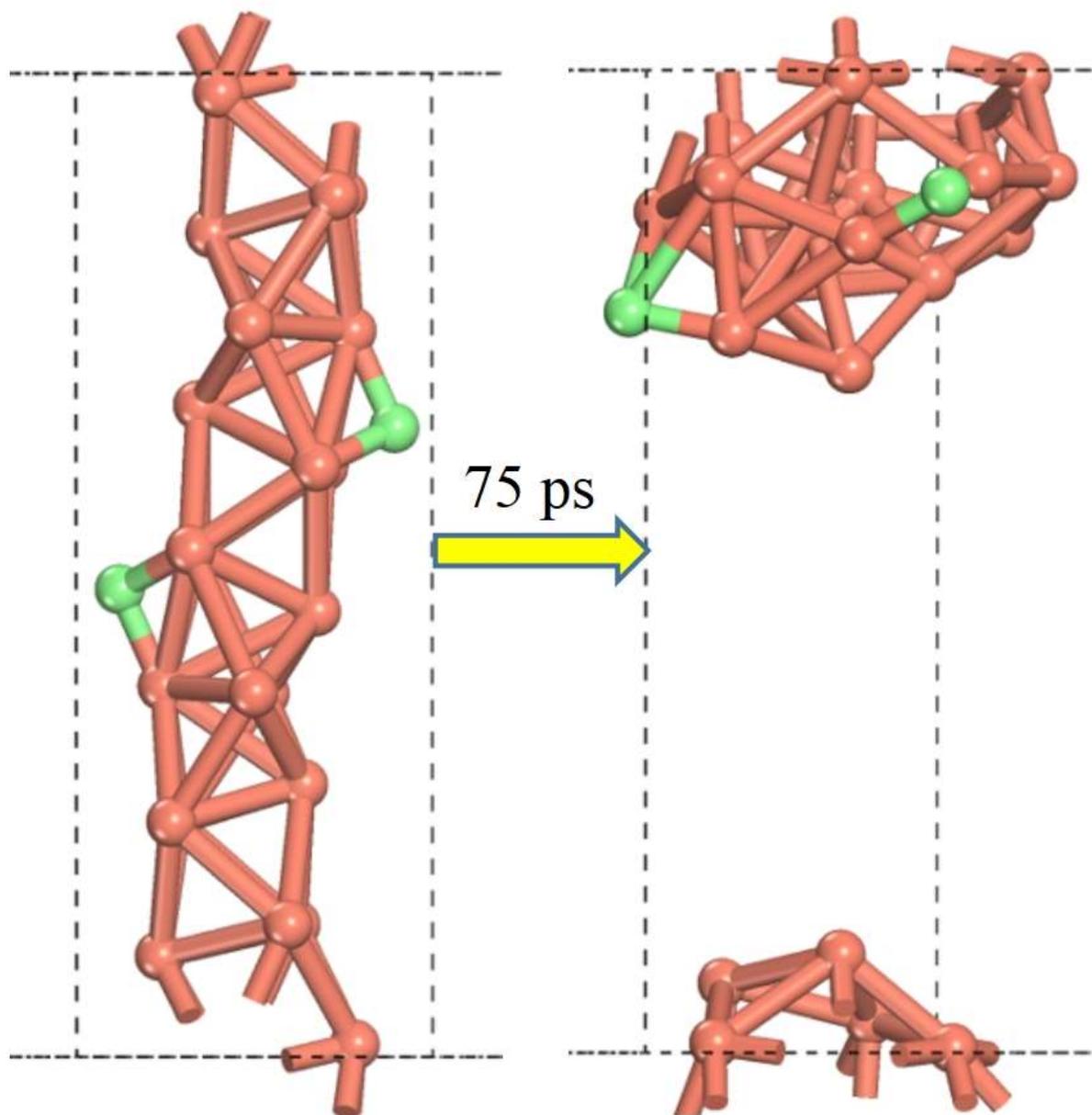


Figure 1c

ACC

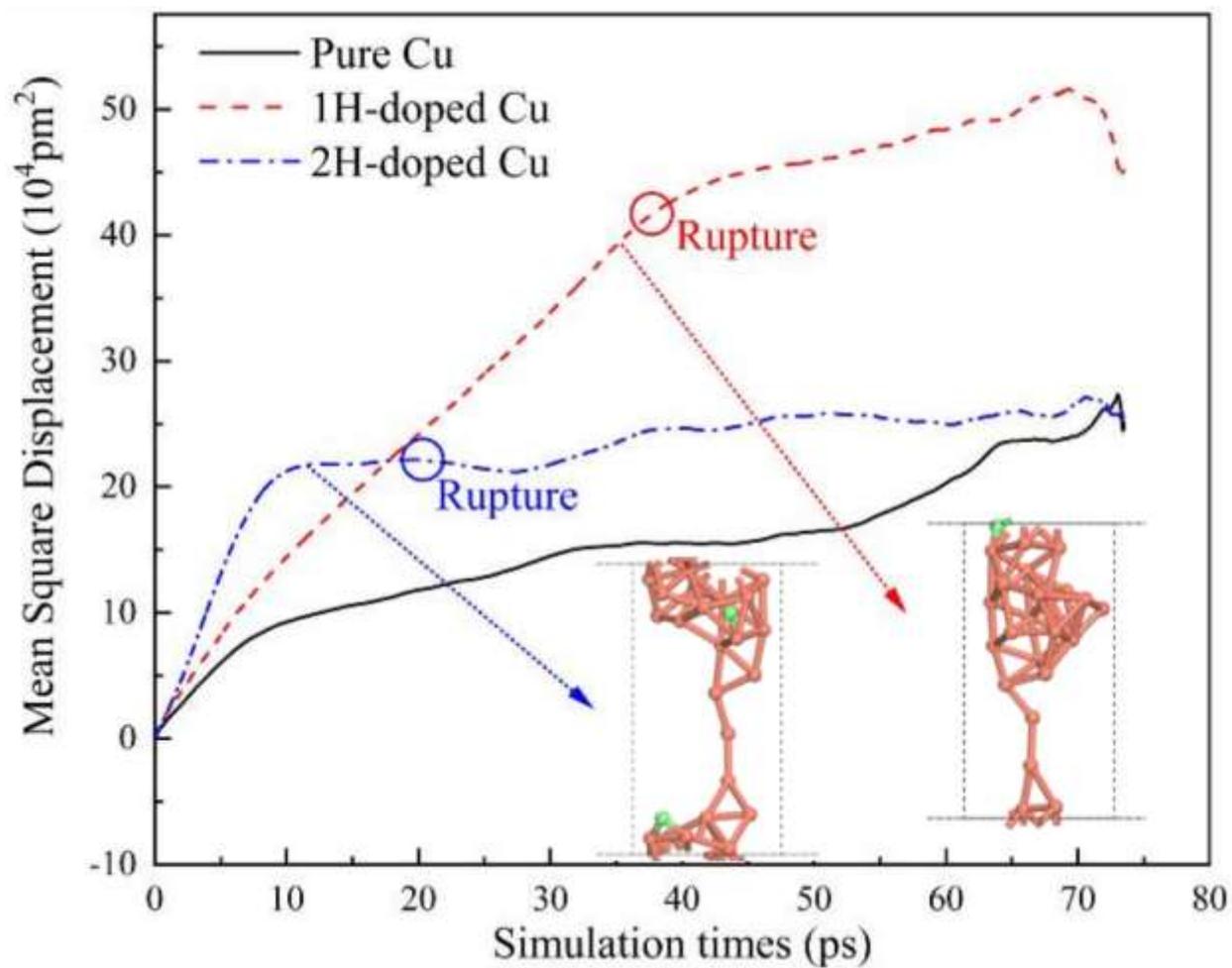


Figure 1d

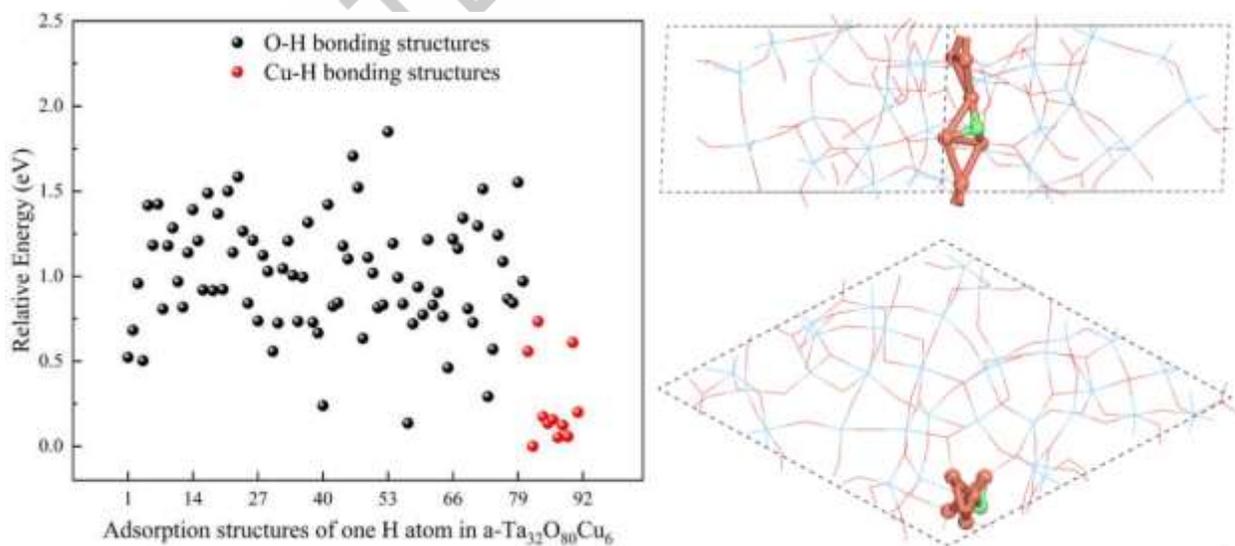


Figure 2a

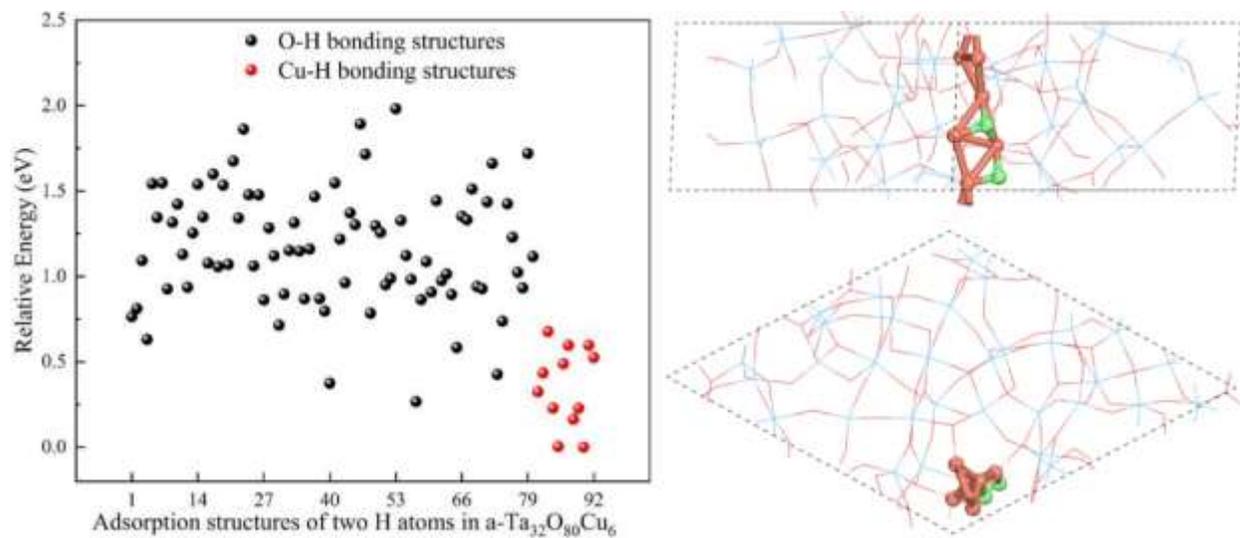


Figure 2b

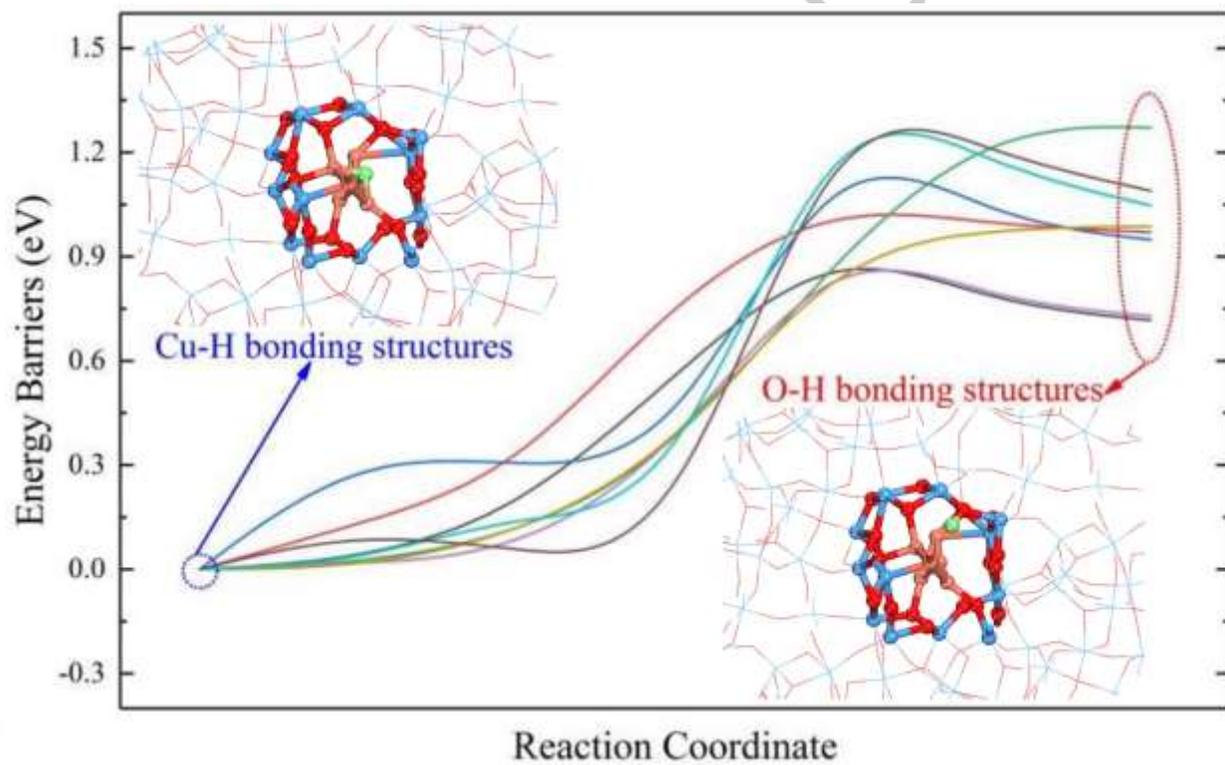


Figure 3

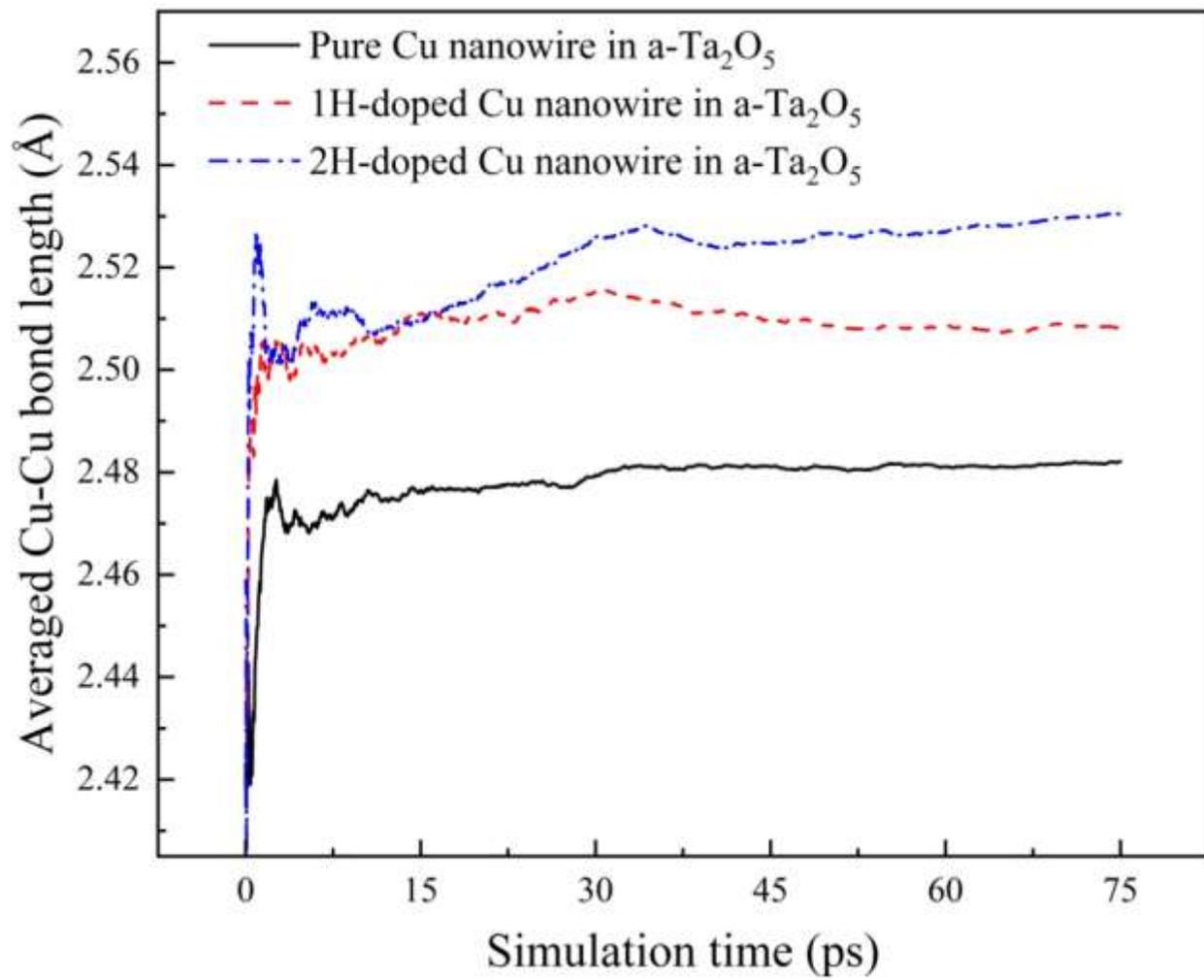


Figure 4a

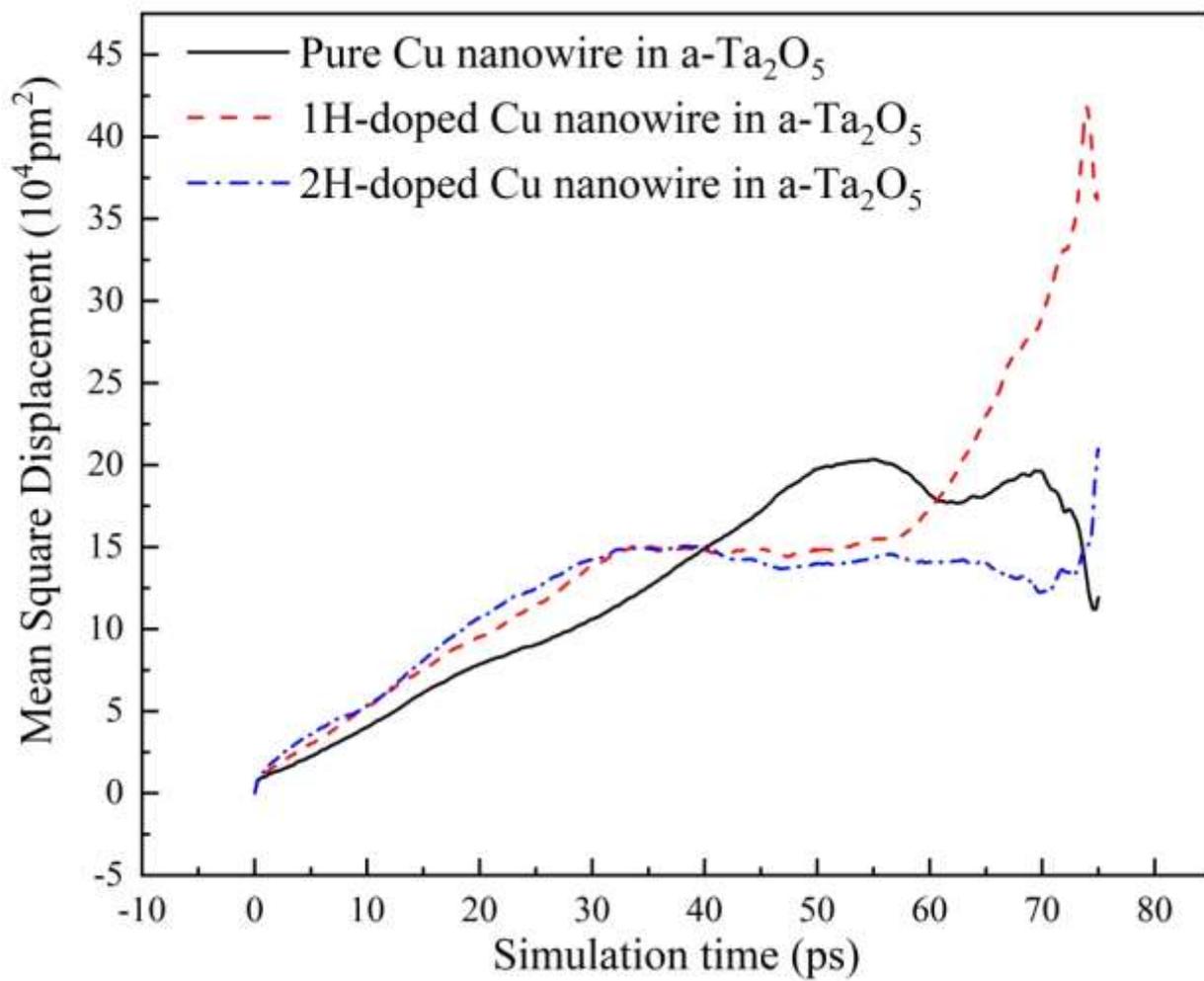


Figure 4b

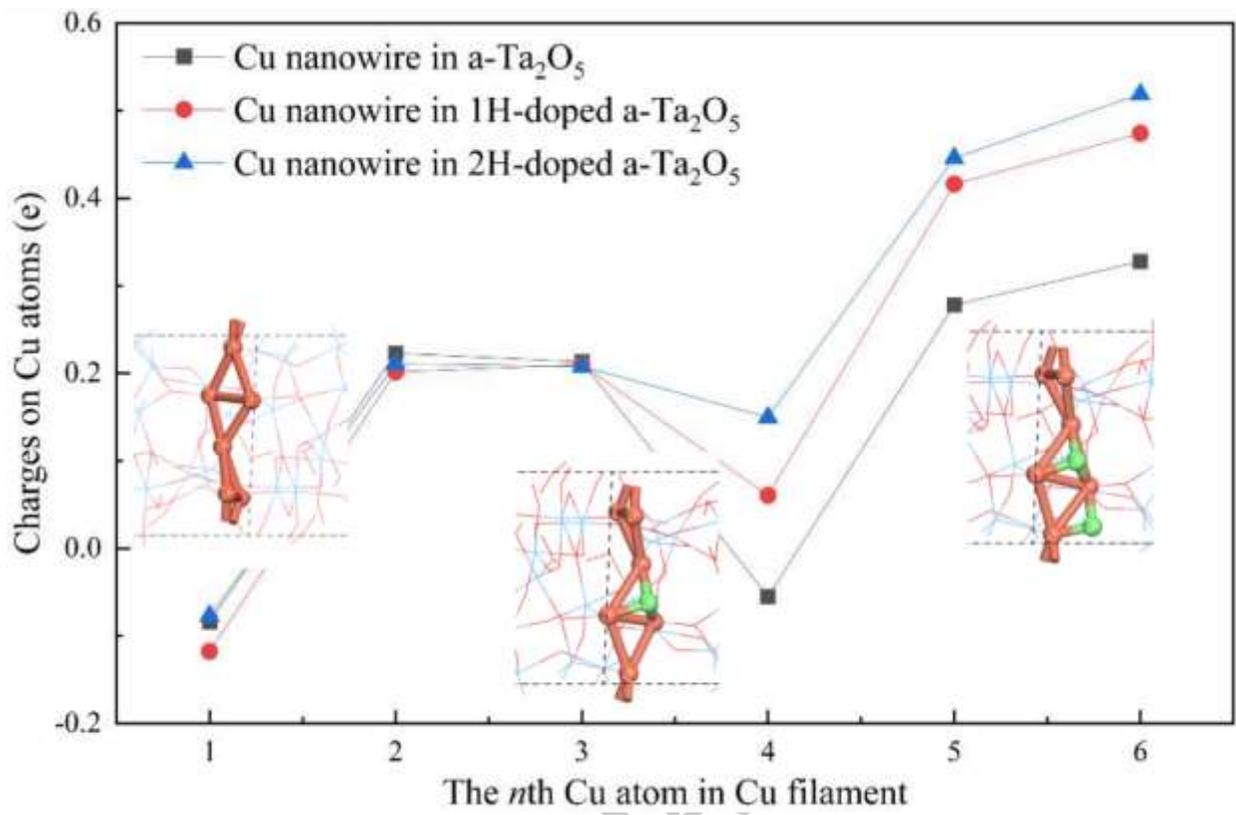


Figure 5

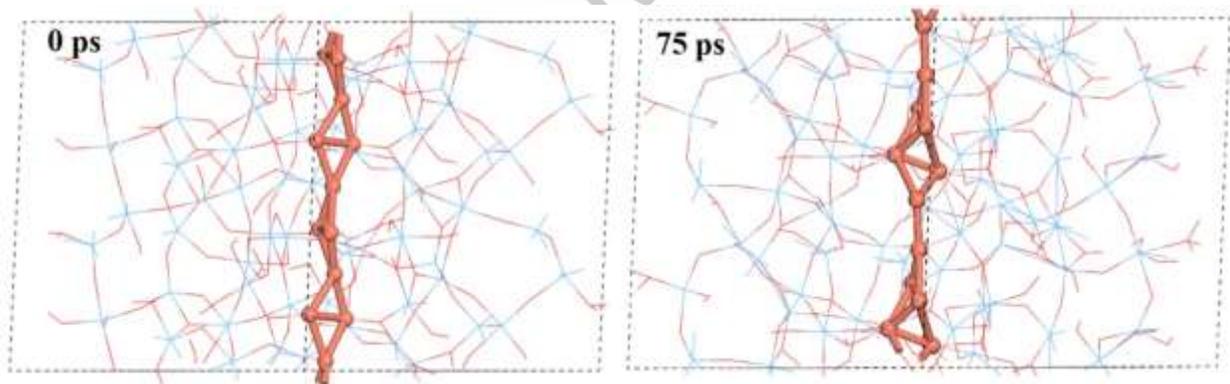


Figure 6a

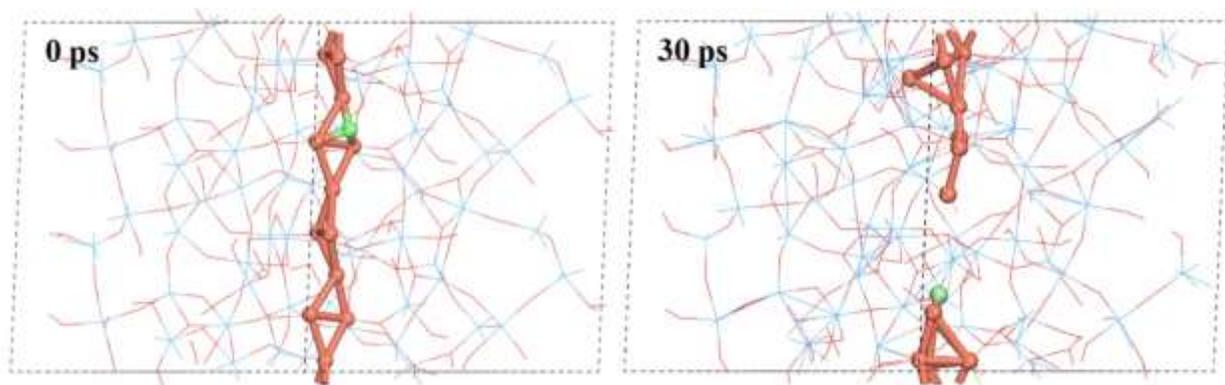


Figure 6b

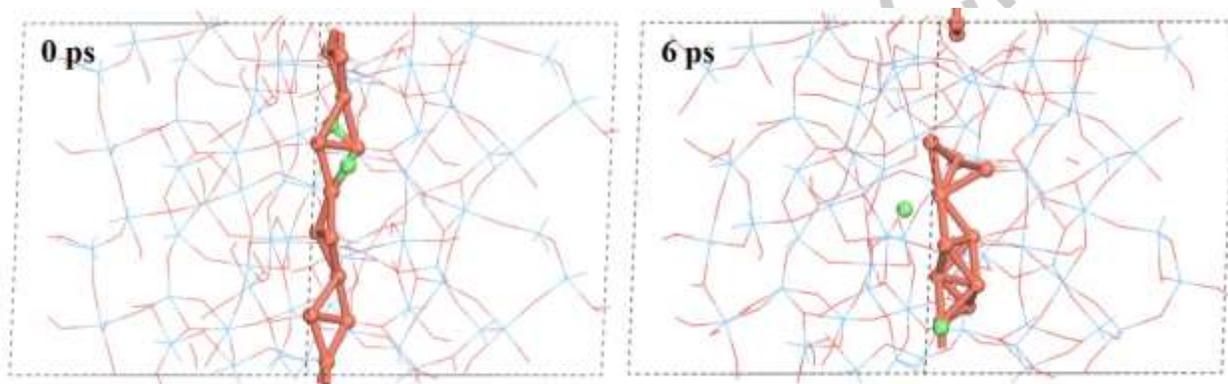


Figure 6c

Supporting information:

Hydrogen-triggered metal filament rupture in Cu-based Resistance Switches

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Table S1. The energy barriers for the migration of one H ion from Cu sites to its adjacent O sites in a-Ta₃₂O₈₀Cu₆.

Migration paths	Energy barriers (eV)
1	0.95
2	1.28
3	1.28
4	0.96
5	0.99
6	1.40
7	1.40
8	1.06

Table S2. Net Bader charges of H ions located in various chemical environments.

Various Systems for the adsorption of H ion(s)	Bader charge (e)
Cu-site in pure Cu filament (1H)	-0.24
Cu-site in pure Cu filament (2H)	-0.27 (averaged)
O-site in one Cu doped a-Ta ₃₂ O ₈₀ (1H)	+0.72
Cu-site in one Cu doped a-Ta ₃₂ O ₈₀ (1H)	-0.37
O-site in a-Ta ₃₂ O ₈₀ with Cu filament (1H)	+0.54
Cu-site in a-Ta ₃₂ O ₈₀ with Cu filament (1H)	-0.20
Cu-site in a-Ta ₃₂ O ₈₀ with Cu filament (2H)	-0.24 (averaged)
Cu-site in a-Ta ₆₄ O ₁₆₀ with Cu filament (1H)	-0.34
Cu-site in a-Ta ₆₄ O ₁₆₀ with Cu filament (2H)	-0.25 (averaged)

Figure S1. The bond lengths for the pure, 1H- and 2H-doped Cu nanowires in the (a) vacuum and (b) a-Ta₃₂O₈₀, respectively.

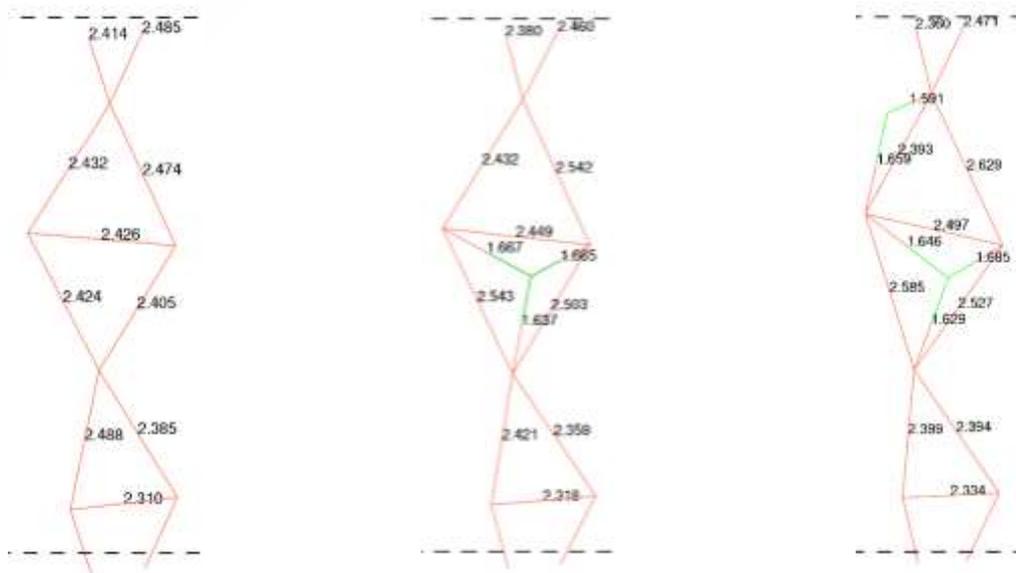
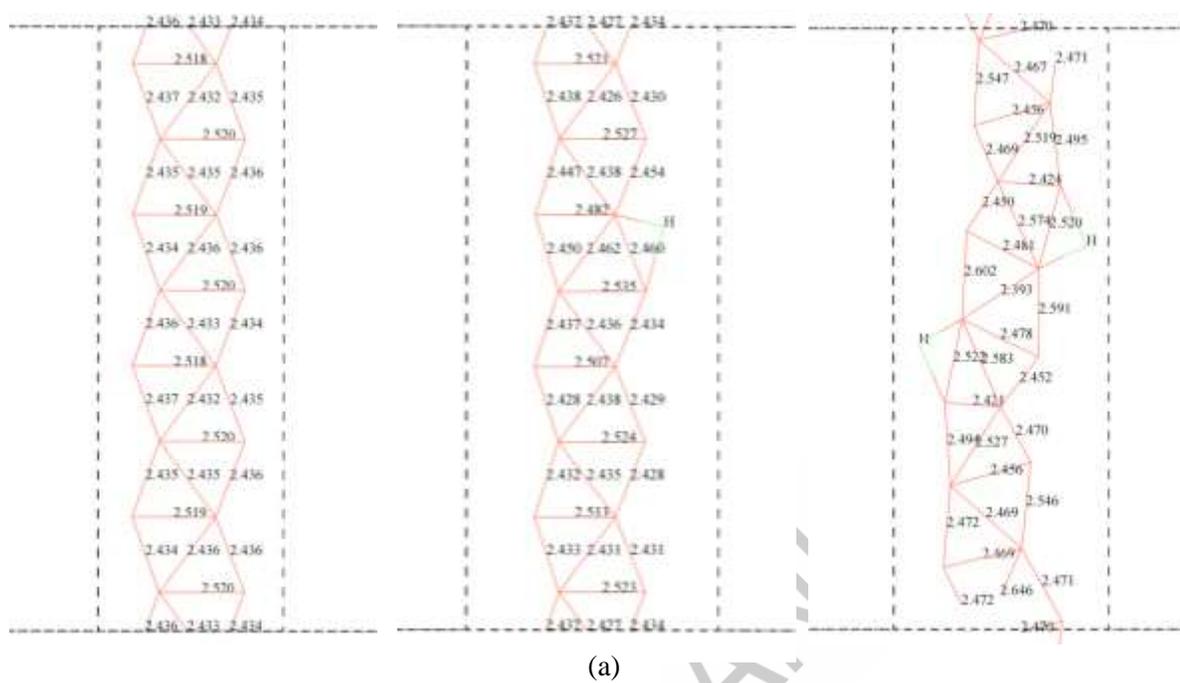


Figure S2. The atomic structures for the migration of one H ion from Cu sites to its adjacent O sites in $a\text{-Ta}_{32}\text{O}_{80}\text{Cu}_6$.

