Molecule Aging

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Abstract: We propose one new concept of "aging of molecules" with no apparent structural changes, which is different from the traditional one with the breaking of chemical bond. Now, IR spectra for the traditional water molecules were changed after long-term electron impact and different potential treatment. Moreover, the performance for hydrogen evolution reaction (HER) using water solution after treatment was decreased obviously. The Density Functional Theory (DFT) calculations indicated the lower activity for HER is origin from comes from the shortened O-H bond length. We hope the construction of new instrument platform with ultrahigh sensitivity and resolution and new theoretical model describing new aging molecules can induce positive effect in energy and life area.

1. Instruction

Molecules or atoms build the world and time can change everything. It is generally known that a new or young matter could become old while with the main functions or properties maintained as time goes on (Fig. 1a, b)[1-3]. Take the human being as an example, when a girl named ***Rose*** becomes an adult at 18, her body will become older and older in the following years as indicated by her face or other organs in her body. Before she dies of old age, she is still exactly the same person as the young ***Rose*** with the main structure or functions maintained. While when she becomes old, her physical strength, ability or energy must be different from that at young age. It means, with the power of time, in a certain time window, due to the aging, a matter is still the matter with some main function maintained although it could become different slowly in some properties before its final death or decomposition.

While in academia of chemistry, the molecules are believed to possess the same properties if their chemical compositions or atomic structures are exactly the same as indicated by some traditional analytical tools[4]. For example, the water molecules, no matter they were formed thousands of years ago or newly formed via the reaction of hydrogen burning ($2H_2+O_2=2H_2O$), people believe that their physics-chemical properties are exactly the same. Based on such "knowledge", in the typical software developed for Density functional theory (DFT) calculation, the atoms, chemical bonds or molecules composed with the same types of elements or atoms are taken exactly the same in different models in different labs. In short, people take it for granted that any molecules with the same chemical compositions or atomic structures are exactly the same in any physics-chemical properties. Obviously, above knowledge is the basis for modern chemistry or science.

So, in modern chemistry, the aging of molecules or atoms in chemistry-based fields has been ignored totally due to the fact that the molecules or atoms are usually very stale in a long time river (Fig. 1c) and the natural aging of a molecule is too slow to be observed in time window of years. Based on known knowledge, people believe that the aging of molecules (including the molecules, ions or radicals), such as H_2O molecules, is negligible. It should be noted here that concept of aging presented here is different from the traditional concept of aging of materials, which refers to the performance decay induced by the degradation or damage of the high-level structure of macromolecules or the breaking of original chemical bonds or the formation of new chemical bonds in polymers [5, 6].

In this work, based on the classic principle that any continuum admits of repeated or successive *division without limit* (Fig. 1d)[7], we propose an opinion about the aging of molecules (Fig. 1e): via a certain treatment in appropriate energy to speed up the aging process of molecules, one could possibly obtain new stable aged molecules with some physics-chemical properties different from the fresh or known ones. Such opinion was further confirmed by experimental results obtained from the ideal model of water molecules. It shows clearly that the water molecules aged by electron attacking present the same IR spectrum as the fresh, indicating the same chemical structure between the fresh and aged water molecules, while their ^{17}O-NMR spectra indicate firmly the difference between the fresh and the aged ones. Significantly, on the surface of the same type of electrocatalyst, we further found that the aged water shows lower HER reactivity than the fresh water. Further DFT calculation along with the NMR results indicates that the low HER reactivity of the aged water probably could be attributed in part to the shortened chemical bonds of O-H in aged water induced by the electron attacking. Such results probably indicate that the electron-attacking adopted here can peeling off some unknown small pieces from electrons, neutrons or protons in H or O atoms, and such gentle peeling off of some unknown small pieces cannot affect the O-H bond too much and then the O-H bond can be maintained apparently as usual but with its length shortened to some extent. The new insights obtained here pave a new way for the developing of new functional materials and extend the boundary of chemical science.

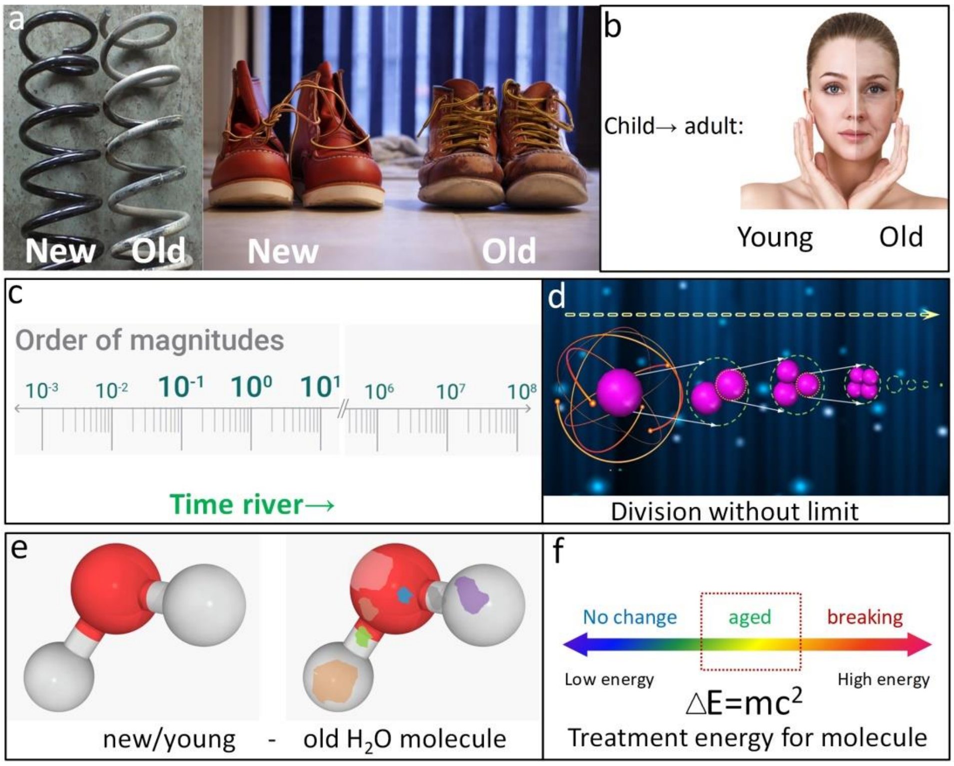

Figure 1. a) Aging of everything. b) Aging of a people. c) The time river in different magnitude. d) Any continuum admits of repeated or successive *division without limit*. e) Scheme to show the aging of water molecules. f) The different treatment energy for the possible aging of molecules.

2. Results and discussion

Herein, we propose that the aging of molecules defined above could be achieved via a certain treatment with appropriate energy to speed up the aging process of molecules by peeling off some unknown tiny pieces maybe from electrons, neutrons or protons into atoms. In this way, one could obtain stable aged molecules with some physics-chemical properties different from the fresh. In this aging treatment (Fig. 1f), if the energy is too low, no tiny pieces could be peeled off and then no change can be made to the atoms or molecules, while if the energy is too high, the treatment can damage the atoms too much and then break the chemical bonds in molecules and then split them into pieces, leading to the formation of new molecules, ions or radicals. Only when the energy for the treatment is appropriate or in the middle level, some tiny pieces can be peeled off from electrons, neutrons or protons in atoms. Such tiny peeling off cannot affect the structure of molecules or atoms too much so that their chemical bonds can be maintained to further maintain the basic structures of molecules, while some physics-chemical properties may vary more or less due to the slight variation of their chemical bonds.

To validate above opinion about the aging of molecules, we take the water molecule as the ideal model since liquid H_2O possesses simple structure. Firstly, we treated pure water molecules via a long-term (2500 h) “boiling” or "cooking" in a steamer at 120°C (Fig. 2a). After such treatment, with some traditional characteristic methods for water, we observed no difference between the “aged” water (named as H_2O-B) and the fresh (named as H_2O-D) without such treatment with the analytic tools we adopted. As shown in Fig. 2b-c (IR, ^{17}O-NMR), H_2O-B shows no observable difference from the fresh in IR and the “full width at half maxima (FWHM)” of NMR spectra. Moreover, as shown in Fig. 2d, the HER reactivity of the H_2O-B in 1 M KOH solution prepared with H_2O-B is almost the same as the fresh water (H_2O-D) on the same catalyst (Pt/C with Pt loading of 20 wt.%) surface. Such fact indicates that the energy of “boiling” adopted here is not high enough to induce detectable “aging” of water molecules or the tiny differences induced by “boiling” cannot be revealed by the analytical tools adopted in this work.

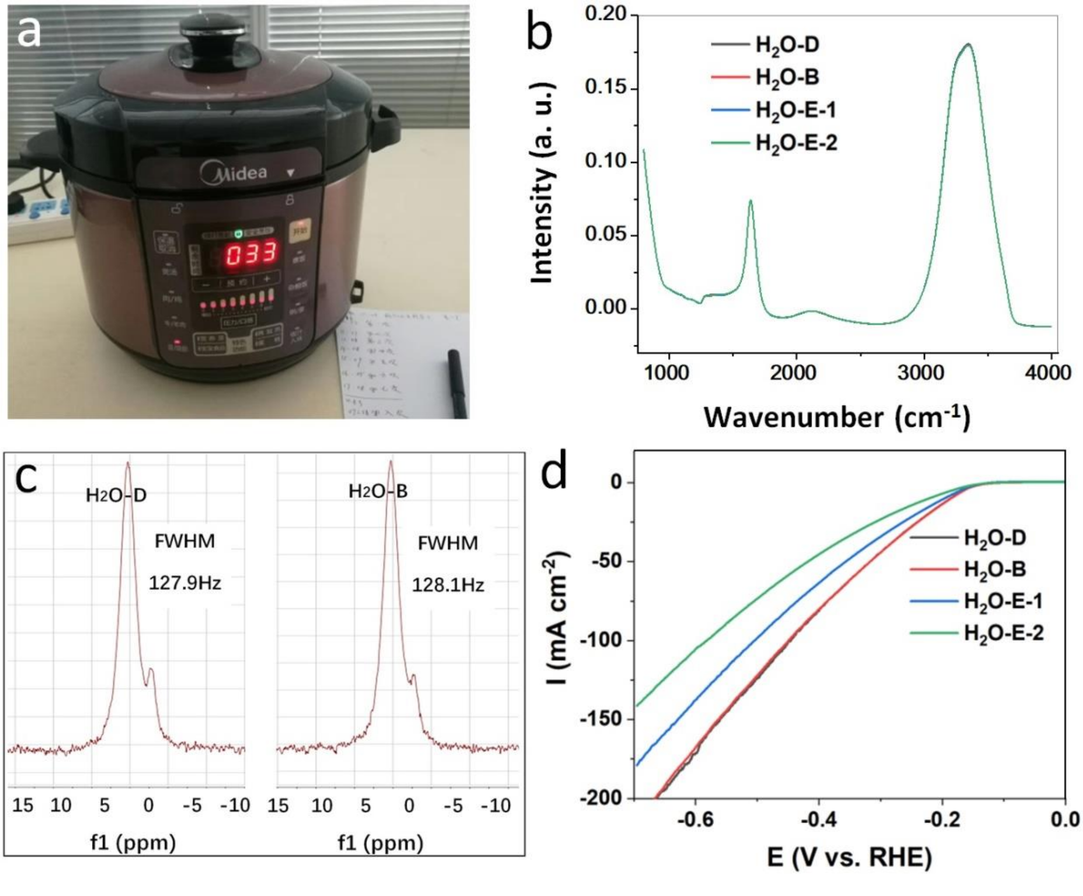

Figure 2 a) Image of the steamer for water aging at 120 °C for 2500 h. b) The IR spectra of four different water samples: H_2O-D, H_2O-B, H_2O-E-1 and H_2O-E-2. c) ^{17}O-NMR spectra for H_2O-D and H_2O-B. d) HER reactivities of four different water samples on commercial Pt/C in 1 M KOH water solution.

Since above “cooking” at 120 °C cannot age water molecules much to induce detectable variation of their physics-chemical properties, we further tried “electron beam” (e-beam) with energy probably higher than “cooking” to attack water molecules. As Figure 3 shows, seven pieces of copper plates with clean smooth surfaces were stacked up tightly with sides sealed with AB glue to form nano-channels between copper plates by sandwiching a thin layer of water between. With a water reservoir sitting on top of the stacker, the water then flows very slowly driven by gravity and capillary force through nano-channels and is collected at the bottom of the stacker. To age the water flowing through the channels, a constant current with density of 0.40 A cm^{-2} flows (at a constant voltage 0.2 V between the left and right sides) through the stacker vertically with electrons to attack the water molecules flowing through the channels. In this way, as shown in Fig. 3a, ideally, each water molecule can be attacked by electrons or e-beam many times before it finally flows out at the bottom of the stacker. By controlling the length of the copper plates or the nano-channels, one can control the attacking times or aging degree of a water molecule by electron attacking, or the longer the plates, more times the water molecules will be attached. In this way, we can study the aging-induced variation of the physics-chemical properties of water. The final water obtained in this way is named as H_2O-E. In this way, two types of aged water samples of H_2O-E-1 and H_2O-E-2 were obtained with two flow channels in different lengths of 20 cm and 25 cm, respectively. In this way, 50 mL of sample H_2O-E-1 was collected from the bottom of the short cell (20 cm×4 cm) in about 9 months, while 50 mL of sample H_2O-E-2 was collected from the long cell (25 cm×4 cm) in about 12 months.

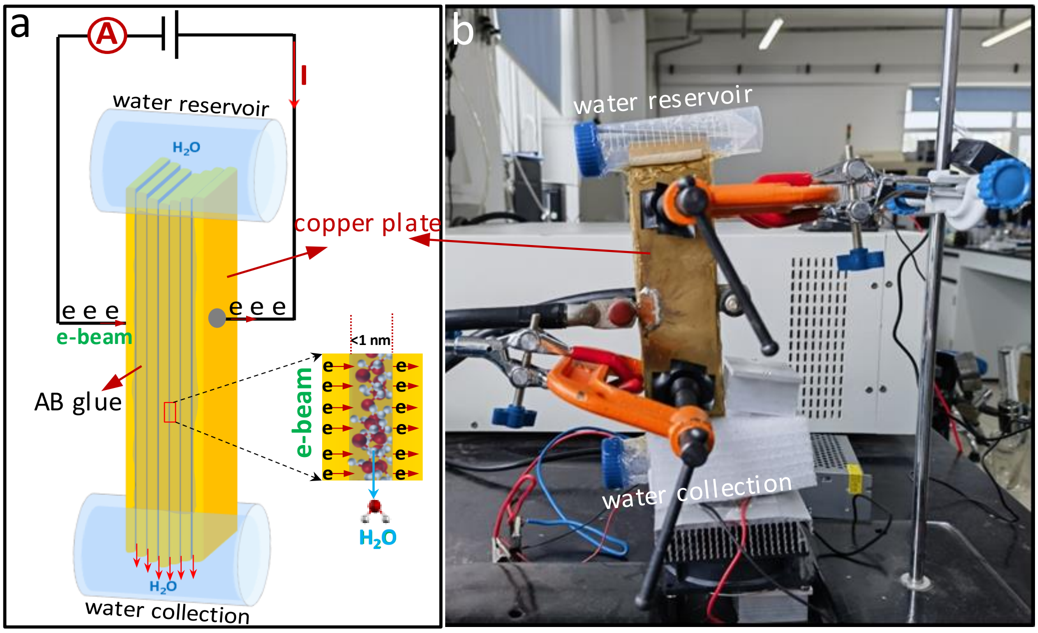

Figure 3. a) Scheme for the setup of water molecule aging via the electron attacking. b)The image of the experimental setup for the aging of water molecules, in which multilayer conductive plate (MCP) made by copper plate, and the right scheme showed the possible mechanism by E-beam.

As shown in Fig. 2b, the IR spectra of these two water samples still show no difference from fresh water, indicating that the main structures of these two types of aged water samples are still the same“chemically” as the traditional water molecules. While surprisingly, different from the boiled water (H_2O-B), the ^{17}O-NMR spectra present clearly (Fig. 4a) the difference of both the “full width at half maxima (FWHM)” and “chemical shift” from the fresh water! It shows that, with the increase of the attacking times of water molecules by electrons, the FWHM for ^{17}O-NMR spectrum decreases step by step while the chemical shift increases step by step. Such variation indicates firmly that the electron-attacking adopted here indeed can induce certain change of H_2O molecules; such change is large enough to be recognized by ^{17}O-NMR. The FWHM of NMR reflects the cluster size of liquid water, the smaller the FWHM the smaller the cluster size of liquid water[8]. So, the decrease of FWHM after aging treatment (Fig. 4a) means the size decrease of the water clusters after getting aged. While the size decrease of water clusters could be attributed to the size decrease of water molecules or the number decrease of water molecules in a cluster. This result confirms that the electron attacking indeed can induce the aging of molecules or the molecules could be aged before its decomposition.

To reveal the possible effect of such tiny difference induced by the aging as shown above in NMR analysis, we further measured the OER reactivity of these two water samples in 1 M KOH solution prepared with these two types of water samples on the same electrode of Pt/C. As shown in Figure 2d, compared with the fresh water without treatment (H_2O-D) or the H_2O-B, we reveal that the electron treatment adopted here can decrease the HER reactivity of water molecules step by step, as indicated by the increase of over potential at the current density of 10 and 100 mA cm^{-2} (Figure 4b). Such fact was further confirmed by the Tafel plots shown in Figure 4c. It shows that the Tafel slope increases step by step after the treatment from 32 mV dec^{-1} to 47 mV dec^{-1}, and 52 mV dec^{-1}, confirming the slower HER kinetics of the aged H_2O molecules shown in Figure 2d[9, 10]. In other words, the aging induced by the electron attacking can deactivate the HER process of water molecules due to the tiny structure variation as indicated by the NMR shown in Figure 4a although without obvious change in their chemical structures indicated by the constant IR spectra in Figure 2b. Such fact indicates for the first time significantly, with certain aging treatments, the obtained molecules with apparently the same chemical structures or compositions as the fresh could present some different properties, meaning the production of brand new materials with new functions for new possible applications. Based on the principle that any continuum admits of repeated or successive *division without limit*[7] (Fig. 1d), the difference observed here probably could be attributed the peeling off of some unknown pieces or particles from the molecules.

To understand the HER reactivity decrease of water molecules after aging treatment, based on the information revealed from the NMR analysis shown above, we further studied the length effect of O-H bond in H_2O on the reactivity of HER on Pt surface by theoretical calculations. Firstly, based on the MD simulations of the stability of H_2O adsorption on **Pt surface**, we obtain four types of stable H_2O molecules with different lengths of O-H bond at minimum local energy and then investigate the HER reactivity of H_2O molecules with slightly different lengths of O-H (L_{OH}) bond (Figure 5a): One H_2O molecule possesses short bond length of 0.964 Å, one is with the normal bond length of 0.976 Å adopted before extensively[11], and the other two (0.990

Å and 1.098 Å) are with longer bond length of about 1.0 Å. It reveals that H_2O molecules with O-H bond in different lengths present different adsorption modes over the same Pt (111) surface. Gibbs free energies for HER based on these H_2O molecules were calculated to evaluate the different reactivity originated from the difference of bond lengths. The HER reactivity gaps are shown in Figure 5b-f. As expected, the H_2O molecule with the longest bond length of 1.098 Å presents the highest HER reactivity as indicated by the smallest energy barrier (eb) of 0.121 eV. When the O-H bond length is shortened step by step, the HER reactivity decreases correspondingly with the following reactivity order of water molecule: H_2O (L_{OH}=1.098 Å, with eb=0.121 eV)>H_2O (L_{OH}=0.990 Å, with eb=0.551 eV)≈H_2O (L_{OH}=0.976 Å, with eb=0.553 eV)>H_2O (L_{OH}=0.964Å, with eb=0.598 eV). Such fact indicates that the shortening of O-H bond from the well-known traditional 0.976Å to 0.964Å indeed can decrease the HER reactivity of H_2O. Based on such results, one can deduce that the observed decrease of cluster size in ^{17}O-NMR probably could be attributed at least in part to the aging-induced shortening of O-H bond in water molecules. As for the lower reactivity of H_2O-E-2 (obtained within 12 months) than H_2O-E-1 (obtained within 9 months), it could be attributed to the different composition between them. As shown in Figure 6, due to the non-ideal surface of the copper plates adopted here, it is inevitable that some water molecules probably will not be attacked seriously by e-beam when they finally flow out from the bottom (Figure 6a), while with the longer channel for water flowing through, more molecules will be aged or the water molecules will be aged more seriously, then such final product collected at the bottom shown in Fig. 3 will present lower HER reactivity since it contains more aged molecules.

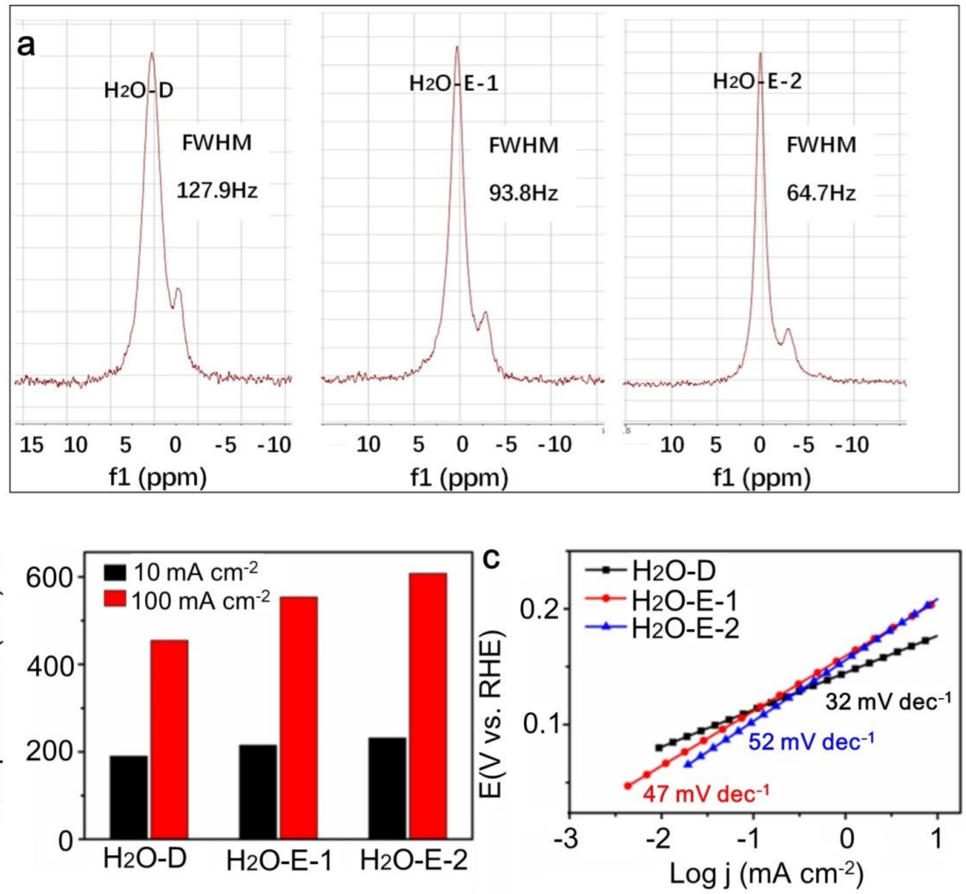

Figure 4. a) ^{17}O-NMR spectra for H_2O-D, H_2O-E-1 and H_2O-E-2. b) Comparison of the HER overpotentials of three different water samples on commercial Pt/C in 1 M KOH water solution at different current densities shown in Fig. 2d. c) Tafel slop analysis for three different water samples during the HER process in 1.0 M KOH solution with different H_2O solvent.

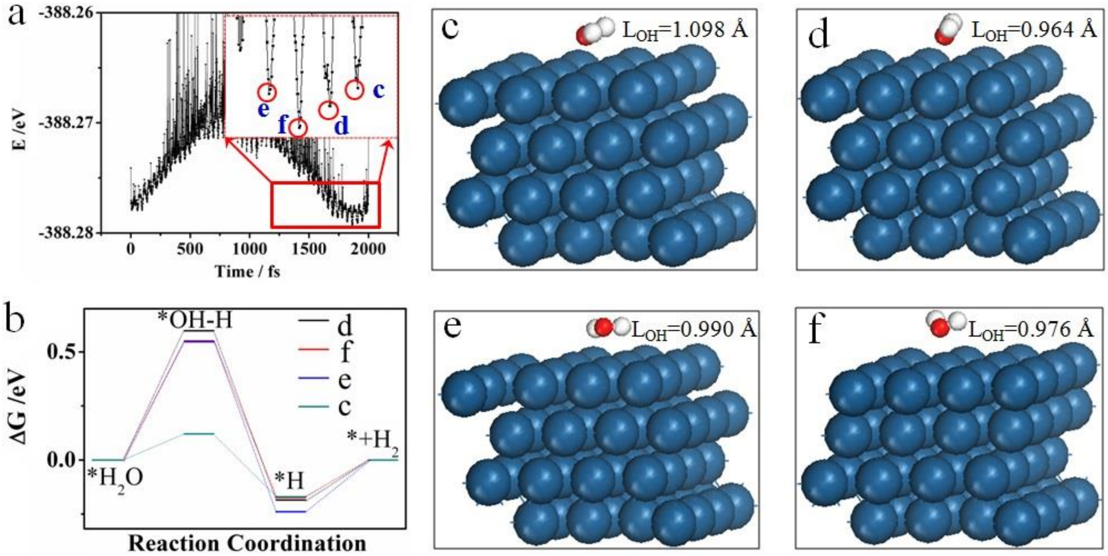

Figure 5.The MD results (a) and the Gibbs free energies (b) for HER based on four H_2O molecules (c-f) with different O-H bond lengths.

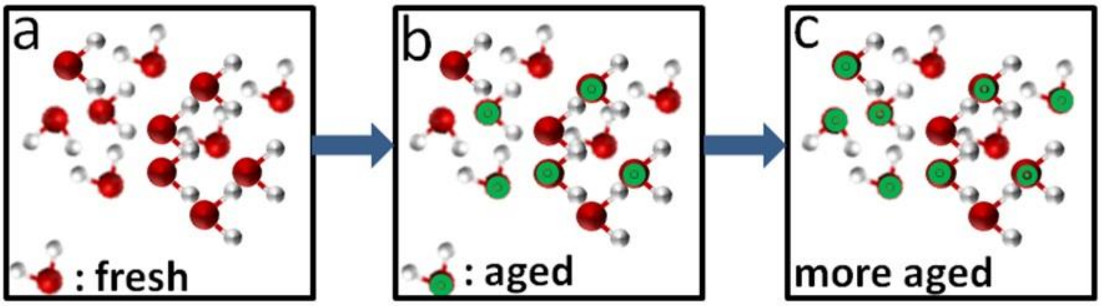

Figure 6. Scheme to show more and more water molecules aged after step-by-step aging.

4. Conclusion

The nature change for matters is closely related to human life, while the matter will all go through aging with the structural collapse by the loss of time. Based on the key scientific questions about the relationship between internal fine structures and reaction processes, we developed an innovative concept called “the aging of molecule” to explain unusual process or mechanism of reaction that is inexplicable by normal theory. The molecules after aging are nearly the same as the original one from the apparent characterization, while the tiny change in atom structure or chemical bond will take place before the molecular disintegration, which induce large change in physical and chemical properties. Here a long-term electron impact treatment has been carried out to destroy water molecules. The treated H2O molecules showed little changes in appearance and by IR characterization, while the NMR results indicated smaller clusters than that before being treated. Moreover, the different HER activities with various water molecules were exhibited due to changed bond lengths. The water molecules with shorten bond length showed lower HER activity comparing with those with elongated bond length, which indicated the long-term electron impact treatment induced bond length shorten named “aging of water molecules”, and the shorter the bond length, the longer the treatment time. In the follow-up work, the reason for shortening the bond length by long-term electron impact treatment will be researched in depth. Based on this new concept, it will provide a new perspective to research the chemical process with the different degrees of aging molecules. Combing with new theoretical model and advanced characterization technologies, it is possible to distinguish the tiny difference in physical and chemical properties of the same kind of atom or molecule from the atoms themselves, and a detection device with “molecule fingerprint” characteristics can be developed to further strengthen the unique performance of these newly discovered "aging molecules". Special treatment can produce new aging molecules with major revolution in energy research, without destroying the appearance of molecules. Then aging will no longer be a negative effect, but with a positive boost to energy and life, which will produce great significance and practical application value closely related to human being.

Material

KOH (99.99%) were purchased from Aladdin. Deionized water (18.25 MΩ cm) was used to prepare all aqueous solutions, obtained by reversed osmosis followed by ion-exchange and filtration (Molecular 1810b). Nafion solution (5 wt%) was purchased from Sigma-Aldrich. All the chemicals were used as purchased without further purification. Commercial Johnson−Matthey Pt/C (20 wt. % Pt loading on carbon) was purchased from Alfa Aesar. All chemicals were purchased from commercial sources and used without further purification.

Physical characterization

The two kinds of water molecules were detected by IR spectra. 1H-NMR was performed on a BRUKER AVANCE-III 500 HD (Switzerland). The Si prism with the Au film on was assembled into a spectroelectrochemical cell that was then fixed in a homemade optics system built in the chamber of a Thermo Fisher IS 50 infrared spectrometer with a liquid nitrogen cooled MCT detector for electrochemical ATR-SEIRAS measurements at an incidence angle of ∼70 °. All ATR-SEIRAS spectra are given in absorbance units defined as $-\log(I/I_0)$, where I and I0represent the sample and reference spectra, respectively.

Electrochemical test

The electrochemical performance of as-synthesized samples was firstly measured in N2-saturated 1.0 M KOH solution with a three-electrode configuration. In order to investigate the change of H2O molecules after electrifying, the electrolytes were prepared with traditional deionized water and those by electrifying. All the electrochemical tests were carried out in N_2-saturated electrolyte at room temperature by a three-electrode system using the CHI750E (Shanghai, Chenhua Co.) electrochemical workstation. Commercial 20 wt.% Pt/C was directly used as the working electrode, a graphite rod was used as the counter electrode, a Hg/HgO electrode was used as the reference electrode. All of the potentials were converted to the reversible hydrogen electrode (RHE) using the equation: $E_{RHE} = E_{SCE} + 0.242 + 0.059*pH$. To prepare the Pt/C modified working electrode, 5 mg of catalyst was first dispersed in 950 μL of ethanol and 50 μL Nafion (5 wt.%) solution under ultrasonication for 30 min to form a homogeneous ink. Then, 10 μL of ink was slowly loaded onto the Φ_4 electrode and dried under room temperature. Linear sweep voltammetry (LSV) measurement was tested with scanning rate of 5 mV s^{-1}.

Theoretical calculation

All structure optimization and energy calculations were performed using PBE function of the PAW potentials within the Vienna ab initio simulation package (VASP) code[12-14]. The energy kinetic cut-off of plane-wave basis functions was 400 eV. A Monkhorst-Pack exchange-correlation functional with a Monkhorst-Pack grid of size 2*2*1 was used to sample the surface Brillouin zone. The electron occupancies were determined using Gaussian broadening with a width of 0.05 eV. Geometries were optimized until the energy was converged to 1.0×10^{-4} eV/atom and the force was converged to 0.05 eV/Å. A vacuum space of 15 Å was inserted in the z direction to prevent any artificial interaction between periodically repeated images under periodic boundary conditions. Four layers of Pt were chose to adsorb H_2O molecules, and the top two layers are optimized with the two layers fixed. To ensure the reliability of the theoretical model of H_2O adsorbed on the surface of Pt/C catalyst, we carried out first-principles molecular dynamics (MD) simulations at 200 K to evaluate the stability of the structures. The MD simulations are carried out in the canonical *NVT* ensemble and the temperature is controlled using the Nosè thermostat. In these simulations, we used *G* point sampling with a time step of 1.0 fs for 2 ps.

Acknowledgements

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References

1. C. C. Zouboulis and E. Makrantonaki, *Clinics in Dermatology*, 2011, **29**, 3-14.
2. R. Noroozi, S. Ghafouri-Fard, A. Pisarek, J. Rudnicka, M. Spólnicka, W. Branicki, M. Taheri and E. Pośpiech, *Ageing Research Reviews*, 2021, **68**, 101314.
3. P. Gkogkolou and M. Böhm, *Dermato-Endocrinology*, 2012, **4**, 259-270.
4. A. Helmenstine, What Is a Molecule? Definition and Examples, https://sciencenotes.org/what-is-a-molecule-definition-and-examples/).
5. P. Rannou, D. Rouchon, Y. F. Nicolau, M. Nechtschein and A. Ermolieff, *Synthetic Metals*, 1999, **101**, 823-824.
6. A. Rjeb, S. Letarte, L. Tajounte, M. C. El Idrissi, A. Adnot, D. Roy, Y. Claire and J. Kaloustian, *Journal of Electron Spectroscopy and Related Phenomena*, 2000, **107**, 221-230.
7. J. L. Bell, in *The Stanford Encyclopedia of Philosophy*, ed. E. N. Zalta, Metaphysics Research Lab, Stanford University, 2022.
8. Z. X. LI Fuzhi, L Mujian, *Acta Scientiae Circumstantiae*, 2004, **24**, 6-9.
9. J. Huang, J. Han, T. Wu, K. Feng, T. Yao, X. Wang, S. Liu, J. Zhong, Z. Zhang, Y. Zhang and B. Song, *ACS Energy Letters*, 2019, **4**, 3002-3010.
10. Y. Shi and B. Zhang, *Chemical Society Reviews*, 2016, **45**, 1529-1541.
11. P. Jiang, Q. Li and J. Lu, *IOP Conference Series: Earth and Environmental Science*, 2018, **178**, 012020.
12. P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953-17979.
13. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1997, **78**, 1396-1396.
14. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.