Local atomic structure modulations activate metal oxide as electrocatalyst for hydrogen evolution in acidic water

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Modifications of local structure at atomic level could precisely and effectively tune the capacity of materials, enabling enhancement in the catalytic activity. Here we modulate the local atomic structure of a classical but inert transition metal oxide, tungsten trioxide, to be an efficient electrocatalyst for hydrogen evolution in acidic water, which has shown promise as an alternative to platinum. Structural analyses and theoretical calculations together indicate that the origin of the enhanced activity could be attributed to the tailored electronic structure by means of the local atomic structure modulations. We anticipate that suitable structure modulations might be applied on other transition metal oxides to meet the optimal thermodynamic and kinetic requirements, which may pave the way to unlock the potential of other promising candidates as cost-effective electrocatalysts for hydrogen evolution in industry.
Hydrogen, when generated directly from water, would be a promising chemical fuel for sustainable energy applications\(^1\). Development of hydrogen evolution reaction (HER), \(2H^+ + 2e^- \rightarrow H_2\), has attracted worldwide interest\(^4\). Platinum (Pt) can effectively catalyse the electrochemical reduction of protons in acidic media to form molecular hydrogen at low overpotentials\(^5\), which remains as the most electrocatalytically active catalyst, but its high cost and low abundance limit large-scale commercial application of electrocatalytic hydrogen evolution\(^5\). Thus, efficient Pt-free catalysts are highly desired for facilitating the global scalability of such potential clean energy technology. However, as a large and important class of chemical compounds, most transition metal oxides fail to electrocatalyse hydrogen evolution in acidic water, although numerous carbides, nitrides, phosphides and sulfides have shown the capacity for this reaction\(^1\)–\(^4\).

As an important oxide, tungsten trioxide (WO\(_3\)) is much more thermodynamically stable in acidic electrolyte than most metal oxides, and it has attracted intense research interests owing to its potential applications in a wide range of fields such as catalysis, photoelectrochemical cells, photochromic devices and gas sensors\(^3\)–\(^18\). Moreover, recent reports have manifested that WO\(_3\) can act as the support of noble metals and in itself possessing electrocatalytic activity for hydrogen evolution\(^19\)–\(^21\). Unfortunately, the adsorption energy of the atomic hydrogen on W-site is undesirable, leading to the poor activity of WO\(_3\) for HER in acidic media. Noteworthy, as the descriptor of catalytic activity\(^22\), the adsorption energies of reactive intermediates can be tuned, in principle, by tailoring the geometric and electronic structures of material, resulting in the enhancement of activity\(^23\). However, modulations of the local structure at the atomic level to tune WO\(_3\) into an active HER catalyst still remains as a great challenge.

Here we present a facile thermal treatment to activate a commercial product of WO\(_3\) into a highly competitive earth abundant catalyst, the dark blue tungsten oxide (WO\(_2.9\)), for electrocatalysing HER in acidic water (see Fig. 1 for schematic mechanism). Experimentally observed results demonstrate that the WO\(_2.9\) with tailored structure exhibits excellent HER activity with a small overpotential of \(-70\) mV at the current density of \(10\) mA cm\(^{-2}\) and a Tafel slope of 50 mV per decade. Further theoretical calculations indicate that its electrocatalytic capacity could be attributed to the modest binding energy with adsorbed atomic hydrogen. The findings in this work may hold the promise for the development of more practical non-Pt catalysts for electrocatalytic hydrogen evolution and other scalable technologies that harness renewable energy and convert it to \(H_2\), for example, the proton exchange membrane electrolysis in acidic environment.

Results

Electron microscopy. To prepare the WO\(_{2.9}\) electrocatalyst, commercially available WO\(_3\) powder was well grinded and thermally treated in a reduction atmosphere, which would readily modulate the local atomic structure of WO\(_3\) (see more details in Methods). The colour of the sample changes from light yellow (commercial product of WO\(_3\)) to dark blue after the modifications (Supplementary Fig. 1). Scanning electron microscope (SEM) images reveal the as-prepared WO\(_2.9\) nanoparticles with a mean diameter of 100 nm, which exhibits negligible difference comparing to the WO\(_3\) sample (Supplementary Fig. 2), indicating that the modification process in this work may not result in the aggregation of the nanoparticles. Moreover, the energy-dispersive spectrometer mapping, together with corresponding SEM image (Supplementary Fig. 3), clearly shows the existence of the elemental W and O in the WO\(_2.9\) sample. To further reveal its structure, a JEM-ARM200F scanning transmission electron microscopy (STEM) fitted with a double aberration corrector for both probe-forming and the imaging lenses is used to perform high-angle annular dark-field (HAADF) imaging. As the contrast exhibits an approximately \(Z^2\) dependency for HAADF imaging, the arrangement of crystallographic structure after modification can be identified directly at the atomic scale. Figure 2 presents the HAADF images of WO\(_3\) and WO\(_{2.9}\) samples, where W atoms are clearly observed (yellow spots for WO\(_3\) and blue spots for WO\(_{2.9}\)). As shown in Fig. 2a, WO\(_3\) displays continuous lattice fringes with lattice spacing of 0.382 and 0.366 nm corresponding to the (002) and (200) atomic planes, respectively (white lines, marked as A and B), whereas WO\(_{2.9}\) exhibits an extended and ordered defect structure (Magnéli phase) with a regularly stair-step shape intermittently (red lines in Fig. 2b)\(^24\). Specifically, the bulk atomic structure of either WO\(_3\) or WO\(_{2.9}\) sample can also be extended to the surface, indicating the similar geometrical structure between bulk and surface (Fig. 2c,d, marked by white and red arrows). We emphasize that the surfaces and main parts of the local structures between WO\(_3\) and WO\(_{2.9}\) are similar, except for the stair-step shape lattice fringes in WO\(_{2.9}\). This suggests that the tailored electronic structure of the stair-case-shaped lattice fringes would be responsible for the enhanced HER performance of WO\(_{2.9}\).

X-ray analyses. In addition to the HAADF-STEM study, Fig. 2e displays the X-ray diffraction (XRD) pattern of the as-synthesized WO\(_{2.9}\) electrocatalyst. The XRD pattern of the WO\(_{2.9}\) sample contains an extra peak that might belong to the WO\(_{3}\) (404) face (JCPDS Card No. 36-0103), and the other peaks are assigned well to monoclinic WO\(_{2.9}\) bulk (JCPDS Card No. 05-0386). On the other hand, the XRD pattern of WO\(_3\) sample illustrates the pure WO\(_3\) phase (Supplementary Fig. 4, JCPDS No. 43-1035). Besides, the characteristic peaks in Raman spectrum of the sample WO\(_{2.9}\) are broad and weak compared with those of sample WO\(_3\) (see details in Supplementary Fig. 5 and Supplementary Table 1), which could be attributed to the local lattice imperfections\(^25\), revealing the absence of partial O atoms in WO\(_{2.9}\) sample. Figure 2f reports our surface analysis for both WO\(_{2.9}\) and WO\(_3\) samples with the X-ray photoelectron spectroscopy (XPS) technique. For the WO\(_{2.9}\) sample, two major tungsten species, W\(^{6+}\) (4f\(_{7/2}\) = 34.7 eV) and W\(^{5+}\) (4f\(_{7/2}\) = 33.3 eV), are found on its surface, showing the existence
of W$^{5+}$ (ref 26). On the other hand, deconvoluted W 4f doublet peaks of the WO$_3$ sample suggest that tungsten is solely in the state of W$^{6+}$ (W 4f$_{7/2} = 34.7$ eV)$^{27}$. Moreover, the peaks in the XPS survey scans of the materials before and after the modifications can be only assigned to the W, O and C elements (Supplementary Fig. 6), indicating the inexistence of other elements$^{28}$. To know the neighbours of the W atoms, the WO$_{2.9}$ sample was thus characterized by means of the W L$_3$-edge X-ray absorption fine structure (XAFS). The W L$_3$-edge white line derives from electron transitions from the 2p$^{3/2}$ state to a vacant 2p$^{1/2}$ state, and Fig. 2g presents the W L$_3$-edge X-ray absorption near-edge structure spectra of the WO$_{2.9}$ sample and the reference samples. The Fourier-transformed spectra of W L$_3$-edge extended XAFS of the samples are shown in Fig. 2h. The peaks in the range 1–2 Å and around 3 Å appear in the curves of bulk WO$_3$ and metallic W samples, respectively, owing to the W–O shell and W–W shell. Thus, the only peak in WO$_{2.9}$ sample at 1–2 Å is believed to be the contribution from W–O binding, indicating the absence of metallic W–W bond, which is consistent with the results of XPS W 4f region that the metallic tungsten species (W$^{0}$, 4f$_{7/2} = 30.0$ eV) could be hardly detected (Supplementary Fig. 7). On the basis of these results, the tungsten species in the as-synthesized catalyst could be the WO$_{2.9}$ phase with only W–O bond.

**Electrochemical hydrogen evolution reaction.** The electrodes for HER were prepared by drop casting a fixed volume and concentration of catalysts from an aqueous suspension onto glassy carbon disc (see more details in Methods). The HER with WO$_{2.9}$ nanoparticles as the catalyst on glassy carbon electrode (GCE) was measured using a standard three-electrode electrochemical configuration in 0.5 M H$_2$SO$_4$ electrolyte deaerated with hydrogen. The electrodes were prepared by depositing approximately one continuous layer of WO$_{2.9}$ sample over the electrode surface area. The polarization curves (not iR corrected) showing the normalized current density versus voltage (j versus V) for the WO$_{2.9}$ catalyst along with commercial Pt/C (5%) and commercial WO$_3$ powder for comparison, are shown in Fig. 3a. Compared with blank glassy carbon, the electrode coated with bulk WO$_3$ exhibits a poor overpotential ($\eta$) value of $−637$ mV at the current density of 10 mA cm$^{-2}$, demonstrating the electro-catalytically inactive for proton reduction kinetics of the commercial WO$_3$ powder. In contrast, WO$_{2.9}$ catalyst exhibits a small $\eta$ value of $−70$ mV at the current density of 10 mA cm$^{-2}$, indicating that the tailored structure effectively reduces the energy input for activating the HER. Moreover, for driving a current density of 20 mA cm$^{-2}$, WO$_{2.9}$ electrocatalyst only requires an overpotential of $−94$ mV (not iR corrected), indicating a performance evidently exceeding most of the reported noble-metal-free HER catalysts (see details in Supplementary Table 2). These results imply that fast electron transfer and HER activation occur on the WO$_{2.9}$ electrocatalyst (Supplementary Movie 1). Further, the linear portions of the Tafel plots (Fig. 3b) were fit to the Tafel equation ($\eta = b \log j + a$, where $j$ is the current density and $b$ is the Tafel slope)$^{29}$, yielding Tafel slopes of $\approx 30$, $50$ and $\approx 120$ mV per decade for Pt/C, WO$_{2.9}$ and WO$_3$ samples, respectively. The turnover frequencies (TOFs) were estimated for the $\eta$ value of $−100$ and $−200$ mV using both theoretical and experimental surface areas for the HER in 0.50 M H$_2$SO$_4$.
Theoretical TOF values, estimated geometrically by assuming inherent activity of these catalysts was evaluated by the exchange current density \(j_0\) for 50 times (Supplementary Note 1). The surface area of the WO\(_{2.9}\) catalyst is about 48.3 m\(^2\) g\(^{-1}\), determined by Brunauer–Emmett–Teller study, and the TOFs (per surface W atom) were calculated to be 8.04 s\(^{-1}\) at –100 mV and 24.76 s\(^{-1}\) at –200 mV. Theoretical TOF values, estimated geometrically by assuming 100-nm spherical particles of WO\(_{2.9}\), can be 4.64 s\(^{-1}\) at –100 mV and 14.29 s\(^{-1}\) at –200 mV. In addition, the HER inherent activity of these catalysts was evaluated by the exchange current density \(j_0\). The \(j_0\) of WO\(_{2.9}\) catalyst is 0.40 mA cm\(^{-2}\) with a surface area of 0.97 cm\(^2\) on the working electrode (0.02 mg loading), which outperforms the value of 5.0 \times 10^{-5} mA cm\(^{-2}\) for bulk WO\(_3\) (Table 1) and can be superior to those for other reported nonprecious HER catalysts (Supplementary Table 2). The high electrode kinetic metrics (including the overpotential of –70 mV at the current density of 10 mA cm\(^{-2}\) and the Tafel slope of 50 mV per decade) and large \(j_0\) (only half lower than the value of 0.93 mA cm\(^{-2}\) for Pt) highlight the exceptional H\(_2\) evolving efficiency of the WO\(_{2.9}\) catalyst.

Cyclic voltammetry (CV) was swept between –0.3 and +0.1 V (versus the reversible hydrogen electrode potential, RHE) were applied to the WO\(_{2.9}\)-decorated working electrodes (Fig. 3c). After 1,000 CV sweeps, the overpotential required to achieve current densities of 10 mA cm\(^{-2}\) shows negligible change (from 70 to 71 mV), which remains higher than those of the benchmark catalysts (Supplementary Table 2). Moreover, we swept the CV towards positive potential up to +1.0 V (versus RHE) with scan rate of 0.02 V s\(^{-1}\) for 50 times (Supplementary Fig. 8). However, the WO\(_{2.9}\) catalyst shows an undesirable degradation of HER performance, indicating that it could hardly withstand excursions to positive potentials. Continuous HER at a static overpotential was also conducted. As shown in Fig. 3d, when an overpotential of –0.1 V was applied, a continuous HER process occurred to generate molecular H\(_2\). The as-measured time-dependent curve is in typical serrate shape, which could be attributed to the alternate processes of bubble accumulation and bubble release (inset in Fig. 3d). The amount of the decay of the WO\(_{2.9}\) catalyst is about 5.9% current loss after 14,000 s, which might be owing to the partial detachment of the catalyst caused by the continuous bubbles releasing or the remaining of H\(_2\) bubbles on the surface of the electrode that hindered the reaction. The current density levelled out at an average of 19.6 mA cm\(^{-2}\) after 14,000 s, showing negligible current density loss even after 1,000 CV cycles. (Fig. 3d). After 1,000 CV sweeps, the overpotential required to achieve current densities of 10 mA cm\(^{-2}\) shows negligible change (from 70 to 71 mV), which remains higher than those of the benchmark catalysts (Supplementary Table 2). Moreover, we swept the CV towards positive potential up to +1.0 V (versus RHE) with scan rate of 0.02 V s\(^{-1}\) for 50 times (Supplementary Fig. 8). However, the WO\(_{2.9}\) catalyst shows an undesirable degradation of HER performance, indicating that it could hardly withstand excursions to positive potentials. Continuous HER at a static overpotential was also conducted. As shown in Fig. 3d, when an overpotential of –0.1 V was applied, a continuous HER process occurred to generate molecular H\(_2\). The as-measured time-dependent curve is in typical serrate shape, which could be attributed to the alternate processes of bubble accumulation and bubble release (inset in Fig. 3d). The amount of the decay of the WO\(_{2.9}\) catalyst is about 5.9% current loss after 14,000 s, which might be owing to the partial detachment of the catalyst caused by the continuous bubbles releasing or the remaining of H\(_2\) bubbles on the surface of the electrode that hindered the reaction. The current density levelled out at an average of 19.6 mA cm\(^{-2}\) after 14,000 s, showing negligible current density loss even after 1,000 CV cycles. (Fig. 3d). After 1,000 CV sweeps, the overpotential required to achieve current densities of 10 mA cm\(^{-2}\) shows negligible change (from 70 to 71 mV), which remains higher than those of the benchmark catalysts (Supplementary Table 2). Moreover, we swept the CV towards positive potential up to +1.0 V (versus RHE) with scan rate of 0.02 V s\(^{-1}\) for 50 times (Supplementary Fig. 8). However, the WO\(_{2.9}\) catalyst shows an undesirable degradation of HER performance, indicating that it could hardly withstand excursions to positive potentials.

Table 1 | Comparison of catalytic parameters of different HER catalysts.

| Catalyst   | Current density \(j_0\) (mA cm\(^{-2}\)) | Corresponding overpotential \(\eta_0\) (mV) | Tafel slope \(\beta\) (mV per decade) | Exchange current density \(j_0\) (mA cm\(^{-2}\)) |
|------------|-----------------------------------------|----------------------------------------|-------------------------------------|-----------------------------------------------|
| WO\(_3\)   | 10                                      | –637                                   | 120                                 | 5.0 \times 10^{-5}                             |
| WO\(_{2.9}\) | 10                                      | –70                                    | 50                                  | 0.40                                          |
| Pt/C\(^{2}\) | 10                                      | –31                                    | 30                                  | 0.93                                          |

HER, hydrogen evolution reaction; RHE, reversible hydrogen electrode.

\(^{2}\)Johnson–Matthey, 20 wt% Pt/XC-72.
after the static overpotential test of the WO$_{2.9}$ catalyst via a gas chromatograph (GC-2014C) with the argon as carrier gas. The total H$_2$ amount is about 95 μmol, which is consistent with the theoretical value of 99.5 μmol by assuming that every electron is used for the reduction of protons.

In addition, we performed the XRD and XPS techniques to determine the structure of the WO$_{2.9}$ catalyst after these electrocatalytic tests. As shown in Supplementary Fig. 9, diffraction peaks in pattern of sample WO$_2.9$ remains at the similar intensity and position compared to those in Fig. 2e, revealing the unchanged local structure of WO$_{2.9}$ catalyst. Moreover, the deconvoluted W 4f doublet peaks of the catalyst after the tests exhibit negligible difference. The dispersion of W$^{5+}$ in both samples, which can be evaluated by the relative XPS intensity ratio of W$^{5+}$ atom to W$^{6+}$ atom, shows negligible change, remaining as 0.182 for the before and after samples. Specifically, we also detected the Pt 4f core level peak region to check for the possible impurities, and the existence of Pt can be thus safely ruled out. All results suggest that the origin of the excellent HER capacity could be attributed to the tailored electronic structure of WO$_{2.9}$ catalyst by means of local atomic structure modulations.

**Density functional theory studies.** On the basis of the above experimental investigations, we thus systematically examined the binding ability of their respective most stable surface, that is, WO$_{2.9}$(010) and WO$_3$(001) by virtue of extensive first-principle density functional theory (DFT) calculations (see details in Fig. 4).

**Stability of WO$_{2.9}$ electrocatalyst.** To further probe the stability of the WO$_{2.9}$ catalyst during electrocatalytic hydrogen evolution in 0.5 M H$_2$SO$_4$, the CV of WO$_{2.9}$ catalyst was swept between $-0.3$ and $+0.1$ V for 10,000 times (Supplementary Fig. 17). As with many metal oxides, WO$_{2.9}$ nanoparticles also suffer from the undesired structure change in acidic water for a long time; they are slightly soluble after these additional accelerated degradation studies, which results in the degradation of electrocatalytic activity. The overpotential increased from $-94$ to $-162$ mV at the current density of 20 mA cm$^{-2}$ after 10,000 CV sweeps. XRD pattern in Supplementary Fig. 18 reveals partial formation of WO$_{2.8}$ phase in catalyst, and the XPS spectrum also shows an enhancement of the W$^{5+}$ doublet peaks in the spectrum from those of fresh WO$_{2.9}$ sample (Supplementary Fig. 19), indicating the high oxygen vacancies of the atomic structure in acidic water for the rigorous tests. It should be noted, however, that the WO$_{2.9}$ catalyst is still much more thermodynamically stable in acidic water than most metal oxides. Further investigation is needed to obtain a clear picture of the exact microscopic changes to their surface chemistry and lattice structure. We believe that, with further research, the deactivation may be reduced or eliminated, for example, by integrating WO$_{2.9}$ nanoparticles with a graphene shell or other nanostructures.

**Discussion**

The WO$_{2.9}$ electrocatalyst prepared in this work exhibits excellent HER activity with a very low cathodic overpotential of $-70$ mV at the current density of 10 mA cm$^{-2}$ and a small Tafel slope of about 50 mV per decade. By modulating the local atomic structure of WO$_3$ at the atomic scale, an extended and ordered defect structure (Magnéli phase) is formed, resulting in preferentially exposed W sites with modified electronic structure that show a greatly enhanced catalytic activity for hydrogen evolution. We anticipate the transition metal oxide materials with suitable metal hydrogen binding energy may also hold the
promises to compete against the best precious metal catalysts available for HER, compared with the well-studied carbides, nitrides, phosphides and sulfides.

Methods
Synthesis of catalyst: In the preparation of the material, a two-step synthesis process was involved. First, 1 g of commercial WO3 (of analytically pure grade, 99.9%, Sinopharm) was carefully ground, which was carried out in a ball mill with the wet grinding method (ethanol, 24 h under rotation speed of 300 r.p.m.). Then, we prepared the thermally treated samples through annealing ground WO3 in hydrogen atmosphere (1 bar, 10% H2, 90% Ar, 100 s.c.c.m. flow) in a tube furnace at 500 °C for 60 min. The resulting powder can be collected after the tube furnace cooling down to room temperature.

Electrochemical measurements. Four microgram of catalyst and 80 μl of 5 wt% Nafion solution (Sigma-Aldrich) were dispersed in 1 ml of 1:4 v/v water/ethanol by at least 30-min sonication to form a homogeneous ink. Then, 5 μl of the catalyst ink (containing 20 μg of catalyst) was loaded onto a GCE of 3 mm in diameter (loading 0.285 mg cm−2). The area of coated electrodes may exceed that of the glassy carbon disc, but we calculate all the current densities using the geometric value. The WO2.9 modified GCE was left to dry at 40 °C. For comparison, GCEs were also modified with commercial WO3 from Sinopharm (99.9%) and Pt/C (5%) from Alfa Aesar.

All electrochemical studies were performed using a CHI 660 potentiostat (CH Instruments, China) in a three-electrode setup with a modified glassy carbon disc, but we calculate all the current densities using the geometric value. The WO2.9 modified GCE was left to dry at 40 °C. For comparison, GCEs were also modified with commercial WO3 from Sinopharm (99.9%) and Pt/C (5%) from Alfa Aesar.

Theoretical calculation. All the spin-polarized calculations were performed with Perdew–Burke–Ernzerhof functional within the generalized gradient approxima-

Catalysts characterization. The crystal structure was determined using XRD (D/MAX 2550 VB/PC) and Raman spectroscopy (Renishaw, inVia + Reflex). The structure of the catalysts was examined by SEM (S-3400N) and TEM (TECNAI F-30, 300 kV). Further, for the chemical states of the elements in catalysts were studied by XPS (ESCALAB 250Xi), and the binding energy of the C 1 s peak at 283.9 eV was taken as an internal reference. W L3-edge absorption spectra (extended XAFS) were performed on the 1W1B beamline of the Beijing Synchrotron Radiation Facility, China, operated at ~200 mA and ~2.5 GeV. W foil and WO3 powders were used as the reference samples. All samples were measured in the transmission mode. Brunauer–Emmett–Teller surface area measurement was performed at 77 K on a Micromeritics ASAP 2460 adsorption analyzer in N2 adsorption mode.

Theoretical calculation. All the spin-polarized calculations were performed with Perdew–Burke–Ernzerhof functional within the generalized gradient approxima-

in which $U$ is the electronic voltage versus SHE, while $P_{H2}$ and $C_{H2}$ are the relative partial pressure of $H_2$ and the relative concentration of $H^+$ in the aqueous solution, respectively. At the standard condition, there are approximations $\Delta G_1 = E_{f2}^\text{H2} + 0.20 \text{eV}$. The adsorption energy ($E_{f2}^\text{H}$) for hydrogen was obtained from the DFT calculation at $0 \text{K}$ relative to gas phase $H_2$ molecule, which is defined as equation (3).

$$E_{f2}^\text{H} = E_{f2}^\text{H2} - E_{f2} - 1/2E_{f1}$$  \hspace{1cm} (3)

where $E_{f2}^\text{H2}$ and $E_{f2}$ are the energy of the surface slab with and without atomic $H$ adsorption, and $E_{f1}$ is the total energy of the $H_2$ molecule in the gas phase. The more negative $E_{f2}^\text{H}$ is, the more strongly the species $H$ binds on surface.

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Author contributions
H.G.Y. conceived the project and contributed to the design of the experiments and analysis of the data. Y.H.L. performed the catalyst preparation, characterizations and wrote the paper. Z.Z.Y. and L.G. conducted the STEM examination and contributed to writing the STEM section. L.F.P., P.F.L. and H.J.Z. collected the electrochemical data. L.R.Z. carried out measurements and data analyses of XAFS. H.F.W. and P.H. conducted DFT calculations and wrote part of the paper (calculations). All the authors discussed the results and commented on the manuscript.

Additional information
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