Supplementary Information for

Hydrogen confined in a single wall carbon nanotube becomes metallic and superconductive nanowire under high pressure

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I. Method and computational details of the simulations

Our molecular dynamics simulations (MDSs) and the structural calculations were performed by using Kohn-Sham self-consistent density-functional theory (DFT) adopting a flexible linear combination of numerical atomic-orbital basis set for the valence electrons and a norm-conserving non-local pseudo-potential for the atomic cores implemented in the SIESTA code. The atomic orbital basis set used was double-$\zeta$ plus polarization orbitals. The accuracies of the energies and the pressures obtained by using DFT for hydrogen under high-pressure depend on the exchange-correlation functionals adopted in the calculations. (see Ref. [28-30] of the text). Systematically analyses of the accuracies of the most commonly used DF-functionals for prediction of the energetics and pressures of hydrogen under high pressure were given by using quantum Monte Carlo (QMC) result as an accurate standard. According to their results it seems that there is no any DF-functional can simultaneously accurately predict the energy and the pressure of hydrogen under high pressure. Fortunately, it was found that vdW-DF has the best global energetics performance while vdW-DF and DF-BLYP functionals have almost the same accuracy for local energetics. For the H@SWNT system considered in this work, the local energetics is more important. We therefore used DF-BLYP functional to calculate the energies at different temperature, while used DF-PBE functional (and LDA) to check the pressures at different temperature, since the latter one has better accuracy of pressure. In order to confirm the metallization of the hydrogen nanowire confined in SWCNT, we also calculation the band structures by using ab initio many-body perturbation theory within GW
approximation. The energy bands are shown in Figure 1(f) of the text. In consist with
the results from the DFT calculations using various exchange-correlation functionals,
we further confirmed that the hydrogen confined in the SWNT becomes metallic at
external hydrostatic pressure $P = 163.5\text{GPa}$. The pressure $P = 163.5\text{GPa}$ reported in this
work is obtained using DF-PBE. The pressure obtained using DF-LDA is about
0.44\text{GPa} higher than that obtained using DF-PBE. It should be noted that this
pressure value is not the pressure “felt” by the hydrogen confined in the SWNT.
SWNTs have very high tensile strength thus the hydrogen filled in the SWNTs can
accumulate to very high density. The pressure on the wall of the SWNT is increasing
with the density of the confined hydrogen (Xia et al. Phys. Rev. B 2002, 65, 155415).
It turns that the same value of pressure is exerted on the confined hydrogen. A
detailed study of the equation of state (EOS) for hydrogen molecules confined in a
SWNT indicated that even if there is not any external pressure exerted on the
$\text{H}_2@\text{SWNT}$ complex, the pressure of the confined hydrogen can be as high as
70-80\text{GPa} (Xia et al. AIP Adv. 2012, 2, 022161). If an external hydrostatic pressure is
applied on the $\text{H}@\text{SWNT}$ the density of the confined hydrogen increases and thus the
pressure on the hydrogen increases rapidly with the external pressure, since the van
der Waals force from the wall of the SWNT go up rapidly when the confined
hydrogen approaches the tube wall. This additional physical pressure added to the
external hydrostatic pressure makes the real pressure on the confined hydrogen much
higher than 163.5\text{GPa}. To evaluate the actual value of the physical pressure, one
needs to study the equation of state (EOS) of the confined hydrogen system and the
elastic strength of the SWNT under the external high pressure. It might be another interesting topic that we don’t study here.

MDSs based on ab initio calculations are usually computationally expensive. The simulation time needed is almost proportional to $N^3$ (where $N$ is the number of the particles in the supercell used), unlike the classical MDSs, or the MDSs based on parametrized transferable tight-binding model (Omata, et al., Physica E 2005, 29, 454-468), where the simulation efficiencies are high and thus larger supercells can be used. Therefore, for ab initio MDSs it is important to use proper size of the supercell incorporated with accurately periodic boundary condition to ensure the accuracy of the results obtained while not wasting the computational resource. To check the size effect of the supercell, we started from a small cell and then increased the size by doubling the size of the supercell to examine the difference of the energies obtained from the different sized supercells. For example, we used three supercells of H@SWNT from a segment of (8, 0) SWNT containing 32 carbon atoms and 11 $H_2$ molecules (22 H atoms), 64 carbon atoms and 22 $H_2$ molecules (44 H atoms), and 128 carbon atoms and 44 $H_2$ molecules (88 H atoms), respectively. They are labeled by $C_{32}H_{22}$, $C_{64}H_{44}$, and $C_{128}H_{88}$, respectively. After the supercells were selected, the ab initio simulations for structural and energy optimization were performed using DF-BLYP functional and using periodic boundary condition along the tube axis (selected as z-axis). The vacuum region in x and y directions were large enough to avoid the lateral mirror interactions. The large vacuum region used in x and y directions ensures the external hydrostatic pressure 3-dimensionally exerted only on
the central H@SWNT while not affected by the lateral image wires. All the atomic coordinates were relaxed with a conjugate gradient algorithm with a tolerance of the maximum force less than 0.01 eV/Å. The real space grid used was represented by an equivalent plane wave cutoff energy of 120 Ry. A k-point mesh of 1×1×8 was used according to the method of Monkhorst-Pack for the Brillouin zone sampling. After the simulations were converged, we find that the energies of C\textsubscript{32}H\textsubscript{22}, C\textsubscript{64}H\textsubscript{44}, and C\textsubscript{128}H\textsubscript{88} are $E = -5246.756099 eV$, $E = -10493.539140 eV$, and $E = -20987.071878 eV$, respectively. Taking C\textsubscript{128}H\textsubscript{88} as a standard, the absolute energy error for C\textsubscript{32}H\textsubscript{22} is 0.21979 meV/atom, and that for C\textsubscript{64}H\textsubscript{44} is 0.02967 meV/atom. It is clear that increasing the size from C\textsubscript{32}H\textsubscript{22} to C\textsubscript{64}H\textsubscript{44}, the energy error is reduced substantially. The energy error for C\textsubscript{64}H\textsubscript{44} almost reaches the accuracy limitation for DFT calculations. Furthermore, we also considered how the size effect may affect the accuracy of the specific heat values obtained if we accept C\textsubscript{64}H\textsubscript{44} as the supercell H@SWNT. In the simulation to mimic the specific heat ‘measurement’ at different temperature $T_i$, where $i=1, 2, 3,...$, we chose $\Delta T = T_{i+1} - T_i = 10K$, or 20K. The energy difference $\Delta E = E(T_{i+1}) - E(T_i)$ is found usually in the range of 140 meV to 280 meV. If we use C\textsubscript{64}H\textsubscript{44} as the supercell H@SWNT, the uncertainty of the energy difference (hence the specific heat value) caused by the size effect of the supercell is estimated in the range of 1% to 2%, which is much less than the thermal fluctuation of the system, as shown in Figure 2 of the text. Therefore, use of C\textsubscript{64}H\textsubscript{44} as the supercell H@SWNT is a proper selection, from which reliable simulation results can be obtained.
The optimized supercell H@SWCNT has radius $r = 3.334\text{Å}$ and has a translational period of $8.65\text{Å}$ along its axial. The confined hydrogen molecules form a cylindrical shell structure along the axis of the SWNT. The average areal density of the hydrogen on the plane perpendicular to the axis is $0.09\text{H}_2/\text{Å}^2$. The linear density of the hydrogen is $2.54\text{H}_2/\text{Å}$. The radius of a (8,0)SWNT without any hydrogen molecule in it is $3.14\text{Å}$. The radial strain of the SWNT caused by the confined hydrogen is $0.062$. A detailed study for the radial strength for H$_2$@SWNT complexes indicated that the acceptable maximum radial strains before the broken of a (5,5)SWNT is $0.12$, and that of a (9,0)SWNT is $0.18$ (Ma et al., Phys. Rev. B 2002, 65, 155430). It is obvious that the H@SWCNT supercell studied in this work is stable, and the wall of the (8,0)SWNT under the pressure of the high density of hydrogen keeps its perfect shape since the radial strain value is only $0.062$.

In the ab initio MDSs, the Parrinello-Rahman dynamics was adopted to simulate an external hydrostatic pressure exerted on the H@SWNT system. When the pressure reaches a value of $205\text{GPa}$, the source of the static pressure is removed and let the system expanding freely until the static pressure on the H@SWNT reaches a fixed pressure of $P_0 = 163.5\text{GPa}$ (accuracy to 163.5374407GPa). At the same time the No̧se dynamics was adopted to simulate a thermal source that is contacted to the system changing the temperature of the system. The time steps of $0.025\text{ fs}$ were used in all the simulations. We adjusted the No̧se mass to a value of $0.05\text{Ry} \cdot \text{fs}^2$ in the simulations to insure that when the temperature reaches a desired value $T_0$ and keeps unchanging with time and the static pressure just reaches the value of $P_0$. When this
condition is satisfied we know that the system reaches a state of quasi-thermodynamic
equilibrium. The time scale needed to reach the quasi-thermodynamic equilibrium
state in our MDSs depends on the temperature of the system which is \( \sim 400 \) fs. In fact,
the H@SWNT and the thermal source can be considered as a combination system to
form an isolated system. The total entropy of the system, \( S = S + S_0 \), where \( S \) and \( S_0 \)
are the entropy of the H@SWNT and the thermal source, respectively. When the
combination system reaches its thermodynamic equilibrium state, \( \delta S = \delta S + \delta S_0 = 0 \)
must be hold. If we use \( U, T, P, \) and \( V \), to present the inner energy, the temperature,
the pressure, and the volume, respectively, for a considered system, then according to
the thermodynamic law, we have

\[
dU = TdS - PdV. \quad (S1)
\]

From Eq.(S1), one has \( \delta S = \frac{1}{T}\delta U + \frac{P}{T}\delta V \) and \( \delta S_0 = \frac{1}{T_0}\delta U_0 + \frac{P_0}{T_0}\delta V_0 \). Then it turns to be:

\[
\delta S = \left( \frac{1}{T} \delta U + \frac{1}{T_0} \delta U_0 \right) + \left( \frac{P}{T} \delta V + \frac{P_0}{T_0} \delta V_0 \right). \quad (S2)
\]

Since the combination system is an isolated one, \( U + U_0 \) keeps constant, and \( V + V_0 \)
also keeps constant. That is to say \( \delta U + \delta U_0 = 0 \), and \( \delta V + \delta V_0 = 0 \). From Eq.(S2) one
has the thermodynamic equilibrium condition:

\[
\delta S = \left( \frac{1}{T} - \frac{1}{T_0} \right) \delta U + \left( \frac{P}{T} - \frac{P_0}{T_0} \right) \delta V = 0. \quad (S3)
\]

Since the inner energy \( U \) and the volume \( V \) of the H@SWNT system are independent
quantities and can change independently, only if the condition of \( T = T_0 \) and \( P = P_0 \)
are true, can the \( Eq.(S3) \) of the thermodynamic equilibrium be satisfied. Because the
combination system is expanding freely, \( P = P_0 \) is always true. When the simulation
is advancing, the desired temperature \( T \) gradual tends to equal to \( T_0 \) and when \( T=T_0 \) is
reached, \( T \) is no longer changing with the simulation time. Thus we know that the system reaches its quasi-thermodynamic equilibrium state at the temperature \( T \). By a series of simulations at different temperature, we can obtain the specific heat of the H@SWNT system, as described in the text. In the practical process of simulations, the Eq. (1) of the text is used in a differential way. At different temperature \( T_i \), the energy of the H@SWNT, \( U(T_i) \), was obtained, which doesn’t contain the contribution from nuclear quantum effects (NQEs). If NQE was considered, an additional energy \( \delta E_{\text{NQE}}(T_i) \) should be added to \( U(T_i) \). In the simulations, \( \Delta T = T_{i+1} - T_i \) was set equal to 10K or 20K. The value of \( \delta E_{\text{NQE}}(T_{i+1}) - \delta E_{\text{NQE}}(T_i) \) should not be very large, because \( \Delta T \) is not very large. As long as the value of \( \delta E_{\text{NQE}}(T_{i+1}) - \delta E_{\text{NQE}}(T_i) \) is not very large, \( \Delta U(T) = U(T_{i+1}) - U(T_i) \), where \( T = T_i + \Delta T / 2 \), can partially reduce the NQEs. Therefore, the NQEs are also partially canceled from the simulated value of specific heat, \( C_p(T) \) = \([\Delta U(T) + P_0 (V(T_{i+1}) - V(T_i))]/\Delta T \), where \( V(T_{i+1}) \) and \( V(T_i) \) are the volumes of the SWNT@H measured at \( T_{i+1} \) and \( T_i \), respectively.

II. The structure of the H@SWNT system and the electronic density distributions of the confined hydrogen

Although the confined hydrogen is very close to the wall of the SWNT, with the closest distance of \( \sim 1.4 \) Å between a H atom and a C atom, there is no any bond formed between a H atom and a C atom. The confined hydrogen and the SWNT formed two sublattices. Under the hydrostatic pressure of 163.5 GPa, the structure of the confined hydrogen substantially changed from the initial molecular structure. The hydrogen molecules are closely packed to form different H-clusters, such as H, H\(_2\), H\(_3\), H\(_4\) and H\(_6\). Some H\(_2\) molecules have bond length longer than 0.74Å of a typical H\(_2\), while other H\(_2\) molecules have bond length shorter than 0.74Å, as the electron
density distributions around two hydrogen atoms shown in Figure 1(b) of the main text. The electron density distribution around a H\textsubscript{4} cluster is also displayed in Figure 1(c). A H\textsubscript{4} cluster is actually formed from two H\textsubscript{2} molecules when they approach closely. For instance, a H\textsubscript{2} molecule has bond length 0.757 Å and another H\textsubscript{2} has bond length 0.743 Å. When they are close to a distance of 0.873 Å, they form a H\textsubscript{4} cluster having an L shape, as shown in Figure 1(c). This configuration is typical for H\textsubscript{4} clusters in the confined hydrogen. Figure 1(d) shows the electron density distribution around a H\textsubscript{6} cluster formed in the confined hydrogen. The H\textsubscript{6} is actually formed by a H\textsubscript{2} molecule joining to a H\textsubscript{4} cluster or two H\textsubscript{3} trimers joining together. The isolated H can also join with other H\textsubscript{2} to form loosely bonded H\textsubscript{3} cluster with bond length in the range from 0.8 Å to 1.0 Å. The formation of these clusters indicates that dissociation and reconstruction of H\textsubscript{2} molecules have taken place. A recent work has shown that hydrogen molecule dissociation took place to form metastable atomic phase under a pressure comparable to that we considered in this work (see Ref. [37] of the text).

![Figure S1](image)

**Figure S1.** The lattice structure of hydrogen confined in a (8,0) SWNT at external hydrostatic pressure of P=163.5GPa, (a) at temperature T=20K, (b) at temperature
T=230K.

The lattice structures of the hydrogen confined in the SWNT for the H@SWNT under a hydrostatic pressure P=163.5GPa are shown in Figure S1. Figure S1(a) shows the structure at temperature T=20K, while Figure S1(b) depicts the structure for T=230K.

In Figure S1(a), we colorized the hydrogen with different colors to distinguish different type of clusters. The black H$_2$ molecules have bond length $\sim$ 0.724Å that is obviously shorter than 0.74Å for typical H$_2$ molecule. The H$_2$ molecules colored in purple blue have bond length from 0.733Å to 0.734Å, while those colored in purple have bond length from 0.738 Å to 0.739 Å. The H$_2$ molecules colored in light blue have bond length from 0.742 Å to 0.743 Å, while those colored in grey have bond length 0.744 Å. The H atoms are colored in red, while the H$_2$ colored in white have bond length from 0.797 Å to 0.798 Å, indicating they are going to dissociate. The hydrogen cluster colored in green represents a H$_4$ cluster with a H$_2$ molecule (bond length 0.759 Å) joined together forming a H$_6$ cluster. The electron cloud around this H$_6$ cluster is shown in Figure 1(d) of the main text. The cluster H$_6$ colored in yellow has the same structure with that colored in green. Although these H$_2$ molecules and other clusters are divided to different categories, each category has a same translational period along the axis forming a one-dimensional lattice with C1 symmetry. The translation period along the axis $\square=5.924\text{Å}$, while the translational repeat distance for each category equals $\square/2 = 2.962 \text{Å}$.

When the temperature rises to 230K that is just above the temperature observed in the jump point of the specific heat shown in Figure 2(b) of the main text, we obtained the structure as shown in Figure S1(b). Using the same colorization method, we see that a same lattice structure as that in Figure S1(a) is observed. In response to very
small thermal expanding coefficient at such a high pressure, the bond lengths of some H$_2$ molecules have tiny changes and the repeat distance changes to $\sqrt[2]{2} \times 2.963$ Å. This confirms that there is no structural phase transition around the jump point. The only possibility for the specific heat drop around T=225K is caused by superconductive to normal state transition. From this figure, we also see that the hydrogen confined in the SWNT is not homogeneous thus we think it may be type II superconductor. According to the Ginsburg-Landau theory used to study the fluctuation in superconductors near the transition temperature, the order parameter represents some average over the neighboring states with similar energy. The fluctuations tend to be very small but become important when we study the properties very close to the transition temperature. (W. A. Harrison, Solid State Theory, TATA McGraw-Hill, Bombay-New Delhi, 1970, p.535). These effects may cause the shape of the curve of the electronic specific heat shows a complicated structure, rather than a single jump point at $T_C$.

III. The phonon frequency spectrum and the contribution of the lattice vibration to the specific heat

The density of state of phonons, which are obtained from first-principles calculations, for the hydrogen confined in the (8,0)SWNT under hydrostatic pressure of 163.5GPa is shown in Figure S2(a). The maximum frequency (maximum phonon energy) of the confined hydrogen is as large as $\omega_m=620$ meV. This large phonon energy leads us to accept large maximum phonon energy $\omega_\theta=277$meV in the electron-phonon spectral density $\alpha^2F(\omega)$. Figure S2(b) shows the molar heat capacity at $P=163.5GPa$ contributed by different terms in Eq. (2) of the main text, including
the contribution from the electrons (both superconductive and normal electrons), that from the lattice vibration for hydrogen confined in the SWNT, and that from the lattice dilation. The component contribution from the lattice vibration, $C_L$, is obtained from the spectrum of the phonon density of states shown in Figure S2(a) by using numerical calculation based on Eq.(3) of the text. Subtracting this contribution and the contribution of the lattice dilation $C_L^{D}$ from the constant-pressure molar heat-capacity shown in Figure 2(b) of the text, we obtained the constant-pressure molar heat capacity of electrons $C_P^e$. The molar heat capacity for the electrons in normal states, $C_n^e$, is also shown by the straight dashed line in this figure.
Figure S2 (a) The phonon density of state for hydrogen confined in a (8,0)SWNT under hydrostatic pressure 163.5 GPa; (b) the molar heat capacity at \( P = 163.5 \text{ GPa} \) contributed by different terms in Eq.(2) of the main text. The red squares indicate the contribution from the electrons (superconductive and normal electrons), the dashed line is that from electrons in normal states, the blue curve is that from lattice vibration of the confined hydrogen, the blue squares give the contribution from lattice dilation, and the total contribution is shown by the black solid dots.

IV. The superconductivity property of the hydrogen nanowire confined in the SWNT

We will use the electron-phonon strong-coupling Eliashberg theory to predict the characteristic superconductivity parameters of the hydrogen nanowire. A systematic description of the theoretical frame can be found in Ref. [35] of the text that summarized the main aspects of the superconductivity theory developing from BCS theory to the strong-coupling Eliashberg theory. The famous McMillan formula and its refined version developed by Allen and Dynes are useful analytical expressions for prediction of the critical temperature of strong-coupling superconductors (McMillan, W. L., *Phys. Rev.* 1968, 167, 331(1968); Allen, P. B., and Dynes, R. C., *Phys. Rev. B* 1975, 12, 905) The most important parameters involved in the Eliashberg equations are the electron-phonon interaction spectral density \( \alpha^2 F(\omega) \), the pairing kernel \( \lambda \) \((i\omega_m - i\omega_n)\) for the electron-phonon interaction to cause the attractive between two electrons around the Fermi energy, and the Coulomb pseudo-potential opposing
superconductivity $\mu^*$. The spectral density $\alpha^2F(\omega)$ can be obtained experimentally from inversion of tunneling measurement data, or from first-principles calculations. For the H@SWNT system, there is no available experimental data on spectral density $\alpha^2F(\omega)$. For the system consists of two sub-lattices, i.e., the SWNT-lattice and the hydrogen lattice. The dynamical pressure delivering on to the SWNT caused by the vibration of hydrogen lattice gives rise to additional atomic displacements on the SWNT. The vibration of the SWNT also delivers dynamical pressure on to the hydrogen lattice to give rise to additional atomic displacements on the hydrogen lattice. In this case, it is difficult to obtain the spectral density $\alpha^2F(\omega)$ by using first-principles calculations. We will use the scaling theorem developed by Coombes and Carbotte (refer to Ref. [35] of the main text) to derive an $\alpha^2F(\omega)$ for the hydrogen nanowire from that of a hydride. The scaling theorem is very useful for the superconductive material when its critical temperature $T_c$ is known. Since the transition temperature $T_c \approx 225K$ of the hydrogen confined in the SWNT is known according to the simulation results to mimic the specific heat “measurements”, we can use this theorem to obtain the electron-phonon interaction spectral density $\alpha^2F(\omega)$ for the hydrogen nanowire. According to the scaling theorem, if the e-p spectral density $\alpha^2F(\omega)$ of a superconductive system is already know. It can be taken as a standard (the base spectral density $\alpha_0^2F(\omega)$) to construct a model $\alpha^2F(\omega)$ for another superconductive system which has the critical temperature $T_c$ already known. Using the model e-p spectral density, the superconductive properties of the system under study can be predicted. We choose $\alpha^2F(\omega)$ for $H_3S$ as the base spectral density to
derive a spectral density for the hydrogen nanowire by use of the scaling theorem. The $\alpha^2F(\omega)$ for H$_3$S was obtained by using \textit{ab initio} calculation, and was provided by Durajski, A. P., et al. in Ref.[17] of the main text. We choose H$_3$S as the base system since its e-p spectral density was obtained under 150GPa that is similar to the pressure 163.5GPa used in our work, and the Tc reported by them is near the value of Tc = 225K found in our work. Furthermore, most studies on compressed hydrogen-rich hydrides confirmed that hydrogen sublattice formed by the compression gives the main contribution to superconductivity (Duan, \textit{et al. Sci. Rep.} 2014, 4, 6968). In consistent, the structures recently found in ScH$_{10}$, and the rare-earth hydrides LaH$_{10}$ and YH$_{10}$ also confirmed the formation of hydrogen sublattice of clathrate-like cage with the metal element located in the center of the cage. (refer to Refs. [19-21] and Ref. [24] of the main text). The superconductive structures of compressed hydrides have a common feature that is characterized by the hydrogen sublattice intercalating the heavier elements, or the cage formed by the hydrogen atoms encapsulating the heavier elements. We think about the H@SWNT system, which has the hydrogen lattice confined in the cage of SWNT. In view of the nanoscale environment, the closest distance between the hydrogen atoms and the carbon atom on the wall of the SWNT is similar to that between the hydrogen atoms and the heavier atoms in the hydrides. The only difference of the local environment between the H@SWNT and that of the hydrides is that the hydrogen atoms in H@SWNT have no chemical bond with the carbon atoms while the hydrogen atoms have chemical bonds with the heavier elementary atoms in hydrides. The hydrogen atoms are more freely in the
H@SWNT, therefore the highest phonon frequency is much higher than that in hydrides, as shown in Figure S2(a). However, the $T_c$ value of the H@SWNT is similar with that in H3S. It indicates that the hydrogen vibration modes with higher frequencies in the phonon frequency spectrum have less contributions to the e-p interaction density $\alpha^2F(\omega)$. Only the hydrogen vibration modes in H@SWNT, which are similar to those in H3S, have main contribution to $\alpha^2F(\omega)$. The hydrogen clusters H$_2$, H$_3$, and H$_4$ found in the hydrogen confined in SWNT and their waggling vibration modes are similar to those found in the hydrides SnH$_4$, SnH$_8$, and SnH$_{12}$ under high compression (ref. to Ref. [18] of the main text). The facts stated above indicate that under high pressure there are certain hydrogen vibration modes exist both in the H@SWNT and the hydrides, which give the main contribution to the high $T_c$ value in these materials. Therefore, the shape of the spectral density $\alpha^2F(\omega)$ of the hydrogen confined in the SWNT should be similar to those for hydrides under similar pressure.

Thus we choose $\alpha^2F(\omega)$ for H$_3$S as the base spectral density to derive a spectral density for the hydrogen nanowire by use of the scaling theorem. According to this theorem, a model spectral density $\alpha^2F(\omega)$ can be constructed by the base spectral $\alpha_0^2F(\omega)$, for instance, the spectral of H$_3$S by the relation:

$$\alpha^2F(\omega) = B\alpha_0^2F(b\omega), \quad (S4)$$

where B and b are adjustable parameters to ensure the $T_c$ obtained by using the strong-coupling superconductivity theory agrees with the known value of $T_c$. We used $b=0.757$, and $B=0.9$ to obtain the model spectral density, as shown in Figure 4(a) of the main text. Then by use of numerical integrations, the useful moments of $\alpha^2F(\omega)$
involved in the Eliashberg equation can be calculated.

\[
\lambda(i\omega_m - i\omega_n) = 2\int_0^{\infty} \frac{\alpha^2 F(\omega) d\omega}{\Omega^2 + (\omega_m - \omega_n)^2},
\]

(S5)

where the imaginary-axial Matsbara frequency \( \omega_n = \pi k_B T (2n - 1) \), \( n = 0, \pm 1, \pm 2, ... \), and \( \omega_m = \pi k_B T (2m - 1) \), \( m = 0, \pm 1, \pm 2, ... \). When \( m = n \), the mass-renormalization parameter \( \lambda = \lambda(0) \) can be obtained:

\[
\lambda = 2\int_0^{\infty} \frac{\alpha^2 F(\omega) d\omega}{\Omega},
\]

(S6)

Using the \( \alpha^2 F(\omega) \) data provided in Fig.4(a), we can obtain the value of \( \lambda = 2.071 \) by use of numerical integration of Eq.(S6).

Another useful moment of the spectral density \( \alpha^2 F(\omega) \) is the characteristic phonon energy \( \omega_{in} \):

\[
\omega_{in} = \exp\left[ \frac{2}{\pi} \int_0^{\infty} \ln(\omega) \frac{\alpha^2 F(\omega) d\omega}{\omega} \right],
\]

(S7)

\( \omega_{in} = 72.611 \text{ meV} \) is obtained by numerically integrating Eq.(S7).

The moment \( \lambda(i\omega_m - i\omega_n) \) is useful if one needs to predict the superconductive properties of the materials by numerically solving the imaginary-axial Eliashberg equations, while the moments \( \lambda \) and \( \omega_{in} \) are useful if one only needs to obtain the critical temperature \( T_c \) by use of the analytical McMillan equation and its refined version. The value of Coulomb pseudo-potential \( \mu^* \) is usually much less than that of \( \lambda \) for strong-coupling superconductors. The value of \( \mu^* = 0.1 \) were used for all the metals in the work of Allen and Dynes (Allen, P. B., and Dynes, R. C., Phys. Rev. B 1975, 12, 905). In principle, \( \mu^* \) should be determined from the numerical solutions from the Eliashberg equations. Durajski, et al., used this method and determined the \( \mu^* = 0.123 \) for H\(_3\)S. Since \( \mu^* \) can be expressed as a function of the \( \mu \), i.e., a pure
instant Coulomb potential on the Fermi surface, we can obtain \( \mu^* \) for the hydrogen nanowire by the Morel-Anderson formula:

\[
\mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{\omega_{el}}{\omega_{ln}} \right)}.
\]  

(S8)

As \( \mu^* = 0.123 \) is the value for H\(_3\)S, Eq.(S8) can be write as

\[
\mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{\omega_{el}}{\omega_{ln}} \right)} = 0.123, \quad \text{ (S9)}
\]

where \( \omega_{ln}^{H_3S} \) denotes the phonon characteristic energy of H\(_3\)S. According to the scale theorem, \( \frac{\omega_{ln}^{H_3S}}{\omega_{ln}^{H_3S}} = \frac{1}{b} = \frac{1}{0.757} = 1.321 \), where \( \omega_{ln}^{H} \) is the phonon characteristic energy of hydrogen lattice confined in the SWNT. As long as the \( \omega_{el} \) of electrons is similar for the H\(_3\)S and the hydrogen nanowire, one can obtain an equation:

\[
0.123 = \frac{\mu}{1 + \mu \ln \left( \frac{\omega_{el}}{\omega_{ln}^{H_3S}} \right)}.
\]  

(S10)

From Eq.(S10) one can obtain an equation:

\[
1 + \mu \ln \left( \frac{\omega_{el}}{\omega_{ln}^{H_3S}} \right) = 7.8517 \mu.
\]

We can obtain the \( \mu^* \) for the hydrogen nanowire:

\[
\mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{\omega_{el}}{\omega_{ln}^{H_3S}} \right)} = \frac{1}{7.8517} = 0.127
\]

The mass-renormalization parameter \( \lambda = 2.071 \) and the characteristic phonon energy \( \omega_{ln} = 72.611 \text{meV} \) from Eq.(S6) and Eq.(S7), respectively, for the hydrogen nanowire are obtained. Furthermore, the spectral weight \( A = \int_0^\infty \alpha^2 F(\omega) d\omega = 128.977 \text{meV} \) and the average phonon energy \( < \omega > = \frac{2A}{\lambda} = 124.555 \text{meV} \) are obtained. These parameters, the maximum phonon energy \( \omega_0 = 277 \text{meV} \) in the spectral density \( \alpha^2 F(\omega) \) and the Coulomb pseudo-potential \( \mu^* = 0.127 \) are very useful
for determination of the critical temperature and/or comparison with those of other strong-coupling superconductors.

Leavens and Carbotte introduced a two-step model for the gap in the real-axial Eliashberg equations (Carbotte, J. P., Rev. Mod. Phys., 1990, 62, 1027; Leavens, C. R., and Carbotte, J. P., J. Low Temp. Phys. 1974, 14, 195):

\[
\Delta(\omega, T) = \begin{cases} 
\Delta_0 & 0 < \omega \leq \omega_0 \\
\Delta_\infty & \omega > \omega_0
\end{cases}, \quad Z_S(\omega, T) = \begin{cases} 
1 + \lambda & 0 < \omega \leq \omega_0 \\
1 & \omega > \omega_0
\end{cases}
\]

Neglecting the phonon scattering factor and taking the limit of \( T = T_C \), the real-axial equation can be linearized in the gap value. A relation, \( \Delta_\infty = -\mu^* \Delta_0 \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right] \) are also obtained. Then an approximation formula is obtained:

\[
1 + \lambda = \int_0^{\omega_0} d\omega' \int_0^{\omega_0} d\omega'' F(\nu) 2f(-\omega') f(\omega') + f(\omega') f(-\omega') - \mu^* \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right], \quad (S11)
\]

The Fermi distribution \( f(\omega') \) decays exponentially as the important frequencies in \( \alpha^2 F(\omega) \) are large compared with \( k_B T \), thus the factor \( \left( \frac{1}{\omega} \right) f(\omega') \) in Eq.(S11) can be replaced by \( \left( \frac{1}{\omega} \right) f(\omega') \). Then one can use Poisson’s frequency sum formula:

\[
\frac{f(-x) - f(x)}{x} = -\frac{\tanh \left( \frac{x}{2k_B T} \right)}{x}, \quad (S12)
\]

The integral in Eq.(S10) is calculated giving

\[
1 + \lambda = 1.13 \omega_0 \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right] - \mu^* \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right], \quad (S13)
\]

where \( \lambda \) is a moment of \( \alpha^2 F(\omega) \) defined as

\[
\lambda = 1.13 \omega_0 \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right] - \mu^* \ln \left[ \frac{1.13\omega_0}{k_B T_C} \right]. \quad (S14)
\]

The critical temperature is given by:
\[ k_B T_C = 1.13 \omega_0 \exp \left[ -\frac{1 + \lambda + \lambda^*}{\lambda + \mu^*} \right]. \quad (S15) \]

From Eq.(S14), we obtain \( \lambda = 2.339 \), and the critical temperature \( T_c = 225K \) is obtained from the semi-quantitative Eq.(S15).

Now, we compare the superconductivity parameters of the hydrogen nanowire with those of the conventional superconductors. It is obvious that the values of the parameters \( \lambda, \omega_{ln} \), and \( \mu^* \) are all in the range of those for other conventional superconductors.

Mitrović et al. (Mitrović, B., Zarate, H. G., Carbotte, J. P., Phys. Rev. B 1984, 29, 184) developed a relation between \( \frac{2\Delta_0}{k_B T_C} \) and the strong-coupling index, \( \frac{T_c}{\omega_{ln}} \), i.e.

\[ 2\Delta_0 / k_B T_C = 3.53 \left[ 1 + 12.5 \left( T_C / \omega_{ln} \right)^2 \ln \left( \omega_{ln} / 2T_C \right) \right]. \quad (S16) \]

The strong-coupling index \( T_C / \omega_{ln} = 0.266 \) is obtained for the hydrogen nanowire. Inserting this value into Eq.(S16), we obtained \( 2\Delta_0 / k_B T_C = 5.500 \). Figure 4(b) in the text shows \( 2\Delta_0 / k_B T_C \) as a function of the strong-coupling index \( T_C / \omega_{ln} \). The dashed curve is from Eq.(S16), and the data points are taken from the data summed in Table I of Ref.[32] of the text. It seems this curve is universal since many of the superconductors including the hydrogen nanowire of this work follow this curve very well.

Another importance quantity is the electron-specific heat jump at \( T_C \). From Figure 3 of the text, we see that the jump value \( \Delta C(T_C) \approx 1.453 \) cal./mol.K, and the ratio of specific heat jump to the specific heat of normal electrons, \( \Delta C(T_C)/C_N(T_C) = \Delta C(T_C)/\gamma T_C = 2.74 \). This value agrees with those of the theoretical prediction of \( \Delta C(T_C)/\gamma T_C = 2.8 \) for many conventional superconductors. We summarize the superconductive parameters of the hydrogen nanowire studied in this work in Table I.
of the main text. It is obvious that these parameters are consistent with the parameters for many known superconductors. The $T_C = 225$K is among the highest values of all-known superconductors. This is reasonable since the maximum phonon energy $\omega_m = 620$meV found for the hydrogen nanowire is remarkable larger than those for other superconductors, the DOS at the Fermi energy and the strong-coupling index $T_C/\omega_m$ are large for the hydrogen nanowire. For the same reason, the $2\Delta_0/k_B T_C$ is large for the nanowire.

The superconductive properties of the nanowire are fully consistent with the electron-phonon strong-coupling superconductive theory. The confined hydrogen molecules dissociate and form small cluster groups such as, H, H$_3$, H$_2$, H$_4$ and H$_6$. But the hydrogen does not react with the SWNT. Thus a pure physical-pressure from the carbon atoms on the tube wall assists the hydrogen becoming metallic and superconductive at much lower pressure than that needed for metallizing bulk hydrogen.

Another point we need to give a discussion. The model SWNT used is a straight isolated tube without any defect on the tube wall. In practice, SWNTs may be bundled and even can be collapse to form $sp^2$-$sp^3$ mixture system under pressure. These difficulties, at this moment, prevent to use accurate $ab$ initio simulations to prove that hydrogen confined in bundles of SWNTs with various defects become metallic and superconductive. Classical MDSs or MDSs with parametrized methods may be used to treat more complicated system. However, the accuracies of those methods can’t give reliable results for phase transition details. The importance of this work is that by
using a simple model H@SWNT structure we have theoretically proved that high density of hydrogen confined in a (8,0) SWNT at pressure of 163.5 GPa, a pressure that is much lower than that need to metallize bulk hydrogen, becomes metallic and superconductive. Metallization and superconductive transition of hydrogen under pressure are a long pursuing and expecting goal. However, for bulk hydrogen, it is difficult to reach this goal, as the pressure needed is too high. Search for new method to lower the high pressure needed to metallize hydrogen is very important. Chemical pressure provided by heavier elements has been proved very efficient to metallize and realize superconductive transition of hydrogen-rich materials at much lower pressure than that need to metallize bulk hydrogen. Through the simulations we also find that physical pressure provided by heavier element C on the SWNT also can substantially lower the pressure of metallization and superconductive transition. Considering both the chemical and physical pressure provided by carbon element on confined hydrogen, it is likely that even if hydrogen are confined in SWNT-bundles, which may have various defects or have been seriously deformed, the confined hydrogen can be metallized and become superconductive under high pressure. In fact, for SWNT-bundles with defects and deformation, the confined hydrogen may distribute in different parts of the material, for instance in the cages of the SWNTs, in the inter-walls of the SWNTs in the bundle, or captured by the defects to form local carbon hydrides. Although the structure of the system is complicated, the hydrogen confined may experience metallization and superconductive transition under compression since both the physical and chemical pressures provided by carbon
element may take important role. This idea needs further tests both by theoretical and experimental studies.

V. Details in GW calculations

GW calculations for the confined hydrogen were performed at the level of one-shot $G_0W_0$ using DFT-PBE as the starting point. In GW, one key quantity is the energy-dependent polarizability of the system, $P$. If represented by the basis functions $\chi_\beta(q,r)$, polarizability takes its matrix representation

$$P_{\beta\beta}(q,\omega) = \frac{2}{V} \sum_k \sum_m \sum_n M_{\beta\beta}^{mn}(k,q) [M_{\beta\beta}^{mn}(k,q)]^* \Theta(E_F - E_{mk}) \Theta(E_{n,k+q} - E_F)$$

$$\times \left[ \frac{1}{E_{mk} - E_{n,k+q} - \omega + i0^+} - \frac{1}{E_{mk} - E_{n,k+q} + \omega + i0^+} \right]$$

where $|m,k\rangle$ and $|n,k+q\rangle$ denote the occupied and the empty bands respectively, the spatial integrals $M_{\beta\beta}^{mn}(k,q) = \int \psi^*_m(k) \chi_\beta^*(q,r) \psi_{n,k+q}(r) d^3r$. In most GW calculations on semiconductor systems, the plasmon-pole approximation (PPA) (Rohlfing, M. et al., Phys. Rev. B 1993, 48, 17791) is frequently used to describe the energy-dependent behavior of $P$. In PPA the matrix elements $P_{\beta\beta}(q,\omega)$ at two frequencies, e.g. $\omega = 0$ and $\omega = i$, are just evaluated. For metallic systems, such as the confined hydrogen studied in this work, PPA might fail to give reasonable band structures. Instead, in this work we explicitly computed $P_{\beta\beta}(q,\omega)$ over a grid of 400 frequencies from zero to ~130 eV. To reduce the computational cost, instead of directly evaluating $P_{\beta\beta}(q,\omega)$, we first calculated the imaginary part of $P$, i.e.

$$\text{Im}P_{\beta\beta}(q,\omega)$$

$$= -\frac{2\pi}{V} \sum_k \sum_m \sum_n \left|M_{\beta\beta}^{mn}(k,q) [M_{\beta\beta}^{mn}(k,q)]^* \right| f_{mk} - f_{n,k+q} \times \delta$$

$$\left[ \omega - (E_{mk} - E_{n,k+q}) \right]$$

(S18)
where $f_{mk}$ and $f_{n,k+q}$ are the occupation numbers. The real part of $P_{\beta\beta}(\mathbf{q},\omega)$ is then simply obtained via the Kramers-Kronig transformation. This method has been employed in the previous work on the quasiparticle band structures of metals copper and silver. Details on the method can be found in Ref. (Yi Z. et al., Phys. Rev. B 2010, 81, 125125). Our GW calculations were carried out by a Gaussian orbital based code (Rohlfing, M. et al., Phys. Rev. B 1995, 52, 1905). Decay constants of 0.3, 1.0, and 3.3 in atomic unit were applied in the calculations.

Clearly, the electronic band structure of the confined hydrogen nanowire obtained by the GW calculation that is shown in Figure 1(f) of the main text has similar feature with that obtained by using DF-BLYP functional as shown in Figure 1 (e) of the main text. This confirms that the confined hydrogen nanowire becomes metallic at an external hydrostatic pressure of 163.5GPa.