Hydrogen spillover phenomenon is well-documented in hydrogenation catalysis but still highly disputed in hydrogen storage. Until now, the existence of hydrogen spillover through metal-organic frameworks (MOFs) remains a topic of ongoing debate and how far the split hydrogen atoms diffuse in such materials is unknown. Herein we provide experimental evidence of the occurrence of hydrogen spillover in microporous MOFs at elevated temperatures, and the penetration depths of atomic hydrogen were measured quantitatively. We have made Matryoshka-type (ZIFs@)_{n-1}ZIFs (where ZIFs = ZIF-8 or ZIF-67) nanocubes, together with Pt nanoparticles loaded on their external surfaces to produce atomic hydrogen. Within the (ZIFs@)_{n-1}ZIFs, the ZIF-8 shell served as a ruler to measure the travelling distance of H atoms while the ZIF-67 core as a terminator of H atoms. In addition to the hydrogenolysis at normal pressure, CO₂ hydrogenation can also trace the migration of H atoms over the ZIF-8 at high pressure.
Hydrogen spillover is a well-known phenomenon in heterogeneous catalysis since the first observation in 1964 on a supported WO₃/Pt system,¹ where migration of hydrogen atoms occurs from the metal phase (e.g., Pt) to the support phase (e.g., WO₃). Generally, hydrogen spillover comprises three connective steps: (i) dissociative chemisorption of molecular hydrogen (H₂) on a metal catalyst, (ii) migration of atomic hydrogen (H) from the metal surface to the adjacent support, and (iii) hydrogen atoms travel on the surface or throughout the bulk support if it is porous.² Different support materials affect the occurrence of hydrogen spillover significantly. For instance, a recent combined theoretical and experimental study shows that hydrogen atom mobility rate over nonreducible supports (Al₂O₃) is about ten orders of magnitude slower than over reducible support (TiO₂).³ Therefore, hydrogen spillover taking place on nonreducible supports is restricted to very short distances. Nevertheless, it can still be observed at elevated temperatures due to a higher kinetic energy.⁴,⁵

Besides metal oxide supports, hydrogen spillover taking place in metal-organic frameworks (MOFs) has also been studied for hydrogen storage at ambient temperature.⁶,⁷ Although many studies report that doping MOFs with metal or supported metal catalysts (that is, bridged MOFs) could enhance H₂ uptakes due to the spillover effect,⁸,⁹ vigorous debates with respect to the spillover through bridged MOFs continue and in general reproducibility of enhanced H₂ storage data are not high. It is more likely that the transportation of H atoms in MOFs competes with Eley-Rideal recombination pathways to form H₂ molecule.²¹,²² In contrast, the ZIF-8 shell serves as a ruler to measure the farthest travelling distance possible of split H atoms while the ZIF-67 core as a terminator of H atoms in this spatial measurement set-up. As the shell thickness of ZIF-8 increases (viz., increasing distance from Pt to ZIF-67), atomic hydrogen concentration decreases dramatically. Thus, on identifying the extent of ZIF-67 decomposition via in-situ gravimetric measurement (under flowing H₂) combined with ex-situ morphological/structural characterizations, we are able to qualitatively measure the concentration of atomic hydrogen arriving at the reactive core of ZIF-67 phase and thereby the penetrating depth of H atoms.

**Results**

**Preparation of Matryoshka-type (ZIFs@)_{n-1}ZIFs.** To ensure identical diffusion pathways of hydrogen atoms starting from the different external surface on ZIFs, it is important to fabricate the highly symmetrical ZIFs structure such as nanocubes since they were bordered by six identical [100] surfaces. Considering that the two representative ZIFs (ZIF-8 and ZIF-67) are isostructural which share the same organic linker (2-methylimidazolate, MeIm), the same crystallographic features (space group I4₃m, a₀ = 16.881 Å in ZIF-8 and 16.908 Å in ZIF-67), but different metal nodes (Zn²⁺ in ZIF-8 and Co²⁺ in ZIF-67), the 4-coordinated Zn²⁺ and Co²⁺ ions are 74 pm and 72 pm in size, respectively, it enables us to combine the two isostructural ZIFs with atomically perfect heterojunctions via multiple heteroepitaxial growth. Firstly, ZIF-67 and ZIF-8 nanocubes were attained respectively by using a surfactant mediated method at room temperature. In our case, surfactant cetyltrimethylammonium bromide (CTAB) molecule functions as a capping agent via interaction between the long hydrocarbon chains and the imidazole linkers in ZIF nodes. It was reported that interaction energies of CTAB with {100}, {110} and {111} facets in ZIF-8 were −775, −395 and −104 kcal/mol, respectively.²³,²⁴ This implies that CTAB molecules mainly adsorb on {100} facets, and slow down the growth rate of {100} facets, leading to the formation of cubic ZIFs exposing with six identical {100} facets. Subsequently, we prepared core-shell structured ZIF-8@ZIF-67 and ZIF-67@ZIF-8, and other Matryoshka-type (ZIFs@ₙ₋₁)ZIFs (e.g., tri-, tetra-, penta-, hexa-, hepta- and octa-layered ZIFs) by stepwise (batch-wise) liquid-phase epitaxial growth. In brief, to construct the (ZIFs@ₙ₋₁)ZIFs (where ZIFs = ZIF-8 or ZIF-67; n = nth ZIFs, n = 1 to 8), we first prepared the first ZIFs cubes (i.e., n = 1) and used the sample as core crystals in a fresh solution containing metal ions, MeIm linker, and CTAB surfactant. Under the crystallisation conditions,
**Structural characterizations.** The topological features of Matryoshka-type ZIFs were clearly confirmed by the corresponding EDX elemental mapping and line scanning in Fig. 3, which provide direct evidence that zinc layers (viz., ZIF-8, highlighted in brown) and cobalt layers (viz., ZIF-67, in purple) are present alternately along the radial direction. An additional proof of the full coverage of a new layer ZIF can be either on the external surface or sandwiched between two previous ZIFs layers.

**Fabrication of ZIFs/metal nanocomposites.** Subsequently, noble metal nanoparticles were immobilized on the above prepared ZIFs by an in-situ reduction method, in which tetrabutylammonium borohydride (R-NBH$_4$) was used as a reducing agent in order to avoid the degradation of ZIFs structure$^{23,27}$ and HAuCl$_4$, H$_2$PtCl$_6$ and AgNO$_3$ methanolic solutions were used as precursor solutions for loading Au, Pt and Ag nanoparticles, respectively. Since the ZIFs have a small theoretical accessible window aperture size of 3.4 Å$^{28}$ the metal precursor and R-NBH$_4$ cannot diffuse into the cavities which resulted in metal nanoparticles being deposited absolutely on the external surface (Fig. 5a–d). The spatial distribution of the loaded nanoparticles on ZIFs was examined by EDX elemental maps and line scans. As shown in Fig. 5i, it clearly indicates that Pt element is located on the six faces of a nanocube. Furthermore, we find that the alignment between the different ZIFs layers is not affected by the encapsulated metal nanoparticles. It means that the epitaxial growth of a new ZIFs phase on the ZIFs/metal hybrid nanocube could still be realized. Along the same line, a series of very complex ZIFs/metal nanocomposites was successfully produced, such as ZIF-67@ZIF-8/Au@ZIF-67, ZIF-67@ZIF-8/Au@ZIF-8/Au@ZIF-8, ZIF-67/Au@ZIF-8, ZIF-67/Au@ZIF-8/Au and ZIF-67/Au@ZIF-8/Au@ZIF-67 (Fig. 5e–h and Supplementary Figs. 16–20). Accordingly, the spatial localization of metal nanoparticles (Au size of 2.8 nm, Pt size of 3 nm or Ag size of 9.4 nm) can be either on the external surface or sandwiched between two ZIFs layers.

**Fig. 1** Schematic representation for the hydrogen spillover over ZIF-8. a The proposed pathway of hydrogen spillover in ZIF-8, which includes dissociative chemisorption of H$_2$ on Pt surface, and subsequent migration of H atoms onto ZIF-8 via spillover and diffusion, finally, hydrogenolysis of ZIF-67 if H atoms arrive the ZIF-67 layer, b ZIF-67@ZIF-8/Pt model catalyst in a cross-section view, c, d the Zn–MeIm–Zn and Co–MeIm–Co linkages the periodic ZIF-8 and ZIF-67 crystals, where the coloured tetrahedrons represent primary building units in ZIFs, and e Schematic of concentration gradient of hydrogen atoms and the coordinate system of the model discussed in the main text, where $l$ is the shell thickness of ZIF-8, and $d$ is the penetration depth of hydrogen atoms.
**Fig. 2** TEM and HAADF-STEM analysis of nano-Matryoshka structured ZIFs. a ZIF-67, b ZIF-67@ZIF-8, c tri-layered ZIF, d tetra-layered ZIF, e, i penta-layered ZIF, f, j hexa-layered ZIF, g, k hepta-layered ZIF, and h, l octa-layered ZIF. The top panel illustrates the synthetic strategy for Matryoshka-type (ZIFs@)_n ZIFs with their 3-dimensional geometrical models. Colour code in the models: purple represents ZIF-67 and brown represents ZIF-8. Scale bars in a–l are 40, 60, 100, 100, 150, 200, 300, 300, 200, 200, 300 and 300 nm, respectively.

**Fig. 3** EDX elemental mapping and line scanning of ZIF-67 and nano-Matryoshka structured ZIFs. a ZIF-67, b ZIF-67@ZIF-8, c tri-layered ZIF, d tetra-layered ZIF, e penta-layered ZIF, f hexa-layered ZIF, g hepta-layered ZIF and h octa-layered ZIF. Colour code: purple represents cobalt; brown represents zinc.
Hydrogen spillover phenomenon. Having thoroughly characterized Matryoshka-type ZIFs/metal nanocubes, we are now in a position to address the issue of hydrogen spillover. We first examined the thermal stabilities of ZIF-67 and ZIF-67/Pt in flowing H₂ by thermogravimetric analysis (TGA), TEM, and XRD. In the TEM images and XRD patterns in Fig. 6a, indeed, we find that ZIF-67/Pt was more readily to be decomposed than the pristine ZIF-67. For instance, the ZIF-67 sample could maintain the cubic morphology and structural integrity with a temperature up to 300 °C (temperature lasting for 4 h). However, after loaded with Pt, the onset temperature for ZIF-67 destruction was dropped to 180 °C (at this temperature for 4 h). In the TGA profiles of Fig. 7a, temperatures at which the weight fraction w reaches 60 wt% (T_w60) for ZIF-67 and ZIF-67/Pt in H₂ flows were 493 °C and 286 °C, respectively. The distinct difference of ΔT_w60 (207 °C) must be interpreted by different mechanisms of ZIF-67 decomposition. In the ZIF-67/Pt system, hydrogen atoms were produced by dissociative adsorption of gaseous H₂ molecules on
Pt surface, which subsequently migrated from the Pt to the ZIF-67 by hydrogen spillover. As the split hydrogen atoms have higher reactivity than H₂, hydrogenolysis of ZIF-67 happened more vigorously, where cobalt–nitrogen single bonds were cleaved and the evolved gases were detected by a mass spectrometer (e.g., NH₃ and CH₄, etc., Supplementary Fig. 21). The reduction that occurred to the divalent cobalt ions was further proved by XRD (Supplementary Fig. 22) and XPS (Supplementary Fig. 23). The derived product was also decorated with nitrogen and carbon as proven from the EDX elemental maps (Supplementary Fig. 23). It was found that smaller Pt sizes are more favourable for the fast spillover of the dissociated H onto and subsequent diffusion over the support, since the smaller Pt can result in higher specific surface areas, more active sites, and greater contacts between the metal nanoparticles and the support (H receptor). In the present work, Pt nanoparticles with an average size of 3 nm were adopted to investigate the hydrogen spillover process.

The activation energies ($E_a$) of the hydrogenolysis of ZIF-67 by H atoms and H₂ molecules were also determined by thermogravimetry. The values of $E_a$ can be calculated from the slope of the plots of $\ln(T^2/\phi)$ versus $1/T$ on the same weight fractional $w$ based on Eq. (1).³⁰

$$\ln\left(\frac{T_1^2}{T_2^2}\right) - \ln\left(\frac{T_1^2}{T_2^2}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

wherein, $T$, $R$ and $\phi$ are the temperature in Kelvin, the molar gas constant and heating rate, respectively. Figure 8a–d displays the TGA curves under different heating rates and the corresponding plots based on Eq. (1). Accordingly, $E_a$ values calculated from the slopes are 116 kJ/mol and 65 kJ/mol for the hydrogenolysis of ZIF-67 by H₂ molecules and H atoms, respectively, which further provides a piece of unambiguous evidence of the hydrogen spillover from Pt to ZIF-67 framework.

In comparison, the thermal stabilities of ZIF-67 and ZIF-67/Pt in an oxidative atmosphere (e.g., air flows) exhibit inappreciable difference ($\Delta T_{w60} \approx 19 ^\circ C$, Fig. 7a). In addition to ZIF-67/Pt, a promoting effect of Au on ZIF-67 decomposition was also observed (Fig. 7b), as H₂ dissociate and subsequent diffuse on the supported Au nanoparticles.³¹ In contrast, there was no significant difference between ZIF-67/Ag and ZIF-67 from the TGA profiles ($\Delta T_{w60} = 13 ^\circ C$, Fig. 7b), revealing that Ag could not dissociate H₂ under the measuring conditions. A previous study indicates that silica support has poor ability for hydrogen atoms migration.³² Therefore, we found that the TGA profile of the mixture of ZIF-67 and SiO₂/Pt (the mass ratio of Pt to ZIF-67 was kept as 3:97) was almost similar to the pristine ZIF-67 ($\Delta T_{w60} = 12 ^\circ C$, Fig. 7d), even though hydrogen atoms were produced on Pt surface. Additionally, hydrogen consumption of ZIF-67 and ZIF-67/M (M = metal nanoparticles) samples were monitored by temperature-programmed reduction (TPR). As displayed in Supplementary Fig. 25, it was found that TPR peaks were shifted to a much lower temperature (240 °C) by addition of Pt and Au, as compared with bare ZIF-67 which occurred at 440 °C. The distinct TPR peak could be assigned to ZIF-67 hydrogenolysis (Co²⁺ → Co⁰ transition) as the temperatures of the reduction peaks were well identical to those of maximum weight loss in TGA profiles. However, no significant change was found in the case of ZIF-67/Ag.

In addition, significant deterioration of ZIF-67 due to hydrogen spillover was also found in the samples of ZIF-67@ZIF-8/ZIF-67/Pt and ZIF-8@ZIF-67/Pt ($\Delta T_{w60}$ were 145 °C and 100 °C, respectively).
respectively, Fig. 7c). It implies that intimate contact between Pt and ZIF-67 facilitates the migration of hydrogen atoms, thereby enhancing the hydrogenolysis of ZIF-67. However, as also revealed in Fig. 7c, such hydrogen spillover enhanced decomposition was not found in the ZIF-8/Pt system. TEM and XRD data suggest that ZIF-8 phase remains intact in both ZIF-8 and ZIF-8/Pt samples under flowing H2 at 300 °C for 4 h (Supplementary Fig. 26). For this reason, no significant H2 consumption was found in the corresponding H2-TPR profiles of ZIF-8 and ZIF-8/Pt samples (Supplementary Fig. 25). Nonetheless, it could not exclude the transfer of hydrogen atoms in the nonreducible ZIF-8. A control experiment by using Zn/Co mixed ZIF and its supported Pt sample showed that the enhanced effect of ZIF-67 decomposition became not so pronounced (ΔTw60 = 30 °C, Fig. 7d), which is caused by a lower H migration rate in the presence of zinc ions (Note: Zn2+ ions possess fully occupied d-orbitals (<10), while Co2+ ions have unsaturated d-orbital (d7)). This is consistent with a previous report showing that ZnO was not as effective as TiO2 at facilitating hydrogen spillover due to its fully filled d-orbital.32 Subsequently, we encapsulated ZIF-67 nanocubes with a ZIF-8 shell to study the hydrogen spillover phenomena. Interestingly, TGA data displayed in Fig. 7d show that a small ΔTw60 (47 °C) of ZIF-67@ZIF-8 and ZIF-67@ZIF-8/Pt was observed as the thickness of ZIF-8 layer was 20 nm. XRD patterns (Fig. 6b) confirm that ZIF-67@ZIF-8/Pt composite with ZIF-8 shell thickness of 20 nm or 50 nm can sustain their structural integrity under flowing H2 at 240 °C for 4 h, indicating that almost no hydrogen atom could access to the ZIF-67 core. However, as the ZIF-8 shell was as thin as 5 nm, the intrusion of atomic hydrogen through ZIF-8 layer was observed even at 220 °C for 4 h, leading the hydrogenolysis of ZIF-67. Our XRD investigation further proved that ZIF-8 phase was unchanged, but ZIF-67 phase was severely destroyed and converted to metallic cobalt. It should be noted that cobalt oxide species were found due to the further oxidation of the derived metallic cobalt during sample characterizations (refer to Supplementary Figs. 22, 23).

As depicted in Fig. 1, it is evident that decomposition rate of ZIF-67 is dominated by the concentration of accessed hydrogen atom in the interface of ZIF-67 and ZIF-8 (C4), where the penetration depth (x) is equal to the thickness of ZIF-8 shell (L). As known, C4 is dominated by the macroscopic diffusion coefficient (Dhk), the distance (x), and the boundary concentration (C0). According to the random walk model for diffusion, Dhk can be expressed as Dhk = a2v, where, a is the distance between two neighbouring adsorption sites of hydrogen atom, and v is the
microscopic jump frequency, and \( z \) is the number of adjacent sites to which H-atoms can hop. Since, the Pt nanoparticles were all located on [100] facets of ZIFs, so the region is a hydrogen atom rich surface. The diffusion of hydrogen atom can be assumed as one-dimensional diffusion (that is, perpendicular to the surface; Fig. 1). Therefore, in this case \( z = 2 \). The \( \nu \) depends on temperature in accordance to the Arrhenius expression:

\[
\nu = \nu_0 \exp \left( \frac{-E_a}{RT} \right),
\]

where \( E_a \) is the activation energy of diffusion, and \( \nu_0 \) is the “attempt frequency” to jump, \( T \) is temperature and \( k_B \) is the Boltzmann constant. In this way, three crucial factors would determine the \( C_x \) over our model catalysts: hydrogen partial pressure (or concentration), temperature, and thickness of ZIF-8 shell. There are two different endings for the hydrogen atoms migrating in MOFs: one is diffusing atomic H through the ZIF-8 matrix (i.e., described by \( C_x \), and the other is Eley-Rideal recombination to form molecular \( \text{H}_2 \) which then desorbs as a “free \( \text{H}_2 \)”. Eley-Rideal recombination step would become predominant as the highly reactive \( \text{H} \) travelling more deeply into the ZIF-8 shell, leading to the concentration attenuation of hydrogen atom.

To further investigate the penetration depth of atomic hydrogen through the ZIF-8 shell. The thickness of ZIF-8 shell could be adjusted as 5 nm, 10 nm, 20 nm, 30 nm and 50 nm by tuning the synthetic parameters. EDX line scanning was used to determine the average thickness of the ZIF-8 coating shell on the ZIF-67 core (as shown in Supplementary Fig. 27). For each catalyst, the Pt content was adjusted in order to maintain a similar surface density (see Method Section). TGA profiles under flowing \( \text{H}_2 \) of various ZIF-67@ZIF-8/Pt with a different coating thickness of ZIF-8 are shown in Fig. 9a, and the weight loss of the corresponding samples soaking at a specific temperature (220, 240 and 260 °C for 4 h) are plotted in Fig. 9d. Apparently, the decomposition rate is dependent on both the ZIF-8 thickness and soaking temperature. For instance, the times for full decomposition of ZIF-67 phase in ZIF-67/Pt and ZIF-67@ZIF-8/Pt (10 nm thickness) are 1.4 h and 2.8 h, respectively, under flowing \( \text{H}_2 \) at 260 °C. In comparison, even with prolonged time to 18 h, no significant weight loss was found for ZIF-67@ZIF-8/Pt (30 nm thickness) sample under similar conditions (Supplementary Fig. 28). The shell thickness-dependent decomposition rate of ZIF-67 is summarised in Fig. 9b, suggesting that a concentration gradient of accessible atomic hydrogen exists along the penetration depth (see the illustration in Fig. 1d), which is the driving force in spillover process. Essentially, the kinetic energy of H atom flux is caused by the dissociation of the H–H bond. Concentration attenuation of hydrogen atom is attributed to the fact that Eley-Rideal recombination of hydrogen atoms yields \( \text{H}_2 \) as travelling through the ZIF-8 shell. As a result, at the same temperature, the degradation rate of ZIF-67 decreases monotonically with increasing the thickness of ZIF-8 shell. Particularly, as illustrated in Fig. 9e, the five \( \text{N}_2–\text{H}_2–\text{N}_2 \) cycles during samples soaking at 260 °C further corroborate that the decomposition of ZIF-67 is caused by hydrogen spillover, which also confirms that ZIF-67 hydrogenolysis is an endothermic process. As the steady state was reached, according to Fick’s first law, the net diffusion flux along the direction \( x \) is proportional to the concentration gradient (1st derivative): 

\[
J = -D \frac{\partial C}{\partial x}.
\]

The calculated concentration gradient is shown in Fig. 9c, verifying that \( J \) strikingly decreases along the penetration depth, which thereby weakens the driven force for hydrogen atom diffusion along the penetration. Furthermore, as shown in Fig. 8e–g, \( E_a \) values of ZIF-67 hydrogenolysis in ZIF-67@ZIF-8/Pt composites are 76, 84, 112 and 114 kJ/mol, when the ZIF-8 shells are 5, 10, 20 and 30 nm, respectively. The increasing \( E_a \) with thicker ZIF-8 implies that the transportation and the population of atomic H depend on the thickness of ZIF-8. This result also suggests that the H migration distance in
ZIFs at low temperature (or ambient temperature) will be short if an extrapolation from the above high temperature data is made.

As mentioned above, hydrogen spillover through MOFs in the gas phase is excluded. Therefore, it is deduced that the resultant H atoms were chemisorbed on ZIFs during hydrogen spillover. Because both MeIm ligand (which is deprotonated from H-MeIM) and ZIFs have been widely reported as N-heterocyclic proton carriers via sharing protons on N–H bonds, we believe that such N–H bonds are also present for the diffusion of H atoms through ZIF-8. The process described in Supplementary Fig. 29 can be further considered in future, following the reported work of a combined electron-proton mobility on reducible TiO$_2$ support which has an energy barrier $E_{\text{act}} = 0.65$ eV and thus is energetically more favourable than other possible diffusion mechanisms (such as oxygen vacancies). As discussed earlier, a hydrogen atom would also combine with another hydrogen atom to generate H$_2$ again (viz., H$_{\text{gas}}$ + H$_{\text{ad}}$ → H$_2$,gas); longer travelling times are spent and thus more recombination events take place along a diffusion path of H atoms. As a result, the concentration of atomic H decreases as the penetration depth increases (Fig. 1e and Supplementary Fig. 30). In addition, since the migration is usually a highly endothermic process, the migration rate of H atoms speeds up pronouncedly at elevated temperatures, which is in good agreement with the decomposition rate of ZIF-67 that increases monotonically with temperature. Again, the above
experimental results suggest that the “hydrogen spillover” in ZIF materials at ambient temperature may not contribute significantly to the enhanced hydrogen storage.

In addition, the effect of hydrogen concentration on hydrogen spillover rate was studied by varying the concentration in H₂/N₂ mixture (at ambient pressure). Taking ZIF-67@ZIF-8/Pt (shell: 20 nm) as an example (Fig. 9f), increasing hydrogen concentration leads to a higher ZIF-67 decomposition rate. This is due to the change of boundary concentration (C₀) of atomic hydrogen at the gas-Pt interface, where higher hydrogen gas concentration gave rise to a higher C₀ (see Fig. 1d).  

However, almost identical TGA profiles were found at hydrogen concentrations of 16% and 20%, due to reaching the equilibrium condition. Furthermore, hydrogen spillover occurring at high pressure (30 bar) was also investigated at temperatures between 160–240 °C. Since TGA apparatus cannot be conducted under high pressure, a fixed bed gas-phase CO₂ hydrogenation reaction was utilized as a probe for ZIF-67 decomposition due to hydrogen spillover at high pressure (30 bar, Fig. 9g). In such a case, Pt nanoparticles were stable to dissociate H₂ molecule which then migrated as H atoms through the ZIF-8 shell to reduce the cobalt ions in the ZIF-67 core. In this process, the activity of CO₂ hydrogenation can be interpreted as originating from the metallic Co derived from hydrolysis of ZIF-67, since cobalt is an active centre for CO₂ hydrogenation towards methane and CO.38,39 In accordance with the above information, the ZIF-8 phase in ZIF-8/Pt sample was quite stable even in a harsh operating condition (240 °C, 30 bar, H₂%=72%). Likewise, in the absence of Pt, the pristine ZIF-67 was not altered after the reaction (30 bar, 240 °C, 12 h, refer to XRD pattern in Supplementary Fig. 31), showing negligible CO₂ conversion over the entire temperature range, similar to the cases of ZIF-8/Pt and SiO₂/Pt. On the contrary, ZIF-67/Pt Totally converted to Co/Pt bimetallic catalysts, which showed the highest CO₂ conversion. A positive correlation was found between the CO₂ conversion and the hydrogen spillover rate. Notably, if the ZIF-67 phase has a close contact with Pt (e.g., ZIF-67/Pt and ZIF-67@ZIF-8@ZIF-67/Pt), the catalysts exhibited higher activities. Obviously, the introduction of ZIF-8 layer between ZIF-67 and Pt, retards the hydrogenolysis rate of ZIF-67, thereby decreasing the CO₂ hydrogenation activity at any measured temperatures. Although hydrogen atoms cannot reduce the ZIF-67@ZIF-8/Pt (shell: 20 nm) at normal atmospheric pressure, it was observed that the ZIF-67 phase in the sample was totally decomposed at 30 bar, suggesting that a higher amount of available hydrogen atoms could migrate to ZIF-67 core at higher pressure. XRD patterns and TEM images of the spent catalyst samples were analysed in Supplementary Fig. 32 to confirm ZIF structures transformation during the reaction.

Discussion

We have demonstrated an ingenious way to prove the spillover of hydrogen atoms in ZIF-8 layer at elevated temperatures, by using a variety of well-defined hybrid ZIFs/Pt nanocubes as probes. Firstly, a simple approach has been developed to fabricate multi-shell structured ZIFs with Matryoshka doll-like features via step-by-step heteropitaxial growth in solution. For core-shell structured ZIF-67@ZIF-8/Pt, the enhanced decomposition of ZIF-67 at low temperatures could be attributed to the hydrogen spillover through the ZIF-8 shell (where molecular H₂ is nonreactive). On the other hand, the hydrogenolysis of ZIF-67 provides direct information about hydrogen atoms spillover which exclusively migrates through [100] facets of ZIF-8 crystalline shell. It is evident that the diffusion behaviour of hydrogen atoms is dominated by the temperature, hydrogen concentration and pressure, and shell thickness. In addition, we have proposed a plausible migration mechanism to elucidate long-distance transport of hydrogen atoms over a ZIF-8 layer, although more theoretical work is still needed for the future investigation of atomic H migration in MOFs.

In contrast to hydrogen spillover phenomenon in hydrogenation catalysis, ambiguity exists about the spillover involved in hydrogen storage enhancement, mostly at ambient temperature. Our experimental results not only provide direct evidence for hydrogen spillover in ZIFs at elevated temperatures, but also set up an upper limit of the migration distance for H atoms diffusing in ZIF-8 phase at elevated temperatures. In terms of hydrogen storage, our findings also indicate that hydrogen spillover in ZIF-8 must have a limited spatial scope (i.e., in the vicinity of noble metal particles) at ambient temperature. The key to measuring the diffusion path of H atoms is that the shell of ZIF-8 serves as a spatial ruler while the core of ZIF-67 functions as a hydrogen atom detector through hydrogenolysis. As demonstrated in the present work, future investigations on hydrogen spillover processes in other MOFs can also be carried out by constructing MOFs and noble-metal nanocomposites with the similar Matryoshka configuration.

Methods

Materials. The following chemicals were used as received without further purification: zinc nitrate hexahydrate (Aldrich, 98%), cobalt (II) nitrate hexahydrate (Aldrich, 98% +), 2-methylimidazole (H-Melm, 99%, Aldrich), cetyl-trimethylammonium bromide (CTAB, 98%, Aldrich), chloroplatinic acid hydrate (Sigma-Aldrich, 99.9% +), gold (III) chloride trihydrate (Sigma, 99.9%), silver nitrate (Merck, 99%), tetrabutylammonium borohydride (R-NBH₄, 98%, Sigma), sodium hydroxide (Merck, 99%), hydrochloric acid (VWR chemical, 33%), methanol (Fisher, 99.9%), and ethanol (Fisher, 99.9%). Deionized water was used for all experiments.

Nanostructure fabrications. For the synthesis of ZIF-67, 0.3 mL of Co(NO₃)₂ aqueous solution (50 g L⁻¹, 0.172 M) was mixed with 2 mL of water and 0.9 mL of H-Melm aqueous solution (200 g L⁻¹, 2.44 M). After stirring for 2 min, 0.2 mL of CTAB aqueous solution (50 g L⁻¹) was added. The mixture was kept stirring for 6 h at room temperature. The purple colour product was harvested through centrifugation and washing (with ethanol for three times). Finally, the product was dispersed in 2 mL of ethanol for TEM analysis and further use. The yield of the product based on Co salts was ca. 91%. For the synthesis of ZIF-8, 0.2 mL of Zn(NO₃)₂ aqueous solution (50 g L⁻¹) was used as the metal source while other parameters were held to identical values as ZIF-67 synthesis. Similarly, in the case of cubic Zn/Co-ZIFs preparation, 0.15 mL of Zn(NO₃)₂ aqueous solution (50 g L⁻¹) and 0.15 mL of Co(NO₃)₂ aqueous solution (50 g L⁻¹) were used as the metal source. To construct multi-layered ZIFs (viz., ZIFs/nanocubes, ZIFs nanocubes, and ZIFs nanocubes), we first prepared ZIFs nanocubes and used them as core crystals in a solution containing metal ions and H-Melm. Usually, the amount of ZIFs core crystals was 0.5 mL at a concentration of 5 mg mL⁻¹, and 0.2 mL of CTAB aqueous solution (50 g L⁻¹) was used in each batch. Other chemicals were added in a similar way as the preparation of ZIF-67 or ZIF-8. As for loading Pt nanoparticles on the ZIF nanocubes, an in-situ reduction method was employed. 40 Briefly, 200 mg of a specific ZIFs was dispersed in 40 mL of methanol by sonication for 10 min, before the addition of 8 mL of H₂PtCl₆ methanolic solution (10 M). The mixture was vigorously stirred for 1 h at room temperature. Then 20 mL of 0.25 M R-NBH₄ methanolic solution (used just after preparation) was injected into the above mixture. After stirring for 30 min, the product was collected through centrifugation and washing procedures (with ethanol twice). The loading amount of Pt was adjusted according to the size of ZIF nanocubes, in order to achieve the same outer surface loading of Pt. For the ZIFs/Pt catalysts (ZIF-67/Pt, ZIF-8/Pt and Zn/Co-ZIF/Pt), the Pt loading amount was maintained as 3 wt%. The immobilization of Au and Ag nanoparticles were prepared in a similar manner but using HAuCl₄ and AgNO₃ as the metal precursors.

Characterization techniques. Sample morphologies of our (ZIFs@n) were investigated with transmission electron microscopy (TEM, JEM-2010, 200 kV) and high-resolution TEM (HRTEM, JEM-2100F, 200 kV). Crystallographic information of these samples was established by X-ray diffraction (XRD, Bruker D8Advance) using Cu Kα radiation. The compositional analysis of our samples was carried out by energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments, Model 7426). The determinations of specific surface areas, pore volume, and pore
size of our samples were made using $N_2$ physisorption isotherms at 77 K (Quan
tachrome NOVA-3000 system). Metal contents in our catalysts were measured by
and inductively coupled plasma optical emission spectrometry (ICP-OES, Optima
7300DV, Perkin Elmer), and the analysis on surface compositions of the samples
was made by X-ray photoelectron spectroscopy (XPS, AXIS-HS, Kratos Analy
tical). The binding energies in our XPS spectra were corrected with the reference
binding energy of adventitious carbon C 1 s at 284.5 eV. TGA results were obtained by
using a Mettler Toledo thermogravimetric analyser at a ramping rate of 3 °C
min$^{-1}$ (sample mass ~20 mg on 150 μL aluminium pan). The total gas flow rate
was set to 120 ml min$^{-1}$. Temperature-programmed reduction analysis (H$_2$–TPR)
was carried out by heating a sample (30 mg) in a quartz tube using HDN analytical
CATLAB instrument. The sample was heated from 50 to 750 °C at 3 °C min$^{-1}$ in
a flow of 5 vol% H$_2$/Ar mixture (60 ml min$^{-1}$ at a total pressure of 1 atm). The system
was stabilized for 10 min at 50 °C to obtain a straight baseline. The amount
of hydrogen consumption and evolved gases (e.g., H$_2$O, NH$_3$, and CH$_4$) were
monitored by a mass spectrometer (MS).

**Catalytic performance evaluations.** The CO$_2$ hydrogenation reactions were
carried out in a continuous flow fixed bed reactor (3/8 inch stainless steel) loading
with 200 mg of ZIF samples. The flowchart of the catalytic experimental set-up is
shown in Supplementary Fig. 33. A gas stream with CO$_2$/H$_2$/N$_2$ = 24%/72%/4% (where
N$_2$ acted as an internal standard) was fed at a flowrate manipulated by a Brooks
mass flow controller. The reactor temperature was monitored with a thermocouple
attached to the centre of catalyst bed. The reactor pressure was tuned
by using a back-pressure gas regulator. Compositions of reactants and products were
determined online with a gas chromatography apparatus equipped with FID and
TCD detectors.

**Data availability**
The data supporting the findings of this study are available upon request from the corresponding author (including data presented in the main text and in the Supple
mentary Information).

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Author contributions
G. Zhan performed the experiments, collected and analysed the data, and wrote the paper. H. C. Zeng contributed towards the project idea, results analysis and paper writing.

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