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Single-atom catalysts (SACs) are witnessing rapid development due to their high activity and selectivity toward diverse reactions. However, it remains a grand challenge in the general synthesis of SACs, particularly featuring an identical chemical microenvironment and on the same support. Herein, a universal synthetic protocol is developed to immobilize SACs in metal–organic frameworks (MOFs). Significantly, by means of SnO$_2$ as a mediator or adaptor, not only different single-atom metal sites, such as Pt, Cu, and Ni, etc., can be installed, but also the MOF supports can be changed (for example, UiO-66-NH$_2$, PCN-222, and DUT-67) to afford M$_x$/SnO$_2$/MOF architecture. Taking UiO-66-NH$_2$ as a representative, the Pt$_1$/SnO$_2$/MOF exhibits approximately five times higher activity toward photocatalytic H$_2$ production than the corresponding Pt nanoparticles (≈2.5 nm) stabilized by SnO$_2$/UiO-66-NH$_2$. Remarkably, despite featuring identical parameters in the chemical microenvironment and support in M$_x$/SnO$_2$/UiO-66-NH$_2$, the Pt$_1$ catalyst possesses a hydrogen evolution rate of 2167 μmol g$^{-1}$ h$^{-1}$, superior to the Cu$_1$ and Ni$_1$ counterparts, which is attributed to the differentiated hydrogen binding free energies, as supported by density-functional theory (DFT) calculations. This is thought to be the first report on a universal approach toward the stabilization of SACs with identical chemical microenvironment on an identical support.

1. Introduction

Single-atom catalysts (SACs), being the ultimate size limit for metal nanoparticles (NPs) in supported catalysts, have captured intensive research interest. With maximized atomic utilization of metal catalysts and almost identical microenvironment, SACs show greatly enhanced activity and selectivity toward diverse catalytic reactions, compared to the traditional metal NPs. However, the isolated single atoms are easy to migrate and sinter during reaction because of the high surface free energy, which remains a considerable challenge. In this context, many substrates, which might present strong coordination bonding and/or considerable charge transfer with isolated single atoms, are selected as the underlying supports of SACs, such as heteroatom-doped carbon materials, metal oxides, etc. Among diverse supports, metal oxides have been intensively investigated due to their abundant metal vacancies and surface OH groups to immobilize single atoms. As an n-type semiconductor, SnO$_2$ is a widely adopted support for metal NPs as it usually provides high stability and strong interaction, the latter of which would improve the catalytic performance of metal sites. It is reported that the Sn$^{2+}$ ion is capable of reducing noble metal ions in situ by oxidizing itself to SnO$_2$. Therefore, SnO$_2$ could also be a suitable support for immobilizing SACs. Meanwhile, to fabricate SACs in reasonable loadings, the most straightforward and effective way is to adopt high-specific-area porous supports, which would enable the accessibility of well-dispersed metal sites.

As a class of porous crystalline materials, metal–organic frameworks (MOFs), featuring very high surface area and high porosity, are recognized to be ideal candidates for stabilizing SACs. In fact, in reference to traditional inorganic supports, MOFs are able to provide abundant pore space and tailored microenvironment, which have been demonstrated to be excellent hosts/supports for metal NPs toward synergetic catalysis in recent years. Nevertheless, the current fabrication of SACs based on MOFs is mostly related to the pyrolysis of MOF precursors. The facile construction of high-loading SACs by directly adopting MOFs has been rarely achieved. These reports are mostly based on two main approaches to MOF-supported SACs. One is to anchor SACs onto M–oxo clusters in MOFs, posing the prior request of the available chelating sites on the clusters, mainly Zr–oxo clusters. The other way is to stabilize SACs by the adjacent coordination atoms in the organic linker. There are respective requirements for particular MOF structures and components in these two strategies, which limit their synthetic universality. Therefore,
In this work, we have integrated the advantages of SnO2 and MOFs as supports and developed a general strategy for the immobilization of diverse SACs, such as Pt, Cu, and Ni, on SnO2-furnished MOFs. Specifically, MOFs are first impregnated with Sn2+ followed by introducing the metal precursor under microwave-assisted conditions. In the subsequent step, the well-dispersed Sn2+ can proceed redox and hydrolysis reactions with introduced metal precursors, giving rise to the deposition of single metal atoms onto SnO2 that is trapped in MOFs, with introduced metal precursors, giving rise to the deposition of single metal atoms onto SnO2 that is trapped in MOFs, as shown in Scheme 1. Remarkably, the representative Pt1/SnO2/UiO-66-NH2 exhibits an excellent activity in the visible-light photocatalytic H2 production (2167 µmol g⁻¹ h⁻¹, TOF = 31 h⁻¹), among the highest H2 production activity in reported MOF photocatalysis and approximately five times higher than its nanoparticle counterpart (denoted PtNPs/SnO2/UiO-66-NH2). Density-functional theory (DFT) calculations reveal that the incorporation of single metal atoms greatly lowers the proton activation barrier, thereby accelerating the H2 evolution.

2. Results and Discussion

2.1. Synthesis and Characterization

The UiO-66-NH2 involving Zr6O4(OH)4 clusters was synthesized by using ZrCl4 and 2-aminoterephthalic acid (Figure S1, Supporting Information), with acetic acid as a modulator in DMF. The Sn2+ impregnated UiO-66-NH2 (alised as Sn2+/UiO-66-NH2) was prepared by microwave-assisted reaction of SnCl2·2H2O and the MOF in acetonitrile. The loading amount of Sn2+ is 12.8 wt% detected by inductively coupled plasma atomic-emission spectrometry (ICP-AES). Powder XRD patterns (Figure S2, Supporting Information) demonstrates the introduction of SnO2 and Pt almost does not affect the stability of UiO-66-NH2 (Figure S5, Supporting Information). Nitrogen sorption isotherms demonstrate that the MOF pore feature is maintained, while the adsorption capacity of Pt1/SnO2/UiO-66-NH2 is slightly reduced due to the mass occupation of introduced components (Figure S6, Supporting Information). The UiO-66-NH2 morphology is almost retained, which can be found in SEM and TEM images (Figure S7, Supporting Information). Close observation in high-resolution TEM (HRTEM) image suggests the particles in 1–2 nm with the lattice fringes and d-spacing of 0.34 and 0.26 nm can be observed (Figure S8, Supporting Information). The UiO-66-NH2 showed a high crystallinity of UiO-66-NH2 (Figure S2, Supporting Information), indicating that Sn2+ ions have been successfully coordinated by the –OH/OH2 groups terminating on the Zr–oxo clusters.

The M1/SnO2/UiO-66-NH2 were subsequently obtained by introducing metal precursors into Sn2+/UiO-66-NH2 under microwave-assisted reaction. This strategy is powerful and general in the fabrication of diverse SACs, including Pt, Cu, Ni, etc. Taking Pt as an example, the Pt1/SnO2/UiO-66-NH2 was prepared by microwave-assisted reaction of Sn2+/UiO-66-NH2 with H2PtCl6 in acetonitrile. The loading amount of Pt is 1.35 wt% detected by ICP-AES. The high crystallinity of UiO-66-NH2 can be well maintained after this modification, as indicated by powder XRD patterns (Figure S2, Supporting Information). The chemical stability investigations for Pt1/SnO2/UiO-66-NH2 demonstrates the introduction of SnO2 and Pt almost does not affect the stability of UiO-66-NH2 (Figure S5, Supporting Information). The peak at 183.2 eV for Sn 3d5/2 is assignable to Sn2+ ions (Figure S4, Supporting Information), indicating that Sn2+ ions have been successfully coordinated by the –OH/OH2 groups terminating on the Zr–oxo clusters.

The M1/SnO2/UiO-66-NH2 were subsequently obtained by introducing metal precursors into Sn2+/UiO-66-NH2 under microwave-assisted reaction. This strategy is powerful and general in the fabrication of diverse SACs, including Pt, Cu, Ni, etc. Taking Pt as an example, the Pt1/SnO2/UiO-66-NH2 was prepared by microwave-assisted reaction of Sn2+/UiO-66-NH2 with H2PtCl6 in acetonitrile. The loading amount of Pt is 1.35 wt% detected by ICP-AES. The high crystallinity of UiO-66-NH2 can be well maintained after this modification, as indicated by powder XRD patterns (Figure S2, Supporting Information). The chemical stability investigations for Pt1/SnO2/UiO-66-NH2 demonstrates the introduction of SnO2 and Pt almost does not affect the stability of UiO-66-NH2 (Figure S5, Supporting Information). Nitrogen sorption isotherms demonstrate that the MOF pore feature is maintained, while the adsorption capacity of Pt1/SnO2/UiO-66-NH2 is slightly reduced due to the mass occupation of introduced components (Figure S6, Supporting Information). The UiO-66-NH2 morphology is almost retained, which can be found in SEM and TEM images (Figure S7, Supporting Information). Close observation in high-resolution TEM (HRTEM) image suggests the particles in 1–2 nm with the lattice fringes and d-spacing of 0.34 and 0.26 nm can be observed (Figure S8, Supporting Information), which correspond to the (110) and (101) planes of tetragonal SnO2 quantum dots, and their particle sizes can match the pore sizes of defective UiO-66. The chemical states of Pt, Sn, and Zr have been examined by X-ray photoelectron spectroscopy (XPS, Figure S9, Supporting Information). The peak of Zr 3d5/2 shifts to higher binding energy from 182.8 to 183.2 eV after modifying Sn2+ to UiO-66-NH2, indicating the possible formation of Sn–O–Zr linkage. Accordingly, the peak at 4873 eV for Sn 3d5/2 is assign able to Sn2+ in Sn2+/UiO-66-NH2. After introducing Pt species in Sn2+/UiO-66-NH2, these XPS peaks shift slightly to higher binding energies of 4874 eV, which reasonably reflects the oxidation of Sn2+ to SnO2 due to the spontaneous redox reaction between Sn2+ and PtCl62– with suitable redox potentials and in accordance with the above HRTEM observation (Figure S8, Supporting Information), yielding Pt1/SnO2/UiO-66-NH2. The binding energy of Pt 4f7/2 locates at 73.1 eV in Pt1/SnO2/UiO-66-NH2, falling in the range between 71.2 and 74.2 eV, which verifies the Pt valence is between 0 and +2 (closer to +2).
To investigate the microstructure of Pt species, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observation was conducted. Single Pt atoms can be identified as bright spots in random distribution, as contrasted by other lighter elements, reflecting that Pt atoms are atomically dispersed while no Pt NPs are observable (Figure 1a).

Given that electron microscope can provide the information of local structure only, X-ray absorption spectroscopy (XAS) was conducted to determine the coordination environment and chemical state of Pt species. In 5d transition metal L3-edge, the peak intensity of X-ray absorption near-edge structure (XANES) is a good indicator of the number of unoccupied d-electron states.[16] As shown in the Pt L3-edge XANES profiles (Figure 1b), the peak intensity of Pt1/SnO2/UiO-66-NH2 is significantly higher than that of Pt foil and closer to that of PtO2, implying the existence of highly oxidized Pt states, which is in agreement with XPS results (Figure S9, Supporting Information). Fourier-transform extended X-ray absorption fine structure (FT-EXAFS) spectrum of Pt1/SnO2/UiO-66-NH2 gives only a main peak at about 1.63 Å, which is assignable to the first shell of the Pt–O bond and no Pt–Cl bond at 1.90 Å (K2PtCl4) or Pt–Pt bond at 2.49 Å (Pt foil) can be found, demonstrating the generation of atomically dispersed Pt sites in Pt1/SnO2/UiO-66-NH2 (Figure 1c). To further verify the Pt1 coordination structure, EXAFS fitting has been performed. The best fitting result for the first shell shows that each Pt atom is coordinated by about 4 oxygen atoms on average (Figure S10, inset, Table S1, Supporting Information). The overall EXAFS analysis on Pt–O4 coordination around the atomically dispersed Pt ions is found to be consistent with the XANES observation of oxidized Pt species.

In addition, the carbon monoxide (CO) adsorption behavior in the DRIFT spectra provides another powerful evidence to determine the dispersion and oxidation state of Pt (Figure 1d). There is only one strong vibration band at 2092 cm⁻¹, ascribed to linearly chemisorbed CO on single Pt atoms, after purging with Ar for 30 min to evacuate gaseous CO. No observable peak in the range of 2080–2030 and 1920–1950 cm⁻¹ indicates the absence of linear- and bridged-adsorbed CO on the Pt clusters, reflecting no significant existence of Pt clusters and/or NPs in Pt1/SnO2/UiO-66-NH2. Accordingly, most Pt species should be atomically dispersed, i.e., single-atomic Pt.[15] Moreover, the location of CO adsorption peak is well retained after purging with Ar, which indicates that the dipole–dipole coupling interaction between adsorbed CO molecules on Pt does not exist, further supporting the isolation of Pt atoms.[10e] The CO adsorption peak appears at 2092 cm⁻¹, a significant blue shift compared to the sharp peak at ≈2030 cm⁻¹ related to CO on Pt0, is ascribed to CO adsorbed on Ptδ+,[15] in good agreement with the oxidation state results from the XAS and XPS spectra.
Interestingly, it is found the pre-introduction of Sn$^{2+}$ in our synthetic process plays a crucial role in the subsequent formation of single Pt atoms. When UiO-66-NH$_2$ was directly treated with H$_2$PtCl$_6$ or a mixture of SnCl$_2$·2H$_2$O and H$_2$PtCl$_6$ by the same microwave-assisted modification (samples were named as Pt/UiO-66-NH$_2$ and Pt-SnO$_2$/UiO-66-NH$_2$, respectively). Pt NPs instead of SACs were obtained (Figures S11–S13, Supporting Information). To further explore the generality of our synthetic strategy to the immobilization of SACs in MOFs, Pt has been replaced by another two metals (Ni and Cu) to afford Ni$_1$/SnO$_2$/UiO-66-NH$_2$ and Cu$_1$/SnO$_2$/UiO-66-NH$_2$. The loading amounts of Ni$^{2+}$ and Cu$^{2+}$ are 0.42 and 0.14 wt%, respectively and the amount of Sn$^{2+}$ remains to be $\approx$12 wt%. Similar to those observed for Pt$_1$/SnO$_2$/UiO-66-NH$_2$, the crystallinity of MOFs can be maintained after modification, as confirmed by powder XRD patterns (Figure S14, Supporting Information). SEM and TEM images indicate the morphologies of MOFs are almost intact and only small particles (about 1–2 nm) identified as SnO$_2$ are found (Figures S15–S17, Supporting Information). Nitrogen sorption isotherms indicate moderately reduced surface area after modification owing to the addition of Sn and Cu (or Ni) species (Figure S18, Supporting Information). Fortunately, we have indeed obtained their corresponding SACs by this synthetic strategy based on the XAS data. The Ni K-edge XANES spectrum of Ni$_1$/SnO$_2$/UiO-66-NH$_2$ indicates that the Ni$^{II}$ oxidation state falls into 0→2 (closer to +2), which is in agreement with XPS results (Figure S19a,b, Supporting Information). The FT-EXAFS spectrum presents a dominated peak at $\approx$1.59 Å respecting to the Ni–O scattering path, and no Ni–Ni bond is detected (Figure S19c, Supporting Information). The six-fold coordinated O atoms in the first-shell of Ni$_1$ center in Ni$_1$/SnO$_2$/UiO-66-NH$_2$ have been resolved by the curve fitting for EXAFS data (Figure S19d, Table S1, Supporting Information). Similar results have been obtained and support the successful formation of single-atom Cu$_1$ with 4 coordinated oxygen atoms in Cu$_{\text{II}}$/SnO$_2$/UiO-66-NH$_2$ (Figure S20, Table S1, Supporting Information).

In addition to the alteration of single-atom metals, the generality of this synthetic strategy has been further demonstrated by replacing the MOF support, UiO-66-NH$_2$, with PCN-222 or DUT-67 (Figures S21 and S22, Supporting Information). All powder XRD patterns and SEM images display that the microstructure of these MOFs remains intact after modification (Figures S23 and S24, Supporting Information). The UV–vis diffuse reflectance spectra show that the incorporation of single atoms has no apparent influence on the intrinsic absorption of the MOFs (Figure S25, Supporting Information). Nitrogen sorption isotherms and pore size distributions for PCN-222 or DUT-67 demonstrate that their surface area and pore size present reasonable decrease after the introduction of SnO$_2$ and Pt species (Figures S26 and S27, Supporting Information). The XANES and EXAFS analyses unambiguously reveal the formation of atomically dispersed Pt species on diverse MOF supports mediated by SnO$_2$ (Figures S28 and S29, Supporting Information), similar to that in Pt$_1$/SnO$_2$/UiO-66-NH$_2$, affording Pt$_1$/SnO$_2$/PCN-222 and Pt$_1$/SnO$_2$/DUT-67.

2.2. Photoelectrochemical Properties

For comparison, Pt NPs (≈2.5 nm) stabilized by SnO$_2$/UiO-66-NH$_2$, namely Pt$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$, were also synthesized via a photochemical deposition process (Figures S30–S32, Supporting Information). UV–vis diffuse reflectance spectrum of UiO-66-NH$_2$ shows a strong absorption in $\approx$300–450 nm, which can be ascribed to the characteristic absorbance of ligand antenna (Figure 2a). The band structure of UiO-66-NH$_2$ calculated from Tauc plots and Mott–Schottky plots shows that it is thermodynamically possible for photocatalytic H$_2$ production (Figure S33, Supporting Information). The absorbance edge is almost identical after modification, which means that all the samples possess similar bandgaps. Photoluminescence (PL) emission spectra are collected under excitation at 385 nm, of which its fluorescent intensity can be an indicator of charge recombination (Figure 2b). As expected, the PL spectra show that the parent MOF has the strongest peak, followed by SnO$_2$/UiO-66-NH$_2$ and Pt$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$ while Pt$_1$/SnO$_2$/UiO-66-NH$_2$ presents significant fluorescence extinction and the weakest fluorescence intensity, which can be explained as its best charge-separation efficiency. Reversed to the PL intensity, Pt$_1$/SnO$_2$/UiO-66-NH$_2$ displays the strongest photocurrent response among all investigated catalysts, suggesting the fastest interfacial charge transfer from UiO-66-NH$_2$ to Pt single-atoms under irradiation (Figure 2c). The above results are also supported by electrochemical impedance spectroscopy (EIS), where Pt$_1$/SnO$_2$/UiO-66-NH$_2$ possesses the smallest radius, indicative of the lowest charge transfer resistance between the catalyst and medium (Figure 2d).

The Cu- and Ni-based samples exhibit similar results to the Pt-based catalysts above. The Cu and Ni NPs were introduced to SnO$_2$/UiO-66-NH$_2$ via impregnation and reduced by NaBH$_4$ to give Cu$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$ and Ni$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$, respectively, for comparison (Figures S34 and S35, Supporting Information). The UV–vis diffuse reflectance, PL photocurrent and EIS measurements for M$_1$/SnO$_2$/UiO-66-NH$_2$, M$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$ (M = Cu and Ni) and SnO$_2$/UiO-66-NH$_2$ display exactly the same trends to the Pt-based samples (Figures S36–S39, Supporting Information). From these results, it is concluded that SACs possess the highest efficiency of charge transfer among all their corresponding counterparts. Further comparison of photoelectrochemical properties for all the three SACs samples, M$_1$/SnO$_2$/UiO-66-NH$_2$ (M = Pt, Cu, and Ni), demonstrates the superior efficiency of Pt$_1$/SnO$_2$/UiO-66-NH$_2$ to Cu$_1$/SnO$_2$/UiO-66-NH$_2$ and Ni$_1$/SnO$_2$/UiO-66-NH$_2$, toward charge separation (Figures S40–S43, Supporting Information).

2.3. Photocatalytic Activity

Encouraged by the above characterizations, we have then investigated catalytic performance of Pt$_1$/SnO$_2$/UiO-66-NH$_2$ for visible-light photocatalytic H$_2$ production by water splitting (Figure 3a). As expected, UiO-66-NH$_2$ shows a poor photocatalytic H$_2$ production rate of $\approx$18.7 µmol g$^{-1}$ h$^{-1}$, possibly attributed to the absence of overlap between the empty metal $d$ orbital and/or the $\pi^*$ orbital of the organic linker and the obstructed electron transfer from the linker to metal.[17] Upon loading Pt NPs, Pt$_{\text{NPs}}$/SnO$_2$/UiO-66-NH$_2$ shows much enhanced activity of $\approx$423 µmol g$^{-1}$ h$^{-1}$, suggesting the critical role of Pt in photocatalysis. Strikingly, Pt$_1$/SnO$_2$/UiO-66-NH$_2$ achieves the highest photocatalytic H$_2$ production rate, 2167 µmol g$^{-1}$ h$^{-1}$ with the apparent quantum efficiency (AQE) of $\approx$2.23% at
380 nm, among all investigated samples, which is ≈116, 8, and 5 times higher than that of UiO-66-NH₂, SnO₂/UiO-66-NH₂ and PtNP/SnO₂/UiO-66-NH₂, respectively, probably on account of maximum utilization of the Pt species. Photocatalytic results show that, irrespective of the metals, the M₁/SnO₂/UiO-66-NH₂ exhibit much higher hydrogen production rate than MNP/SnO₂/UiO-66-NH₂ and other counterparts (Figure S44, Supporting Information), demonstrating that single-atom metal dramatically boosts the photocatalytic activity. Furthermore, Pt₁/SnO₂/UiO-66-NH₂ outperforms the other M₁/SnO₂/UiO-66-NH₂ (M = Cu and Ni) and displays the highest activity (Figure 3a).

It is believed that the Pt behaves as a cocatalyst to trap electrons for hydrogen evolution; its low overpotential is responsible for the high performance. The recycling experiments indicate no noticeable activity drop occurs to all M₁/SnO₂/UiO-66-NH₂ (Figure 3b; Figure S45, Supporting Information). Powder XRD patterns, SEM, TEM, and HRTEM images confirm that the MOF crystallinity and structural integrity are well maintained and no Pt NPs can be found after reaction (Figures S46 and S47, Supporting Information). The atomically dispersed status of catalytic metal centers in these catalysts is also verified by EXAFS and CO adsorption behavior in the DRIFT spectra for

Figure 2. a) UV–vis spectra, b) PL emission spectra (λ<sub>ex</sub> = 385 nm), c) photocurrent responses, and d) EIS Nyquist plots for Pt₁/SnO₂/UiO-66-NH₂, PtNP/SnO₂/UiO-66-NH₂, SnO₂/UiO-66-NH₂, and UiO-66-NH₂.

Figure 3. a) Photocatalytic hydrogen production rates for Pt₁/SnO₂/UiO-66-NH₂, Cu₁/SnO₂/UiO-66-NH₂, Ni₁/SnO₂/UiO-66-NH₂, PtNP/SnO₂/UiO-66-NH₂, SnO₂/UiO-66-NH₂, and UiO-66-NH₂. b) Performance in three consecutive runs of photocatalytic recycling for Pt₁/SnO₂/UiO-66-NH₂.
M1/SnO2/UiO-66-NH2 after reaction (Figures S48 and S49, Supporting Information). These results highlight the good stability of M1/SnO2/UiO-66-NH2 in the photocatalytic process.

Electron paramagnetic resonance (EPR) was conducted to illustrate the charge transfer and further reveal the mechanism in the photocatalytic process (Figure S50, Supporting Information). The EPR spectrum of Pt1/SnO2/UiO-66-NH2 gives signals at g values of 2.001, 2.006, and 2.029 upon visible-light irradiation for 60 s in the solvent of acetonitrile with triethylamine as a sacrificial agent. The three EPR signals can be attributed to O2•– trapped in Zr–oxo clusters, while the g value of 2.001 may overlap with the signal of oxygen vacancies. It is assumed that the adsorbed O2 molecules accept electrons from electron-trapped Zr–oxo clusters based on the ligand-to-cluster charge transfer (LCCT) process. Inspired by the above results, the overall reaction mechanism of Pt1/SnO2/UiO-66-NH2 involved in the system can be proposed: (1) the electron–hole pairs are generated from the photoexcited amino functionalized organic linker (antenna) under visible light irradiation; (2) electrons are transferred to Zr–oxo clusters via LCCT process; and (3) electrons further migrate to the single Pt atoms for subsequent proton reduction. Remarkably, Pt1/SnO2/UiO-66-NH2 gives stronger EPR signals than Pt NP/SnO2/UiO-66-NH2, SnO2/UiO-66-NH2, and UiO-66-NH2, which could be attributed to the greatly accelerated electron transfer in the optimized SACs. Furthermore, the strongest EPR signals of Pt1/SnO2/UiO-66-NH2 among all investigated SACs is in well line with its superior catalytic performance (Figure S50, Supporting Information).

According to the above experimental results, the activity of photocatalytic H2 production can be significantly improved with SACs. DFT calculations were carried out to figure out the role of SACs in Pt1/SnO2/UiO-66-NH2 (Figure 4a; Section S3 and Table S2, Supporting Information). The Gibbs free energy (∆G<sub>H^*/e^−</sub>) represents the free energy barrier of proton reduction, a key step of photocatalytic H2 production; the absolute value approaching to 0 eV is favorable to the H2 production activity of the photocatalyst. The Pt1/SnO2/UiO-66-NH2 is able to significantly reduce the ∆G<sub>H^*/e^−</sub> to −0.28 eV (Figure 4b). The extremely low value of ∆G<sub>H^*/e^−</sub> would not only expedite electron–proton acceptance to form H<sup>+</sup>, but also guarantee the fast hydrogen desorption. The ∆G<sub>H^*/e^−</sub> value of PtNP/SnO2/UiO-66-NH2 is calculated to be −0.50 eV, which means that its overall free energy barrier is higher than that in Pt1/SnO2/UiO-66-NH2 (Figure 4c). Therefore, the single Pt atoms not only maximize the Pt utilization but also feature extremely low absolute value of ∆G<sub>H^*/e^−</sub> to facilitate hydrogen generation. In comparison, the ∆G<sub>H^*/e^−</sub> values of Cu1/SnO2/UiO-66-NH2 and Ni1/SnO2/UiO-66-NH2 are calculated to be 0.39 and 0.46 eV, respectively, slightly higher than that of Pt1/SnO2/UiO-66-NH2, which is consistent with experimental catalytic results and further illustrates the higher activity of the latter. Given the identical chemical microenvironment and support, the fabrication of M1/SnO2/UiO-66-NH2 indeed provides an ideal SAC platform to differentiate the intrinsic activity of diverse single-atom metal species.

3. Conclusion

We have developed a general, two-step approach toward the immobilization of single-atom metal sites (M = Pt, Cu, and Ni) in diverse MOFs (UiO-66-NH2, PCN-222 and DUT-67), by supporting SnO2 as a mediator/adapter onto metal–oxo clusters via microwave-assisted modification. The SnO2 offers strong interaction to stabilize the SACs, and the high surface area and high porosity of MOFs extend the dispersion distance of metal

![Figure 4. a) Calculated free energy diagram of catalyst loaded to Uio-66-NH2 for photocatalytic H2 production. b,c) Geometric structures of H+ of Pt/H2 in Pt/SnO2/UiO-66-NH2 (b) and Pt NPs (c). The cyan, gray, red, and green balls represent Pt, Sn, O, and H atoms, respectively.](image)
atoms and guarantees their accessibility in catalysis. Particularly, thanks to the maximum utilization of metal atoms, the atomically dispersed Pt in PtI/SSO2/UO-66-NH2 displays the best photocatalytic hydrogen activity up to 2167 µmol g⁻¹ h⁻¹, superior to that of CuI/SSO2/UO-66-NH2 (1265 µmol g⁻¹ h⁻¹) and NiI/SSO2/UO-66-NH2 (654 µmol g⁻¹ h⁻¹), and far outperforming their corresponding metal NPs and other counterparts. DFT calculations reveal that the single Pt atoms possess a lower forming their corresponding metal NPs and other counterparts.

Keywords

H₂ production, metal–organic frameworks, photocatalysis, single-atom catalysts

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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