Incorporating Transition-Metal Phosphides Into Metal-Organic Frameworks for Enhanced Photocatalysis

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Abstract: Metal-organic frameworks (MOFs) have been shown to be an excellent platform in photocatalysis. However, to suppress electron–hole recombination, a Pt cocatalyst is usually inevitable, especially in photocatalytic H₂ production, which greatly limits practical application. Herein, for the first time, monodisperse, small-size, and noble-metal-free transitional-metal phosphides (TMPs; for example, Ni₅P, Ni₃P₃), are incorporated into a representative MOF, UiO-66-NH₃, for photocatalytic H₂ production. Compared with the parent MOF and their physical mixture, both TMPs@MOF composites display significantly improved H₂ production rates. Thermo-dynamic and kinetic studies reveal that TMPs, behaving similar ability to Pt, greatly accelerate the linker-to-cluster charge transfer, promote charge separation, and reduce the activation energy of H₂ production. Significantly, the results indicate that Pt is thermodynamically favorable, yet Ni₅P is kinetically preferred for H₂ production, accounting for the higher activity of Ni₅P@UiO-66-NH₃ than Pt@UiO-66-NH₃.

Introduction

With the rapid depletion of conventional energy sources and associated environmental issues, increasing renewable energy demand is being intensively pursued. The conversion of solar energy to chemical energy or high valued chemicals, by means of photocatalysis, has been recognized to be an attractive solution and intensively studied. Amongst diverse photocatalytic processes, photocatalytic water splitting to generate H₂, an ideal and very promising future fuel, is being the most studied reaction. However, the currently reported photocatalysts toward this conversion suffer from severe photogenerated electron-hole (e–h) recombination, insufficient reaction sites, and low efficiency, posing significant challenge for further practical application. The most urgent task along this research line is to develop suitable photocatalytic systems with efficient photocatalysts greatly promoting charge separation toward hydrogen production.

The introduction of cocatalyst has been well established to be the most effective way to suppress the charge recombination, provide adequate active sites and reduce activation energy for H₂ evolution. Noble metals (e.g., Pt) are well-known as the most used and efficient cocatalysts. However, their high-cost and limited-reserves drive the demand to explore non-precious metal cocatalysts with low cost and high efficiency. Transition-metal phosphides (TMPs), such as Ni₅P, Ni₃P₃, Co₃P, etc., have been recently reported as promising noble-metal-alternative cocatalysts toward photocatalytic hydrogen production due to their unique structural and electronic properties. Despite significant progress on this aspect, two challenging issues arise out of those previous reports: 1) The activity comparison between TMPs and Pt remains a topic of debate. Some reports suggest that H₂ production rate of the TMP cocatalysts is even higher than Pt.[4b,e,6c] whereas some other studies believe that the TMP activity is lower than Pt.[4a,d,6b] The former explains this phenomenon based on the kinetic results, while the latter explains it from the perspective of electrochemistry by comparing the on-set overpotential in the polarization curves, in which the on-set overpotential of Pt is lower than that of TMPs. Therefore, the current interpretation and understanding on TMP cocatalyst might be one-sided, and further in-depth study and complete understanding are highly desired. 2) The large particle sizes of TMPs and small interface contact with semiconductors. Although some nanostructured TMPs have been synthesized via the surfactant-assisted strategy, their high surface energy gives rise to a strong tendency to agglomeration during the reaction.[3b] Most of TMPs in previous reports were prepared from the precursors of metal salts, oxides, etc.,[4–6] where the resultant large particle sizes of TMPs cause very limited interface contact, or even in a physical mixture form, between TMPs and semiconductors, detrimental to photocatalysis.

In addition to cocatalyst, the development of optimized photocatalyst is of great importance for improving charge separation. In contrast to the traditional solid semiconductors, porous materials feature high porosity and high surface area, not only favorable to the dispersion and accessibility of cocatalysts but also beneficial to the transport of substrates and products.[7] Moreover, they enable charge carriers short-
ened migration path to reach the substrates that are diffused inside the pores, resulting in efficient e-h separation. In this context, metal-organic frameworks (MOFs),[9] a class of crystalline porous materials constructed by metal ions/cluster and organic ligands, have been recognized their great potential in photocatalysis.[10–11] Not limited to the advantages of porous solids mentioned above, the high crystallinity of MOFs has a positive effect on charge separation and photocatalysis, as the structural defects usually behave as recombination centers of e-h pairs. In fact, it has been well accepted that MOFs possess congenial capability to encapsulate small guest nanoparticles (NPs) for synergistic catalysis.[12] Therefore, MOF might be an ideal platform for incorporating small-size and highly dispersed TMP NPs for enhanced photocatalytic H₂ production.

With the aforementioned in mind, we have pre-synthesized tiny monodisperse TMPs (Ni₅P, Ni₅₂P₃) and Pt NPs in similar sizes (≈10 nm) and assembled them into a representative MOF, UiO-66-NH₂ (Zr₅O₄(OH)₄(BDC-NH₂)₆, BDC-NH₂ = 2-amino-1,4-benzenedicarboxylic acid), to give the corresponding composites, denoted Ni₅P@UiO-66-NH₂, Ni₅₂P₃@UiO-66-NH₂ and Pt@UiO-66-NH₂, respectively (Scheme 1). Significantly, the TMPs greatly boost the photocatalytic H₂ production performance and Ni₅P NPs exhibit even higher H₂ production rate than Pt NPs. While energy level analysis and linear sweep voltammetry (LSV) reveal that Pt is thermodynamically favorable, Ni₅P is kinetically preferred, as supported by the photoelectrochemical measurements. The superior H₂ production of Ni₅P to Pt should be a balanced result between thermodynamics and dynamics. More importantly, by taking Ni₅P as a representative example, it is unambiguously demonstrated that Ni₅P behaves a similar role to Pt, accelerating the link-to-cluster charge transfer (LCCT) in photocatalytic process, based on electronic spin resonance (ESR) and ultrafast transient absorption (TA) spectroscopy, the latter of which presents similar real-time photoexcited carrier dynamics between Ni₅P and Pt.

To our knowledge, in addition to the only report on the physical mixture of MOF and large sizes of TMPs toward photocatalysis,[6c] this is the first attempt on incorporating monodisperse and small TMPs into MOFs for photocatalysis.

Results and Discussion

The TMPs (e.g. Ni₅P, Ni₅₂P₃) with uniform sizes of ≈10 nm were synthesized in nitrogen atmosphere (Figure S1 in the Supporting Information, SI).[3] Their phase purity was confirmed based on powder X-ray diffraction (XRD) profiles (Figure S2). The obtained TMPs were dispersed in DMF with ZrCl₄ and 2-aminoterephthalic acid to afford Ni₅P@UiO-66-NH₂ and Ni₅₂P₃@UiO-66-NH₂ with good crystallinity, in a regular octahedral shape and ≈1 µm sizes (Figure S2 and S3). Upon encapsulation in the MOF, the TMPs remain to be ≈10.0 nm, in a uniformly dispersed form inside the MOF particles, as verified by transmission electron microscopy (TEM) observation (Figure 1a,b and Figure S4).

For control experiments, Pt NPs with sizes of ≈10 nm were synthesized and Pt@UiO-66-NH₂ of ≈1 µm was fabricated with a similar method as above (Figure S1 and S3). The Pt NPs present good dispersion in the MOF particles (Figure 1c,d and S5). Not limited to the particle sizes, the loading amount of the cocatalyst and the BET surface areas of all the three MOF composite photocatalysts are similar (Figure S6 and Table S1). All their UV-vis diffuse reflectance spectra inherit the feature of UiO-66-NH₂ and almost exhibit the same band gap, indicating their similar light harvesting behavior (Figure S7). All these important features make it fair for their activity comparison with a focus on their different cocatalysts, Ni₅P, Ni₅₂P₃, and Pt NPs. In addition, the lowest unoccupied molecular orbital (LUMO) level of UiO-66-NH₂, which has been estimated by Mott-Schottky mea-

**Scheme 1.** Schematic illustration for the synthesis of TMPs and TMPs@UiO-66-NH₂.

**Figure 1.** TEM images of a, b) Ni₅P@UiO-66-NH₂ (inset: size distribution of Ni₅P NPs) and c, d) Pt@UiO-66-NH₂ (inset: size distribution of Pt NPs).
surement (Figure 2a), is $-0.62$ V (vs. NHE, pH 6.8). This value is lower than the potential for H$_2$O reduction ($-0.40$ V vs. NHE, pH 6.8), suggesting its feasibility toward H$_2$ production.

Encouraged by the above information, photocatalytic H$_2$ production by water splitting was conducted under visible light irradiation. In stark contrast to the negligible H$_2$ production rate of pristine UiO-66-NH$_2$ (2.1 $\mu$mol g$^{-1}$ h$^{-1}$), both TMPs@UiO-66-NH$_2$ exhibit exponential enhancement of photocatalytic activity. The Ni$_2$P@UiO-66-NH$_2$ shows H$_2$ production rate of 293.2 $\mu$mol g$^{-1}$ h$^{-1}$, $\approx 80$ times higher than the MOF. Strikingly, with the help of similar cocatalyst contents, Ni$_2$P@UiO-66-NH$_2$ and Pt@UiO-66-NH$_2$ possess over two orders of magnitude activity enhancement, 409.1 and 378.0 $\mu$mol g$^{-1}$ h$^{-1}$, respectively (Figure 2b, S8 and Table S3), which are even tens of times higher than all physical mixtures of TMPs/Pt and UiO-66-NH$_2$ (Table S4). The results reflect the formation of TMP-MOF and Pt-MOF Schottky junction, where TMPs and Pt steer the rapid charge transfer from the MOF to the cocatalyst, suppressing e-h recombination and thereby achieving excellent efficiency of proton reduction. Further recycling experiments for Ni$_2$P@UiO-66-NH$_2$ suggest the well retained activity in the consecutive three catalytic runs (Figure 2c). Powder XRD, ICP and TEM results provide the evidences on its structural maintenance during the reaction (Figure S9 and S10).

It is well accepted that, for photocatalytic H$_2$ reduction in the presence of sacrificial agent, the law of reaction thermodynamics needs to be followed:

$$E_{CB} > E_{H_2/2} + E_R$$  \hspace{1cm} (1)

Where $E_{CB}$ is the energy of conduction band (or LUMO) of the photocatalyst, $E_{H_2/2}$ is the potential for H$_2$O reduction, and $E_R$ is the overpotential for water reduction. Though UiO-66-NH$_2$ is theoretically able to give electrons for proton reduction as characterized above, its hydrogen production rate is very low. Introducing cocatalyst can significantly reduce $E_R$ and improve the hydrogen production rate. The ability of a cocatalyst to lower $E_R$ can be reflected by the on-set overpotential of the hydrogen evolution reaction (HER) process.\textsuperscript{[14]} It is apparent that the on-set overpotential of Pt NPs is much lower than that of Ni$_2$P and Ni$_{12}$P$_5$ NPs (Figure 2d and S11), unambiguously demonstrating that Pt is thermodynamically superior to Ni$_2$P and Ni$_{12}$P$_5$. Meanwhile, the work function of Pt is larger, which means that the driving force of photo-generated electron transfer to Pt is greater.\textsuperscript{[3a,b]} Therefore, from the perspective of thermodynamics, Pt is undoubtedly one of the best cocatalysts, which is consistent with the previous findings\textsuperscript{[3]} and the capability to accept electrons follows the order of Pt $>$ Ni$_2$P $>$ Ni$_{12}$P$_5$.

Following the thermodynamic principle, the activity of Pt@UiO-66-NH$_2$ should be much higher than the other two. Unexpectedly, Ni$_2$P@UiO-66-NH$_2$ has been confirmed to be more active. This result illustrates that the capability of accepting electrons is not the only criterion to evaluate a cocatalyst. The electron transfer kinetics between MOF and the cocatalyst should be taken into account as well. To this end, combined characterizations have been adopted. Steady-
state photoluminescence (PL) spectra under excitation at 380 nm show that the MOF and all composites give a broad band centered at ≈ 450 nm, whereas the intensity is distinctly different and follows UiO-66-NH₂ > Ni₃P@UiO-66-NH₂ > Pt@UiO-66-NH₂ > Ni₅P@UiO-66-NH₂ (Figure 3a). The reduced intensity of PL signal in the composites in reference to the MOF reveals rapid electron transfer from the MOF to Pt and the most efficient electron transfer takes place in the Ni₃P composite. Photocurrent results disclose the e-h separation efficiency of photocatalysts and stay in line with the PL trend. As expected, the photocurrent of the parent MOF gets greatly enhanced after incorporating cocatalyst NPs, where Ni₃P@UiO-66-NH₂ exhibits the strongest photocurrent response, followed by Pt@UiO-66-NH₂, Ni₅P@UiO-66-NH₂ and UiO-66-NH₂ (Figure 3b), indicating the promoted separation of e-h pairs via the formation of MOF-cocatalyst Schottky junction and the best charge transfer in Ni₃P@UiO-66-NH₂ under light irradiation. This argument is also verified by electrochemical impedance spectroscopy (EIS) characterization (Figure 3c), in which all composites exhibit smaller radii than the parent MOF and Ni₅P@UiO-66-NH₂ presents the smallest radius, indicative of its lowest resistance of interfacial charge transfer. It is surprising that all kinetic data are miraculously consistent with the photocatalytic hydrogen production rate. Therefore, although Pt is easier to accept electrons from UiO-66-NH₂ than Ni₃P based on thermodynamic analysis, from the kinetic data and the photocatalytic results, we are able to reach the conclusion that the electrons migrate more efficiently from the MOF to Ni₃P than Pt, and followed by Ni₅P. By integrating thermodynamic and kinetic factors, it is ready to conclude that the overall trend of promoting charge separation capability is Ni₃P > Pt > Ni₅P, matching with the experimental results.

In order to further rationalize the results above, by taking Ni₃P and Pt as representative examples, mechanistic information from electron spin resonance (ESR) and ultrafast transient absorption (TA) spectroscopy has been gleaned. The Pt is recognized to accelerate the link-to-cluster charge transfer (LCCT) process in photocatalytic hydrogen production, where oxygen-centered active sites in Zr-oxo clusters can be generated. To our delight, a new ESR signal at \( g_{\text{iso}} = 2.003 \) (close to the value of free electrons, \( g_e = 2.0023 \)) emerges in all samples (Figure 3d). The much higher signal intensity is similarly observed in both Ni₅P@UiO-66-NH₂ and Pt@UiO-66-NH₂ than that in the parent MOF, which demonstrates the LCCT process and verifies the similar role of Ni₅P and Pt, being a cocatalyst. The differentiated intensity of ESR signal and photocatalytic activity can be ascribed to the different ability of the cocatalyst to accelerate LCCT process. Furthermore, ultrafast TA spectroscopy was resorted to track in real time the charge carrier dynamics for these photocatalysts. The TA spectra are similar whether or not a cocatalyst is introduced, indicating that the cocatalysts do not significantly affect the MOF light absorption, as also supported by UV-vis spectra (Figure S7). Compared with Pt@UiO-66-NH₂ and UiO-66-NH₂, Ni₅P@UiO-66-NH₂ exhibits a weaker stimulated emission (SE) signal (–) in the range of 420–530 nm when probed at the same delay times.
(Figure 4a and S12), indicative of efficient excited state quenching by Ni$_2$P. This is consistent with the PL intensities observed in Figure 3a, which also shows that Ni$_2$P quenches the PL of UiO-66-NH$_2$ more effectively than Pt. Moreover, there is a strong photoinduced absorptive peak at ≈650 nm that can be observed for Ni$_2$P and Pt loaded UiO-66-NH$_2$, but not for pure UiO-66-NH$_2$, suggesting that this feature is likely an indication of excited state charge transfer from UiO-66-NH$_2$ to cocatalysts.\[16\]

To further unveil the excited state dynamics of these photocatalysts, their TA kinetics of excited state absorption (ESA) at 650 nm are compared (Figure S13). All kinetics traces can be fitted by a three-exponential decay function (fitting parameters in Table S2) (Figure 4b). The average relaxation lifetime is 367.4, 238.5 and 284.7 ps for UiO-66-NH$_2$, Ni$_2$P@UiO-66-NH$_2$ and Pt@UiO-66-NH$_2$, respectively. Accurate assignment of these multiple time constants is challenging as they could arise from charge transfer, various trapping processes and/or intrinsic lifetime heterogeneities. Nonetheless, the facts that the average relaxation lifetime of Ni$_2$P@UiO-66-NH$_2$ is shorter than Pt@UiO-66-NH$_2$ and that both are shorter than pure UiO-66-NH$_2$ indicate that charge transfer from UiO-66-NH$_2$ to Ni$_2$P is more efficient than to Pt, again consistent with the higher photocatalytic activity of Ni$_2$P@UiO-66-NH$_2$.\[16,17\]

In addition, apparent activation energy ($E_a$), an important parameter combining thermodynamic and dynamic factors to reflect the difficulty of a reaction, can be evaluated based on the temperature-dependent PL spectra. With the temperature increasing, the PL peak intensity gradually decreases (Figure 4c and S14), and the $E_a$ can be estimated by the following Arrhenius equation:\[18\]

$$ I(T) = I_0/(1 + A \exp (-E_a/k_B T)) $$

According to the equation, the $E_a$ values of UiO-66-NH$_2$, Pt@UiO-66-NH$_2$ and Ni$_2$P@UiO-66-NH$_2$ are 69.2, 66.3 and 57.7 meV, respectively. The change trend of $E_a$ is exactly opposite to that of hydrogen production rate (Figure 4c and S15). This result, once again, suggests that the cocatalysts reduce the reaction energy barrier and boost the reaction activity. The lower $E_a$ of Ni$_2$P@UiO-66-NH$_2$ nicely supports its better performance than Pt@UiO-66-NH$_2$ in our system.

### Conclusion

In this work, small-size and monodisperse NPs of TMPs, for the first time, have been rationally incorporated into a MOF for photocatalysis. For control, Pt NPs have also been assembled into the MOF particle. Both TMPs and Pt have been demonstrated to be the similar role of cocatalyst to accept the electrons and promote the charge transfer. The electron-injected TMPs and Pt encompassed by the MOF are easily accessible to protons for photocatalytic H$_2$ production. As a result, the activity of Ni$_2$P@UiO-66-NH$_2$ outperforms all other counterparts, even Pt@UiO-66-NH$_2$, unambiguously demonstrating that this is an integrated performance between...
thermodynamic and kinetic results, though the Pt possesses much more favorable thermodynamics than TMs. As expected, a series of photoelectrochemical and spectroscopic observations elucidate the underlying electron-transfer mechanism and manifest the faster kinetics and more efficient charge separation in NiP@UiO-66-NH₂ than Pt@UiO-66-NH₂ and others. We believe this work will not only enable in-depth understanding on the charge transfer in MOF composites, but also provide inspirations for building efficient and noble-metal-free MOF-based and even other porous material-based photocatalytic systems.

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**Conflict of interest**

The authors declare no conflict of interest.

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