NiII Coordination to Al-Based Metal–Organic Framework Made from 2-Aminoterephthalate for Photocatalytic Overall Water Splitting

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Abstract: The aluminum-based metal–organic framework (MOF) made from 2-aminoterephthalate is a photocatalyst for oxygen evolution. This MOF can be modified by incorporating NiII cations into the pores through coordination to the amino groups, and the resulting MOF is an efficient photocatalyst for overall water splitting.

Photocatalytic water splitting has been extensively investigated since it offers a way to replace fossil fuels with carbon-free and sustainable hydrogen energy. A number of studies on water splitting have focused on the half reaction, namely, the evolution of \( \text{O}_2 \) or \( \text{H}_2 \) in the presence of a sacrificial agent, and most photocatalysts for water splitting are composites.\[1–9\] In general, the efficiency of photocatalytic reactions is enhanced by cocatalysts, because they lower the activation energy barrier and act as reactive sites.\[10–15\] Metal–organic frameworks (MOFs), in which metal ions are coordinated to organic ligands forming one-, two-, or three-dimensional structures, possess semiconductor-like attributes and can be promising photocatalysts. Examples include UiO-66 for water reduction as well as MIL-101(Cr) and bismuth-based MOFs for water oxidation.\[16–21\] So far, no MOF has been reported to be a photocatalyst for overall water splitting. The aluminum-based MOF derived from 2-aminoterephthalic acid \( \text{H}_2\text{ATA} \) (hereafter, Al-ATA MOF) consists of \( \text{Al}(	ext{OH})_2 \) octahedra linked by the carboxylate groups of 2-aminoterephthalates, \( \text{ATA}^2^- \). Al-ATA MOF is a photocatalyst for oxygen evolution from water, with the benzene ring of \( \text{ATA}^2^- \) as the site for \( \text{O}_2 \) evolution.\[22\] It is known that compounds of NiII ions are efficient cocatalysts for hydrogen production,\[23–32\] and the amino groups of Al-ATA MOF present in the pores can act as ligands for the NiII cations. Thus, if NiII ions are incorporated into Al-ATA MOF by coordination to the amino groups, the resulting modified MOF (hereafter, Al-ATA-Ni MOF) would have both the \( \text{H}_2 \) and \( \text{O}_2 \) evolution units in close proximity and hence might be an efficient photocatalyst for overall water splitting. In this Communication, we confirm this hypothesis.

We first examine the coordination environment of the Ni atoms and their oxidation state in Al-ATA-Ni MOF by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) measurements (Figure 1). The overall XANES profile (Figure 1a) of Al-ATA-Ni MOF is similar to that of Ni(NO\(_3\))\(_2\), with a much weaker pre-edge peak at ca. 8333.0 eV. The latter indicates that the Ni atoms of Al-ATA-Ni MOF are in an oxidation state of around +2 and are octahedrally coordinated. The

Figure 1. a) Ni K-edge XANES spectra. b) EXAFS Fourier transforms of Al-ATA-Ni, Ni(NO\(_3\))\(_2\), NiO, and Ni foil. c) Wavelet transforms for the \( k^2 \)-weighted Ni K-edge EXAFS signals for the first (lower panel) and higher (upper panel) coordination shells of Al-ATA-Ni. The vertical dashed lines are a guide for the eye. Label on x-axis: \( k \) (Å\(^{-1}\)).
EXAFS Fourier transform and wavelet transform (WT) are presented in Figure 1b,c. The assignment of the signals from 1.0 to 4.0 Å to either Ni–N(O) or Ni–Ni interactions is based on the detailed EXAFS WT analysis (Figures S1 and S2 in the Supporting Information). For Al-ATA-Ni MOF, the WT intensity maximum near 4.5 Å⁻¹ is well resolved at a distance of 1.6 Å and is assigned to the Ni–N and Ni–O bonding. No obvious signal is detected for Ni–Ni bonding, which would have a WT maximum near 7.5 Å⁻¹ at distances of 2.14–2.58 Å. The WT maximum near 6.3 Å⁻¹ resolved at a distance of 3.21 Å is assigned to the Ni–Al bonding. These results indicate that the Ni atoms are isolated rather than forming Ni nanocrystals. Our EXAFS curve-fitting analysis reveals that the coordination number of the nearest-neighbor N and O atoms surrounding an isolated Ni atom is 5.5 at a distance of roughly 2.05 Å (Figure S3 and Table S1 in the Supporting Information), further confirming an octahedral coordination for Ni²⁺ ions in the pores of Al-ATA-Ni MOF.

Comparison of the FTIR spectra and XRD patterns of Al-ATA and Al-ATA-Ni MOFs provides more structural information about Al-ATA-Ni MOF. In the FTIR spectra (Figure 2a), the new band centered at 754 cm⁻¹ is assigned to a Ni–N bond. The peaks centered at 1099 and 2933 cm⁻¹ (i.e., the C–N and N–H stretching vibrations of the amino group, respectively) decrease in intensity after Ni²⁺ incorporation. This is expected because the Ni–N bond formation would weaken the C–N and N–H bonds as a consequence of electron transfer from N to Ni²⁺. Furthermore, the intensity associated with the O–H vibration (3200–3700 cm⁻¹) is stronger for Al-ATA-Ni MOF than for Al-ATA MOF, suggesting the coordination of HO⁻ anion to Ni²⁺.

The XRD patterns of Al-ATA and Al-ATA-Ni MOFs (Figure S4) show that the peak positions of Al-ATA-Ni MOF are identical to those of Al-ATA MOF; suggesting that incorporation of Ni²⁺ ions neither destroys Al-ATA MOF, nor replaces the Al³⁺ ions of Al-ATA MOF. This result is expected, given that the incorporation of Ni²⁺ into Al-ATA MOF proceeds at room temperature, and that no MOF materials can be obtained when the organic ligand H₂ATA and Ni(NO₃)₂ are mixed at room temperature. The SEM images (Figure S5) suggest that Al-ATA and Al-ATA-Ni MOFs have the same morphology composed of small particles less than 100 nm. No significant difference is observed for the particle size. The analysis of N₂ adsorption–desorption isotherms (Figure S6) shows a smaller BET surface area for Al-ATA-Ni (262.6 m²g⁻¹) than for Al-ATA (961.2 m²g⁻¹), further suggesting the coordination of Ni²⁺ with ATA.

Based on the above results, the probable local environment of a Ni²⁺ ion incorporated into Al-ATA MOF can be depicted as in Figure 2b. The Ni²⁺ cation present in a pore is coordinated to the amino N of one ATA²⁻, one O of an AlO₆ octahedron, and four OH groups. The pore of Al-ATA MOF has the dimensions 8.6 Å × 14.3 Å, which can accommodate one Ni²⁺ (the ionic radius of a hydrated Ni²⁺ cation is approximately 4.04 Å).

The results of the photocatalytic reaction over Al-ATA-Ni MOF in pure water are presented in Figure 3a. H₂ and O₂ are produced in the stoichiometric ratio of 2:1, suggesting that the detected H₂ and O₂ are generated from water splitting. The H₂ and O₂ evolution stops either when the light is turned off or when Al-ATA-Ni MOF is absent, showing that the reaction is a photocatalytic process. Furthermore, no H₂ and O₂ was detected over Al-ATA MOF under the same conditions. To confirm the effect of the Ni²⁺ cation on the photocatalytic overall water splitting, we carry out the half reactions in the presence of sacrificial agents (namely, 30 mg AgNO₃ and 6 mL CH₃OH as sacrificial reagents for the oxygen and hydrogen evolution reactions, respectively). The O₂ evolution rate over Al-ATA-Ni MOF is much higher than that over Al-ATA MOF (155 vs. 16.5 μmolh⁻¹) (Figure 3b). For H₂ evolution, Al-ATA MOF is inactive while Al-ATA-Ni MOF is active with a rate of 36.0 μmolh⁻¹ (Figure 3c). Thus, the Ni²⁺ ions in Al-ATA-Ni MOF act as the H₂ evolution sites, and also improve the efficiency of the O₂ evolution.

To probe the role of the incorporated Ni²⁺ cations in enhancing the photocatalytic performance, we analyzed the linear sweep voltammetry (LSV) curves for Al-ATA and Al-ATA-Ni MOFs. The photocurrent of Al-ATA MOF increases...
as the bias becomes more negative, suggesting its p-type semiconducting behavior (Figure 4). Al-ATA-Ni MOF displays a higher current than Al-ATA MOF in the dark as well as under UV/Vis light irradiation. In addition, Al-ATA-Ni MOF has a more positive redox peak under UV/Vis irradiation than in the dark (0.30 vs. 0.10 V against Ag/AgCl sat. KCl). This redox peak is associated with the conversion of Ni$^{2+}$ to Ni$^+$, and the UV/Vis light irradiation promotes a positive shift of 0.2 V for Al-ATA-Ni MOF.$^{[24,35]}$ A similar phenomenon is observed for NiCl$_2$ solution, i.e., exposure to UV/Vis light lowers the potential for the Ni$^{2+}$ to Ni$^+$ transformation (Figure S7). Therefore, it is reasonable to conclude that UV/Vis light plays an important role in assisting the conversion from Ni$^{2+}$ to Ni$^+$. The formation of Ni$^+$ ions is essential for the photocatalytic H$_2$ evolution over Al-ATA-Ni MOF, since they act as active sites. The formation of Ni$^+$ ions over Al-ATA-Ni MOF under UV/Vis light irradiation is confirmed by both Tengs blue color reaction and EPR spectra (Figures S8 and S9).

Al-ATA-Ni MOF displays an oxidation peak at 1.05 V (vs. Ag/AgCl sat. KCl), which is attributed to the characteristic interconversion between Ni$^{2+}$ and Ni$^{3+}$.$^{[36,37]}$ However, this peak is weakened upon light irradiation, suggesting that under light irradiation Ni$^{2+}$ is preferentially reduced to Ni$^+$ rather than oxidized to Ni$^{3+}$. This result implies that the active site for O$_2$ evolution is not Ni, and is consistent with our previous results.$^{[22]}

Our previous study$^{[22]}$ showed that when Al-ATA MOF is exposed to light, a photogenerated electron in ATA$^2-$ moves across the AlO$_6$ octahedron to react with Ag$^+$ of the sacrificial agent, while a photogenerated hole is left in the benzene ring to oxidize water giving rise to O$_2$. In Al-ATA-Ni MOF, it is most likely that a photogenerated electron is transferred to the Ni$^{2+}$ ion coordinated to the amino group of ATA$^2-$, while the photogenerated hole stays in the benzene ring, oxidizing water to O$_2$. The oxidation half reaction of Al-ATA-Ni MOF is the same as that of Al-ATA MOF.
We explored further the effect of Ni$^{2+}$ ions on the photoresponsive behavior and photogenerated charge carriers. Figure 5a shows the UV/Vis diffuse reflectance spectra (DRS) of Al-ATA and Al-ATA-Ni MOFs. The Ni incorporation induces little change in the photoresponsive behavior of Al-ATA MOF. Both samples display an absorption edge at about 451 nm, which corresponds to a band gap of 2.75 eV. The weak absorption between 450–650 nm of Al-ATA-Ni MOF may be related to the d–d transition of the Ni$^{2+}$ cations in an octahedral environment. No obvious difference of the peak position of the photoluminescence (PL) spectra is observed between Al-ATA and Al-ATA-Ni MOFs (Figure 5b), which is consistent with the DRS results. However, the emission intensity of Al-ATA-Ni MOF is much lower than that of Al-ATA MOF, indicating that Al-ATA-Ni MOF separates electron–hole pairs more efficiently than Al-ATA MOF does, which agrees well with the observation that the O$_2$ evolution rate is higher over Al-ATA-Ni than over Al-ATA MOF.

The photoelectrical results are consistent with the photoluminescence results (Figure 6). The transient photocurrent response under UV/Vis light illumination is higher over Al-ATA-Ni MOF (1.7 μA) than that over Al-ATA MOF (1.1 μA). This result suggests that Ni$^{2+}$ incorporation increases the efficiency of electron–hole separation, and therefore results in a greater number of free photogenerated charge carriers. The electrochemical impedance spectra (EIS) of both samples display one dominant semicircle, whose diameter is related to charge-transfer resistance. The typical Nyquist plots reveal a smaller charge-transfer resistance for Al-ATA-Ni than for Al-ATA MOF, suggesting a faster photogenerated charge transfer kinetics at the Al-ATA-Ni MOF electrode. After the simulation of an equivalent circuit diagram, the charge-transfer resistance ($R_{ct}$) of Al-ATA-Ni/FTO electrode was determined to be 3.7 × 10$^4$ Ω, which is smaller than that of Al-ATA/FTO (6.9 × 10$^4$ Ω).

In summary, Al-ATA-Ni MOF is a photocatalyst for overall water splitting. The Ni$^{2+}$ cation coordinated to the amino group of ATA$^2@$ acts as the H$_2$ evolution site and enhances the O$_2$ evolution at the benzene ring bearing the amino group. In designing heterogeneous and homogeneous photocatalysts for overall water splitting, it would be important to assemble both H$_2$ and O$_2$ evolution units in proximity.

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Conflict of interest
The authors declare no conflict of interest.
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