

Intrinsic White-Light-Emitting Metal–Organic Frameworks with Structurally Deformable Secondary Building Units

Chengdong Peng⁺, Xueling Song⁺, Jinlin Yin, Guiyang Zhang, and Honghan Fei^{*}

Abstract: The secondary building units in metal–organic frameworks (MOFs) are commonly well-defined metal–oxo clusters or chains with very limited structural strain. Herein, the structurally deformable haloplumbate units that are often observed in organolead halide perovskites have been successfully incorporated into MOFs. The resultant materials are a rare class of isorecticular MOFs exhibiting large Stokes-shifted broadband white-light emission, which is probably induced by self-trapped excitons from electron–phonon coupling in the deformable, zigzag $[\text{Pb}_2\text{X}_3]^+$ ($X = \text{Cl}, \text{Br}, \text{or I}$) chains. In contrast, MOFs with highly symmetric, robust haloplumbate chains only exhibit narrow UV–blue photoemission. The designed MOF-based intrinsic white-light photoemitters have a number of advantages over hybrid inorganic–organic perovskites in terms of stability and tunability, including moisture resistance, facile functionalization of photoactive moieties onto the organic linkers, introduction of luminescent guests.

White-light-emitting diodes (WLEDs) are of particular importance in solid-state lighting technology, which has the potential to significantly cut energy consumption and decrease greenhouse gas emission.^[1] They are generally produced utilizing blue InGaN LEDs coated with a yellow-emitting YAG:Ce phosphor or near-UV InGaN LEDs with a blend of red-, green-, and blue-emitting phosphors.^[2] However, these multicomponent strategies have problems such as intrinsic color balance, self-adsorption, and device complication.^[2–5] Thus, single-source white-light emitters are a major target in developing WLEDs.

Recently, broadband white-light emission as an intrinsic property has been realized in (110)-oriented corrugated 2D or 1D organolead halide perovskites, which is attributed to the formation of self-trapped excitons.^[6–12] This promising class of white-light emitters is amenable to crystal engineering for further enhancing their photoluminescence properties.^[13–18] However, the intrinsic moisture instability of lead perovskites has not been fully addressed.^[19]

Luminescent metal–organic frameworks (MOFs) are considered to be an ideal platform for single-phase white-

light photoemitters, owing to their capability to organize multiple photoemissive components into a single lattice.^[20,21] MOFs with open topology offer unique advantages since a vast array of bulky luminescent groups can be attached onto the organic ligands via postsynthetic modification.^[22,23] In addition, the permanent porosity of MOFs will bring opportunities to encapsulate luminescent guest molecules.^[24,25] The well-defined pore environment along with multiple luminescent centers either on the framework or residing in the porosity make MOFs a very promising alternative to the conventional white-light-emissive phosphors.

To date, the vast majority of white-light-emitting MOFs are obtained by controlling the relative amount of rare earth (RE) metals with characteristic f–f emission.^[26] However, the high demand for RE elements has led to a dramatic 49-fold price increase from 2001 to 2011.^[27] Other white-light-emitting MOFs either exhibit ligand-based luminescence or are based on metal-to-ligand/ligand-to-metal charge transfer (MLCT/LMCT) or a combination of both.^[28,29] Among them, very few emit broadband white-light emission spanning the entire visible spectrum with high color-rendering index (CRI).^[30]

Herein, we describe the incorporation of structurally deformable lead halide units, which are often observed in organolead halide perovskites, into MOFs. The deformable $[\text{Pb}_2\text{X}_3]^+$ ($X = \text{Cl}, \text{Br}, \text{or I}$) 1D chains as the secondary building units (SBUs) were interconnected by 1,4-benzenedicarboxylate (bdc) as the strut to afford a series of white-light-emitting MOFs ($[\text{Pb}_2\text{X}_3]^+[\text{O}_2\text{C}(\text{C}_6\text{H}_4)\text{CO}_2^-]_2[(\text{CH}_3)_2\text{NH}_2^+]_3$ ($X = \text{Cl}, \text{Br}, \text{or I}$), which we denote as TMOF-5(X), TMOF = Tongji University). Upon near-UV excitation, the resultant materials are a rare class of isorecticular MOFs with tunable band gaps that feature intrinsic broadband emission with a high color-rendering index (CRI) of up to 89, satisfying the color properties required by WLED. In addition, the MOF-based photoemitters are air/moisture resistant and provide a versatile platform for further functionalization and tunability.

The solvothermal reaction of PbCl_2 , bdc, and perchloric acid in DMF/EtOH afford needle-like colorless crystals of TMOF-5(Cl). X-ray crystallography reveals that TMOF-5(Cl) consists of doubly interpenetrated nets defined in the tetragonal crystal system, which is due to the tetragonal arrangement of the 1D rod-shaped $[\text{Pb}_2\text{Cl}_3]^+$ SBUs in each independent framework (Figure 1a and Figure S1). The lead halide SBUs comprise asymmetric Pb_2Cl_2 units in a distorted square geometry, which propagate along the c axis via μ_2 -Cl in a zigzag manner with $\text{Pb}-(\mu_2)\text{Cl}-\text{Pb}$ bond angles of $132.885(6)^\circ$ (Figure 1b). In contrast to the conventional 1D metal–oxo SBUs in MIL-53 and MOF-74,^[31,32] both the Pb_2Cl_2 units and

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Enhanced Electrocatalytic Oxygen Evolution by Exfoliation of a Metal–Organic Framework Containing Cationic One-Dimensional $[\text{Co}_4(\text{OH})_2]^{6+}$ Chains

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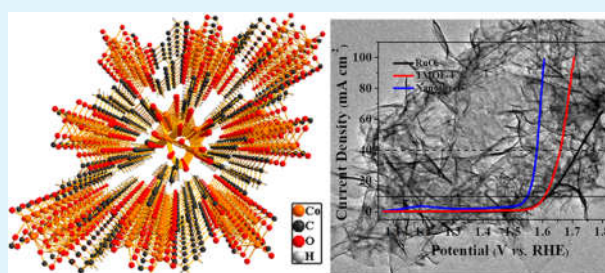
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Supporting Information

ABSTRACT: Metal–organic frameworks (MOFs) are an emerging class of heterogeneous electrocatalyst, though the focus for the vast majority of them has been on employing them as a precursor for carbon materials or as a host material for encapsulating catalytically active species. Herein, we report the preparation of a metal–organic nanosheet with one-dimensional (1-D) $[\text{Co}_4(\text{OH})_2]^{6+}$ chains via delamination of a 3-D MOF. The resultant atomically thin nanosheets are highly active, robust, and recyclable oxygen evolution reaction (OER) electrocatalysts with a low overpotential 318 mV (without iR compensation) to achieve a current density of 10 mA cm^{-2} .

These values along with the small Tafel slope (54 mV dec^{-1}) exhibit a superior performance to the bulk MOF precursor and the benchmark RuO_2 catalyst under the identical condition. The electrochemical studies ascribe the excellent OER activity to the high surface area, accessible Co^{II} sites, and good charge transfer of the nanosheets.

KEYWORDS: metal–organic frameworks, exfoliation, metal–organic nanosheets, electrocatalysis, oxygen evolution reaction



Electrochemical water splitting provides a promising alternative to produce hydrogen fuels and to store the electricity from sustainable sources, which include hydrogen evolution reaction (HER)¹ and oxygen evolution reaction (OER).² Particularly, the oxidative half-reaction of the OER process is an inherently sluggish reaction, which involves a four-electron transfer process coupled with breaking of the O–H bonds and the O–O bond formation.^{3,4} Although ruthenium (Ru) and iridium (Ir) oxides have been widely used to be the state-of-the-art efficient OER electrocatalysts,^{5,6} endowing highly active electrocatalysts based on earth-abundant elements is greatly needed.^{7,8}

Metal–organic frameworks (MOFs) are a class of crystalline microporous materials with exceptionally high surface area and tunable functionality,^{9–12} which are essentially desirable in OER electrocatalysis.^{13,14} The vast majority of MOF-based electrocatalysts studies focused on preparing the porous carbon materials via pyrolysis as well as encapsulation of catalytically active species into the MOF hosts.^{15–18} However, these MOF-derived materials often lead to partial decomposition of the open MOF framework and/or a significant sacrifice in the long-range well-ordered porosity, thus undesirable for diffusion of catalytic substrates. An efficient earth-abundant OER catalyst often requires all three properties of (a) high surface area, (b) unsaturated metal catalytic sites, and (c) high electrical conductivity.^{3,4} Meanwhile, the typical metal–carboxylate structural motifs residing in MOFs are electrically non-

conductive and coordinatively saturated, thus limiting their efficiencies in electrocatalysis.¹⁹

Exfoliation of the bulk materials into atomically thin nanosheets is an advantageous approach to expose the catalytically active sites, thus significantly improving the electrocatalytic performance.^{4,20–22} The vast majority of the 2D ultrathin nanosheets are prepared from layered inorganic materials with strong intralayer covalent bonds.²³ In contrast, exfoliation of MOFs to realize ultrathin metal–organic nanosheets with less robust coordination bonds are rather challenging, and only a few examples were reported.^{21,22} Although less explored in the literature, the exfoliated MOF nanosheets with an ordered array of the open metal catalytic sites as well as infinite one-dimensional metal–oxo chains for electron transport will be an excellent platform for electrocatalysis.

Co-based OER electrocatalysts are regarded as one of the most promising alternatives to noble-metal-based OER catalysts in view of their rich oxidation states and excellent electron conductivity.^{23–25} Herein, we reported a rational “top-down” synthetic strategy to afford ultrathin Co^{II} –organic nanosheets consisting of one-dimensional $[\text{Co}_4(\text{OH})_2]^{6+}$ chains as an active, recyclable water oxidation electrocatalyst. In contrast to

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