Research paper

Bio-inspired assembly of cubane-adjustable polyoxometalate-based high-nuclear nickel clusters for visible light-driven hydrogen evolution

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ABSTRACT

By artificial mimic of the natural [FeFe]-hydrogenases, a series of polyoxometalate-based high-nuclear Ni clusters containing a varying number of $\{Ni_4O_4\}$ cubane cores, $K_{1.5}Na_{26.5}[\{Ni_4(OH)_3(PO_4)\}_4(A\text{-}PW_9O_{34})_4]\cdot62H_2O$ (**1**), $Na_{28}[\{Ni_4(OH)_3(PO_4)\}_4(A\text{-}PW_9O_{34})_2(B\text{-}PW_9O_{34})_2]\cdot102H_2O$ (**2**), and $Na_{28}[\{Ni_4(OH)_3(VO_4)\}_4(B\text{-}PW_9O_{34})_4]\cdot74H_2O$ (**3**), were synthesized and systematically characterized. Compounds **1**−**3** contain $\{Ni_{16}(XO_4)_4(OH)_{12}\}$ (X = P, V) core encapsulated by the trivacant $A\text{-}/B\text{-}\{PW_9O_{34}\}$ ligands. Compounds **1**−**3** as homogeneous catalysts for visible-light-driven H_2 evolution indicate that they not only show high photocatalytic performance (High TON of 578.8, 679.1, and 931.1 for **1**−**3** were achieved, respectively), but also their catalytic performance was improved with the increasing number of $\{Ni_4O_4\}$ cubanes. Multiple stability experiments confirm that compounds **1**−**3** maintain their structure intact under the photocatalytic conditions. The above research provides a platform for mimicking the structures of natural hydrogenases to further explore more efficient and inexpensive H_2 evolution catalysts.

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1. Introduction

Hydrogen production from artificial photosynthesis (AP) is an intriguing approach to storing and converting solar energy into renewable and non-fossil-based fuels [1–9]. The exploration of H_2 evolution catalysts (HECs) to satisfy the requirements of the commercial application is currently a formidable yet exceedingly engaging challenge. As more and more biological functions of the cubane-like $[Fe_4S_4]$ cluster in natural photosystem I (PSI) were discovered, biomimetic chemistry of $[Fe_4S_4]$ and related clusters has become an important subject [10–14]. Such biomimetic molecular clusters i) are based on earth-abundant elements, which holds great potential for large-scale commercial application, ii) have well-defined composition and molecular structures allowing the exploration of structure-property relationship and mechanistic features of the catalytic H_2 evolution reactions (HERs), and iii) may help tune H_2 evolution performance at the molecular level. Their unique advantages offer breakthrough points for constructing highly efficient and well-defined molecular HECs.

Polyoxometalates (POMs) is a sub family of soluble anionic metal-oxo clusters constituted by W, Mo, V, Nb, or Ta ions in high oxidation states [15–19]. They possess oxygen-rich surfaces and proved to be ideal inorganic building blocks for targeting transition metal (TM) cubane clusters [20–26], as elucidated in a recent review of our group [27]. What's more important is that the introduction of TM into POMs could help tune the band gap structures and even broaden the spectrum absorption of such molecular clusters from UV to the visible-light region, thereby providing the possibility for the synthesis of visible-light-driven POM-based HECs.

In an effort to develop more efficient, more viable, and low-cost molecular catalysts to realize the widespread use of solar energy, we have been focused on designing and synthesizing $\{M_4O_4\}$ cubane and/or $\{M_3O_4\}$ quasi-cubane core-containing photocatalysts to mimic the natural photosystem (PS). At the outset of our work, we have mimicked the oxygen-evolving complex (OEC)

{Mn$_4$O$_5$Ca} of PSII and successfully prepared a series of POM-based water oxidation catalysts (WOCs) [21,22]. Given that the "footprint" of {M$_4$O$_4$} cubane core is very close to the natural [Fe$_4$S$_4$] cubane cluster of [FeFe]-hydrogenases, as an extension of our work, we intend to take a step further to probe the generality of such biomimetic POM-based metal clusters as visible-light-driven HECs. However, we noticed that there is almost no relevant work for reference [28,29]. Only one Ni-cubane-encapsulating POM exhibits H$_2$ evolution activity under visible-light illumination hitherto [30], even though various types of polyoxotungstates with photocatalytic H$_2$ evolution activities under UV-light irradiation have already been reported [31–40]. It means that building POM-based TM-cubane clusters is a big challenge in current synthetic chemistry. As a consequence, in order to trace some instructive laws in this field, some key questions remain to be addressed: Which of the transition metal elements presents the optimal choice for POM-based HECs? How to synthesize TM cubane-containing POMs to achieve fine adjustment of the number of cubane? What is the relationship between the number of cubane and catalytic performance? If we could prepare a series of reliable structural paradigms, it may help shed light on these issues, and therefore, in the longer term, design and develop more efficient HECs with controlled active site and structure.

As we know, among the first-row TM elements, nickel is the ninth most abundant element in the Earth's crust [41]. It belongs to the same group as Pt on the periodic table, a best performing catalyst discovered to date for HER, but is much cheaper than Pt [3]. In nature, hydrogenase enzymes based on earth-abundant metals (nickel is one of them) can efficiently catalyze H$_2$ production with a turnover frequency (TOF) as high as 9000 s^{-1} [42,43]. Theoretical calculations show that Ni site of the hydrogenase plays an essential role in the hydrogen evolution reaction (HER) [44]. Given all that, Ni is a preferable choice for TM-substituted POM-based HECs. Meanwhile, it is noteworthy that subtle geometry variation of lacunary POMs enables their isomeric species to have different reactivity when coordination with TM metals. Hence, by ingenious use of the reactivity difference of isomeric forms of {PW$_9$O$_{34}$}$^{9-}$ toward TM metals, we now have succeeded in preparing three stable POM-based high-nuclear nickel clusters: K$_{1.5}$Na$_{26.5}$[{Ni$_4$(OH)$_3$(PO$_4$)}$_4$(A-PW$_9$O$_{34}$)$_4$]·62H$_2$O (**1**), Na$_{28}$[{Ni$_4$(OH)$_3$(PO$_4$)}$_4$(A-PW$_9$O$_{34}$)$_2$(B-PW$_9$O$_{34}$)$_2$]·102H$_2$O (**2**), and Na$_{28}$[{Ni$_4$(OH)$_3$(VO$_4$)}$_4$(B-PW$_9$O$_{34}$)$_4$]·74H$_2$O (**3**). Compounds **1**−**3** contain a varying number of {Ni$_4$O$_4$} cubane core (one, three, and five {Ni$_4$O$_4$} cubane cores corresponding to **1**, **2**, **3**, respectively), reminiscent of the [Fe$_4$S$_4$] cubane cluster of [FeFe]-hydrogenases. Their successful preparation provides the possibility for systematical investigation on visible-light-driven H$_2$ evolution activities of POM-based complexes. Compounds **1**−**3** as the homogeneous catalysts for visible-light-driven H$_2$ evolution have been investigated in detail and high TON of 578.8 for **1**, 679.1 for **2**, and 931.1 for **3** were achieved, respectively. Further exploration of structure-performance relationship revealed that the catalytic activity improved with increasing number of {Ni$_4$O$_4$} cubane. Furthermore, the reusability and stability of compounds **1**−**3** in the photocatalytic system were also examined in detail. We also carried out photophysical studies and initially put forward the HER mechanism of compounds **1**−**3**.

2. Results and discussion

2.1. Synthesis and structures of **1**−**3**

Directional synthesis of cubane-containing POMs is a significant challenge and commonly frustrated by the absence of a reliable synthetic strategy. It is well-known that lacunary derivatives of

POMs can be obtained by the removal of one or more {MO$_6$} octahedra from their corresponding saturated species, which, in some cases, will result in positional isomers. It is the subtle variation of geometry that enables the isomeric species to have different reactivity. Two common trivacant isomers of Keggin ions, A-α-{PW$_9$O$_{34}$}$^{9-}$ and B-α-{PW$_9$O$_{34}$}$^{9-}$ are such cases. As shown in Fig. S1, the central PO$_4$ tetrahedron in A-α-{PW$_9$O$_{34}$}$^{9-}$ is exposed at its base, whereas in B-α-{PW$_9$O$_{34}$}$^{9-}$ it exposed at its apex. This determines that B-α-{PW$_9$O$_{34}$}$^{9-}$ is much easier to form cubane structure than A-α-{PW$_9$O$_{34}$}$^{9-}$ when coordination with TM metals. So this raises a question if one can apply this difference to modulate the number of TM-cubanes. By use of different isomeric forms as reactive precursors, we have obtained a series of POM-based high-nuclear Ni clusters containing a varying number of {Ni$_4$O$_4$} cubanes. Using A-typed isomer as starting materials without or with partial conversion from type A to type B, compounds **1** and **2** containing one and three cubane cores were synthesized respectively; only use of B-typed isomer compounds **3** containing five cubane cores were synthesized. This new method of using isomers of POMs to regulate the resulting structure opens a promising avenue for directional synthesis of POM-based complexes. In addition, several important synthetic factors should be emphasized. Firstly, the pH of reaction solution should be in the range 8.0–9.0. It is crucial for the assembly of compounds **1**−**3**. Beyond this pH range, negligible or no crystalline products were obtained in the same reaction system. Secondly, the reaction temperature plays an important role in synthesizing compounds **1**−**3**. Compound **1** was synthesized at room temperature. At a too high temperature, no target product is obtained. Compounds **2** and **3** were synthesized by refluxing the reaction solution because high temperature favors isomerization from type A to type B and favors bridging ligand {VO$_4$} coordination with Ni^{2+} and B-α-{PW$_9$O$_{34}$}$^{9-}$. Without refluxing, negligible or no crystalline products of compounds **2** and **3** were isolated. Thirdly, the presence of {PO$_4$} or {VO$_4$} is required to stabilize the hexadecanuclear-Ni clusters. We have also been devoted ourselves to synthesize a compound containing more than three {Ni$_4$O$_4$} cubane units. Using NiCl$_2$·6H$_2$O, Na$_8$H[B-α-PW$_9$O$_{34}$], and Na$_3$PO$_4$·12H$_2$O as the starting materials, we changed a lot of synthetic conditions. However, to our disappointed, we have not got aimed product. Considering the various coordination spheres of vanadium atom and similar bond length of V-O with P-O, Na$_3$PO$_4$·12H$_2$O was replaced by NaVO$_3$, and then compound **3** containing a central {Ni$_4$(VO$_4$)$_4$} core encapsulated by four{(B-α-PW$_9$O$_{34}$)(NiOH)$_3$} units was obtained, in which there are five {Ni$_4$O$_4$} cubane units in all.

Compound **1** (Fig. 1c) contains a high-nuclearity nickel−phosphate cluster {Ni$_{16}$(PO$_4$)$_4$(OH)$_{12}$} ({**Ni16-1**}) (Fig. 1b) and four A-α-[PW$_9$O$_{34}$]$^{9-}$ units (Fig. 1a). The whole {**Ni16-1**} cluster is well encapsulated by four lacunary A-α-{PW$_9$O$_{34}$} POM units, allowing the nickel−phosphate cluster to be well isolated without terminal H$_2$O coordinating to the central nickel ions. From another point of view, compound **1** can be viewed as a tetramer comprising four tetra-nickel-substituted Keggin fragments {Ni$_4$(OH)$_3$(A-α-PW$_9$O$_{34}$)} (Fig. 1d), connected with four {PO$_4$} linkers (Fig. 1e). Alternatively, compound **1** can also be viewed as a central {Ni$_4$(PO$_4$)$_4$} core (Fig. 1g) wrapped by four {(A-α-PW$_9$O$_{34}$)(NiOH)$_3$} units (Fig. 1f) with idealized Td symmetry. Such a {Ni$_4$(PO$_4$)$_4$} core comprises a central {Ni$_4$O$_4$} cubane unit (Fig. 1h), which is structurally analogous to the [Fe$_4$S$_4$] cubane. In the {Ni$_4$O$_4$} cubane unit, the Ni−O distances are in the range 2.073(18)–2.138(17) Å and the Ni···Ni distances range from 3.077(10) to 3.189(10) Å. It's noted that compound **1** is isostructural to recently reported [{Co$_4$(OH)$_3$(PO$_4$)}$_4$(PW$_9$O$_{34}$)$_4$]$^{28-}$ [20,21].

Compound **2** crystallizes in the monoclinic space group C2/c. Compound **2** (Fig. 2d) consists of one central {Ni$_{16}$(PO$_4$)$_4$(OH)$_{12}$} ({**Ni16-2**}) core (Fig. 2b), two lacunary A-α-{PW$_9$O$_{34}$} POM units