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Facile and Reproducible Electrochemical Synthesis of the Giant Polyoxomolybdates

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Cite This: *J. Am. Chem. Soc.* 2021, 143, 20059−20063
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ABSTRACT: Giant polyoxomolybdates are traditionally synthesized by chemical reduction of molybdate in aqueous solutions, generating complex nanostructures such as the highly symmetrical spherical $\{Mo_{102}\}$ and $\{Mo_{132}\}$, ring-shaped $\{Mo_{154}\}$ and $\{Mo_{176}\}$, and the gigantic protein sized $\{Mo_{368}\}$, which combines both positive and negative curvature. These complex polyoxometalates are known to be highly sensitive to reaction conditions and are often difficult to reproduce, especially $\{Mo_{368}\}$, which is often produced in yields far below 1%, meaning further investigation has always been limited. While the electrochemical properties of these materials have been studied, their electrochemical synthesis has not been explored. Herein, we demonstrate an alternative reliable synthetic method by means of electrochemistry. By using electrochemical synthesis, we have shown the synthesis of various reported polyoxomolybdates, along with some unreported structures with unique features that have yet to be reported by traditional synthetic methods. The six different giant polyoxomolybdates that were obtained via electrochemical synthesis range from the spherical $\{Mo_{102-x}Fe_x\}$ and $\{Mo_{132}\}$ to the ring-shaped $\{Mo_{148}\}$ and $\{Mo_{154-x}\}$, as well as the largest known polyoxometalate $\{Mo_{368}\}$, with improved yield (up to 26.1% for $\{Mo_{368}\}$), increased reproducibility, and shorter crystallization time compared to chemical reduction methods.

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Polyoxometalates (POMs) are inorganic metal oxide clusters, commonly composed of molybdenum or tungsten,[1] self-assembled by condensation of $\{MO_x\}_n$ building blocks in aqueous conditions at low pH.[2] As a family, their structural diversity and the tunability of the bulk electronic properties have proved of interest for fields such as analytical chemistry, energy storage materials, electronics, and catalysis.[3−5] Despite the illusion of triviality in their synthesis, the self-assembly process for POMs can be influenced by subtle changes to a wide range of factors such as metal salts, heteroatoms, cations, reducing agents, temperature, pH, rate of addition, sequence of additions, and more.[6−8] These factors often make POM synthesis highly irreproducible especially when it comes to larger and more complex structures. One of the most complex structures, and the largest POM known to date, is a giant polyoxomolybdate consisting of 368 Mo atoms, $\{Mo_{368}\}$, which exhibits a lemon-shaped structure and was first reported in 2002.[9] A follow-up report in 2004 demonstrated an improved procedure to shorten the period required to obtain the cluster to 2 days by increasing the concentration of electrolyte.[10] Curiously, there are no reports regarding the synthesis since then, as opposed to other small clusters such as Keggin and Wells−Dawson types.[11] Within our laboratories we have found the procedures for larger polyoxometalates, and in particular $\{Mo_{368}\}$ are challenging to reproduce.[12]

The term molybdenum blue (MB), applied to reduced polyoxomolybdates, derives from the deep-blue coloration of solutions consisting of various Mo species such as ball-shaped Keplerate $\{Mo_{102}\}$,[13,14] nanowheel $\{Mo_{154}\}$,[15] and nano-hedgehog $\{Mo_{368}\}$.[9] The characteristic hue is achieved by partial reduction of molybdate clusters in acidic media. Besides MBs, other giant polyoxomolybdates of more reduced molybdate clusters are known as molybdenum browns,[16] such as the highly reduced ball-shaped Keplerate $\{Mo_{132}\}$.[17] One of the most important factors required to make large molybdenum anion clusters $\{(MoO_x)_y\}$ (i.e., where $y > 36$) is the choice of reducing agents, often sodium dithionite ($Na_2S_2O_4$), hydrazine ($N_2H_4{\cdot}HCl$ or $N_2H_4{\cdot}H_2SO_4$), or other organic reductants.[18] The intrinsic properties and quantities of different reducing agents have been found to be the trigger for the formation of different clusters.[19] In 2017, Sahin et al. observed the formation of a characteristic blue solution upon undertaking cyclic voltammetry (CV) experiments on molybdate salts, suggesting the formation of MB species was possible,[20] but neither were crystals isolated nor was structural characterization reported of the amorphous product formed on the electrode surface.

Herein, we report the synthesis of a number of giant polyoxomolybdates in aqueous conditions by using the electrochemical technique chronopotentiometry (CP) to yield the following compounds:

1. $[H_{16}Mo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$
2. $[Mo_{154}O_{462}H_{14}(H_2O)_{70}][Mo_{154}O_{462}H_{14}(H_2O)_{58}(SO_4)_6]^{40-}$
3. $[Mo_{142}O_{432}(H_2O)_{58}H_{14}]^{26-}$
4. $[Mo_{36}O_{112}(H_2O)_{16}]\subset[Mo_{150}O_{442}(OH)_{10}(H_2O)_{61}]^{22-}$
5. $[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$

Received: September 27, 2021
Published: November 23, 2021

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https://doi.org/10.1021/jacs.1c10198
J. Am. Chem. Soc. 2021, 143, 20059−20063

6. $[Mo_{102}O_{282}(H_2O)_{66}(SO_4)_{12}]^{12-}$
7. $[Fe_{25}Mo_{77}O_{257}(H_2O)_{91}(SO_4)_{12}]^{12-}$

In the synthesis of **1**, an equimolar mixture of sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$, 0.75 M) and sulfuric acid (H_2SO_4, 0.75 M) in water solvent at pH 0.9 was placed in a H-cell separated by a glass frit and was subjected to electrochemical reduction whereby the current was held at 100 μA in a two-electrode setup. The low current ensures a slow and steady stream of charge passes through, reducing the metal ions with little to no parasitic reaction such as through the hydrogen evolution reaction (HER) (Figure 1). Within minutes,

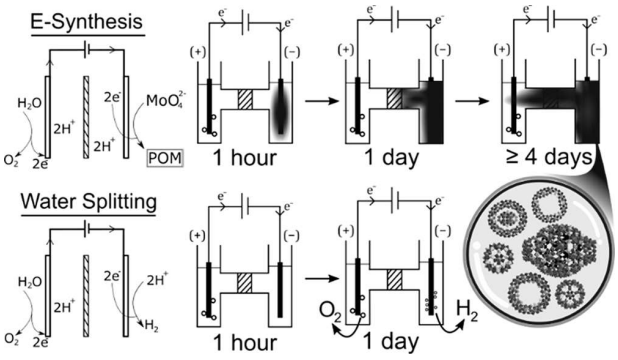

Figure 1. Schematic representation of the difference between electrochemical synthesis of POM and water splitting by addition of a molybdate source in acidic media. Left chamber (anode) and right chamber (cathode). Top: Colorization of the solution indicating the MB species formation around the cathode surface during electrochemical synthesis (E-synthesis). Bottom: Hydrogen evolution from the cathode during water splitting.

formation of a deep blue solution appeared around the cathode, and its diffusion was observed, continuing up the cathodic chamber of the H-cell until it was dark. As the experiment proceeded, transit of the reduced ions across the channel to the anodic chamber was observed (Figure 1, top). After electrolysis, the elongated hexagonal-shaped crystalline product was collected, and unit cell checks on several of these crystals confirmed them to comprise $\{Mo_{368}\}$. The $\{Mo_{368}\}$ structure[9] was confirmed by multiple unit cell check using crystals prepared in several electrochemical synthesis repeats under the optimized conditions.

It is therefore clear from these results that introduction of the molybdate species during electrolysis suppresses the HER. The electrons produced in the oxygen evolution reaction (OER) are then utilized in the reduction of molybdate species in solution. The notion is similar to that of the electron-coupled-proton buffer (ECPB),[21,22] with one major difference. Instead of utilizing POM as an electron sponge, the electrons are used as the reducing agent that triggers the self-assembly of the POM. An overall water splitting process in acidic media can be split into two half-reactions.

Hydrogen evolution reaction (HER):

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (1)$$

Oxygen evolution reaction (OER):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

The half-reaction for reduction of Mo(VI) to $\{Mo_{368}\}$ is thought to be as follows:

$$368Mo^{VI} + 112e^- \rightarrow \{Mo^{V}_{112}Mo^{VI}_{256}\} \equiv \{Mo_{368}\} \quad (3)$$

When coupled with the OER, the overall process can be denoted:

$$368Mo^{VI} + 56H_2O \rightarrow \{Mo^{V}_{112}Mo^{VI}_{256}\} + 28O_2 + 112H^+ \quad (4)$$

Based on eq 4, excess protons yielded in the equation would result in a pH drop in the system as the reaction proceeds. Indeed, the pH of the solution decreased over the course of the reaction from $pH_{initial} = 0.90$ to $pH_{final} = 0.71$, while in the course of the experiment, evolution of a gas was observed in the anodic chamber. Thus, eq 4 can be considered a simplified model of the processes at play (see SI Section 7 for a more detailed version of eq 4).

The electrodes used in the electrochemical synthesis were platinum (Pt). When carbon-based electrodes were utilized instead under the same experimental conditions, no crystals were obtained. The leaching of Pt into the electrolyte that may catalyze the formation of $\{Mo_{368}\}$ in the solution phase was ruled to be unlikely by ICP, as these experiments indicated that no Pt traces were present in the solution after the experiment. The absence of crystals when the reaction was performed on carbon-based electrodes is not clear yet. One theory is that the superior ability of Pt for water-splitting, due to a low Volmer and Tafel barrier,[23] has a similar effect on the electrochemical synthesis of POM.[24,25]

Upon exposure of the mother liquor of **1** to aerobic conditions for 2 weeks, cuboid-shaped crystals **2**, $\{Mo_{154}\}$, form (see Table S2). These were shown to consist of a $\{Mo_{154}\}$-type MB, which forms a 1D chain linked by Mo−O−Mo bonds between wheels (Figure S7b). The chains are further bridged by sulfate groups on the outer rim of the wheel (Figure 2) to form a 2D sheet. This is the first observation where sulfate coordination and bridges are present on this nanowheel $\{Mo_{154}\}$.

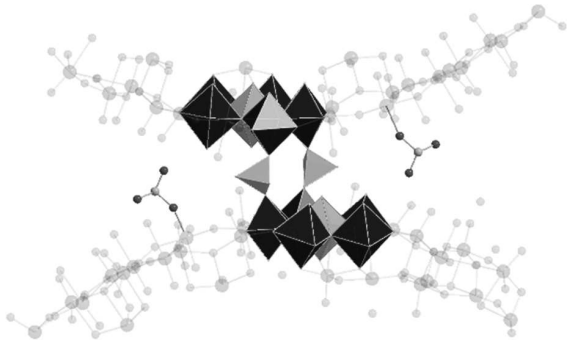

Figure 2. Highlighted sulfate bridges that link the $\{Mo_{154}\}$ wheel on one of the axes of the 2D plane (orange: sulfate and blue: molybdate).

One of the possible explanations for the formation of this new $\{Mo_{154}\}$ derivative is that the decomposition of $\{Mo_{368}\}$ to smaller building blocks (e.g., Mo_1, Mo_2, and Mo_5) occurs first. The building blocks then undergo spontaneous self-assembly to $\{Mo_{154}\}$.[26] The second possible explanation is that the $\{Mo_{154}\}$ could be present in the reduced solution when the experiment is first completed, and this species crystallizes over time, while the $\{Mo_{368}\}$ is deconstructed to smaller Mo species and redissolved in the aqueous phase. Following the isolation of **2**, a derivative of $\{Mo_{154}\}$ known as $\{Mo_{152}\}$[27] was synthesized directly via

https://doi.org/10.1021/jacs.1c10198
J. Am. Chem. Soc. 2021, 143, 20059−20063

electrochemical synthesis and does not possess the described sulfate groups.

To develop the electrochemical synthesis methodology further, pH and the type of acid used were varied (Figure 3).

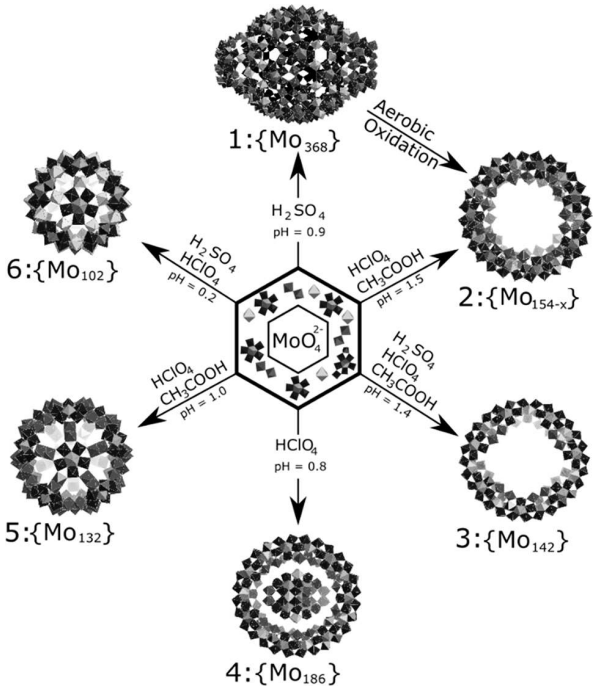

Figure 3. Schematic representation of the six giant polyoxomolybdates produced by the electrochemical synthesis reported in this study under different conditions.

By mixing H_2SO_4, $HClO_4$, and CH_3COOH with sodium molybdate, a defected nanowheel, **3**, $\{Mo_{142}\}$,[28] was synthesized via electrolysis. When H_2SO_4 was replaced with $HClO_4$, **4**, $\{Mo_{186}\}$ was formed.[29] Upon mixing H_2SO_4 and $HClO_4$ with Na_2MoO_4, formation of **6**, a $\{Mo_{102}\}$ cluster, was observed (see Table S2).

The formation of **4** was confirmed by unit-cell measurement, which is consistent with the unit cell previously reported by Cronin et al.[29] In that work we hypothesized that the $\{Mo_{186}\}$ cluster could only be synthesized in a flow-reactor system due to the fact that the synthesis occurred in a nonequilibrium reaction system with controlled input of reducing agent and acid. The advantage of an electrochemical synthesis is the presence of an electrochemical gradient intrinsic to an electrochemical setup. Ball-shaped Keplerates from molybdenum blue $\{Mo_{102}\}$ and brown $\{Mo_{132}\}$ families have also been obtained by our method. The $\{Mo_{102}\}$ that was synthesized via electrochemical synthesis possesses a different unit cell than reported in the literatures (see Table S2). When $FeSO_4$ and acetic acid were added to the perchloric acid and the pH raised to 1.4, a new cluster, $\{Mo_{77}Fe_{25}\}$ **7**, was formed, which has a structure similar to $\{Mo_{102}\}$ and $\{Mo_{72}Fe_{30}\}$ (see structure description in SI Section 6). By adding CH_3COOH and $HClO_4$ with Na_2MoO_4 and reducing the solution for 10 days, **5**, $\{Mo_{132}\}$,[17] was obtained and confirmed by a unit-cell check.

Next, electrochemical characterization of a solution from the electrochemical synthesis of **1** was undertaken. A three-electrode setup was employed with a glassy carbon electrode (GCE) as the working electrode, Pt as the counter electrode, and Ag/AgCl (3.0 M KCl) as the reference electrode. When CV was carried out in H_2SO_4 solution (Figure 4, gray), a reduction wave

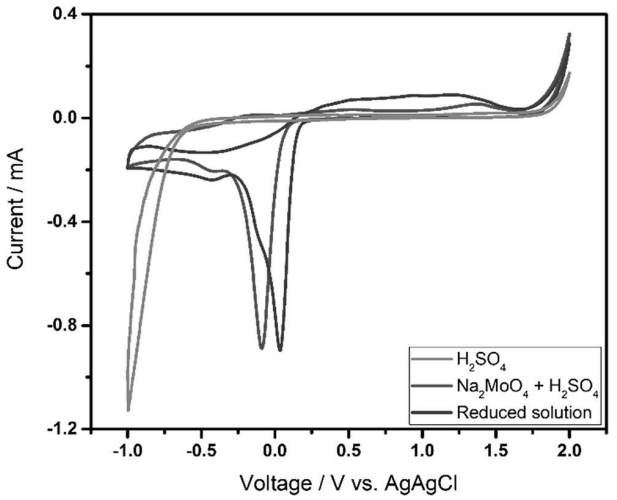

Figure 4. Cyclic voltammetry of the different solutions; scan rate: 10 mV s^{-1}. Gray: blank solution of just 0.75 M H_2SO_4, red: 0.75 M Na_2MoO_4 + H_2SO_4, blue: reduced solution after electrochemical synthesis of **1**, containing higher nuclearity MB species.

originating from HER was observed at −0.8 V vs Ag/AgCl. The HER peak was not present in the case of both of Na_2MoO_4 + H_2SO_4 (Figure 4, red) and the solution from the electrochemical synthesis of **1** (Figure 4, blue).

Additional experiments were performed by increasing the pH under which the electrochemical synthesis was done. When the pH was raised to 3, the solution did not turn deep blue as observed at lower pH. Instead, a light blue solution was observed, and an aggregate of a molybdenum oxide polymer was formed as a white solid at the bottom of the cathodic chamber. It was noted that all the experiments with CH_3COOH yielded a white precipitate in the cell. In another case, when H_3PO_4 was added to the solution of Na_2MoO_4, a blue solution resulted through electrolysis with no solid present. When this blue solution was placed on a glass slide, immediate crystallization was observed and a polyoxomolybdenum(V) phosphate framework[30] was seen (see Table S1 for detailed conditions and yield for all the compounds synthesized).

In conclusion, we have shown that electrochemical synthesis is a valuable addition to the synthetic chemists' toolkit in the field of polyoxometalate chemistry. We have demonstrated that electrochemical synthesis can produce giant polyoxometalates, which are challenging to synthesize or unknown by other routes, with higher yield on average. By allowing selective redox transformation in the absence of chemical redox agents, which could contaminate the synthesis, electrochemical synthesis improves the reproducibility of POM synthesis and can potentially allow access to novel materials as demonstrated here. This facile electrochemical synthesis method opens the gate for all scientists to easily prepare giant polyoxomolybdates, facilitating their application to other fields. Electrochemical synthesis is shown to have significant potential for the reproducible synthesis of known compounds, specifically $\{Mo_{368}\}$ and its homologues, as well as a means to form new self-assembled metal oxide nanostructures, unknown by chemical reduction methods. Future work, by varying transition metals, exploring the role of electrode materials, cations,

https://doi.org/10.1021/jacs.1c10198
J. Am. Chem. Soc. 2021, 143, 20059−20063

concentrations, solvents, organic linkers, and electrode materials, and attempting chronoamperometry with various fixed potentials, offers great opportunities to unveil the versatility and tunability of the electrochemical synthesis of POMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c10198.

Experimental protocols and additional characterization (PDF)

Accession Codes

CCDC 2112046−2112048 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by LCs EPSRC grants (Grants EP/J015156/1; EP/L023652/1; EP/I033459/1; EP/J015156/1; EP/K023004/1; EP/L023652/1) and the ERC Advanced Grant (ERC-ADG, 670467 SMART-POM). The authors would like to thank Dr. Pablo Martinez-Bulit for help with the single-crystal X-ray diffraction at the beginning of the project and his mentorship toward M.T.-K.N.

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