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Introduction
Massive discharge of \( \text{CO}_2 \) resulting from the combustion of limited fossil fuels is leading to global warming, which has driven people to find effective ways to alleviate this crisis.\(^{1-4} \) Photocatalytic reduction of \( \text{CO}_2 \) to valuable hydrocarbon fuels, such as methane (\( \text{CH}_4 \)), provides a promising ‘one stone two birds’ approach to realize the purpose of eliminating energy shortage and environmental challenges.\(^{5-8} \) Nevertheless, the accomplishment of this catalytic reaction means that chemically inert \( \text{CO}_2 \) molecule absorbed on the catalyst has to undergo proton-assisted multi-electron transfer process; it is a rather challenging task for catalyst design because of uncontrollable multi-electron supply and complicated photocatalytic reaction mechanism.\(^{7, 8} \) Moreover, heterogeneous nature of the catalyst in principle is also indispensable in view of practical application.\(^{7} \) So far, the heterogeneous catalysts, especially those applied in photocatalytic reduction of \( \text{CO}_2 \) to \( \text{CH}_4 \), mainly focus on nano-sized semiconductor materials or composites,\(^{18-21} \) because their rich interfacial modification and structural stability that are beneficial for photocatalytic \( \text{CO}_2 \) reduction reaction (\( \text{CO}_2 \text{RR} \)) towards high activity and good photocatalytic durability.\(^{22-27} \) It is well-known that these inorganic nanomaterials are stable, but their indistinct active sites and even electrons donor are commonly unsuitable for explanation of the photocatalytic reaction mechanism.\(^{28} \) Also, the introduction of noble metal co-catalysts or heterojunction sometimes would raise the cost and/or cover the surface active sites to obstruct the incident light absorption, which results in reduced photoconversion efficiency. Consequently, the construction of crystalline inorganic heterogeneous catalyst with well-defined active site and multi-electron source would be a better choice for obtaining multi-electron reductive hydrocarbon fuel and investigating mechanism of photocatalytic \( \text{CO}_2 \text{RR}. \)\(^{29} \)

Photocatalytic reduction of \( \text{CO}_2 \) to value-added methane (\( \text{CH}_4 \)) has been a promising strategy for energy sustainable development, but it is challenging to trigger this reaction because of its necessary eight-electron transfer process. In this work, efficient photocatalytic \( \text{CO}_2 \)-to-\( \text{CH}_4 \) reduction reaction was achieved for the first time in aqueous solution by using two crystalline heterogeneous catalysts, \( \text{H}[	ext{Na}_2\text{K}_4\text{Mn}_6\text{Mo}_{12}\text{O}_{40}](\text{H}_2\text{O})_4\text{I}_{12} \cdot 21\text{H}_2\text{O} (\text{NENU-605}) \) and \( \text{H}[	ext{Na}_2\text{CoMn}_6\text{Mo}_{12}\text{O}_{40}](\text{H}_2\text{O})_4\text{I}_{12} \cdot 16\text{H}_2\text{O} (\text{NENU-606}) \). Both compounds have similar host inorganic polyoxometalate (POM) structures constructed with strong reductive \( \text{P}_4\text{Mo}_{12}\text{O}_{40}^{2-} \) units, homo/hetero transition metal ions (\( \text{Mn}^{2+}/\text{Co}^{2+} \)) and alkali metal ions (\( \text{K}^+/\text{Na}^- \)). It is noted that the \( \text{P}_4\text{Mo}_{12}\text{O}_{40}^{2-} \) cluster including six \( \text{Mo}^{6+} \) atoms served as a multi-electron donor in the case of photocatalytic reaction, while the transition metal ions were treated as catalytically active sites for adsorbing and activating \( \text{CO}_2 \) molecule. Additionally, the presence of alkali metal ions was believed to assist the capture of more \( \text{CO}_2 \) for photocatalytic reaction. Synergistic combination of the above-mentioned components in \text{NENU-605} and \text{NENU-606} effectively facilitates the accomplishment of required eight-electron transfer process for \( \text{CH}_4 \) evolution. Furthermore, \text{NENU-606} involving hetero-metallic active sites finally exhibited higher \( \text{CH}_4 \) generation selectivity (85.5%) than \text{NENU-605} (76.6%).

Hetero-metallic Active Sites Coupled with Strong Reductive Polyoxometalate for Selectively Photocatalytic \( \text{CO}_2\text{-to-CH}_4 \) Conversion in Water
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\( \text{CO}_2 \) conversion to valuable hydrocarbon fuels has been the focus of extensive investigations in recent years.\(^{30-35} \) A lot of classic POM units or POM-based derivatives often exhibit favourable responses to specific catalytic reactions, in that the relevant active sites and electron transfer of catalytic reaction can be explained by their crystal structures.\(^{36-40} \) However, the dissolvability of traditional POM cluster has been a major limiting
factor for the catalytic durability that needs to be primarily considered. So, the structural stability is the prerequisite for POM chemistry applied in any heterogeneous catalysis. As far as we know, high dimensional POM-included inorganic architecture compared with POM monomer usually shows good structural insolubility and extended solar spectrum absorption range, which has been investigated in many photo-simulated catalytic reactions such as water splitting, organic degradation, etc. Among them, fast and reversible multi-electron transfer character of POM subunit plays an extremely important role in promoting photocatalytic performance. In this context, POM-assembled inorganic complex is also believed to have advantages in the field of heterogeneous photocatalytic CO₂RR. In particular, if the POM component within structure can offer CO₂ molecule sufficient electrons, then multi-electron oriented reductive products would be achievable.

Herein, we report two stable POM-containing inorganic compounds, H₂[(Na₂K₂Mn₄(PO₄)₃(H₂O)₆)·{[Mo₆O₃0(OH)₃(HPO₄)₂(PO₄)₂]·(Mn₆(H₂O)₆)}·16H₂O (NENU-605) and H₂[(Na₂CoMn₄(PO₄)₃(H₂O)₆)·{[Mo₆O₃0(OH)₃(HPO₄)₂(PO₄)₂]·(Co₆(H₂O)₆)}·21H₂O (NENU-606), which have very similar host skeletons but different catalytic active species. It is noted that assembling {P₄Mo⁶V₆} (P₄Mo⁶V₆) units with strong reducibility into structures enables NENU-605 and NENU-606 with efficient heterogeneous photocatalytic CO₂-to-CH₄ reduction ability in water. To our knowledge, this is the first report of {P₄Mo⁶V₆}-based crystalline inorganic materials applied in photocatalytic CO₂RR. Photocatalytic analysis revealed that the synergistic combination of strong reductive {P₄Mo⁶V₆} units (donating electrons) and the first-row transition metal active centres (Mn⁶⁺/Co⁶⁺) in NENU-605 and NENU-606 effectively boosts the necessary eight-electron reduction process for CH₄ evolution. Furthermore, heterometallic active sites of NENU-606 finally exhibited higher CH₄ generation selectivity (85.5%) in photocatalytic CO₂RR than that of NENU-605 (76.6%). Besides, the coordination effect of alkali metal ions can also assist the accomplishment of photocatalytic reaction by influencing CO₂ absorption ability of title compounds. At the same time, crystalline and heterogeneous nature of these stable inorganic POM-included compounds also provides some insight for photocatalytic CO₂RR mechanism.

Results and discussion

Figure 1. Simplified (a-d) and real (e-h) three-shell nested subunit for NENU-605. (a, e) The innermost shell (central PO₄³⁻ group); (b, f) The shuttle-shaped second shell (Na₂K₂Mn₄⁺); (c, g) The cage-like outermost shell (Mn₆(PO₄)₃⁶⁻); (d, h) The overall three-shell nested substructure. Colour code: P yellow, O red, Na orange, K light purple, Mn green, Mo light blue.

NENU-605 and NENU-606 were prepared by hydrothermal synthesis method with slight difference in the use of metal salts and organic templates, and they can be clearly distinguished by colour and shape of crystals (Figure S1). Single crystal X-ray diffraction analysis reveals that NENU-605 and NENU-606 crystallize in the same I₄₁/aac tetragonal space group and have very similar pure inorganic matrix composed of three kinds of independent Mn⁶⁺/Co⁶⁺, Mn⁴⁺ ions, Na⁺ /K⁺ /Na⁺ ions, {P₄Mo⁶V₆} polyanions, phosphate anions and water molecules (Figure S2). The overall three-dimensional (3D) architecture of these two compounds is assembled with nesting subunits by using PO₄³⁻ and O²⁻ bridges. Such a nested substructure in NENU-605 can be described as a three-shell assembly where the PO₄³⁻ group is the innermost shell (Figure 1a). Four µ₂-O atoms of the PO₄³⁻ connect with four six-coordinated Mn₁ and four K₁ atoms of outward, and that these Mn₁ and K₁ atoms establish two types of metal-based tetrahedrons respectively. The interpenetrating coupling of two tetrahedrons forms a twisted hexahedron whose diagonal-linked vertexes are occupied by Mn₁ or K₁ atoms. Meanwhile, the top and down surfaces of this hexahedron are then capped by two Na atoms to build the shuttle-shaped second shell (Figure 1b). By 16 PO₄³⁻ and 8 O²⁻ groups, the second shell further communicates with outer four Mn₂ atoms and four (Mo⁶V₆) rings. Each Mn₂ atom is coordinated by five O atoms from four PO₄³⁻ anions and one O atom from coordinated water molecule (Figure S3) and is surrounded by four (Mo⁶V₆) rings made of six edge-sharing (Mo⁶V₆) octahedrons. It is noted that every (Mo⁶V₆) ring supported by four PO₄³⁻ anions constitutes a strong reductive component, P₄Mo⁶V₆ ⁴₅⁻ which includes six Mo⁶⁺ atoms (Figure S4). Interestingly, these Mn₂ atoms and (Mo⁶V₆) rings can construct peripherally larger distorted hexahedron in the same interpenetrating way as the second shell; diagonal-linked vertexes are occupied by Mn₂ atoms or (Mo⁶V₆) rings that can be treated as the third shell (Figure 1c). In such a way, a three-shell nested substructure is formed (Figure 1d). To better understand the further evolution of this nested subunit, it has been simplified as a distorted hexahedral entity whose eight
vertexes are taken up by Mn2 atoms and (Mo\textsuperscript{VI}) rings, as shown in Figure 2a-b. These Mn2 atoms and (Mo\textsuperscript{VI}) rings serve as nodes to contact with adjacent eight subunits in Mn2-to-Mn2 and (Mo\textsuperscript{VI})-Mn3-(Mo\textsuperscript{VI}) modes (Figure 2c), which finally gives rise to the 3D inorganic structure of NENU-605 (Figure 2d). The linkage of Mn2-to-Mn2 is achieved by two µ\textsubscript{4}-O atoms from two PO\textsubscript{4}\textsuperscript{3-} groups (Figure S5), moreover the locations of K1 atoms are fully replaced by Na atoms (Figure S7). The most important difference between these two compounds is that original Mn atom sites in the lattice of NENU-605 are partially substituted by Co atoms, and the doping ratio (1:3) of Co/Mn in NENU-606 is determined by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Besides, if the nested substructure and Mn2/Mn3 atom are regarded as B-connected nodes and linkers respectively, then the skeletons of NENU-605 and NENU-606 feature a unimodal topology with the Schl"afli symbol of 4\textsuperscript{8}·6\textsuperscript{7} (Figure S8).

The phase purity and thermal stability of NENU-605 and NENU-606 were demonstrated by well-matched powder X-ray diffraction (PXRD) patterns and thermogravimetric analysis, respectively (Figure S9 and S10). As showed in Figure S9a, b, these two compounds also can remain stable when being soaked in aqueous solutions at different pH values for several days, which indicated that their structures have strong acid and alkali resistance.\textsuperscript{50} Besides, in order to confirm the heterogeneous catalytic nature, the structural stability of title compounds was tested again under the conventional condition of photocatalytic CO\textsubscript{2}RR. It is obvious that the PXRD patterns of all treated crystals remain intact, indicating there was no phase transition or structural collapse occurred. A broad UV-vis absorption range of 200-600 nm for NENU-605 and NENU-606 revealed that they indeed have better light-harvesting ability than single POM cluster, whose absorption mainly focuses on ultraviolet region (200-400nm).\textsuperscript{51,53} On this foundation, the band gaps of 3.20 (NENU-605) and 2.57 eV (NENU-606) were evaluated by Kubelka–Munk (KM) method (Figure S11), unveiling the potential for these two compounds being as semiconducting photocatalysts. At the same time, Mott-Schottky measurements at frequencies of 1000, 1500, and 2000 Hz were used to determine the LUMO positions of NENU-605 and NENU-606 such that the occurrence of photocatalytic CO\textsubscript{2}RR and relevant reductive products can be simply inferred (Figure S12-13). As we can see, the LUMO locations of compounds are more negative than the reduction potentials required for producing CO (0.53V vs. NHE) and CH\textsubscript{3} (-0.24V vs. NHE), indicating that the electrons can be transferred to CO\textsubscript{2} molecule for further reduction reaction.

Taking above features of NENU-605 and NENU-606 into consideration, photocatalytic CO\textsubscript{2}RR was conducted under pure CO\textsubscript{2} (1.0 atm, 293 K) atmosphere in aqueous solution with triethanolamine (TEOA) as a sacrificial agent (TEOA/H\textsubscript{2}O = 2:28 mL, pH ≈ 10.5). In addition, [Ru(bpy)]\textsubscript{2}Cl\textsubscript{2}·4H\textsubscript{2}O (0.01 mmol) as auxiliary photosensitizer (PS) was added into reaction system for increasing visible-light absorption.\textsuperscript{29} Because of the matched LUMO positions between PS and catalysts (Figure S14-15), photo-generated electrons were allowed to migrate from PS to catalysts. During the whole photoreduction process, gaseous CH\textsubscript{4} and CO were the main reactive products detected by gas chromatography, while trace amount of HCOOH was produced in the aqueous solution as detected by ion chromatograph. Moreover, no competitive H\textsubscript{2} produced during the whole reaction (Figure S16). With the increasing irradiation time, the yields of CO and CH\textsubscript{4} increase simultaneously at different reaction rate (Figure 3a-b). The amount of CH\textsubscript{4} for NENU-605 reached up to 170 nmol (i.e., 894.7 nmol g\textsuperscript{-1} h\textsuperscript{-1}) after 19 h. By contrast, the maximum production of CH\textsubscript{4} for NENU-606 achieved 402 nmol (i.e., 1747.8 nmol g\textsuperscript{-1} h\textsuperscript{-1}) after 23 h (Figure 3c). Moreover, they finally exhibit very high selectivity (CH\textsubscript{4} over CO) of 76.6% (NENU-605) and 85.5% (NENU-606), respectively (Figure S17). It is significant that this is the first report of heterogeneous POM-based catalysts applied in photocatalytic CO\textsubscript{2}RR that exhibited such high selectivity of CH\textsubscript{4}, although the corresponding CH\textsubscript{4} outputs are still very low that needs to be greatly improved. The CO amounts determined after reaction were 267.0 nmol g\textsuperscript{-1} h\textsuperscript{-1} (NENU-605) and 295.7 nmol g\textsuperscript{-1} h\textsuperscript{-1} (NENU-606), and the relevant parameters including TONs and TOFs about this photocatalytic system were summarized in Table S1. NENU-606 obviously has higher photocatalytic CH\textsubscript{4} selectivity than NENU-605, which can be further proofed by their distinguishing transient photocurrent responses and electrochemical impedance spectra (Figure S17). The higher photocurrent response and smaller size of the Nyquist plot for NENU-606 represented better separation efficiency of photo-induced electron-hole pairs and faster interfacial charge transfer process than NENU-605. Such differences in the charge separation and the kinetics of charge transfer probably resulted from the different active sites in NENU-605 (homometallic Mn\textsuperscript{III} ions) and NENU-606 (heterometallic Mn\textsuperscript{III}/Co\textsuperscript{II} ions). Additionally, a series of reference experiments were carried out to explore the importance of each component in the photocatalytic reaction system, and the results are summed up in Table S1. As we can see, in the absence of POM-based catalyst, TEOA, PS, CO\textsubscript{2} or light illumination, no detectable products were observed in the reaction system. The photocatalytic durability of compounds was tested to confirm their heterogeneous nature. From the time course plots of CH\textsubscript{4} evolution, the POM-containing catalysts maintain almost unchanged activities.
NENU-605 is a dimer, one (Mn VI) atom sandwiched between two (P₆Mo₆O₃₉) units, displaying similar connection mode as NENU-605 and NENU-606. When the NENU-607 was synthesized and used as catalyst in the identical condition of photocatalytic reaction, only a little amount of CO (47 nmol) and CH₄ (70 nmol) were detected, which manifested that the light-induced CO₂ reduction process was more likely occurred on the active Mn⁶⁺ ions (NENU-605) or Mn⁶⁺/Co⁷⁺ ions (NENU-606). Strong reductive P₆Mo₆O₃₉ cluster including six Mo⁶⁺ atoms in the case of redox theoretically can offer multi-electron for CO₂RR. Because each Lewis acid metal active site in title compounds was surrounded by four P₆Mo₆O₃₉ units, therefore the achieved photo-stimulated CO₂-to-CH₄ conversion seems to be understandable. As for the higher CH₄ selectivity of NENU-606 than that of NENU-605, we speculated that the interaction between hetero-metallic Mn⁶⁺/Co⁷⁺ ions was more beneficial than between homo-metallic Mn⁶⁺ ions in terms of adsorption and activation of CO₂ molecule. Besides, reaction medium was also found to be an important factor in influencing the catalytic result. When the aqueous solution was replaced by dry MeCN (entry 9, Table S1), no noticeable reduction products can be detected in the photocatalytic system. Additionally, the generation of reduction products relies on the participation of H₂O solvent, as demonstrated in Figure S27. Moreover, the further increase of reductive products is also related to the increased amount of H₂O solution. All the above cases have suggested the importance of H₂O as proton donor for the CO₂-to-CH₄ reduction reaction.

Figure 3. Amounts of CH₄ and CO produced as a function of the time of visible-light irradiation over (a) NENU-605 and (b) NENU-606; (c) Total product yield and selectivity of gas products in photocatalytic CO₂RR; (d) The Mass spectra of ¹³CCH₄ recorded under a ¹³CO₂ atmosphere. The reaction with catalyst (10 mg) in the H₂O/TEOA (14:1 v/v, 30 mL) solution was irradiated using a Xe lamp filtered to produce light in the range of 420-800 nm.

Figure 4. Proposed mechanism for the photocatalytic reduction of CO₂ to CH₄ for NENU-605 and NENU-606.

Based on the analysis of related experimental results, a speculative reaction mechanism with respect to photocatalytic CO₂-to-CH₄ conversion of these two crystaline POM-containing compounds, as well as possible photo-generated electrons transport pathway, were proposed (Figure 4). Firstly, the photosensitizer in system absorbs sunlight to generate photo-excited electrons from HOMO and then transport them to catalyst through the matched LUMO assistance of H₂O/(OH)⁻. Because each Lewis acid metal active site in title compounds was surrounded by four P₆Mo₆O₃₉ units, therefore the achieved photo-stimulated CO₂-to-CH₄ conversion seems to be understandable. The small amount of CO (47 nmol) and CH₄ (70 nmol) were detected, which manifested that the light-induced CO₂ reduction process was more likely occurred on the active Mn VI ions. Strong reductive P₆Mo₆O₃₉ cluster including six Mo VI atoms in the case of redox theoretically can offer multi-electron for CO₂RR. Because each Lewis acid metal active site in title compounds was surrounded by four P₆Mo₆O₃₉ units, therefore the achieved photo-stimulated CO₂-to-CH₄ conversion seems to be understandable. As for the higher CH₄ selectivity of NENU-606 than that of NENU-605, we speculated that the interaction between hetero-metallic Mn VI/Co VII ions was more beneficial than between homo-metallic Mn VI ions in terms of adsorption and activation of CO₂ molecule. Besides, reaction medium was also found to be an important factor in influencing the catalytic result. When the aqueous solution was replaced by dry MeCN (entry 9, Table S1), no noticeable reduction products can be detected in the photocatalytic system. Additionally, the generation of reduction products relies on the participation of H₂O solvent, as demonstrated in Figure S27. Moreover, the further increase of reductive products is also related to the increased amount of H₂O solution. All the above cases have suggested the importance of H₂O as proton donor for the CO₂-to-CH₄ reduction reaction.
electron transfer process of CO\textsubscript{2}-to-CH\textsubscript{4} reduction. In addition, because of low local concentration of CO\textsubscript{2} around the typical catalysts can make the reaction suffer from slow kinetics\textsuperscript{56,57} thus the coordination of alkali metal cations in NENU-605 and NENU-606 architectures are helpful for effectively physical adsorb CO\textsubscript{2} molecules through non-covalent interactions,\textsuperscript{58,59} which could lower the overpotential and Gibbs free energy $\Delta G$ diagrams of the chemical reduction of CO\textsubscript{2}.

Conclusions

In summary, this is the first report of inorganic POM-containing crystalline materials as heterogeneous catalysts applied in photocatalytic CO\textsubscript{2}RR, and the significant CO\textsubscript{2}-to-CH\textsubscript{4} conversion in the aqueous phase was realized. Both of NENU-605 and NENU-606 have almost identical 3D host structures composed of three-shell nested substructures, which was further assembled by $\{P\text{Mo}_6\}$ cluster, first-row transition metals and alkali metals. Because of the strong reducibility and electron-enrichment of $\{P\text{Mo}_6\}$ unit, sufficient electrons can be transported to metal-active sites under the effect of photo-stimulated redox reaction for the activation and reduction of CO\textsubscript{2} molecule. In virtue of the synergistic coupling of structural components, these compounds finally exhibit high photocatalytic CH\textsubscript{4} selectivity (76.6%, NENU-605; 85.5%, NENU-606). Especially for NENU-606 with hetero-metallic active sites, the interaction between Mn\textsuperscript{II} and Co\textsuperscript{II} ions are found to be more efficient for photocatalytic CO\textsubscript{2}RR than between homo-metallic Mn\textsuperscript{II} ions in NENU-605. Notably, the introduction of $\{P\text{Mo}_6\}$ building block not only endows NENU-605 and NENU-606 with favorable structural rigidity, but also indeed facilitates the accomplishment of eight-electron transfer process of CH\textsubscript{4} formation by delivering sufficient electrons. We anticipate that such a feasible strategy, embedding strong reducing component into visible-light sensitized catalyst architecture, could inspire more enthusiasm to construct stable inorganic networks for effective reduction of CO\textsubscript{2} to other high-valued hydrocarbons and further enhance their photocatalytic activity.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


Two reductive polyoxometalate (POM)-based heterogeneous photo-catalysts display highly selective CO$_2$-to-CH$_4$ conversion in water.