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COMMUNICATION

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Selective photocatalytic production of CH₄ using Zn-based polyoxometalate as a nonconventional CO₂ reduction catalyst†

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Efficient and selective production of CH₄ through the CO₂ reduction reaction (CO₂RR) is a challenging task due to the high amount of energy consumption and various reaction pathways. Here, we report the synthesis of Zn-based polyoxometalate (ZnPOM) and its application in the photocatalytic CO₂RR. Unlike conventional Zn-based catalysts that produce CO, ZnPOM can selectively catalyze the production of CH₄ in the presence of an Ir-based photosensitizer (Tl₃) through the photocatalytic CO₂RR. Photophysical and computation analyses suggest that selective photocatalytic production of CH₄ using ZnPOM and Tl₃ can be attributed to (1) the exceptionally fast transfer of photogenerated electrons from Tl₃ to ZnPOM through the strong molecular interactions between them and (2) effective transfer of electrons from ZnPOM to *CO intermediates due to significant hybridization of their molecular orbitals. This study provides insights into the design of novel CO₂RR catalysts for CH₄ production beyond the limitations in conventional studies that focus on Cu-based materials.

New concepts

There have been fundamental limitations to the selection of elements for the design and synthesis of CO₂RR catalysts. For example, metallic Zn or Zn-based materials are known as CO producing catalysts, and CH₄ producing catalysts have been limited to Cu-, Ru- and Ir-based materials. To the best of our knowledge, this is the first report that Zn-based materials including POMs can be used as a CH₄ producing catalysts. Our study suggests that the overlap between the orbitals of catalytic elements and intermediate species (e.g., Zn in ZnPOM and *CO) plays a significant role in multistep electrochemical reactions such as the CO₂RR. Conventionally, the underlying mechanism for the CO₂RR has been explained mostly in terms of the binding energy between catalysts and intermediate species. This is also why there have been fundamental limitations on the selection of elements for the design and synthesis of CO₂RR catalysts. In this regard, our study provides insights and broadens the material library for the design and synthesis of novel CO₂RR catalysts, especially for the selective production of hydrocarbons including CH₄. Considering that POMs can be considered as a 0-D nanomaterial with a well-defined structure, this study can offer a basis for understanding the structure-performance relationship of nanocatalysts.

Introduction

The carbon dioxide (CO₂) reduction reaction (CO₂RR) into valuable chemicals using renewable energy resources is a promising

technology for both ensuring sustainable growth and mitigating environmental problems.^{1–4} In principle, useful chemicals, such as carbon monoxide (CO), formic acid (HCOOH), and hydrocarbons, can be produced and consumed in a carbon-neutral manner by exploiting the CO₂RR.^{5–7} Despite recent important progress, the CO₂RR is a still challenging task that consumes a large amount of energy and results in low product yield/selectivity for a specific chemical. The difficulty stems from the high stability of CO₂ molecules, the complexity of the CO₂RR involving the transfer of multiple protons and electrons, and the presence of competing reactions.^{8–10} These problems necessitate the development of efficient and selective catalysts for the CO₂RR.^{11–16} However, there have been fundamental limitations to the selection of elements in the design and synthesis of CO₂RR catalysts (Scheme 1a). For example, most transition metals (coloured grey in Scheme 1a) favor hydrogen evolution reactions (HERs) rather than the CO₂RR. Among diverse chemicals

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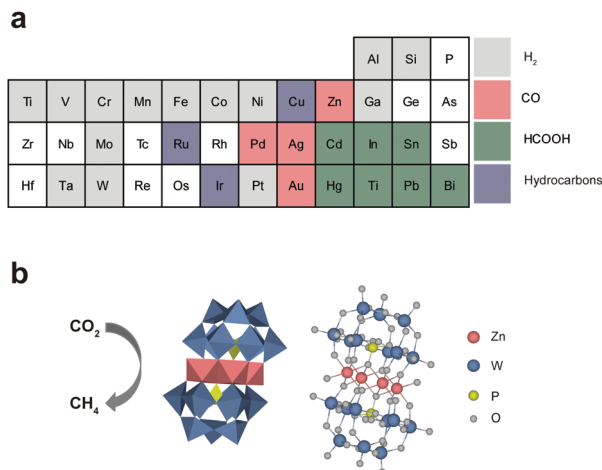
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Scheme 1 Production of various chemicals from the CO₂RR. (a) Classification of the main chemical produced by each element in the periodic table through the CO₂RR: hydrogen (grey), CO (pink), formic acid (green), and hydrocarbons (purple). (b) Structure of ZnPOM and its application as a CO₂RR catalyst for the selective production of CH₄.

from the CO₂RR, the production of hydrocarbons requires the formation of multiple stable intermediate states and the incorporation of more electrons and protons than other CO₂RR products. For example, eight electrons and protons are required to produce CH₄, whereas only two are required to produce CO or HCOOH. As a result, only a few elements, such as Cu,¹⁷ Ru,¹⁸ and Ir,¹⁹ are available for the design of the CO₂RR catalysts for CH₄ production (purple), whereas more diverse elements are available for CO (pink) and HCOOH (green). In this regard, the development of CO₂RR catalysts for CH₄ production has been mostly focused on Cu-based materials due to their low cost.^{20–22}

On the other hand, polyoxometalates (POMs) are considered promising electrocatalysts due to their molecular nature with uniform active sites, structural diversity, and rich electrochemistry.²³ In particular, sandwich-type POMs have been demonstrated as efficient and robust multi-electron transfer catalysts because they can stably embed various transition metal ions between metal oxide clusters.^{24,25} For example, it is reported that POMs can serve as homogeneous water splitting catalysts: POMs with Co- and Ru-based active sites for oxygen evolution reactions^{26,27} and POMs with Mn-, Ni-, and Cu-based ones for the HER.^{28–30} In addition, POMs can rapidly scavenge photogenerated charge carriers from light harvesting materials through strong electrostatic interactions and allow effective photochemical water splitting.^{31–34} Despite such unique and promising features, POMs have rarely been studied as CO₂RR catalysts; even POMs with a Cu-based active site were only tested for the HER.³⁰ Among the reported POMs for the CO₂RR, only a few POMs, which have highly complicated structures and are thus very difficult to synthesize, allow CH₄ production while most POMs can catalyse CO production more efficiently than CH₄.^{35–37}

In this study, we first report the synthesis of a simple Zn-based POM (ZnPOM) and its application in a selective photochemical CO₂RR to CH₄. ZnPOM was readily prepared under mild conditions and its molecular structure was investigated using

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) analyses. ZnPOM showed catalytic activity for the CO₂RR and allowed highly selective CH₄ production under visible light irradiation in the presence of Ir-based photosensitizers (Tir3). The selectivity against CH₄ was 97.8% when ZnPOM was used as a CO₂RR catalyst (Scheme 1b). Static and time-resolved photoluminescence analyses revealed that photoexcited electrons of Tir3 photosensitizers rapidly transfer to ZnPOM. Density of states (DOS) calculations showed that ZnPOM can have strong electronic interactions with a bound CO intermediate (*CO) due to the significant overlap of the d-orbital of Zn in ZnPOM and the p-orbital of C in *CO, while metallic Zn cannot due to having no overlap. This explains how Zn—known as a CO-producing catalyst^{38,39}—in ZnPOM can lead to selective production of CH₄. This study provides insights for more flexible design and synthesis of CO₂RR catalysts, especially for CH₄ production.

Results and discussion

We synthesized ZnPOM with a molecular formula of [Zn₄-(PW₉O₃₄)₂]^{10–} for the CO₂RR. There are a family of sandwich-type phosphotungstate POMs ([M(II)₄(PW₉O₃₄)₂]^{10–}) embedded with various transition metal ions [M(II)=Co²⁺, Ni²⁺, Mn²⁺, Cu²⁺] (MPOM). However, to the best of our knowledge, there is no report on the synthesis of sandwich-type POMs with Zn ions. Conventionally, Zn- and Cu-based materials are known to produce CO and hydrocarbons, respectively, upon the CO₂RR. Thus, we prepared ZnPOM and CuPOM and compared their catalytic activity for the CO₂RR (Scheme 1b). It is expected that ZnPOM can be prepared by the same method for the synthesis of CuPOM, which was reported by Hill *et al.*,³⁰ due to the similarity between Zn and Cu ions in terms of valence charge and ionic radius (74 and 73 pm, respectively).

First, we investigated the properties and molecular structure of ZnPOM by using various characterization methods. The as-prepared ZnPOM was completely dissolved in an aqueous solution (Fig. S1, ESI†). According to dynamic light scattering and zeta potential (Fig. 1a) analyses, the average diameter and zeta potential of ZnPOM were 0.83 nm and –26.13 mV, respectively. These results are consistent with those of other sandwich-type POMs²⁹ and confirm the molecular nature of ZnPOM rather than the particulate counterpart. XPS analysis confirmed the presence of Zn, W, K, and O atoms of ZnPOM (Fig. S2, ESI†). However, P was not identified possibly due to its relatively low content. Fourier-transform infrared (FT-IR) spectroscopy also showed peaks corresponding to P–O and W–O bands of sandwich-type POMs (Fig. S3, ESI†).³⁰ To investigate the molecular structure of ZnPOM, we obtained crystallographic data using single crystal XRD after the crystallization of supersaturated ZnPOM from hot water (Table S1, ESI†). As expected, the crystal structure and atomic arrangement of ZnPOM (K₁₀[Zn₄(H₂O)₂(PW₉O₃₄)₂]·24H₂O) were almost identical to those of CuPOM, except for the types of transition metal ions embedded in metal-oxo clusters (*i.e.*, Zn²⁺ vs. Cu²⁺). The simulated XRD pattern from the single crystal XRD analysis well matched the measured

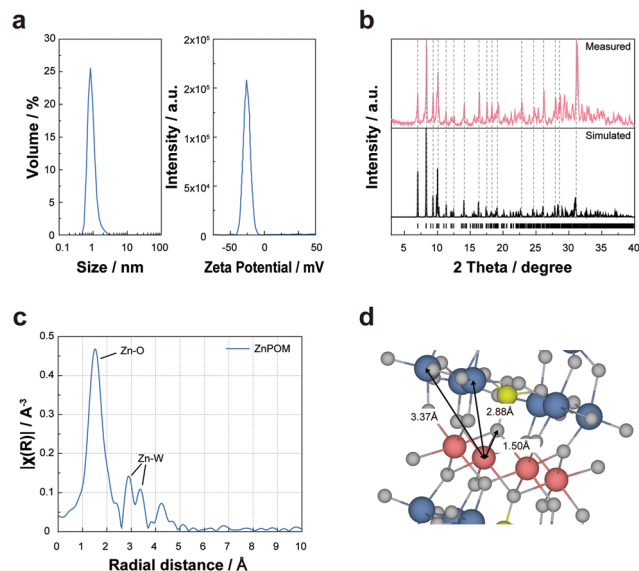


Fig. 1 Characterization of ZnPOM. (a) Dynamic light scattering (left) and zeta potential (right) analyses of ZnPOM. (b) Simulated and measured XRD patterns of ZnPOM. (c) EXAFS analysis showing the distance between Zn and its nearest neighbouring elements in ZnPOM. (d) A graphical illustration showing the molecular structure of ZnPOM and coordination environment of Zn^{2+} ions in ZnPOM.

powder XRD pattern (Fig. 1b). ZnPOM was further characterized by EXAFS analysis to check the coordination environment of Zn ions in ZnPOM (Fig. 1c and d, ESI†). The distances between Zn^{2+} and the nearest neighbouring elements in ZnPOM were 1.5 (Zn–O), 2.88 (Zn–W1), and 3.37 Å (Zn–W2), which were similar to those in CuPOM, respectively (Fig. S4, ESI†). All these results confirmed the successful synthesis of molecular CuPOM by the same method as that of ZnPOM. High purity of the synthesized ZnPOM (>99.9%) was confirmed by ^{31}P NMR (Fig. S5, ESI†).

Next, physicochemical properties of ZnPOM were investigated for the CO_2RR . First, cyclic voltammetry (CV) of ZnPOM was conducted in 0.1 M KHCO_3 saturated with Ar or CO_2 gas (Fig. 2a). For both cases, there was rapid increase of current density without saturation at highly negative potentials possibly due to the HER. However, there was a pair of redox peaks at around -0.5 V vs. a reversible hydrogen electrode (RHE; -0.9 V vs. standard hydrogen electrode [SHE]) only when CO_2 was purged, suggesting a possibility of ZnPOM as a CO_2RR catalyst. Encouraged by these results, we carried out photochemical CO_2RR using ZnPOM in the presence of Ir-based photosensitizers (Tir3) because ZnPOM has no or a negligible absorbance in the visible light region (Fig. 2b and Fig. S6, ESI†). Tir3 was chosen as a photosensitizer because it has sufficiently high reducing power for the CO_2RR with the lowest unoccupied and highest occupied molecular orbital (LUMO and HOMO) levels of -3.08 and -5.62 eV vs. vacuum (-1.36 and 1.18 V vs. SHE), respectively.⁴⁰ Tir3 had strong absorption in the UV and visible light region up to 500 nm. Interestingly, the absorbance of Tir3 with ZnPOM was significantly higher than their respective absorbance and arithmetic sum (Fig. 2b), suggesting strong molecular interactions between positively charged Tir3 and negatively charged ZnPOM. The

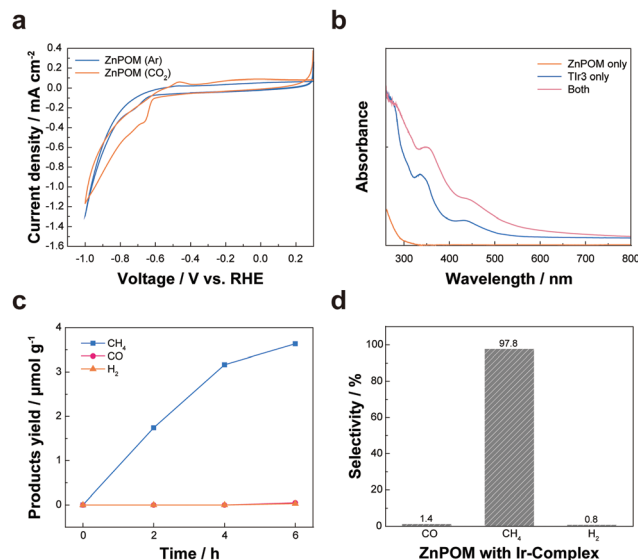


Fig. 2 Photochemical CO_2RR using ZnPOM as a catalyst and Tir3 as a photosensitizer. (a) CV analysis of ZnPOM in 0.1 M KHCO_3 saturated with Ar or CO_2 gas. (b) UV/visible absorbance spectra of each component and both in 0.1 M KHCO_3 . (c) Production and (d) selectivity of various chemicals upon photochemical CO_2RR using 30 μM ZnPOM, 0.1 mM Tir3, and 0.05 M Na_2SO_3 under visible light irradiation. The selectivity of each product was calculated after 6 h of photochemical CO_2RR by considering the number of electrons required to produce each.

wavelength-dependent apparent quantum yield of our photocatalytic CH_4 production system showed the maximum efficiency at 400 nm and was in accordance with the absorbance spectra (Fig. S7, ESI†). CV analysis showed that Tir3 has no activity towards the CO_2RR and can strongly interact with ZnPOM, as can be expected from the increase of current density of the redox pair at around -0.5 V vs. RHE in the presence of both (Fig. S8, ESI†). On the other hand, CuPOM had not only a negligible absorbance in the visible light region but also weak interactions with Tir3 in terms of absorbance (Fig. S9, ESI†).

Photochemical reactions were conducted using ZnPOM (or CuPOM) to check its activity as a CO_2RR catalyst without any external bias. Tir3 and Na_2SO_3 were used as a photosensitizer and a sacrificial electron donor, respectively. Under the optimum conditions with Tir3 at 0.1 mM, ZnPOM at 30 μM , and Na_2SO_3 at 50 mM, only CH_4 was selectively produced with negligible or erroneous amounts of H_2 and CO (Fig. S10, ESI†). Under continuous visible light irradiation, the amount of CH_4 linearly increased and reached 4.16 μmol per unit mass of ZnPOM after 6 h (Fig. 2c). There were no other liquid products. Although the CH_4 production yield of this study is not record-high, it was comparable to those in previous reports on the photocatalytic CO_2RR (Table S2, ESI†). The product selectivity of ZnPOM towards a certain chemical (A) was calculated using the following equation that considers the number of electrons (n) required to make each product (Fig. 2d):

Selectivity (%) for A

$$= \frac{\text{mole of A} \times n}{(\text{mole of CH}_4 \times 8) + (\text{mole of CO} \times 2) + (\text{mole of H}_2 \times 2)}$$

where n is 2 for H_2 and CO , and 8 for CH_4 . Surprisingly, the selectivity of ZnPOM against CH_4 was 97.8% whereas those against CO and H_2 were only 3.0 and 2.3%, respectively. The stability of ZnPOM was studied by a recycling test (Fig. S11, ESI†). There was no noticeable decrease of CH_4 production yield until the third cycle. Because Ir is also known to generate CH_4 ,¹⁹ we carried out photochemical CO_2RR reactions without ZnPOM. Tlr3 alone showed no activity for the CO_2RR and led to the production of hydrogen only (Fig. S12, ESI†). For comparison, CuPOM, CoPOM, and NiPOM were also tested for photochemical CO_2RR under the same conditions (Fig. S13 and S14, ESI†). Although CuPOM also allowed the production of CH_4 , it was much less efficient than ZnPOM in terms of productivity (0.42 vs. $4.16 \mu\text{mol g}^{-1}$ for 6 h) and selectivity (69.5 vs. 97.8%). However, CoPOM²⁶ and NiPOM²⁹ exhibited poor performance for the CO_2RR , as expected from the previous reports about their application in oxygen and hydrogen evolution reactions, respectively. As shown in the absorbance measurement above, ZnPOM (Fig. 2b) showed stronger electrostatic interactions with Tlr3 than CuPOM (Fig. S9, ESI†). This partly explains why ZnPOM exhibited a higher activity than CuPOM for photocatalytic CO_2RR to CH_4 . Taken together, these results indicate that ZnPOM acts as an electrocatalyst for CH_4 production. These are very interesting results in the sense that metallic Zn and Cu are known to produce CO and hydrocarbons upon the CO_2RR , respectively.

Static and dynamic photoluminescence quenching analyses were performed to confirm the electron transfer pathway in our photocatalytic system. Strong photoluminescence of Tlr3 in the range of 500–700 nm was dramatically quenched as the concentration of ZnPOM increased (Fig. 3a). Photoluminescence of Tlr3 disappeared immediately after the addition of ZnPOM, which can be observed even by the naked eye. Because the LUMO level of Tlr3 (-0.8 V vs. RHE) is more negative than that of ZnPOM (-0.6 V vs. RHE), one can expect that photoexcited electrons from Tlr3 can be transferred to ZnPOM, resulting in photoluminescence quenching (Fig. S8b and c, ESI†). To quantify the charge transfer dynamics, the photoluminescence lifetime of Tlr3 was recorded in the absence and presence of an electron donor (Na_2SO_3) or ZnPOM (Fig. 3b). The photoluminescence lifetime of Tlr3 dramatically decreased from 820 to 64 ns after the addition of ZnPOM, which well agrees with the static photoluminescence quenching results. In contrast, there was little change in the lifetime after the addition of Na_2SO_3 , which rules out the reductive quenching pathway of Tlr3. Thus, we can conclude that the main charge transfer pathway in this catalytic network follows the oxidative quenching pathway (Fig. 3c). Based on the ratio between the photoluminescence of Tlr3 without (I_0) and with ZnPOM (I), the bimolecular rate constant (K_{SV}) was calculated from the Stern–Volmer equation (Fig. S15, ESI†). K_{SV} for Tlr3 and ZnPOM was $1.76 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, which is remarkably fast compared to those in previously reported catalytic systems (Table S3, ESI†).

DOS calculations from density functional theory were carried out to unveil the molecular mechanism for the selective production of CH_4 by ZnPOM. Because metallic Zn and Zn-based materials are known to produce CO ,^{41,42} we compared the DOS

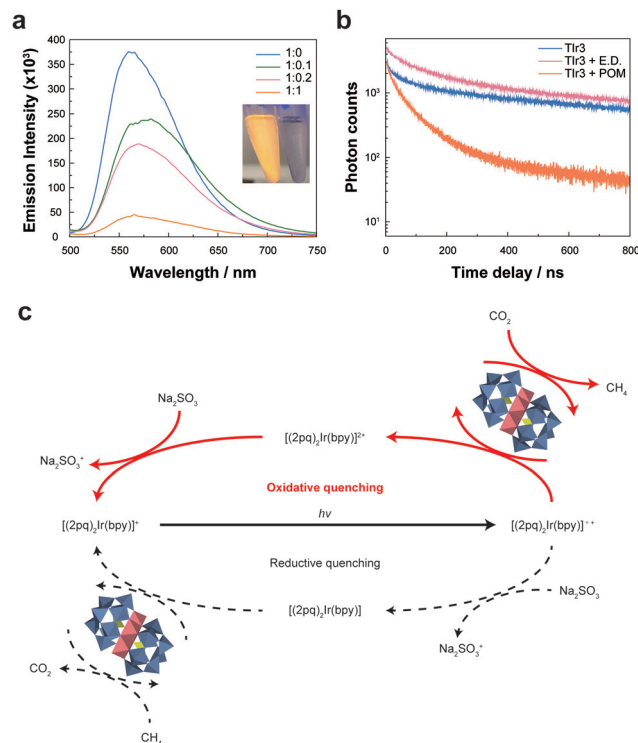
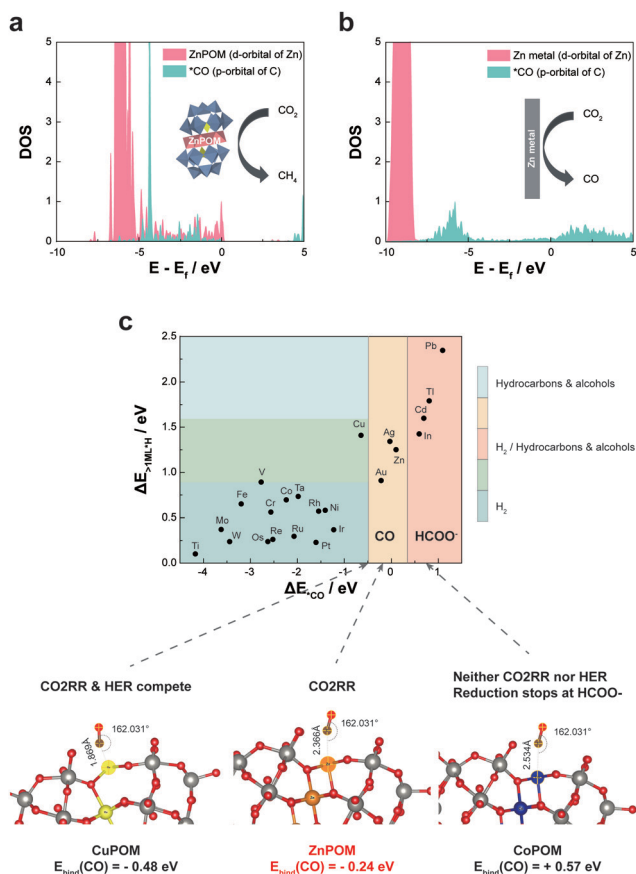


Fig. 3 Photophysical analysis of photocatalytic CO_2RR systems. (a) Static photoluminescence spectra of Tlr3 (50 μM) without (blue line) and with ZnPOM at different concentration ratios of Tlr3 and ZnPOM. The inset shows a photograph of Tlr3 solutions under UV light without (left) and with (right) ZnPOM (50 μM). (b) Time-correlated single-photon counting for lifetime measurements of Tlr3 without and with POM or sacrificial electron donor (E.D.) Na_2SO_3 . (c) A suggested mechanistic pathway for the photocatalytic CO_2RR to CH_4 using ZnPOM and Tlr3.

of Zn ions in ZnPOM with that of metallic Zn. In addition, one of the most important factors determining the products of the CO_2RR is electronic interactions between catalysts and intermediate states.^{21,43} In particular, $^*\text{CO}$ is an important intermediate for the production of CH_4 . Our calculations showed that the DOS of the Zn atom (d-orbital) in ZnPOM significantly overlaps with that of the C atom (p-orbital) in $^*\text{CO}$ (Fig. 4a). In contrast, the DOS of the metallic Zn does not overlap with that of the C atom (p-orbital) in $^*\text{CO}$ (Fig. 4b). Thus, one can expect that the strong electronic hybridization between ZnPOM and the $^*\text{CO}$ intermediate allows the facile transfer of electrons for further reactions of $^*\text{CO}$ to CH_4 . To investigate the reaction mechanism more in detail, the binding energy between the key intermediate $^*\text{CO}$ and POMs was calculated (Fig. 4c). The binding energies of CuPOM, ZnPOM, and CoPOM were -0.48 , -0.24 , and $+0.57$ eV, respectively. Our results are consistent with the previous report on the relationship between the $^*\text{CO}$ binding energy and product selectivity in the CO_2RR .¹ While CuPOM strongly binding to $^*\text{CO}$ led to competition between the HER and CO_2RR , CoPOM, which cannot easily bind with $^*\text{CO}$, has poor activity for the CO_2RR (Fig. S14, ESI†). In contrast, ZnPOM binding neither too strongly nor too weakly with $^*\text{CO}$ is advantageous for the selective production of CH_4 .

In this study, we first report the synthesis of ZnPOM as a CO_2RR catalyst for the selective production of CH_4 upon

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Elemental and structural characterization

The elemental composition of ZnPOM was characterized by K-alpha X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific, USA). FT-IR spectra were measured on a Varian 670-IR (Agilent Technologies, USA) using KBr pellets. UV/visible absorbance of each material was confirmed with a V-730 UV-Visible spectrophotometer (JASCO, Japan). For X-ray diffraction (XRD) analysis, microcrystals of ZnPOM were obtained by crystallization in the supersaturated solution. Single-crystal and powder XRD data were collected by an R-Axis RAPID II (Rigaku, Japan) and a powder XRD D2 PHASER (Bruker, USA), respectively. Extended X-ray absorption fine structure (EXAFS) analysis was performed at the beamline 6D of the Pohang Light Source in the Pohang Accelerator Laboratory in Korea. The ZnPOM particle size was analysed with a Zeta sizer (Malvern, England). ^{31}P NMR spectra were collected by an AVANCE III HD (Bruker, USA).

Electrochemical and photochemical characterization

Cyclic voltammetry (CV) was carried out with a WMOG1000 multichannel potentiostat (WonA Tech CO. Ltd, Korea) in a three-electrode configuration: a working electrode, glassy carbon; a reference electrode, Ag/AgCl; a counter electrode, fluorine-doped tin oxide coated with 100 nm thick Pt; electrolyte, 0.1 M KHCO_3 (pH 7.0) saturated with Ar or CO_2 gas; and scan rate, 10 mV s^{-1} . For the optimal photochemical CO_2RR , 4 mL of a 0.1 M KHCO_3 solution with 30 μM ZnPOM, 0.1 mM Ir-complex, and 0.05 M Na_2SO_3 in 0.1 M KHCO_3 was used in a 10 mL vial. Gas products were collected from a sealed reaction vessel using an air-tight syringe (1 mL) and analysed with a GC-2010 plus gas chromatograph (Shimadzu Co., Japan) equipped with an FID and MICRO-PAKED ST column (Shinwa Chemical Industries Ltd, Japan). Product yields were calculated by dividing the amount of products by the amount of catalyst. Liquid products were measured using a Water 2410 HPLC (Waters, USA). A 300 W Xe lamp equipped with a 400 nm cut-on filter (100 mW cm^{-2}) was used as a light source.

Photoluminescence quenching analysis

TiR3 (50 μM) was mixed with POM at molar ratios of 1:0, 1:0.1, 1:0.5, and 1:1 in distilled water. The photoluminescence intensity of the prepared solutions was recorded with a FLS920 (Edinburgh Instruments, UK) and a PC1 (ISS, USA). Bimolecular rate constant (KSV) from photoluminescence quenching was calculated through Stern-Volmer plot by maximum photoluminescence intensity for each mixture ratio.

Time-correlated single photon counting for lifetime measurements

The photoluminescence lifetime of TiR3 was recorded with and without potential quenchers (e.g., ZnPOM or Na_2SO_3) using a FluoTime300 time-correlated single photon counting setup (TCSPC) (PicoQuant, Berlin, Germany). A LDH-D-C-450 pulsed diode laser coupled with a PDL 820 laser diode driver (<70 ps pulse width and 196 kHz–40 MHz repetition rate) was used as a photoexcitation source. The time-resolved exciton decay was measured with a PicoHarp 300E TCSPC module and a PMA-C

182-N-M photomultiplier tube. Fitting was carried out using FluoFit software to calculate the corresponding photoluminescence lifetimes.

Density functional theory calculations

The Vienna Ab initio Simulation Package (VASP)⁴⁴ was used to calculate relaxed structures and density of states. The generalized gradient approximation (GGA) method was adopted to describe the exchange correlation functional. The pseudopotentials generated under the projector-augmented wave (PAW) method⁴⁵ were used and the energy cutoff for the plane wave basis set was set to 500 eV. The force criterion for optimizing the atomic positions was $5 \times 10^{-3} \text{ eV \AA}^{-1}$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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