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Cite this: *Nanoscale*, 2024, **16**, 16451

Modulated assembly and structural diversity of heterometallic Sn–Ti oxo clusters from inorganic tin precursors†

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Through modulating the multidentate ligands, solvent environments, and inorganic tin precursors during the synthesis processes, we have successfully prepared a series of unprecedented heterometallic Sn–Ti oxo clusters with structural diversity and different physiochemical attributes. Initially, two **Sn₆Ti₁₀** clusters were synthesized using trimethylolpropane as a structure-oriented ligand and SnCl₄·5H₂O as a tin source. Then, when a larger pentadentate ligand di(trimethylolpropane) was used instead of trimethylolpropane and aprotic acetonitrile solvent was introduced into the reaction system, four low-nuclearity Sn–Ti oxo clusters were discovered, including two **Sn₁Ti₁**, one **Sn₂Ti₂** and one **Sn₂Ti₆**. Finally, two mixed-valence state clusters, **Sn^{II}₄Sn^{IV}₂Ti^{IV}₁₄** and **Sn^{II}₄Sn^{IV}₄Ti^{IV}₂₀**, were obtained by transforming the tin precursor from SnCl₄·5H₂O to SnCl₂·2H₂O and adjusting the acetonitrile solution with trace acetic acid/formic acid. **Sn₈Ti₂₀** is the highest-nuclearity heterometallic Sn–Ti oxo cluster to date. Moreover, comparative electro-catalytic CO₂ reduction experiments were carried out, and it was concluded that the **Sn₈Ti₂₀**-decorated electrode showed the most satisfactory performance due to the influence of mixed-valence states of the Sn atoms and the charging effects provided by 20 Ti⁴⁺ ions. This study presents important guiding significance for the design, synthesis and application optimization of functional heterometallic nanoclusters.

Received 26th June 2024,
Accepted 9th August 2024

DOI: 10.1039/d4nr02644f

rsc.li/nanoscale

Introduction

Studying the formation mechanisms, structures, and properties of clusters not only builds a bridge between atoms/molecules and condensed states of matter, but also helps us to conduct precise research on molecular materials.¹ Therefore, in recent years, the chemistry of metal oxo clusters (MOCs) has developed rapidly and MOCs with accurate atomic structural information have been synthesized continuously.^{2–6} Doping heteroatoms with metal oxides is considered one of the most effective ways to improve the catalytic performance of materials.^{7,8} This might occur because the composite material produces synergistic effects to improve its catalytic performance.^{9,10} Similarly, heterometallic oxo clusters combine the characteristics of MOCs and the interaction

between different kinds of metals in their composition, thus giving the materials unique physical and chemical properties.^{11–16} However, although both homometallic Ti- and Sn-oxo clusters have been extensively reported, the number of heterometallic Sn–Ti oxo clusters is relatively small at present. Extensive research in this field has been limited to the discovery of a few Sn–Ti oxo clusters with low nuclearity (≤ 11), such as {Sn₁Ti₁},^{17,18} {Sn₁Ti₂},^{19,20} {Sn₃Ti₁},²¹ {Sn₄Ti₁},²² {Sn₂Ti₆},²³ {Sn₄Ti₆},²⁴ and {Sn₆Ti₅}.²⁵ Very recently, we prepared three dual-layered Sn–Ti oxo clusters, two {Sn₂Ti₁₂} and one {Sn₆Ti₁₄}, which were functionalized with 1,10-phenanthroline and showed interesting optical limiting effects.²⁶ Therefore, it is necessary to develop high-nuclearity Sn–Ti oxo clusters to enrich their structures and expand applications.

In the synthesis of tin oxo clusters, organotin compounds have been used as the main tin sources, while a few examples have been prepared using inorganic tin sources. There is a significant difference between organotin and inorganic tin precursors in the synthesis reactions.^{27–30} Moreover, unlike the single valence state of organic tin sources, inorganic tin precursors have two different valence states: +2 and +4.^{23,31,32} In addition, an important advantage of MOCs is that their modifiable surface organic ligands can regulate the structures of the obtained clusters and improve their properties.^{33–35}

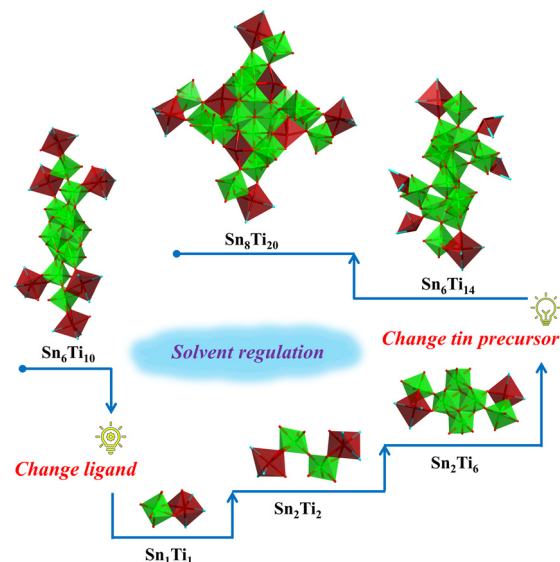
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Compared with organotin precursors, inorganic tin precursors not only are more environmentally friendly, but also more easily break Sn–X (F, Cl, Br, I, *etc.*) bonds, which are more likely to be modified by functional organic ligands during the reaction process.³⁰

Usually, the multiple coordination modes of multidentate ligands can meet the spatial requirements and stabilize MOCs to the greatest extent.^{36–38} Herein, polyhydroxyalkanes with multiple mildly acidic hydroxyl groups were selected as the protecting ligands for the construction of heterometallic Sn–Ti oxo clusters, including trimethylolpropane (H₃TPP) and di(trimethylolpropane) (H₄DTPP). Through comprehensively adjusting solvents, tin precursors, temperature and other synthetic factors, the modulated assembly of a series of Sn–Ti oxo clusters was achieved (Table 1). As a result, seven intermediates were successfully identified, including two Sn₆Ti₁₀ clusters (TOC-51 and TOC-52), two Sn₁Ti₁ clusters (TOC-53 and TOC-54), one Sn₂Ti₂ cluster (TOC-55), one Sn₂Ti₆ cluster (TOC-56), and one Sn₆Ti₁₄ cluster (TOC-57), guiding to the targeted Sn₈Ti₂₀ cluster (TOC-58) eventually (Scheme 1). Among these, TOC-57 and TOC-58 show interesting mixed Sn²⁺/Sn⁴⁺ valences which were proved by bond-valence sum (BVS) calculations (Tables S5 and S6†), X-ray photoelectron spectroscopy (XPS) analysis (Fig. 1) and the charge balancing principle. The windmill-like structure of TOC-58 embodies a unique structural aesthetic. The core size of TOC-58 is ~0.8 × 2.2 nm, and its nuclearity of 28 exceeds those of currently known heterometallic Sn–Ti oxo clusters (≤20). Electrocatalytic CO₂ reduction (CO₂RR) studies were conducted on three large clusters (TOC-51, TOC-57 and TOC-58), and the experimental results showed that the formate Faradaic efficiency (FE_{formate}) of the electrode derived from TOC-58 with the largest {Sn₈Ti₂₀} core and mixed Sn²⁺/Sn⁴⁺ valences reached above 66% at –1.0 (vs. RHE).

Results and discussion

In the initial stage of this research, using SnCl₄·5H₂O, trimethylolpropane and Ti(OⁱPr)₄ as raw materials, a colorless crystal of TOC-51 was synthesized by allowing it to stand at room temperature for 6 days after heating at 80 °C for 3 days in a mixture of 1,4-dioxane solvent and ethyl acetate. Ethyl



Scheme 1 Illustration of the synthetic route from intermediates (Sn₆Ti₁₀, Sn₁Ti₁, Sn₂Ti₂, Sn₂Ti₆, and Sn₆Ti₁₄) to the largest Sn₈Ti₂₀.

acetate is easily hydrolyzed and will gradually produce acetic acid and ethanol during the reaction. As shown in Fig. 2a, single-crystal X-ray diffraction analysis indicates that trimethylolpropane collaborates with the auxiliary ligand HAC to form the hamburger-like structure of TOC-51. The protected inorganic Sn₂Ti₈ core is linked with two {Sn₂Ti(TPP)(HTPP)Cl₆} units by four μ₂-O to form the whole TOC-51 cluster. The bread slices of the hamburger are {Sn₂Ti(TPP)(HTPP)Cl₆} moieties. The Sn₂Ti₈ core in the middle of the structure is composed of two μ₄-O and two μ₃-O connecting eight Ti atoms, while two Sn atoms are bonded to the Ti atoms by μ₂-OH. In fact, there are two ways for O atoms in H₃TPP to participate in the coordination. One is that two O atoms take part in the coordination and the other is that all three O atoms take part in the coordination. The Sn₂Ti₈ core is surrounded by six trimethylolpropanes, two acetic acids, and six Cl atoms. For the two Sn atoms in Sn₂Ti₈, there are two H₂O molecules participating in their 6-coordination, respectively. Meanwhile, the acetic acid in TOC-51 can be replaced with propionic acid to form another new cluster TOC-52 (Fig. 2e). Although the two clusters are structurally identical except for modifying the same sites with

Table 1 Summary of the composition and reaction conditions of TOC-51 to TOC-58

Compound	Ligand	Sn source	Solvent	Formula
TOC-51	H ₃ TPP	SnCl ₄ ·5H ₂ O	1,4-Dioxane	[Sn ^{IV} Ti ^{IV} (μ ₄ -O) ₂ (μ ₃ -O) ₂ (μ ₂ -O) ₄ (μ ₂ -OH) ₂ (TPP) ₆ (HTPP) ₄ (Ac) ₂ (H ₂ O) ₂ Cl ₁₈]·2(1,4-D)
TOC-52	H ₃ TPP		Propionic acid	[Sn ^{IV} Ti ^{IV} (μ ₄ -O) ₂ (μ ₃ -O) ₂ (μ ₂ -O) ₄ (μ ₂ -OH) ₂ (TPP) ₆ (HTPP) ₄ (Pr) ₂ (H ₂ O) ₂ Cl ₁₈]·2(1,4-D)
TOC-53	H ₄ DTPP		Acetonitrile	[Sn ^{IV} Ti ^{IV} (DTPP)(Ac)Cl ₃]
TOC-54	H ₄ DTPP		Propionic acid	[Sn ^{IV} Ti ^{IV} (DTPP)(Pr)Cl ₃]
TOC-55	H ₄ DTPP		1,4-Dioxane	[Sn ^{IV} Ti ^{IV} (μ ₂ -O)(DTPP) ₂ (H ₂ O) ₂ Cl ₆]
TOC-56	H ₄ DTPPs		Propionic acid	H ₂ [Sn ^{IV} Ti ^{IV} (μ ₂ -O) ₆ (DTPP) ₄ Cl ₆]
TOC-57	H ₄ DTPP	SnCl ₂ ·2H ₂ O	Acetic acid	[Sn ^{IV} Sn ^{IV} Ti ^{IV} (μ ₄ -O) ₂ (μ ₃ -O) ₄ (μ ₂ -O) ₈ (DTPP) ₆ (HDTTP) ₂ Cl ₁₄]
TOC-58	H ₄ DTPP		Formic acid	[Sn ^{IV} Sn ^{IV} Ti ^{IV} (μ ₄ -O) ₈ (μ ₃ -O) ₄ (μ ₂ -O) ₁₀ (DTPP) ₁₂ Cl ₁₂]

Abbreviations: H₃TPP = trimethylolpropane; H₄DTPP = di(trimethylolpropane); HPr = propionic acid; HAC = acetic acid; 1,4-D = 1,4-dioxane.

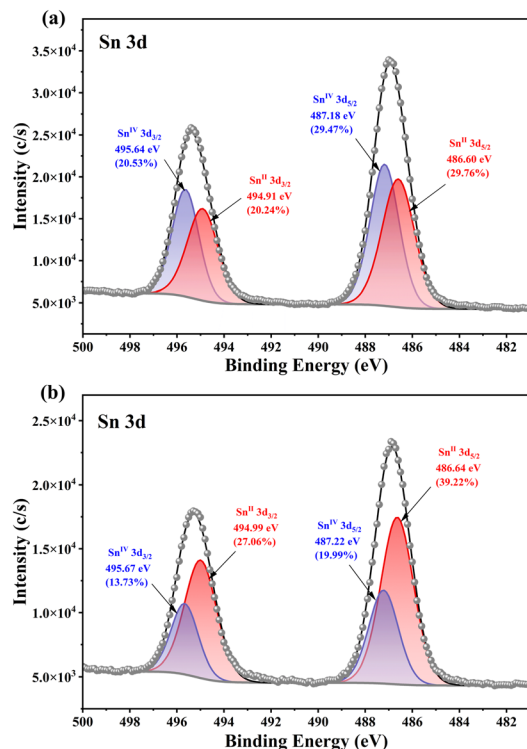


Fig. 1 XPS spectra of Sn 3d of TOC-57 (a) and TOC-58 (b).

different carboxylic acids, they are different in the packing modes (Fig. 2c and f). Both Sn atoms and Ti atoms exist with 6-coordination and +4 valence in the above two $\text{Sn}_6\text{Ti}_{10}$ clusters (TOC-51 and TOC-52).

When only replacing the small-sized tridentate ligand H_3TPP with the larger pentadentate ligand H_4DTPP , there was

no crystal growth in the original solvent environment. Through debugging the solvent, it was found that when aprotic solvent CH_3CN was used, four new heterometallic Sn–Ti oxo clusters (TOC-53–TOC-56) were constructed with different auxiliary solvents (Fig. 3). TOC-53 was formed by the synergistic coordination of the organic ligand H_4DTPP and the auxiliary ligand HAc from the decomposition of ethyl acetate solvent molecules. Just as the acetic acid in TOC-51 can be substituted by propionic acid to obtain TOC-52, the acetic acid in TOC-53 also can be replaced by propionic acid to give rise to TOC-54. The packing diagrams of TOC-53 and TOC-54 are also dissimilar (Fig. S1b and S2b†). TOC-55 can be seen as the connection of two TOC-51 clusters through a $\mu_2\text{-O}$ between two Ti atoms, relying on H_2O molecules to stabilize the 6-coordinate mode of Sn atoms. When we reduced the dosage of propionic acid to 50 μL while keeping the other conditions unchanged, TOC-56 was found. As shown in Fig. 3, TOC-56 can be regarded as the insertion of two DTPP ligands protecting four Ti atoms in the middle of the TOC-55 structure. In these four Sn–Ti heterometallic oxo clusters (TOC-53–TOC-56), Sn atoms and Ti atoms also exist in 6-coordinated and +4 valence states. Furthermore, energy dispersive spectroscopy (EDS) and plasma emission spectroscopy (ICP) analyses matched well with the obtained crystallographic results (Fig. S12–S15 and Table S7†).

Nevertheless, the cluster nuclearity was unable to further increase through continually adjusting the dosage of propionic acid or replacing propionic acid with other stronger/weaker acids. To break this deadlock, we considered introducing an inorganic tin raw material as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with better reactivity. Fortunately, TOC-57 with a larger $\text{Sn}_6\text{Ti}_{14}$ core was obtained by changing the tin source from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ to $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and adjusting the acetonitrile solution with trace acetic acid (Fig. 4a). The cluster structure of TOC-57 can be seen to trans-

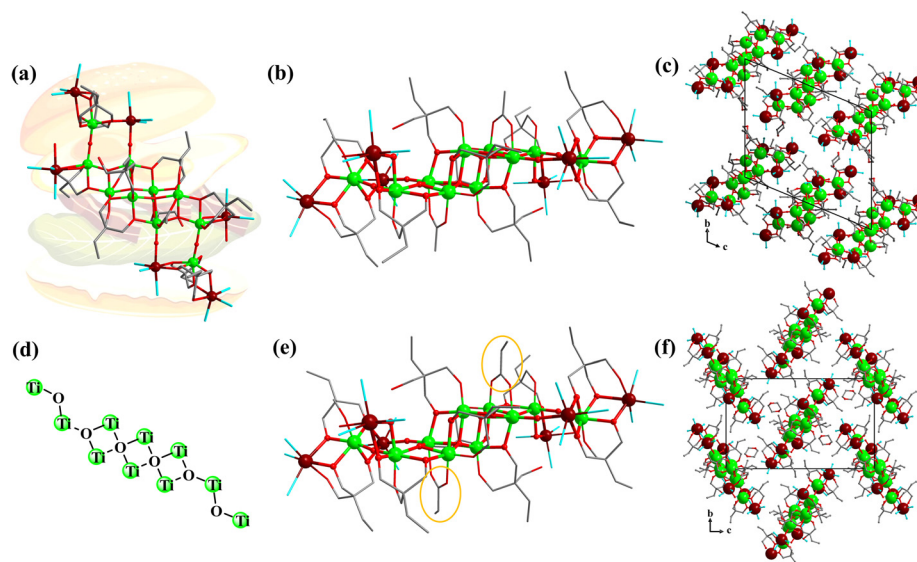


Fig. 2 (a and b) Hamburger-like structure of TOC-51. (c) Packing mode of TOC-51. (d) Connection diagram of Ti atoms through bridging an O atom in TOC-51. (e) Cluster structure of TOC-52, highlighting the Pr ligands. (f) Packing mode of TOC-52. Color codes: dark red, Sn; green, Ti; blue, Cl; gray, C; red, O. H atoms were omitted for clarity.

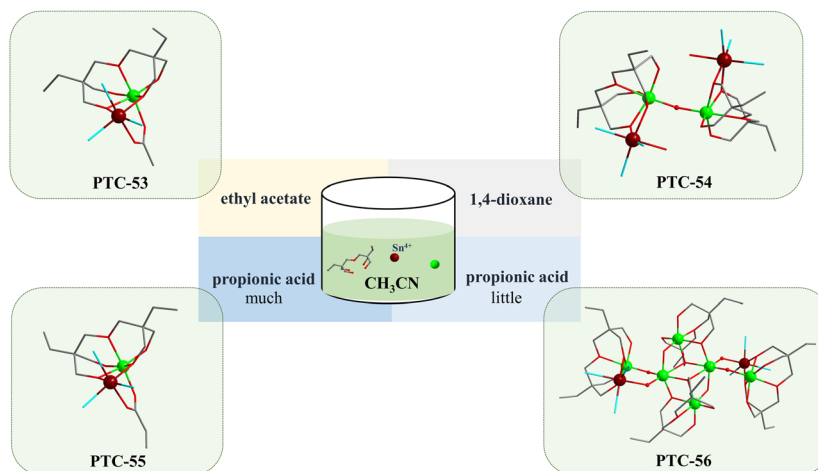


Fig. 3 Synthetic conditions and cluster structures of TOC-53–TOC-56.

form the four Ti atoms protected by DTPP ligands in the middle of **TOC-56** into a $\text{Sn}_4\text{Ti}_{12}$ inorganic core encircled by DTPP ligands, to achieve a further increase in the number of cluster cores. Interestingly, BVS calculations (Table S5†) and XPS analysis (Fig. 1a) showed that the tin ions in **TOC-57** were in mixed-valence states due to the partial oxidation of the initial Sn^{2+} ions during the synthesis process. The four Sn atoms in the $\text{Sn}_4\text{Ti}_{12}$ inorganic core display 3-coordination and +2 valence states. Therein, two Sn^{2+} ions are bridged with Ti atoms by two O atoms from two DTPP ligands and the other two Sn^{2+} ions are linked with Ti atoms by a $\mu_2\text{-O}$. The 12 Ti atoms in the inorganic core $\text{Sn}_4\text{Ti}_{12}$ are connected together by 4 $\mu_2\text{-O}$, 2 $\mu_3\text{-O}$, and 2 $\mu_4\text{-O}$. There are 6- and 7-coordination modes for Ti atoms, with two out of 14 Ti atoms being 7-coordinated.

Based on the above synthesis results, we can clearly see that the assembly of heterometallic Sn–Ti oxo clusters was greatly affected by solvents and the pH value of the solution also played an important role in the assembly of the cluster core in this system. Accordingly, when we further replaced acetic acid with more acidic formic acid and the other conditions remained unchanged from those for **TOC-57**, a highly symmetric high-nuclearity Sn–Ti oxo cluster **TOC-58** was synthesized (Fig. 5b). The cluster core of **TOC-58** is $\text{Sn}_8\text{Ti}_{20}$, which represents the nuclearity record in the existing heterometallic Sn–Ti oxo clusters. The results of single-crystal X-ray diffraction show that it crystallizes in a cubic system with the space group $I\bar{4}3d$. The atomic ratio of Sn to Ti was determined to be 8 : 20.09 through ICP analysis (Table S7†), which is consistent with the structural analysis results. The cluster core size of

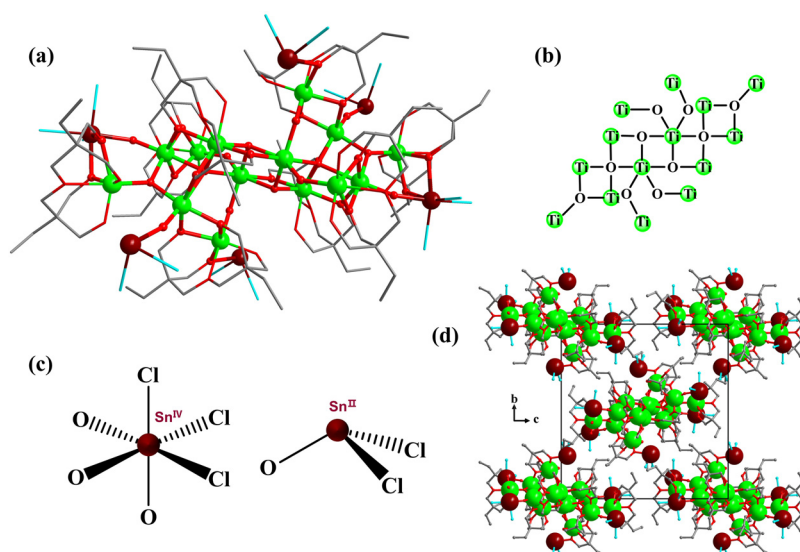


Fig. 4 (a) The cluster structure of **TOC-57**. (b) Connection diagram of Ti atoms through bridging an O atom in **TOC-57**. (c) Coordination spheres of the Sn atoms in **TOC-57**. (d) The packing mode of **TOC-57**.

TOC-58 is $\sim 2.2 \times 0.8$ nm (Fig. 5e). The crystal structure analysis reveals that **TOC-58** has a central scale structure, and the whole cluster is like a windmill. At the top of the four blades of the windmill there are $\{\text{SnTi}(\text{DTPP})\text{Cl}_3\}$ units, and the internal inorganic core is $\text{Sn}_4\text{Ti}_{16}$ (Fig. 5a). The $\text{Sn}_4\text{Ti}_{16}$ inorganic core of **TOC-58** consists of four $\mu_4\text{-O}$ bridged $\{\text{SnTi}_3\}$ tetranuclear parts and four Ti atoms are connected by four $\mu_2\text{-O}$. The two adjacent $\{\text{SnTi}_3\}$ tetranuclear moieties are connected by a $\mu_4\text{-O}$, and the linker between two opposite $\{\text{SnTi}_3\}$ tetranuclear parts is one $\mu_2\text{-O}$ bridge. Moreover, each of the four Ti atoms forming the central scale has a $\mu_2\text{-O}$ attached to a Ti atom. Four Ti atoms and four $\{\text{SnTi}_3\}$ tetranuclear moieties are distributed before and after in a regular pattern. The $\text{Sn}_4\text{Ti}_{16}$ inorganic core is surrounded by eight DTPP ligands. The tin atoms in **TOC-58** are also in mixed-valence states as proved by BVS calculations (Table S6†) and XPS analysis (Fig. 1b). Different from the 3-coordination mode of Sn^{2+} ions in **TOC-57** (Fig. 4c), the Sn^{2+} ions in **TOC-58** adopt the 5-coordination mode (Fig. 5c). The 5-coordination tin atoms are connected to the 7-coordination Ti atoms by a $\mu_4\text{-O}$. In addition, the Ti^{4+} ions in **TOC-58** are located in the $\{\text{TiO}_7\}$ or $\{\text{TiO}_6\}$ coordination geometry. Among the 20 Ti atoms, four are 7-coordinated which are distributed in four cubes, respectively. Because inorganic tin precursors are used, the Sn^{4+} ions in all clusters (**TOC-51**–**TOC-58**) are located in the $\{\text{SnO}_3\text{Cl}_3\}$ coordination octahedra. By analysing the TG curve of **TOC-58** (Fig. S19d†), it was observed that the skeleton of the compound remained relatively stable until ~ 300 °C. Beyond this temperature, ligand detachment and structural decomposition occurred.

Sn containing materials are regarded as suitable CO_2RR electrocatalysts to produce formic acid.^{39–46} Considering that **TOC-51**, **TOC-57** and **TOC-58** present potential active sites of Sn atoms (Fig. S7†), their applications in electrocatalysis were studied. First, linear sweep voltammetry (LSV) profiles of the three sample-modified working electrodes were measured in 0.5 M KHCO_3 solution filled with N_2 or CO_2 (Fig. 6a). It was clear that the current densities of **TOC-51**-, **TOC-57**- and **TOC-58**-derived electrodes in CO_2 -saturated electrolyte were higher than those in N_2 -saturated electrolyte, revealing the capacity of the CO_2RR . The **TOC-58**-modified electrode displayed the lowest initial potential, indicating the fastest electrocatalytic kinetics. The liquid product of the CO_2RR was detected by nuclear magnetic resonance spectroscopy (Fig. S25†), and the analysis demonstrated that formate was the only liquid product. The $\text{FE}_{\text{formic}}$ was measured by ion chromatography (Fig. S26†), and the values for H_2 (Fig. S27†) and CO (Fig. S28†) were measured by gas chromatography.

As shown in Fig. 6b, the $\text{FE}_{\text{formate}}$ of the **TOC-51**-modified electrode shows little difference under different voltages with the highest value being $\sim 51\%$ at -1.0 V (vs. RHE). The electrode modified with **TOC-57** exhibits the lowest $\text{FE}_{\text{formate}}$ at -0.7 (vs. RHE) and it increases to around 57% at -1.0 V (vs. RHE). The highest $\text{FE}_{\text{formate}}$ of the electrode modified with **TOC-58** exceeds 66% at -1.0 (vs. RHE). Although the number of Sn active sites in **TOC-58** is less than that in **TOC-57**, it contains more Ti^{4+} to achieve better charging effects.²⁴ Meanwhile, the mixed-valence states of Sn atoms show better catalytic activity than the single valence state.³¹ These compre-

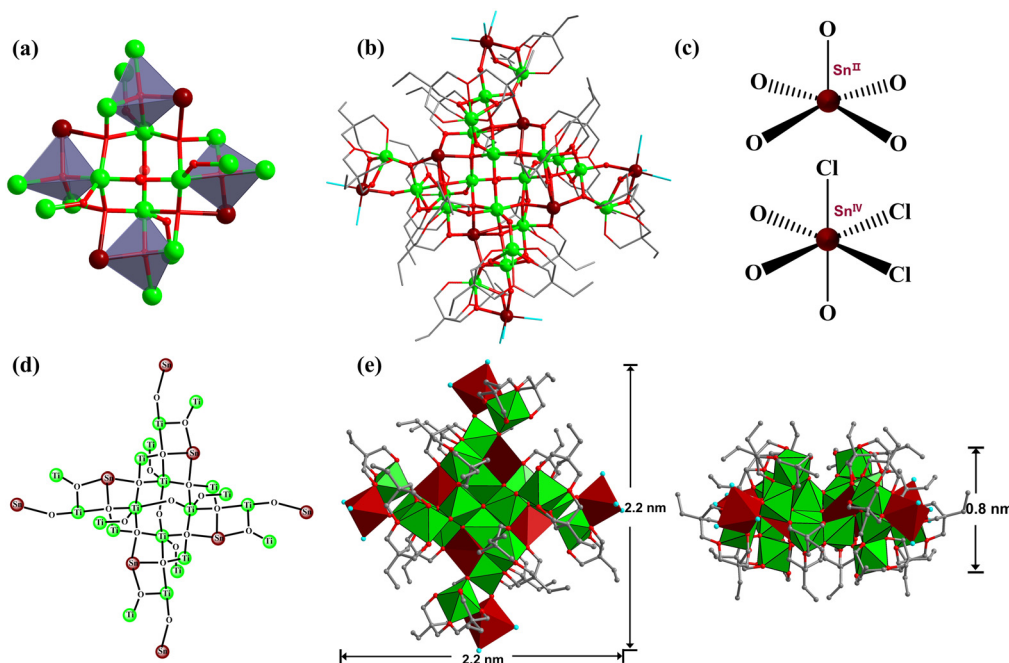


Fig. 5 (a) Multifaceted view of the $\text{Sn}_4\text{Ti}_{16}$ internal inorganic core in **TOC-58**. (b) The cluster structure of **TOC-58**. (c) Coordination spheres of the Sn atoms in **TOC-58**. (d) Connection diagram of Ti and Sn atoms through bridging an O atom in **TOC-58**. (e) Polyhedral representations of the $\text{Sn}_8\text{Ti}_{20}$ core of **TOC-58**.

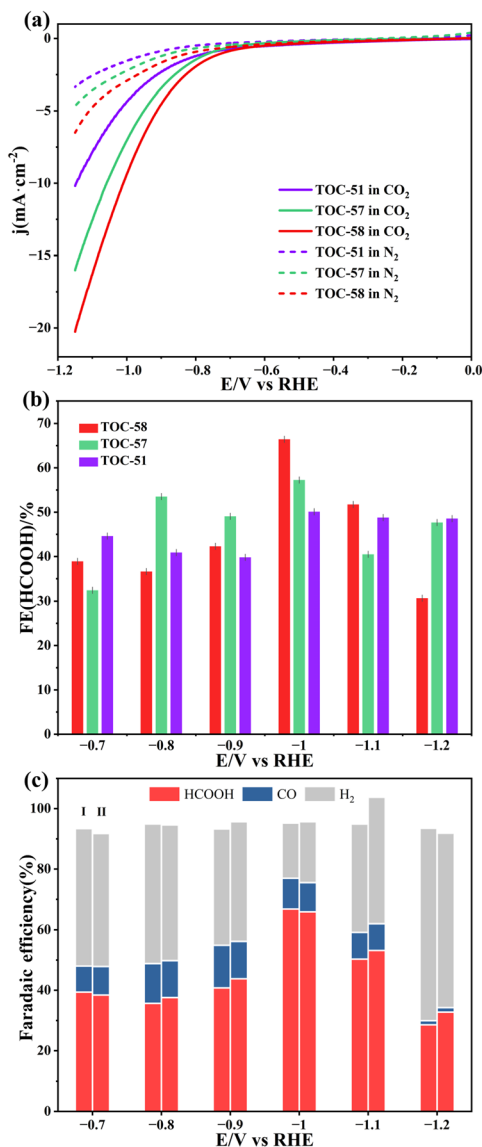


Fig. 6 (a) LSV profiles of TOC-51-, TOC-57- and TOC-58-decorated electrodes in N₂- or CO₂-saturated 0.5 M KHCO₃ solution. (b) Comparative FEs of formates for TOC-51-, TOC-57- and TOC-58-derived electrodes at various potentials. (c) Faradaic efficiencies for formate H₂ and CO at different potentials of the TOC-58-decorated electrode, showing the results of two different experiments (I and II).

hensive factors make TOC-58 exhibit the best catalytic effect. The stability of these cluster decorated electrodes was confirmed by the well-maintained mass spectrometry and XPS spectra after electrocatalysis (Fig. S31–S33†).

Conclusions

In conclusion, we used inorganic tin precursors and functional tridentate H₃DPP and pentadentate H₄DTPP ligands to direct the assembly of heterometallic Sn–Ti oxo clusters. A family of compounds with various nuclearities was successfully con-

structed by adjusting the solvents and changing the inorganic tin sources. Therein, Sn₈Ti₂₀ (TOC-58) presents the highest nuclearity and the largest size in the heterometallic Sn–Ti oxo cluster field. Moreover, mixed Sn²⁺/Sn⁴⁺ valent states have been achieved by the introduction of SnCl₂·2H₂O during synthesis. Both the mixed-valence states of Sn atoms and the charging effects of Ti⁴⁺ ions show influence on the electrocatalytic activity of these heterometallic Sn–Ti oxo clusters, with the TOC-58-decorated electrode exhibiting the highest FE_{formate} (over 66%). This work not only enriches the structural diversity of Sn–Ti oxo clusters, but also provides an efficient strategy for improving their physiochemical performance.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data for TOC-51 to TOC-58 have been deposited at the Cambridge Crystallographic Data Centre (CCDC) deposition numbers 2365528 to 2365535.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Natural Science Foundation of Fujian Province (2022J02013) and the National Natural Science Foundation of China (22271284).

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