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# Stepwise assembly of thiacalix[4]arene-protected Ag/Ti bimetallic nanoclusters: accurate identification of catalytic Ag sites in CO<sub>2</sub> electroreduction†

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The accurate identification of catalytic sites in heterogeneous catalysts poses a significant challenge due to the intricate nature of controlling interfacial chemistry at the molecular level. In this study, we introduce a novel strategy to address this issue by utilizing a thiacalix[4]arene (TC4A)-protected Ti-oxo core as a template for loading Ag<sup>1+</sup> ions, leading to the successful synthesis of a unique Ag/Ti bimetallic nanocluster denoted as Ti<sub>8</sub>Ag<sub>8</sub>. This nanocluster exhibits multiple surface-exposed Ag sites and possesses a distinctive "core-shell" structure, consisting of a {Ti<sub>4</sub>@Ag<sub>8</sub>(TC4A)} core housing a {Ti<sub>2</sub>O<sub>2</sub>@Ag<sub>4</sub>(TC4A)<sub>2</sub>} motif and two {Ti@Ag<sub>2</sub>(TC4A)} motifs. To enable a comprehensive analysis, we also prepared a Ti<sub>2</sub>Ag<sub>4</sub> cluster with the same {Ti<sub>2</sub>O<sub>2</sub>@Ag<sub>4</sub>(TC4A)<sub>2</sub>} structure found within Ti<sub>8</sub>Ag<sub>8</sub>. The structural disparities between Ti<sub>8</sub>Ag<sub>8</sub> and Ti<sub>2</sub>Ag<sub>4</sub> provide an excellent platform for a comparison of catalytic activity at different Ag sites. Remarkably, Ti<sub>8</sub>Ag<sub>8</sub> exhibits exceptional performance in the electroreduction of CO<sub>2</sub> (eCO<sub>2</sub>RR), showcasing a CO faradaic efficiency (FE<sub>CO</sub>) of 92.33% at -0.9 V vs. RHE, surpassing the FE<sub>CO</sub> of Ti<sub>2</sub>Ag<sub>4</sub> (69.87% at -0.9 V vs. RHE) by a significant margin. Through density functional theory (DFT) calculations, we unveil the catalytic mechanism and further discover that Ag active sites located at {Ti@Ag<sub>2</sub>(TC4A)} possess a higher  $\epsilon_d$  value compared to those at {Ti<sub>2</sub>O<sub>2</sub>@Ag<sub>4</sub>(TC4A)<sub>2</sub>}, enhancing the stabilization of the \*COOH intermediate during the eCO<sub>2</sub>RR. This study provides valuable insights into the accurate identification of catalytic sites in bimetallic nanoclusters and opens up promising avenues for efficient CO<sub>2</sub> reduction catalyst design.

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## Introduction

The electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) offers a promising approach for the conversion of CO<sub>2</sub> into valuable chemical fuels.<sup>1,2</sup> Ag-based nanomaterials have gained significant attention as electrocatalysts for the eCO<sub>2</sub>RR, demonstrating remarkable selectivity towards CO generation.<sup>3-6</sup> Despite substantial advancements in the synthesis of mono-disperse Ag nanoparticles with enhanced catalytic activity, their surface structures remain challenging to precisely characterize and define.<sup>7,8</sup> This limitation hinders the investigation of the structure-activity relationship. Consequently, it is crucial to attain synthetic control over the coordination environments of active Ag sites, enabling the creation of well-defined catalytic centers. Such control holds immense potential for elucidating

the structure-activity relationship of Ag nanocatalysts, thereby facilitating efficient catalysis.

In the realm of Ag catalysis, pre-transition metal oxides (*e.g.*, TiO<sub>2</sub>) have gained significant prominence as substrates for the stabilization of Ag nanoparticles featuring surface-exposed catalytic sites.<sup>9-13</sup> The interplay between the oxide substrate and the active metal site manifests unique physical properties, thus prompting extensive investigations into the structural characteristics and reactive models of Ag-TiO<sub>2</sub> materials.<sup>14</sup> By establishing a close association between titanium-oxo clusters (TOCs) and TiO<sub>2</sub>,<sup>15-24</sup> Ag-doped TOCs can be considered as molecular counterparts of bulk Ag-TiO<sub>2</sub> nanomaterials. Previous studies have successfully synthesized certain crystalline Ag-TOCs,<sup>25-31</sup> although the Ag sites were predominantly embedded within the TOCs as single atoms or clusters, impeding direct interaction with the reactants. Consequently, the controlled assembly of Ag-TOCs featuring surface-exposed Ag catalytic sites and the precise identification of their catalytic centers have posed significant challenges. Regarding the cluster assembly, ligands are the most important prerequisites that we should consider. Thiacalix[4]arene, a macrocyclic compound featuring four phenol units bridged by four S-

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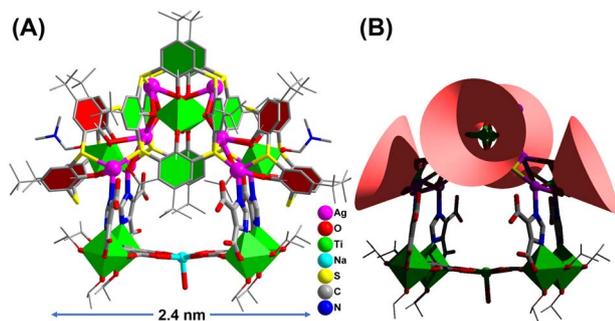


Fig. 1 Single-crystal X-ray structure of  $\text{Ti}_8\text{Ag}_8$ .

groups, has caught our attention, the oligomers of which are favourable to form typical tetranuclear  $\text{M}_4\text{-TC4A}$  units to fabricate high-nuclearity clusters.<sup>32–37</sup> According to soft and hard acid/base theory, the  $\text{Ti}^{4+}$  ion is a hard Lewis acid with a strong coordination affinity for phenolic oxygen, while  $\text{Ag}^{1+}$  is a soft Lewis acid that exhibits an affinity for soft bases, such as the S atom. It has here been assumed that if O-philic  $\text{Ti}^{4+}$  and S-philic  $\text{Ag}^{1+}$  ions participate in an assembly with TC4A, it would result in unexplored bimetallic clusters with unique geometric and/or electronic structures. Despite the existence of TC4A-protected TOCs<sup>38–40</sup> and Ag nanoclusters,<sup>41–46</sup> the synthesis of TC4A-stabilized Ag/Ti bimetallic clusters has yet to be reported in the literature.

Herein we provide a cluster model to accurately identify the Ag catalytic sites in  $\text{CO}_2$  electroreduction. Through the synergistic assembly of TC4A and 4,5-imidazoledicarboxylic acid ( $\text{IdcH}_2$ ), we synthesized the first calixarene-protected  $\text{Ag}^{1+}/\text{Ti}^{4+}$  bimetallic cluster of  $\text{Ti}_8\text{Ag}_8$  with the formula of  $[\text{HNaTi}_8\text{Ag}_8\text{-O}_2(\text{TC4A})_4(\text{HIdc})_6(\text{PrO})_{10}(\text{DMF})_2(\text{H}_2\text{O})]$  (Fig. 1). The big cluster has a composite structure with two kinds of surface-exposed Ag sites, including the Ag(I) sites in the two  $\{\text{Ti}@Ag_2(\text{TC4A})\}$  and the Ag(II) sites in the  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$  units. We have carefully studied the formation path of  $\text{Ti}_8\text{Ag}_8$  and crystallized four structural intermediates,  $\text{Ti}_1\text{Ag}_1$ ,  $\text{Ti}_2\text{Ag}_2$ ,  $\text{Ti}_2\text{Ag}_{2.6}$  and  $\text{Ti}_2\text{Ag}_4$ , by controlling synthesis conditions. Interestingly,  $\text{Ti}_2\text{Ag}_4$  was exactly identical to the  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$  unit in  $\text{Ti}_8\text{Ag}_8$ , thus providing a perfect cluster model for comparing the catalytic activity of different Ag sites. The  $\text{Ti}_8\text{Ag}_8$  cluster was found to be an excellent  $\text{eCO}_2\text{RR}$  catalyst, which exhibited high reactivity and selectivity to CO (92.33% FE at  $-0.9$  V vs. RHE), outperforming  $\text{Ti}_2\text{Ag}_4$ . The DFT method was used to calculate the free energy change of each elementary step in the conversion mechanism from  $\text{CO}_2$  to CO, and in the competing hydrogen evolution reaction (HER). It was demonstrated that the Ag centers located on  $\{\text{Ti}@Ag_2(\text{TC4A})\}$  could stabilize the  $^*\text{COOH}$  intermediates in the  $\text{CO}_2$  electroreduction better than those located on  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$ .

## Results and discussion

### Synthesis and characterization

The synthesis of  $\text{Ti}_8\text{Ag}_8$  was accomplished through a one-pot solvothermal reaction using  $\text{Ag}(\text{O}_2\text{CCF}_3)$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ , TC4A, and

$\text{IdcH}_2$  in a 2 mL solution of  $^i\text{PrOH}/\text{DMF}$  ( $v/v = 1:2$ ) at  $80^\circ\text{C}$  for 2 days. This reaction yielded yellow prismatic crystals with a high yield of 60%. The composition of  $\text{Ti}_8\text{Ag}_8$  was determined using electrospray ionization-mass spectrometry (ESI-MS), which revealed a +2 signal at  $m/z = 2663.46$ , corresponding to the species  $[\text{H}_3\text{NaTi}_8\text{Ag}_8\text{O}_2(\text{TC4A})_4(\text{Idc})_6(\text{PrO})_4]^{2+}$  (Fig. S33<sup>†</sup>). The molar ratio of Ti:Ag:Na in  $\text{Ti}_8\text{Ag}_8$  was determined through inductively coupled plasma (ICP) analysis (Table S2<sup>†</sup>), yielding a ratio of approximately 8:8:1, which is consistent with the findings from crystallography analysis. The geometrical structure of  $\text{Ti}_8\text{Ag}_8$  was found to be rather complicated, resembling a “hand basket”, which can be divided into two parts. The handle of the basket is composed of a core-shell  $\{\text{Ti}_4@Ag_8@(\text{TC4A})_4\}$  substructure (Fig. 2A), while the bottom of the basket is formed by one  $\{\text{Ti}_4\text{Na}(\text{Idc})_6\}$  substructure (Fig. 2B). The  $\{\text{Ti}_4@Ag_8(\text{TC4A})_4\}$  substructure can be further divided into two  $\{\text{Ti}@Ag_2(\text{TC4A})\}$  motifs (Fig. 2C) and one  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$  motif (Fig. 2D). Upon inspecting the structure of  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$ , it was observed that each of the two completely deprotonated TC4A molecules accommodated an apical  $\text{Ti}^{4+}$  ion within their lower-rim tetraphenolic pocket, which are further fused together through two  $\mu_2\text{-O}^{2-}$  to form  $\{\text{Ti}_2\text{O}_2@(\text{TC4A})_2\}$  units. Additionally, the two  $\text{Ti}^{4+}$  ions inside the cage exhibited octahedral  $\text{TiO}_6$  formations. The  $\text{Ag}_4$  array sandwiched between two calix entities formed a trapezium-like geometry. Among them, two exposed Ag(I) sites (Ag1 and Ag2) were located in an  $\text{O}_3\text{S}_2$  environment defined by two phenoxide, one  $\mu_2\text{-O}^{2-}$ , and two S (Ag–S: 2.558(2)–2.589(2) Å and Ag–O: 2.499(2)–2.645(2) Å), while the Ag3 and Ag4 sites were fully coordinated and embedded within the cluster. In the  $\{\text{Ti}@Ag_2(\text{TC4A})\}$  unit, TC4A accommodated the apical  $\text{Ti}^{4+}$  ion within its lower-rim tetraphenolic pocket, with two of the four S arms bridging to two  $\text{Ag}^{1+}$  ions. The four equivalent Ag(II) sites (Ag5–Ag8) were in an  $\text{O}_2\text{S}_2\text{N}$  environment defined by two phenoxide (Ag–O: 2.696(9)–2.894(2) Å), two S (Ag–S: 2.487(2)–2.573(8) Å), and one imidazole N. The Ag–O bonds were relatively long, suggesting weaker interactions. One  $\{\text{Ti}_2\text{O}_2@Ag_4(\text{TC4A})_2\}$  and two  $\{\text{Ti}@Ag_2@TC4A\}$  units were coupled together through four Ag–S bonds and six Ag–O bonds to form the  $\{\text{Ti}_4@Ag_8@(\text{TC4A})_4\}$  substructure. In the  $\{\text{Ti}_4\text{Na}(\text{Idc})_6\}$  substructure, the two Idc ligands at the bottom each bridged two  $\text{Ti}^{4+}$  ions to form two  $\{\text{Ti}_2(\text{Idc})\}$  units, which were further bridged by a  $\text{Na}^+$  ion to create a planar  $\{\text{Ti}_4\text{Na}(\text{Idc})_2\}$  layer. The other four protonated Idc ligands acted as bridges between the  $\{\text{Ti}@Ag_2\text{TC4A}\}$  and  $\{\text{Ti}_4\text{-Na}(\text{Idc})_2\}$  units. In this way, the two substructures of  $\{\text{Ti}_4@Ag_8@(\text{TC4A})_4\}$  and  $\{\text{Ti}_4\text{Na}(\text{Idc})_6\}$  were joined together by four Ag–N bonds (Ag–N: 2.220(5)–2.246(2) Å) to form the final  $\text{Ti}_8\text{Ag}_8$  cluster.

### Tracking of the assembly process of $\text{Ti}_8\text{Ag}_8$

To understand the formation of  $\text{Ti}_8\text{Ag}_8$ , tracking its evolution process by mass spectrometry was performed. Firstly, the structural formation could be conveniently probed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) of the crystalline samples of  $\text{Ti}_8\text{Ag}_8$  in the positive mode, using  $\text{CH}_2\text{Cl}_2$  as a solvent (Fig. 3A). The pattern showed abundant fragment signals. The most dominant  $m/z$  peak at 1993.7 was attributed to the  $[\text{HTi}_2\text{Ag}_4\text{O}_2(\text{TC4A})_2]^{1+}$



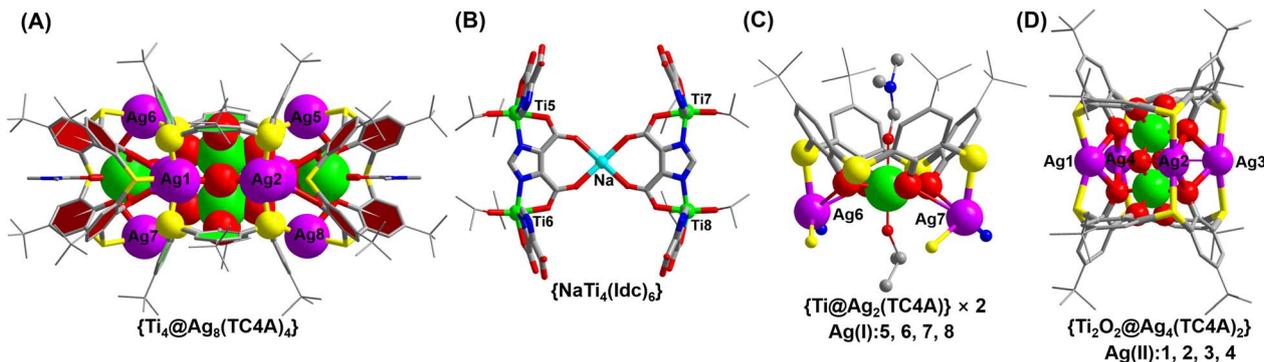


Fig. 2 Detailed local structures of  $\{\text{Ti}_4\text{Ag}_8(\text{TC4A})_4\}$  (A),  $\{\text{Ti}_4\text{Na}(\text{Idc})_6\}$  (B),  $\{\text{Ti@Ag}_2(\text{TC4A})\}$  (C) and  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  (D).

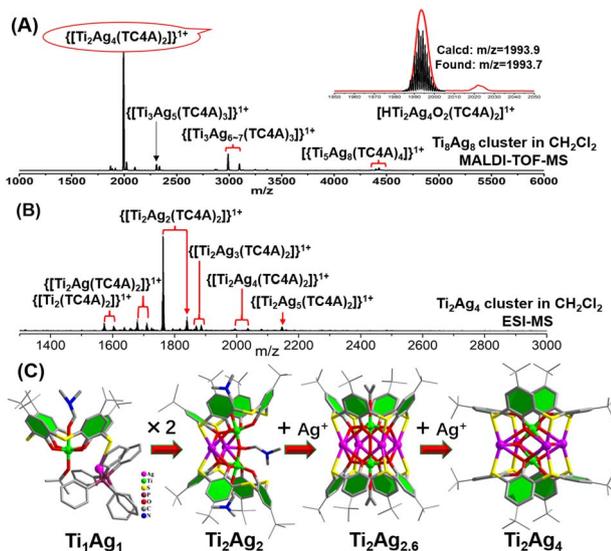


Fig. 3 (A) Positive-ion mode MALDI-TOF-MS of  $\text{Ti}_8\text{Ag}_8$  dissolved in  $\text{CH}_2\text{Cl}_2$ . Inset: zoomed-in experimental and simulated ESI-MS of  $[\text{HTi}_2\text{Ag}_4\text{O}_2(\text{TC4A})_2]^{1+}$ ; (B) positive-ion mode ESI-MS of  $\text{Ti}_2\text{Ag}_4$  dissolved in  $\text{CH}_2\text{Cl}_2$ . (C) Structures of the  $\text{TiAg}_1$ ,  $\text{Ti}_2\text{Ag}_2$ ,  $\text{Ti}_2\text{Ag}_{2.6}$  and  $\text{Ti}_2\text{Ag}_4$  clusters.

species, which corresponded to the  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  unit in  $\text{Ti}_8\text{Ag}_8$ . Interestingly, this intermediate could be crystallized and structurally resolved. The  $\text{Ti}_2\text{Ag}_4$  cluster was synthesized by the reaction of TC4A and  $\text{Ag}(\text{OAc})$  with  $\text{Ti}(\text{O}^i\text{Pr})_4$  in  $\text{CH}_3\text{CN}/\text{DMF}$ . Structure determination revealed that the structure of  $\text{Ti}_2\text{Ag}_4$  was exactly the same as that of the  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  unit in  $\text{Ti}_8\text{Ag}_8$ . This “core-shell” structure had a high chemical stability. One can see that only a peak corresponding to  $[\text{HTi}_2\text{Ag}_4\text{O}_2(\text{TC4A})_2]^{1+}$  was observed in the MALDI-TOF-MS of  $\text{Ti}_2\text{Ag}_4$  in  $\text{CH}_2\text{Cl}_2$ , indicating that the cluster retained its integrity in solution (Fig. S35<sup>†</sup>). However, under the hard ionization conditions of ESI-MS, the pattern of  $\text{Ti}_2\text{Ag}_4$  showed an abundance of cluster fragments (Fig. 3B). Signals corresponding to the units of  $\{\text{Ti}_2\text{@Ag}_{4-x}(\text{TC4A})_2\}^{1+}$  ( $x = 0-4$ ) can be found, which indicated that the four  $\text{Ag}^{1+}$  ions in  $\text{Ti}_2\text{Ag}_4$  could be gradually dropped. The removal of  $\text{Ag}^{1+}$  ions indicated that the  $\text{Ti}_2\text{Ag}_4$  cluster originated from the  $\{\text{Ti}_2\text{O}_2\text{@}(\text{TC4A})_2\}$  unit, whose surface abundance of S/O sites provided binding sites for the  $\text{Ag}^{1+}$  ions. The crystallography

data of structural intermediates  $\text{Ti}_1\text{Ag}_1$ ,  $\text{Ti}_2\text{Ag}_2$ , and  $\text{Ti}_2\text{Ag}_{2.6}$  help us precisely determine the structural model of the product generated upon fragmentation. These intermediates were all crystallized in the same system by a slight change in the reaction conditions. For  $\text{Ti}_1\text{Ag}_1$ , the TC4A unit kept one  $\text{Ti}^{4+}$  ion within the bowl, with one S arm binding to one  $\text{Ag}(\text{PPh}_3)_2$  unit. For  $\text{Ti}_2\text{Ag}_2$ , two  $\{\text{Ti@TC4A}\}$  units were bridged by one  $\mu_2\text{-O}^{2-}$  ion and two  $\text{Ag}^{1+}$  ions, forming an asymmetrical semi-closed cage.  $\text{Ti}_2\text{Ag}_{2.6}$  also contained a  $\{\text{Ti}_2\text{O@}(\text{TC4A})_2\}$  core, with a total number of 2.6  $\text{Ag}^{1+}$  ions embedded in the waist in a disordered manner.

In the ESI-MS of  $\text{Ti}_2\text{Ag}_4$ , a distinctive signal corresponding to  $[\text{Na}_2\text{Ti}_2\text{Ag}_5\text{O}_2(\text{TC4A})_2]^{1+}$  was observed. This signal was formed by the binding of  $\text{Ag}^{1+}$  to the  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  core, suggesting that the  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  could serve as a seed for further growth. The primary question at this point was whether  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  could be further transformed into  $\text{Ti}_8\text{Ag}_8$ . Remarkably, the crystal of  $\text{Ti}_8\text{Ag}_8$  can be directly obtained from the solvothermal reaction of  $\text{Ti}_2\text{Ag}_4$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ , and  $\text{IdcH}_2$  in  $^i\text{PrOH}/\text{DMF}$  at  $80^\circ\text{C}$  for 2 days. Fig. 4 illustrates the time-dependent ESI-MS analysis of the mother liquor at different time intervals during the reaction. In the initial stage, the signals in the low  $m/z$  region closely resembled those observed in the ESI-MS of  $\text{Ti}_2\text{Ag}_4$ . However, as the reaction progressed, new signals emerged in the high  $m/z$  region. Specifically, peaks corresponding to the units of  $[\text{H}_3\text{NaTi}_3\text{Ag}_8\text{O}_2(\text{TC4A})_3(\text{Idc})(^i\text{PrO})_2(\text{DMF})_2]^{2+}$  ( $m/z = 3633.70$ ) and  $[\text{HTi}_4\text{Ag}_8\text{O}_2(\text{TC4A})_4(\text{OH})]^{1+}$  ( $m/z = 3988.76$ ) were detected at 4 hours and 8 hours, respectively. These fragments can be regarded as a combination of one  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  unit and one or two  $\{\text{Ti@Ag}_2(\text{TC4A})\}$  units. At the 24 hour mark, a +2 peak of  $[\text{H}_3\text{NaTi}_6\text{Ag}_8\text{O}_2(\text{TC4A})_4(\text{Idc})_5(^i\text{PrO})_3]^{2+}$  ( $m/z = 2500.30$ ) was observed, which is formed by the  $\{\text{Ti}_4\text{@Ag}_8(\text{TC4A})_4\}$  substructure bridging  $\text{Ti}^{4+}$  with Idc ligands. After 48 hours of reaction, the ESI-MS results of the mother liquid exhibited a series of +2 peaks within the  $m/z$  range of 2600–2900. Among them, the prominent peaks at 1 g and 1 h were assigned to  $[\text{H}_3\text{Na}_2\text{Ti}_8\text{Ag}_8\text{O}_2(\text{TC4A})_4(\text{Idc})_6(^i\text{PrO})_5(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{H}_4\text{NaTi}_8\text{Ag}_8\text{O}_2(\text{TC4A})_4(\text{Idc})_6(^i\text{PrO})_6(\text{H}_2\text{O})]^{2+}$ , respectively, confirming the formation of the  $\text{Ti}_8\text{Ag}_8$  cluster. These findings clearly demonstrated that  $\text{Ti}_8\text{Ag}_8$  could be derived from the  $\{\text{Ti}_2\text{O}_2\text{@Ag}_4(\text{TC4A})_2\}$  unit, following a small-to-large assembly pathway.

Thus, with the aid of the crystal structures of intermediate clusters, cluster fragment information, and growth paths



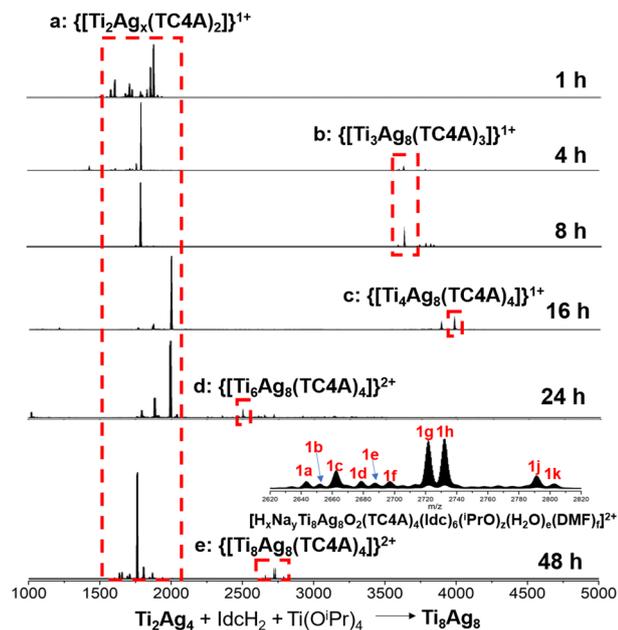


Fig. 4 Time-dependent ESI-MS in the range of  $m/z$  1000–5000 for the reaction of  $\text{Ti}_2\text{Ag}_4$ ,  $\text{Ti}(\text{O}i\text{Pr})_4$  and  $\text{IdcH}_2$  in  $i\text{PrOH}/\text{DMF}$  at  $80^\circ\text{C}$  at 1 h, 4 h, 8 h, 16 h, 24 h and 48 h.

revealed by time-dependent mass spectrometry, a comprehensive bottom-up evolution route for this series of TC4A-protected Ag/Ti bimetallic nanoclusters can be presented (Fig. S13<sup>†</sup>). In the initial stage, TC4A captures  $\text{Ti}^{4+}$  ions, leading to the formation of TOCs such as  $\{\text{Ti}@\text{TC4A}\}$  and  $\{\text{Ti}_2\text{O}_2@\text{TC4A}\}_2$ . The abundance of S/O sites on these TOCs enables them to act as substrates for the adsorption of  $\text{Ag}^{1+}$  ions, giving rise to the clusters of  $\text{Ti}_1\text{Ag}_1$ ,  $\text{Ti}_2\text{Ag}_2$ ,  $\text{Ti}_2\text{Ag}_{2.6}$  and  $\text{Ti}_2\text{Ag}_4$ . These structures can be separated through crystallization under different conditions. Moving forward, the  $\{\text{Ti}@\text{Ag}_2(\text{TC4A})\}$  and  $\{\text{Ti}_2\text{O}_2@\text{Ag}_4(\text{TC4A})_2\}$  units combine to form  $\{\text{Ti}_3@\text{Ag}_6(\text{TC4A})_3\}$  and  $\{\text{Ti}_4@\text{Ag}_8(\text{TC4A})_4\}$ . Subsequently,  $\text{Ti}^{4+}$  ions are bridged to the  $\{\text{Ti}_4@\text{Ag}_8(\text{TC4A})_4\}$  substructure by the  $\text{Idc}^{2-}$  ligands, culminating in the formation of the final  $\text{Ti}_8\text{Ag}_8$  cluster.

### Electrochemical $\text{CO}_2$ reduction

Generally, the coordination and geometry environments to the Ag sites in Ag-based catalysts have an important effect on their catalytic activity. However, due to the lack of structural models, accurately comparing the catalytic activity of different Ag sites at the molecular level proves to be challenging. Upon detailed comparison of the XPS data for the clusters of  $\text{Ti}_2\text{Ag}_4$  and  $\text{Ti}_8\text{Ag}_8$ , we observed a slight difference in the binding energies of the Ag species between them, with the binding energy of Ag in  $\text{Ti}_2\text{Ag}_4$  approximately 0.1 eV lower compared to that of Ag in  $\text{Ti}_8\text{Ag}_8$  (Fig. S26 and S27<sup>†</sup>). The subtle differences in their binding energies indicate variations in the local electronic structure and bonding characteristics between  $\text{Ti}_2\text{Ag}_4$  and  $\text{Ti}_8\text{Ag}_8$ . Geometrically, the active Ag atoms in  $\text{Ti}_8\text{Ag}_8$  could be divided into two nonequivalent groups: the four Ag(I) sites in two  $\{\text{Ti}@\text{Ag}_2(\text{TC4A})\}$  and the two exposed Ag(II) sites in  $\{\text{Ti}_2\text{O}_2@\text{Ag}_4(\text{TC4A})_2\}$ . The structural differences between  $\text{Ti}_8\text{Ag}_8$  and

$\text{Ti}_2\text{Ag}_4$  provided an ideal platform for an accurate comparison of  $\text{eCO}_2\text{RR}$  activities for those Ag sites.

The  $\text{eCO}_2\text{RR}$  activities of the  $\text{Ti}_8\text{Ag}_8$  and  $\text{Ti}_2\text{Ag}_4$  electrocatalysts were examined in a standard three-electrode configured H-type electrolytic cell with a 0.5 M  $\text{KHCO}_3$  electrolyte. Linear sweep voltammetry (LSV) studies showed that  $\text{Ti}_8\text{Ag}_8$  exhibited a much higher current density and a more positive onset potential in a  $\text{CO}_2$  flow electrolyzer, as compared with an Ar purged one, indicating that  $\text{Ti}_8\text{Ag}_8$  had  $\text{CO}_2$  reduction activity (Fig. 5A). The cyclic voltammetry (CV) studies of  $\text{Ti}_8\text{Ag}_8$  in a proton-deficient organic solution showed similar results (Fig. S41<sup>†</sup>). For comparison, the LSV of  $\text{Ti}_2\text{Ag}_4$  exhibits much lower current density. Fig. 5B compares the FE of the CO formation for the two clusters. Only CO and  $\text{H}_2$  were detected by gas chromatography. No other liquid product had been formed according to the  $^1\text{H}$  NMR spectra.  $\text{Ti}_8\text{Ag}_8$  exhibited a higher  $\text{FE}_{\text{CO}}$  than  $\text{Ti}_2\text{Ag}_4$  over the selected potential range from  $-0.6$  V to  $-1.2$  V. It achieved the maximum  $\text{FE}_{\text{CO}}$  of 92.33% at  $-0.9$  V, which was much higher than the corresponding value of 69.87% for  $\text{Ti}_2\text{Ag}_4$ . The CO partial current density ( $J_{\text{CO}}$ ) for the two clusters was also calculated (Fig. 5C), and the  $J_{\text{CO}}$  of  $\text{Ti}_8\text{Ag}_8$  reached  $23.46 \text{ mA cm}^{-2}$  at  $-1.2$  V vs. RHE, which was at least 2.5 times larger than that of  $\text{Ti}_2\text{Ag}_4$  ( $9.50 \text{ mA cm}^{-2}$ ). This indicates an improved catalytic activity and selectivity of  $\text{Ti}_8\text{Ag}_8$  for the electrocatalytic  $\text{CO}_2\text{RR}$ .

To find the underlying reasons for the performance differences between the two clusters, the Tafel slope was used to characterize their reaction kinetics in the electrolyte. The Tafel slope of  $\text{Ti}_8\text{Ag}_8$  was found to be smaller than that of  $\text{Ti}_2\text{Ag}_4$ , indicating that  $\text{Ti}_8\text{Ag}_8$  had more favorable reaction kinetics of CO formation, which may be due to the more efficient charge transfer and larger active surface of  $\text{Ti}_8\text{Ag}_8$  during the catalytic

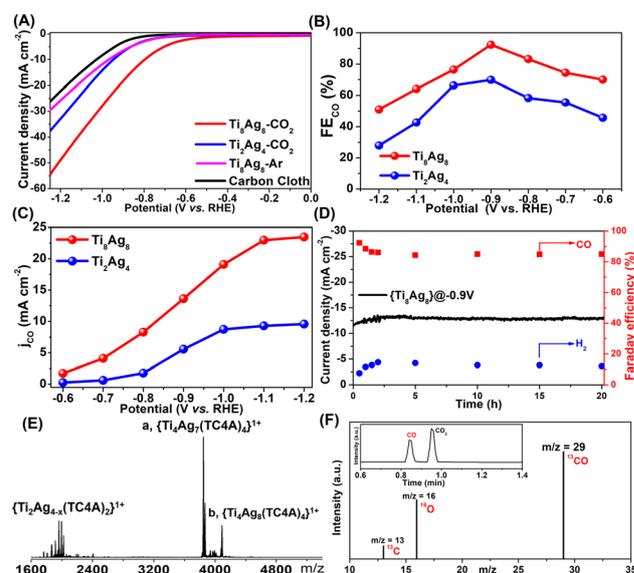


Fig. 5 (A) LSV curves in  $\text{CO}_2$ -saturated 0.5 M  $\text{KHCO}_3$  solution; (B) the  $\text{FE}_{\text{CO}}$  values at different applied potentials in  $\text{CO}_2$ -saturated 0.5 M  $\text{KHCO}_3$  solution; (C) the  $\text{CO}$  partial current density ( $J_{\text{CO}}$ ); (D) stability tests of the electrocatalysts for  $\text{CO}_2$  reduction; (E) ESI-MS of  $\text{Ti}_8\text{Ag}_8$  electrocatalysts after reaction; (F) GC-MS of  $^{13}\text{CO}$  recorded under a  $^{13}\text{CO}_2$  atmosphere.



process (Fig. S45<sup>†</sup>). To verify this, the electrochemically active surface area (ECSA) was characterized (Fig. S46<sup>†</sup>). By plotting  $\Delta J/2 = (J_a - J_c)/2$  at  $-0.12$  V vs. RHE against the scan rate, the calculated electrochemical  $C_{dl}$  of  $\text{Ti}_8\text{Ag}_8$  is  $6.18 \text{ mF cm}^{-2}$ , higher than that of  $\text{Ti}_2\text{Ag}_4$  ( $5.54 \text{ mF cm}^{-2}$ ), which indicated that  $\text{Ti}_8\text{Ag}_8$  had a faster reaction speed in the  $\text{CO}_2\text{RR}$  process and had more active sites to contact with electrolyte.

The electrochemical stability of  $\text{Ti}_8\text{Ag}_8$  was evaluated with chronopotentiometry at  $-0.9$  V vs. RHE. The current density and  $\text{FE}_{\text{CO}}$  kept almost stable during 20 h continuous electrolysis, indicative of the excellent reaction stability of  $\text{Ti}_8\text{Ag}_8$  (Fig. 5D). We also recovered the catalyst after the reaction and conducted ESI-MS measurements. The ESI-MS pattern showed two strong signals that corresponded to  $[\text{HTi}_4\text{Ag}_8\text{O}_2(\text{TC4A})_4(-^i\text{PrO})_2(\text{H}_2\text{O})]^{1+}$  and  $[\text{H}_2\text{Ti}_4\text{Ag}_7\text{O}_2(\text{TC4A})_4]^{1+}$ . This indicated that the core structure of  $\{\text{Ti}_4@_{\text{Ag}_8}(\text{TC4A})_4\}$  was still stable (Fig. 5E). Additionally, EDS analysis of the catalyst after the reaction indicated that the Ti and Ag elements remained in a 1 : 1 ratio (Fig. S50<sup>†</sup>). XPS analysis showed no significant change in the binding energy of the Ag element in the catalyst before and after the reaction, signifying the preservation of its coordination environment (Fig. S51<sup>†</sup>). Transmission electron microscopy (TEM) revealed the presence of clusters in the solution as discrete particles, with an average particle size of approximately 3 nanometers, consistent with the cluster size measured by SCXRD, further confirming the stability of the catalyst (Fig. S52<sup>†</sup>). To further determine the C origin of the products, an isotopic experiment was performed under similar catalytic conditions, but by using  $^{13}\text{CO}_2$  as the C source. The production of  $^{13}\text{CO}$  ( $m/z = 29$ ) was then studied by using GC-MS, which showed that the generated CO came from  $\text{CO}_2$  (Fig. 5F).

DFT calculations were performed to investigate the reactivity of the two clusters. The calculation models,  $\text{Ti}_8\text{Ag}_8\text{-m}$  and  $\text{Ti}_2\text{Ag}_4\text{-m}$ , were optimized based on the crystal structures, by simplifying  $^i\text{Bu}$  groups of benzene rings to H atoms and  $^i\text{PrO}$  groups to MeO groups. In addition, the  $\text{Ti}_4\text{Na}(\text{Idc})_6$  groups in  $\text{Ti}_8\text{Ag}_8$  were removed to create active sites to build  $\text{Ti}_4\text{Ag}_8\text{-m}$ . The Gibbs free energy diagrams of the  $\text{CO}_2\text{RR}$  and HER are shown in Fig. 6. The proposed pathway for the  $\text{CO}_2$  reduction to CO was  $\text{CO}_2(\text{g}) \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow \text{CO}(\text{g})$ . The calculated Gibbs free energies of the  $\text{CO}_2\text{RR}$  revealed that the formation of  $^*\text{COOH}$  was the rate determining step. The Gibbs free energy that was calculated for the formation of  $^*\text{COOH}$  on the Ag site on the  $\{\text{Ti}@_{\text{Ag}_2}(\text{TC4A})\}$  unit in  $\text{Ti}_4\text{Ag}_8\text{-m}$  was 1.01 eV, which was much lower than the corresponding Gibbs free energy for the  $\{\text{Ti}@_{\text{Ag}_2}(\text{TC4A})\}$  unit in  $\text{Ti}_2\text{Ag}_4\text{-m}$  (1.42 eV). This result suggested that the Ag sites on  $\{\text{Ti}@_{\text{Ag}_2}(\text{TC4A})\}$  were more energetically favorable for the catalysis of the  $\text{CO}_2$  conversion to CO than those on  $\{\text{Ti}_2\text{O}_2@_{\text{Ag}_4}(\text{TC4A})_2\}$ . The Gibbs free energies of the adsorptions were also calculated to illustrate the HER reactivities of  $\text{Ti}_8\text{Ag}_8$  and  $\text{Ti}_2\text{Ag}_4$ . The high Gibbs free energies of the  $\text{H}^*$  adsorption revealed that both  $\text{Ti}_8\text{Ag}_8$  (1.63 eV) and  $\text{Ti}_2\text{Ag}_4$  (2.00 eV) were unfavorable in the formation of  $\text{H}_2$ . By comparing the Gibbs free energy diagrams of the  $\text{CO}_2\text{RR}$  and HER, we found that  $\text{Ti}_4\text{Ag}_8\text{-m}$  had a higher selectivity for the CO formation, as compared with  $\text{Ti}_2\text{Ag}_4\text{-m}$ .

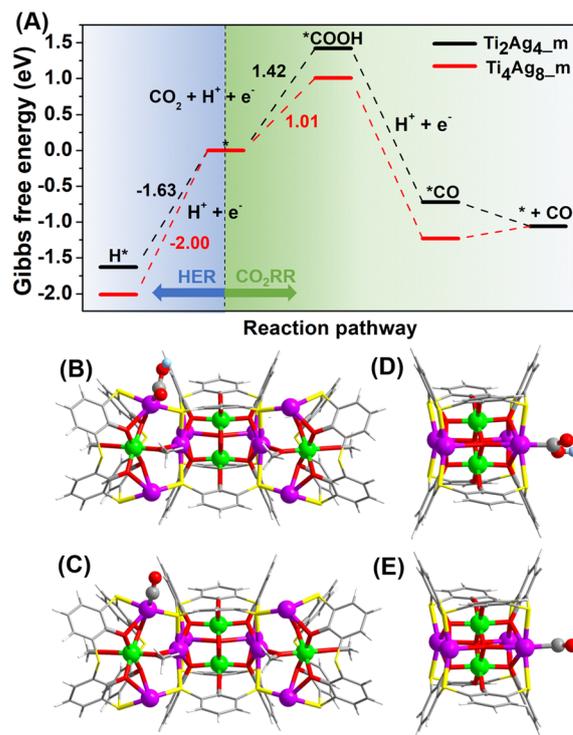


Fig. 6 (A) Free energy diagrams for the  $\text{CO}_2\text{RR}$  and HER on  $\text{Ti}_4\text{Ag}_8\text{-m}$  (red) and  $\text{Ti}_2\text{Ag}_4\text{-m}$  (black); the calculation optimized structures of COOH adsorbed on  $\text{Ti}_4\text{Ag}_8\text{-m}$  (B) and  $\text{Ti}_2\text{Ag}_4\text{-m}$  (C); the calculation optimized structures of CO adsorbed on  $\text{Ti}_4\text{Ag}_8\text{-m}$  (D) and  $\text{Ti}_2\text{Ag}_4\text{-m}$  (E).

To further unravel the mystery of the differences in catalytic performances, the d-band center ( $\varepsilon_d$ ) of the Ag sites in  $\text{Ti}_4\text{Ag}_8\text{-m}$  and  $\text{Ti}_2\text{Ag}_4\text{-m}$  was calculated to evaluate their reactivity as active sites, since  $\varepsilon_d$  has been proposed as a benchmark descriptor for transition metal reactivity.<sup>47</sup> Our calculations showed markedly different electronic properties for the two nonequivalent Ag sites (Fig. S53<sup>†</sup>). In  $\text{Ti}_4\text{Ag}_8\text{-m}$ , the  $\varepsilon_d$  value of the four Ag(i) sites in  $\{\text{Ti}@_{\text{Ag}_2}(\text{TC4A})\}$  is  $-0.34$  eV, which is 0.06 eV higher than that of the two surface-exposed Ag(ii) sites in  $\{\text{Ti}_2\text{O}_2@_{\text{Ag}_4}(\text{TC4A})_2\}$ . As a comparison, the four Ag(ii) sites in  $\text{Ti}_2\text{Ag}_4\text{-m}$  also exhibit a lower  $\varepsilon_d$  value of  $-0.44$  eV, suggesting that the Ag(i) sites in  $\{\text{Ti}@_{\text{Ag}_2}(\text{TC4A})\}$  are more active than Ag(ii) in the  $\{\text{Ti}_2\text{O}_2@_{\text{Ag}_4}(\text{TC4A})_2\}$  unit. Furthermore, the projected density of states (PDOS) showed that the active Ag(i) sites in  $\text{Ti}_4\text{Ag}_8\text{-m}$  underwent a stronger hybridization with the adsorbed COOH and CO than those in  $\text{Ti}_2\text{Ag}_4\text{-m}$  (Fig. S55<sup>†</sup>). It is important to stress that the results from the DFT calculations were consistent with the corresponding experimental results. The combined theoretical and experimental investigations have thereby resulted in a fundamental understanding of the  $\text{CO}_2\text{RR}$  mechanism involving different Ag active sites on the Ag/Ti bimetallic clusters.

## Conclusions

In summary, we have for the first time compared  $\text{eCO}_2\text{RR}$  atomic-level activities for different Ag sites on Ag-based catalysts. We synthesized and characterized an atomically precise



bimetallic  $\text{Ti}_8\text{Ag}_8$  cluster using a calixarene-protected Ti-oxo core as a substrate for loading  $\text{Ag}^{1+}$  ions. The  $\text{Ti}_8\text{Ag}_8$  clusters contain two groups of surface-exposed Ag catalytic sites, located on the  $\{\text{Ti}_2\text{O}_2@\text{Ag}_4(\text{TC4A})_2\}$  and  $\{\text{Ti}@\text{Ag}_2(\text{TC4A})\}$  units, respectively. We traced the assembly path of  $\text{Ti}_8\text{Ag}_8$  and successfully isolated  $\{\text{Ti}_2\text{O}_2@\text{Ag}_4(\text{TC4A})_2\}$  in the  $\text{Ti}_2\text{Ag}_4$  cluster alone. The  $\text{eCO}_2\text{RR}$  test showed that both clusters were good electrocatalysts for the reduction of  $\text{CO}_2$  to CO, but the performance of  $\text{Ti}_8\text{Ag}_8$  was significantly superior to that of  $\text{Ti}_2\text{Ag}_4$ . Also, DFT was used to calculate the free energy change of each elementary step for converting  $\text{CO}_2$  into CO and the competing HER, revealing the difference in activity between the Ag sites on the  $\{\text{Ti}@\text{Ag}_2(\text{TC4A})\}$  and  $\{\text{Ti}_2\text{O}_2@\text{Ag}_4(\text{TC4A})_2\}$  units. This work clearly demonstrated that subtle changes in the coordination geometry of catalytic sites can greatly affect the catalytic performance; thus, the attainment of the atomic structures of nanoclusters is of critical importance, which could provide a valuable reference for rational design of cluster structures to achieve efficient catalysis.

## Data availability

The data that support the findings of this study are available in the main text and the ESI.†

## Author contributions

C. L. and J. Y. supervised the project and conceived the idea. Y. Q. T. carried out synthesis, characterization and electrochemical experiments of clusters. C. L. and Y. Q. T. wrote the manuscript. L. L. W. undertook the calculations for this article. All authors discussed the experimental results.

## Conflicts of interest

There are no conflicts of interest to declare.

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