Chemical Science

EDGE ARTICLE



Cite this: Chem. Sci., 2023, 14, 10212

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 1st June 2023 Accepted 4th September 2023

DOI: 10.1039/d3sc02793g

rsc.li/chemical-science

Introduction

The electrochemical CO₂ reduction reaction (eCO₂RR) offers a promising approach for the conversion of CO₂ into valuable chemical fuels.^{1,2} Ag-based nanomaterials have gained significant attention as electrocatalysts for the eCO₂RR, demonstrating remarkable selectivity towards CO generation.³⁻⁶ Despite substantial advancements in the synthesis of monodisperse Ag nanoparticles with enhanced catalytic activity, their surface structures remain challenging to precisely characterize and define.^{7,8} 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



Yi-Qi Tian, Wen-Lei Mu, Lin-Lin Wu,* Xiao-Yi Yi, 🕩 Jun Yan 🕩 * and Chao Liu 🕩 *

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 Ag¹⁺ ions, leading to the successful synthesis of a unique Ag/Ti bimetallic nanocluster denoted as Ti₈Ag₈. This nanocluster exhibits multiple surface-exposed Ag sites and possesses a distinctive "core-shell" structure, consisting of a {Ti₄@Ag₈(TC4A)₄} core housing a {Ti₂O₂@Aq₄(TC4A)₂} motif and two {Ti@Aq₂(TC4A)} motifs. To enable a comprehensive analysis, we also prepared a Ti_2Ag_4 cluster with the same $\{Ti_2O_2@Ag_4(TC4A)_2\}$ structure found within Ti_8Ag_8 . The structural disparities between Ti₈Ag₈ and Ti₂Ag₄ provide an excellent platform for a comparison of catalytic activity at different Ag sites. Remarkably, Ti₈Ag₈ exhibits exceptional performance in the electroreduction of CO₂ (eCO₂RR), showcasing a CO faradaic efficiency (FE_{CO}) of 92.33% at -0.9 V vs. RHE, surpassing the FE_{CO} of Ti₂Ag₄ (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@Ag₂(TC4A)} possess a higher ε_{d} value compared to those at {Ti₂O₂@Ag₄(TC4A)₂}, enhancing the stabilization of the *COOH intermediate during the eCO₂RR. This study provides valuable insights into the accurate identification of catalytic sites in bimetallic nanoclusters and opens up promising avenues for efficient CO₂ reduction catalyst design.

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

In the realm of Ag catalysis, pre-transition metal oxides (e.g., TiO_2) have gained significant prominence as substrates for the stabilization of Ag nanoparticles featuring surface-exposed catalytic sites.9-13 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-TiO₂ materials.¹⁴ By establishing a close association between titanium-oxo clusters (TOCs) and TiO₂,¹⁵⁻²⁴ Ag-doped TOCs can be considered as molecular counterparts of bulk Ag-TiO₂ nanomaterials. Previous studies have successfully synthesized certain crystalline Ag-TOCs,²⁵⁻³¹ 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-

View Article Online

View Journal | View Issue

Hunan Provincial Key Laboratory of Chemical Power Sources, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, Hunan, P. R. China. E-mail: chaoliu@csu.edu.cn

[†] Electronic supplementary information (ESI) available: X-ray crystallographic file in CIF format, and full experimental and computational details. CCDC 2262773-2262777. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3sc02793g



groups, has caught our attention, the oligomers of which are favourable to form typical tetranuclear M_4 -TC4A units to fabricate high-nuclearity clusters.^{32–37} According to soft and hard acid/base theory, the Ti⁴⁺ ion is a hard Lewis acid with a strong coordination affinity for phenolic oxygen, while 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 Ti⁴⁺ and S-philic 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 TOCs³⁸⁻⁴⁰ and Ag nanoclusters,^{41–46} the synthesis of TC4Astabilized 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 CO₂ electroreduction. Through the synergistic assembly of TC4A and 4,5-imidazoledicarboxylic acid (IdcH₂), we synthesized the first calixarene-protected Ag^{1+}/Ti^{4+} bimetallic cluster of Ti₈Ag₈ with the formula of [HNaTi₈Ag₈- $O_2(TC4A)_4(HIdc)_6(^{i}PrO)_{10}(DMF)_2(H_2O)]$ (Fig. 1). The big cluster has a composite structure with two kinds of surface-exposed Ag sites, including the Ag(1) sites in the two {Ti@Ag₂(TC4A)} and the Ag(II) sites in the $\{Ti_2O_2@Ag_4(TC4A)_2\}$ units. We have carefully studied the formation path of Ti₈Ag₈ and crystallized four structural intermediates, Ti₁Ag₁, Ti₂Ag₂, Ti₂Ag_{2,6} and Ti₂Ag₄, by controlling synthesis conditions. Interestingly, Ti_2Ag_4 was exactly identical to the $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$ unit in Ti_8Ag_8 , thus providing a perfect cluster model for comparing the catalytic activity of different Ag sites. The Ti₈Ag₈ cluster was found to be an excellent eCO₂RR catalyst, which exhibited high reactivity and selectivity to CO (92.33% FE at -0.9 V vs. RHE), outperforming Ti_2Ag_4 . The DFT method was used to calculate the free energy change of each elementary step in the conversion mechanism from CO₂ to CO, and in the competing hydrogen evolution reaction (HER). It was demonstrated that the Ag centers located on {Ti@Ag2(TC4A)} could stabilize the *COOH intermediates in the CO₂ electroreduction better than those located on $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$.

Results and discussion

Synthesis and characterization

The synthesis of Ti_8Ag_8 was accomplished through a one-pot solvothermal reaction using $Ag(O_2CCF_3)$, $Ti(O^iPr)_4$, TC4A, and

IdcH₂ in a 2 mL solution of ⁱPrOH/DMF (v/v = 1:2) at 80 °C for 2 days. This reaction yielded yellow prismatic crystals with a high yield of 60%. The composition of Ti₈Ag₈ was determined using electrospray ionization-mass spectrometry (ESI-MS), which revealed a +2 signal at m/z = 2663.46, corresponding to the species $[H_3NaTi_8Ag_8O_2(TC4A)_4(Idc)_6(^iPrO)_4]^{2+}$ (Fig. S33[†]). The molar ratio of Ti: Ag: Na in Ti8Ag8 was determined through inductively coupled plasma (ICP) analysis (Table S2[†]), yielding a ratio of approximately 8:8:1, which is consistent with the findings from crystallography analysis. The geometrical structure of Ti₈Ag₈ 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 {Ti₄@Ag₈@(TC4A)₄} substructure (Fig. 2A), while the bottom of the basket is formed by one $\{Ti_4Na(Idc)_6\}$ substructure (Fig. 2B). The $\{Ti_4(a)Ag_8(TC4A)_4\}$ substructure can be further divided into two {Ti@Ag2(TC4A)} motifs (Fig. 2C) and one {Ti₂O₂@Ag₄(TC4A)₂} motif (Fig. 2D). Upon inspecting the structure of $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$, it was observed that each of the two completely deprotonated TC4A molecules accommodated an apical Ti⁴⁺ ion within their lowerrim tetraphenolic pocket, which are further fused together through two μ_2 -O²⁻ to form {Ti₂O₂@(TC4A)₂} units. Additionally, the two Ti⁴⁺ ions inside the cage exhibited octahedral TiO₆ formations. The Ag4 array sandwiched between two calix entities formed a trapezium-like geometry. Among them, two exposed Ag(1) sites (Ag1 and Ag2) were located in an O_3S_2 environment defined by two phenoxide, one μ_2 -O²⁻, 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 {Ti@Ag₂(TC4A)} unit, TC4A accommodated the apical Ti^{4+} ion within its lower-rim tetraphenolic pocket, with two of the four S arms bridging to two Ag^{1+} ions. The four equivalent Ag(n) sites (Ag5-Ag8) were in an O₂S₂N 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 {Ti2O2@Ag4(TC4A)2} and two {Ti@Ag2@TC4A} units were coupled together through four Ag–S bonds and six Ag–O bonds to form the $\{Ti_4 \otimes Ag_8 \otimes (TC4A)_4\}$ substructure. In the ${Ti_4Na(Idc)_6}$ substructure, the two Idc ligands at the bottom each bridged two Ti⁴⁺ ions to form two ${Ti_2(Idc)}$ units, which were further bridged by a Na⁺ ion to create a planar {Ti₄Na(Idc)₂} layer. The other four protonated Idc ligands acted as bridges between the {Ti@Ag2TC4A} and {Ti4- $Na(Idc)_2$ units. In this way, the two substructures of ${Ti_4@Ag_8(TC4A_{4}$ and $\{Ti_{4}Na(Idc)_{6}\}$ were joined together by four Ag-N bonds (Ag–N: 2.220(5)–2.246(2) Å) to form the final Ti_8Ag_8 cluster.

Tracking of the assembly process of Ti₈Ag₈

To understand the formation of Ti_8Ag_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 Ti_8Ag_8 in the positive mode, using CH₂Cl₂ as a solvent (Fig. 3A). The pattern showed abundant fragment signals. The most dominant m/zpeak at 1993.7 was attributed to the $[HTi_2Ag_4O_2(TC4A)_2]^{1+}$ **Chemical Science**



 $\label{eq:Fig.2} \mbox{ Detailed local structures of $$Ti_4@Ag_8(TC4A)_4$ (A), $$Ti_4Na(ldc)_6$ (B), $$Ti_aAg_2(TC4A)$ (C) and $$Ti_2O_2@Ag_4(TC4A)_2$ (D) and $$Ti_2O_2@Ag_4(TC4A)_4$ (D) a$



Fig. 3 (A) Positive-ion mode MALDI-TOF-MS of Ti_8Ag_8 dissolved in CH_2Cl_2 . Inset: zoomed-in experimental and simulated ESI-MS of $[HTi_2Ag_4O_2(TC4A)_2]^{1+}$; (B) positive-ion mode ESI-MS of Ti_2Ag_4 dissolved in CH_2Cl_2 . (C) Structures of the TiAg, Ti_2Ag_2 , $Ti_2Ag_{2,6}$ and Ti_2Ag_4 clusters.

species, which corresponded to the ${Ti_2O_2(aAg_4(TC4A)_2)}$ unit in Ti₈Ag₈. Interestingly, this intermediate could be crystallized and structurally resolved. The Ti_2Ag_4 cluster was synthesized by the reaction of TC4A and Ag(OAc) with Ti(O¹Pr)₄ in CH₃CN/DMF. Structure determination revealed that the structure of Ti_2Ag_4 was exactly the same as that of the ${Ti_2O_2@Ag_4(TC4A)_2}$ unit in Ti₈Ag₈. This "core-shell" structure had a high chemical stability. One can see that only a peak corresponding to [HTi₂Ag₄O₂(- $TC4A_{2}^{1+}$ was observed in the MALDI-TOF-MS of $Ti_{2}Ag_{4}$ in CH₂Cl₂, indicating that the cluster retained its integrity in solution (Fig. S35[†]). However, under the hard ionization conditions of ESI-MS, the pattern of Ti₂Ag₄ showed an abundance of cluster fragments (Fig. 3B). Signals corresponding to the units of $\{Ti_2 (Ag_{4-x}(TC4A)_2)\}$ (x = 0-4) can be found, which indicated that the four Ag^{1+} ions in Ti_2Ag_4 could be gradually dropped. The removal of Ag¹⁺ ions indicated that the Ti₂Ag₄ cluster originated from the {Ti₂O₂@(TC4A)₂} unit, whose surface abundance of S/O sites provided binding sites for the Ag¹⁺ ions. The crystallography

data of structural intermediates Ti_1Ag_1 , Ti_2Ag_2 , and $Ti_2Ag_{2.6}$ 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 Ti_1Ag_1 , the TC4A unit kept one Ti^{4+} ion within the bowl, with one S arm binding to one Ag(PPh_3)₂ unit. For Ti_2Ag_2 , two {Ti@TC4A} units were bridged by one μ_2 -O²⁻ ion and two Ag¹⁺ ions, forming an asymmetrical semi-closed cage. $Ti_2Ag_{2.6}$ also contained a { $Ti_2O@(TC4A)_2$ } core, with a total number of 2.6 Ag¹⁺ ions embedded in the waist in a disordered manner.

In the ESI-MS of Ti₂Ag₄, a distinctive signal corresponding to $[Na_2Ti_2Ag_5O_2(TC4A)_2]^{1+}$ was observed. This signal was formed by the binding of Ag^{1+} to the $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$ core, suggesting that the $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$ could serve as a seed for further growth. The primary question at this point was whether {Ti₂- $O_2(a)Ag_4(TC4A)_2$ could be further transformed into Ti_8Ag_8 . Remarkably, the crystal of Ti₈Ag₈ can be directly obtained from the solvothermal reaction of Ti_2Ag_4 , $Ti(O^iPr)_4$, and $IdcH_2$ in ¹PrOH/DMF at 80 °C for 2 days. Fig. 4 illustrates the timedependent 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 Ti₂Ag₄. However, as the reaction progressed, new signals emerged in the high m/z region. Specifically, peaks corresponding to the units of $[H_3NaTi_3Ag_8O_2(TC4A)_3(Idc)(^iPrO)_2(DMF)_2]^+$ (m/ z = 3633.70 and $[HTi_4Ag_8O_2(TC4A)_4(OH)_2]^+$ (m/z = 3988.76) were detected at 4 hours and 8 hours, respectively. These fragments can be regarded as a combination of one $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$ unit and one or two {Ti@Ag₂(TC4A)} units. At the 24 hour mark, a +2 peak of $[H_3NaTi_6Ag_8O_2(TC4A)_4(HIdc)_5(^{1}PrO)_3]^{2+}$ $(m/z) = (m/z)^{2+}$ 2500.30) was observed, which is formed by the $\{Ti_4 (a) Ag_8 (TC4A)_4\}$ substructure bridging Ti4+ 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 $[H_3Na_2Ti_8Ag_8O_2(TC4A)_4(Idc)_6(^{i}PrO)_5(H_2O)_2]^{2+}$ and to $[H_4NaTi_8Ag_8O_2(TC4A)_4(Idc)_6(^{i}PrO)_6(H_2O)]^{2+}$, respectively, confirming the formation of the Ti₈Ag₈ cluster. These findings clearly demonstrated that Ti₈Ag₈ could be derived from the {Ti₂O₂@- $Ag_4(TC4A)_2$ 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

8



Fig. 4 Time-dependent ESI-MS in the range of m/z 1000–5000 for the reaction of Ti₂Ag₄, Ti(OⁱPr)₄ and IdcH₂ in ⁱPrOH/DMF at 80 °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[†]). In the initial stage, TC4A captures Ti⁴⁺ ions, leading to the formation of TOCs such as {Ti@(TC4A)} and {Ti₂O₂@(TC4A)₂}. The abundance of S/O sites on these TOCs enables them to act as substrates for the adsorption of Ag¹⁺ ions, giving rise to the clusters of Ti₁Ag₁, Ti₂Ag₂, Ti₂Ag_{2.6} and Ti₂Ag₄. These structures can be separated through crystallization under different conditions. Moving forward, the {Ti@Ag₂(TC4A)} and {Ti₂-O₂@Ag₄(TC4A)₂} units combine to form {Ti₃@Ag₆(TC4A)₃} and {Ti₄@Ag₈(TC4A)₄}. Subsequently, Ti⁴⁺ ions are bridged to the {Ti₄@Ag₈(TC4A)₄} substructure by the Idc²⁻ ligands, culminating in the formation of the final Ti₈Ag₈ cluster.

Electrochemical CO₂ 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 Ti_2Ag_4 and Ti_8Ag_8 , we observed a slight difference in the binding energies of the Ag species between them, with the binding energy of Ag in Ti_2Ag_4 approximately 0.1 eV lower compared to that of Ag in Ti_8Ag_8 (Fig. S26 and S27[†]). The subtle differences in their binding energies indicate variations in the local electronic structure and bonding characteristics between Ti_2Ag_4 and Ti₈Ag₈. Geometrically, the active Ag atoms in Ti₈Ag₈ could be divided into two nonequivalent groups: the four Ag(1) sites in two {Ti@Ag₂(TC4A)} and the two exposed Ag(II) sites in {Ti₂- $O_2(aAg_4(TC4A)_2)$. The structural differences between Ti_8Ag_8 and

 Ti_2Ag_4 provided an ideal platform for an accurate comparison of eCO_2RR activities for those Ag sites.

The eCO2RR activities of the Ti8Ag8 and Ti2Ag4 electrocatalysts were examined in a standard three-electrode configured H-type electrolytic cell with a 0.5 M KHCO₃ electrolyte. Linear sweep voltammetry (LSV) studies showed that Ti₈Ag₈ exhibited a much higher current density and a more positive onset potential in a CO₂ flow electrolyzer, as compared with an Ar purged one, indicating that Ti₈Ag₈ had CO₂ reduction activity (Fig. 5A). The cyclic voltammetry (CV) studies of Ti₈Ag₈ in a proton-deficient organic solution showed similar results (Fig. S41[†]). For comparison, the LSV of Ti2Ag4 exhibits much lower current density. Fig. 5B compares the FE of the CO formation for the two clusters. Only CO and H₂ were detected by gas chromatography. No other liquid product had been formed according to the ¹H NMR spectra. Ti₈Ag₈ exhibited a higher FE_{CO} than Ti₂Ag₄ over the selected potential range from -0.6 V to -1.2 V. It achieved the maximum FE_{CO} of 92.33% at -0.9 V, which was much higher than the corresponding value of 69.87% for Ti₂Ag₄. The CO partial current density (I_{CO}) for the two clusters was also calculated (Fig. 5C), and the J_{CO} of Ti₈Ag₈ reached 23.46 mA cm⁻² at -1.2 V vs. RHE, which was at least 2.5 times larger than that of Ti_2Ag_4 (9.50 mA cm⁻²). This indicates an improved catalytic activity and selectivity of Ti₈Ag₈ for the electrocatalytic CO₂RR.

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 Ti_8Ag_8 was found to be smaller than that of Ti_2Ag_4 , indicating that Ti_8Ag_8 had more favorable reaction kinetics of CO formation, which may be due to the more efficient charge transfer and larger active surface of Ti_8Ag_8 during the catalytic



Fig. 5 (A) LSV curves in CO₂-saturated 0.5 M KHCO₃ solution; (B) the FE_{CO} values at different applied potentials in CO₂-saturated 0.5 M KHCO₃ solution; (C) the CO partial current density (J_{CO}); (D) stability tests of the electrocatalysts for CO₂ reduction; (E) ESI-MS of Ti₈Ag₈ electrocatalysts after reaction; (F) GC-MS of ¹³CO recorded under a ¹³CO₂ atmosphere.

process (Fig. S45[†]). To verify this, the electrochemically active surface area (ECSA) was characterized (Fig. S46[†]). By plotting $\Delta J/2 = (J_a - J_c)/2$ at -0.12 V vs. RHE against the scan rate, the calculated electrochemical $C_{\rm dl}$ of **Ti₈Ag₈** is 6.18 mF cm⁻², higher than that of **Ti₂Ag₄** (5.54 mF cm⁻²), which indicated that **Ti₈Ag₈** had a faster reaction speed in the CO₂RR process and had more active sites to contact with electrolyte.

The electrochemical stability of Ti₈Ag₈ was evaluated with chronopotentiometry at -0.9 V vs. RHE. The current density and FE_{CO} kept almost stable during 20 h continuous electrolysis, indicative of the excellent reaction stability of Ti₈Ag₈ (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 [HTi₄Ag₈O₂(TC4A)₄(-ⁱPrO)₂(H₂O)]¹⁺ and [H₂Ti₄Ag₇O₂(TC4A)₄]¹⁺. This indicated that the core structure of $\{Ti_4 (a)Ag_8(TC4A)_4\}$ 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[†]). 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[†]). 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[†]). To further determine the C origin of the products, an isotopic experiment was performed under similar catalytic conditions, but by using ¹³CO₂ as the C source. The production of ¹³CO (m/z = 29) was then studied by using GC-MS, which showed that the generated CO came from CO₂ (Fig. 5F).

DFT calculations were performed to investigate the reactivity of the two clusters. The calculation models, Ti₄Ag₈m and Ti₂Ag₄m, were optimized based on the crystal structures, by simplifying ^tBu groups of benzene rings to H atoms and ⁱPrO groups to MeO groups. In addition, the Ti₄Na(Idc)₆ groups in Ti_8Ag_8 were removed to create active sites to build $Ti_4Ag_8_m$. The Gibbs free energy diagrams of the CO₂RR and HER are shown in Fig. 6. The proposed pathway for the CO₂ reduction to CO was $CO_2(g) \rightarrow *COOH \rightarrow *CO \rightarrow CO(g)$. The calculated Gibbs free energies of the CO₂RR revealed that the formation of *COOH was the rate determining step. The Gibbs free energy that was calculated for the formation of *COOH on the Ag site on the {Ti@Ag₂(TC4A)} unit in Ti₄Ag₈m was 1.01 eV, which was much lower than the corresponding Gibbs free energy for the {Ti@Ag₂(TC4A)} unit in Ti₂Ag₄m (1.42 eV). This result suggested that the Ag sites on {Ti@Ag2(TC4A)} were more energetically favorable for the catalysis of the CO₂ conversion to CO than those on $\{Ti_2O_2 \otimes Ag_4(TC4A)_2\}$. The Gibbs free energies of the adsorptions were also calculated to illustrate the HER reactivities of Ti₈Ag₈ and Ti₂Ag₄. The high Gibbs free energies of the H* adsorption revealed that both Ti_8Ag_8 (1.63 eV) and Ti_2Ag_4 (2.00 eV) were unfavorable in the formation of H₂. By comparing the Gibbs free energy diagrams of the CO₂RR and HER, we found that Ti₄Ag₈m had a higher selectivity for the CO formation, as compared with Ti₂Ag₄_m.



Fig. 6 (A) Free energy diagrams for the CO₂RR and HER on Ti₄Ag₈_m (red) and Ti₂Ag₄_m (black); the calculation optimized structures of COOH absorbed on Ti₄Ag₈_m (B) and Ti₂Ag₄_m (C); the calculation optimized structures of CO absorbed on Ti₄Ag₈_m (D) and Ti₂Ag₄_m (E).

To further unravel the mystery of the differences in catalytic performances, the d-band center (ε_d) of the Ag sites in Ti₄Ag₈_m and Ti₂Ag₄_m was calculated to evaluate their reactivity as active sites, since ε_d has been proposed as a benchmark descriptor for transition metal reactivity.47 Our calculations showed markedly different electronic properties for the two nonequivalent Ag sites (Fig. S53[†]). In Ti₄Ag₈, m, the ε_d value of the four Ag(1) sites in ${Ti}(aAg_2(TC4A))$ is -0.34 eV, which is 0.06 eV higher than that of the two surface-exposed Ag(II) sites in $\{Ti_2O_2(a)Ag_4(TC4A)_2\}$. As a comparison, the four Ag(II) sites in Ti₂Ag₄m also exhibit a lower ε_d value of -0.44 eV, suggesting that the Ag(1) sites in ${Ti@Ag_2(TC4A)}$ are more active than Ag(II) in the ${Ti_2O_2@Ag_4(-$ TC4A)₂ unit. Furthermore, the projected density of states (PDOS) showed that the active Ag(I) sites in Ti₄Ag₈m underwent a stronger hybridization with the absorbed COOH and CO than those in Ti₂Ag₄_m (Fig. S55[†]). 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 CO2RR mechanism involving different Ag active sites on the Ag/Ti bimetallic clusters.

Conclusions

In summary, we have for the first time compared eCO_2RR atomic-level activities for different Ag sites on Ag-based catalysts. We synthesized and characterized an atomically precise

bimetallic Ti₈Ag₈ cluster using a calixarene-protected Ti-oxo core as a substrate for loading Ag^{1+} ions. The Ti_8Ag_8 clusters contain two groups of surface-exposed Ag catalytic sites, located on the {Ti₂O₂@Ag₄(TC4A)₂} and {Ti@Ag₂(TC4A)} units, respectively. We traced the assembly path of Ti₈Ag₈ and successfully isolated $\{Ti_2O_2@Ag_4(TC4A)_2\}$ in the Ti_2Ag_4 cluster alone. The eCO2RR test showed that both clusters were good electrocatalysts for the reduction of CO₂ to CO, but the performance of Ti₈Ag₈ was significantly superior to that of Ti₂Ag₄. Also, DFT was used to calculate the free energy change of each elementary step for converting CO₂ into CO and the competing HER, revealing the difference in activity between the Ag sites on the ${Ti}_{a}Ag_{2}(TC4A)$ and ${Ti}_{2}O_{2}(Ag_{4}(TC4A)_{2})$ 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.

Acknowledgements

This work was supported by the Natural Science Foundation of Hunan Province (2023JJ30650), the Central South University Innovation-Driven Research Programme (2023CXQD061) and the Fundamental Research Funds for the Central Universities of Central South University (2022ZZTS0527). We are grateful for resources from the High-Performance Computing Center of Central South University.

Notes and references

- 1 J. A. Turner, Science, 1999, 285, 687-689.
- 2 P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo and E. H. Sargent, *Science*, 2019, **364**, 350–359.
- 3 G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou,
 Z. Wen and L. Dai, *Chem. Soc. Rev.*, 2021, 50, 4993–5061.
- 4 L. Qin, F. Sun, X. Ma, G. Ma, Y. Tang, L. Wang, Q. Tang, R. Jin and Z. Tang, *Angew. Chem., Int. Ed.*, 2021, **60**, 26136–26141.

- 5 J. Y. Xu, L. Xiong, X. Cai, S. S. Tang, A. C. Tang, X. Liu, Y. Pei and Y. Zhu, *Chem. Sci.*, 2022, **13**, 2778–2782.
- 6 J. Wang, F. Xu, Z.-Y. Wang, S.-Q. Zang and T. C. W. Mak, Angew. Chem., Int. Ed., 2022, 61, e202207492.
- 7 I. Chakraborty and T. Pradeep, *Chem. Rev.*, 2017, **117**, 8208–8271.
- 8 R. Jin, C. Zeng, M. Zhou and Y. Chen, *Chem. Rev.*, 2016, **116**, 10346–10413.
- 9 P. Liu, Y. Zhao, R. Qin, S. Mo, G. Chen, L. Gu, D. M. Chevrier,
 P. Zhang, Q. Guo, D. Zang, B. Wu, G. Fu and N. Zheng, *Science*, 2016, 352, 797–800.
- 10 J. Wan, W. Chen, C. Jia, L. Zheng, J. Dong, X. Zheng, Y. Wang, W. Yan, C. Chen, Q. Peng, D. Wang and Y. Li, *Adv. Mater.*, 2018, **30**, 1705369.
- 11 L. DeRita, S. Dai, K. L. Zepeda, N. Pham, G. W. Graham,
 X. Pan and P. Christopher, *J. Am. Chem. Soc.*, 2017, 139, 14150–14165.
- 12 H. Guan, J. Lin, B. Qiao, X. Yang, L. Li, S. Miao, J. Liu, A. Wang, X. Wang and T. Zhang, *Angew. Chem., Int. Ed.*, 2016, 55, 2820–2824.
- 13 W. N. Wang, W. J. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay and P. Biswas, J. Am. Chem. Soc., 2012, 134, 11276–11281.
- 14 S. Chen, Z. N. Chen, W. H. Fang, W. Zhuang, L. Zhang and J. Zhang, *Angew. Chem., Int. Ed.*, 2019, **58**, 10932–10935.
- 15 P. Coppens, Y. Chen and E. Trzop, *Chem. Rev.*, 2014, **114**, 9645–9661.
- 16 W. H. Fang, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 2018, 47, 404–421.
- 17 L. Rozes and C. Sanchez, *Chem. Soc. Rev.*, 2011, **40**, 1006–1030.
- 18 P. D. Matthews, T. C. King and D. S. Wright, *Chem. Commun.*, 2014, **50**, 12815–12823.
- 19 Y. Lv, J. Cheng, A. Steiner, L. Gan and D. S. Wright, *Angew. Chem., Int. Ed.*, 2014, **53**, 1934–1938.
- 20 C. Zhao, Y. Z. Han, S. Dai, X. Chen, J. Yan, W. Zhang, H. Su, S. Lin, Z. Tang, B. K. Teo and N. Zheng, *Angew. Chem., Int. Ed.*, 2017, 56, 16252–16256.
- 21 G. Zhang, C. Liu, D. L. Long, L. Cronin, C. H. Tung and Y. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 11097–11100.
- 22 W. H. Fang, L. Zhang and J. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 7480–7483.
- 23 M. Y. Gao, F. Wang, Z. G. Gu, D. X. Zhang, L. Zhang and J. Zhang, *J. Am. Chem. Soc.*, 2016, **138**, 2556–2559.
- 24 J. X. Liu, M. Y. Gao, W. H. Fang, L. Zhang and J. Zhang, Angew. Chem., Int. Ed., 2016, 55, 5160-5165.
- 25 S. Chen, W.-H. Fang, L. Zhang and J. Zhang, *Angew. Chem.*, *Int. Ed.*, 2018, **57**, 11252–11256.
- 26 X. Fan, F. Yuan, D. Li, S. Chen, Z. Cheng, Z. Zhang, S. Xiang, S.-Q. Zang, J. Zhang and L. Zhang, *Angew. Chem., Int. Ed.*, 2021, **60**, 12949–12954.
- 27 G. H. Chen, D. J. Li, Y. P. He, S. H. Zhang, F. P. Liang and J. Zhang, *Inorg. Chem.*, 2020, 59, 14861–14865.
- 28 X. M. Luo, C. H. Gong, X. Y. Dong, L. Zhang and S. Q. Zang, Nano Res., 2021, 14, 2309–2313.

- 29 Y. Z. Yu, Y. Guo, Y. R. Zhang, M. M. Liu, Y. R. Feng, C. H. Geng and X. M. Zhang, *Dalton Trans.*, 2019, 48, 13423–13429.
- 30 Y. J. Liu, P. Shao, M. Y. Gao, W. H. Fang and J. Zhang, *Inorg. Chem.*, 2020, **59**, 11442–11448.
- 31 M. Y. Gao, K. Wang, Y. Y. Sun, D. J. Li, B. Q. Song, Y. H. Andaloussi, M. J. Zaworotko, J. Zhang and L. Zhang, *J. Am. Chem. Soc.*, 2020, **142**, 12784–12790.
- 32 M. M. Deegan, T. S. Ahmed, G. P. A. Yap and E. D. Bloch, *Chem. Sci.*, 2020, **11**, 5273–5279.
- 33 H. T. Han, L. Kan, P. Li, G. S. Zhang, K. Y. Li, W. P. Liao, Y. L. Liu, W. Chen and C. H. T. Hu, *Sci. China: Chem.*, 2021, 64, 426–431.
- 34 D. T. Geng, X. Han, Y. F. Bi, Y. C. Qin, Q. Li, L. L. Huang,
 K. Zhou, L. J. Song and Z. P. Zheng, *Chem. Sci.*, 2018, 9, 8535–8541.
- 35 M. Liu, W. P. Liao, C. Hu, S. C. Du and H. J. Zhang, *Angew. Chem., Int. Ed.*, 2012, **51**, 1585–1588.
- 36 X. X. Hang, B. Liu, X. F. Zhu, S. T. Wang, H. T. Han, W. P. Liao, Y. L. Liu and C. H. Hu, *J. Am. Chem. Soc.*, 2016, 138, 2969–2972.
- 37 S. T. Wang, X. H. Gao, X. X. Hang, X. F. Zhu, H. T. Han, X. K. Li, W. P. Liao and W. Chen, *J. Am. Chem. Soc.*, 2018, 140, 6271–6277.

- 38 X. Wang, Y. N. Yu, Z. Wang, J. Zheng, Y. F. Bi and Z. P. Zheng, *Inorg. Chem.*, 2020, **59**, 7150–7157.
- 39 Y. Q. Tian, Y. S. Cui, J. H. Zhu, C. Q. Xu, X. Y. Yi, J. Li and C. Liu, *Chem. Commun.*, 2022, 58, 9034–9037.
- 40 Y. Q. Tian, Y. S. Cui, W. D. Yu, C. Q. Xu, X. Y. Yi, J. Yan, J. Li and C. Liu, *Chem. Commun.*, 2022, **58**, 6028–6031.
- 41 Z. Wang, L. Li, L. Feng, Z. Y. Gao, C. H. Tung, L. S. Zheng and D. Sun, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200823.
- 42 Z. Wang, H. F. Su, Y. W. Gong, Q. P. Qu, Y. F. Bi, C. H. Tung, D. Sun and L. S. Zheng, *Nat. Commun.*, 2020, **11**, 308.
- 43 Z. Wang, F. Alkan, C. M. Aikens, M. Kurmoo, Z. Y. Zhang,
 K. P. Song, C. H. Tung and D. Sun, *Angew. Chem., Int. Ed.*, 2022, 61, e202206742.
- 44 S. Q. Li, L. F. Dai, Y. Q. Tian, Y. X. Yi, J. Yan and C. Liu, *Chem. Commun.*, 2023, **59**, 575–578.
- 45 Z. J. Guan, J. L. Zeng, Z. A. Nan, X. K. Wan, Y. M. Lin and Q. M. Wang, *Sci. Adv.*, 2016, 2, e1600323.
- 46 Z. J. Guan, F. Hu, S. F. Yuan, Z. A. Nan, Y. M. Lin and Q. M. Wang, *Chem. Sci.*, 2019, **10**, 3360–3365.
- 47 J. K. Nørskov, T. Bligaard, J. Rossmeisl and C. H. Christensen, *Nat. Chem.*, 2009, **1**, 37–46.