

Polyoxometalate-modified AgAu nanoalloy electrocatalysts for highly efficient nitrate-to-ammonia conversion

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(Dedicated to Late Prof. M. T. Pope for his pioneering work on polyoxometalates)

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ABSTRACT: Electrocatalytic nitrate(NO_3^-) reduction technology can simultaneously realize the remediation of nitrate pollution in water and distributed ammonia(NH_3) synthesis. To meet the demand for efficient nitrate removal and ammonia resource recovery under practical water treatment conditions, it is of great significance to develop high-performance NO_3^- electroreduction catalysts suitable for near-neutral environments. However, the sluggish kinetics of multi-proton-coupled electron transfer in neutral media typically lead to unsatisfactory ammonia yields. To handle this issue, we design the lacunary polyoxometalate(POM)-modified AgAu nanoalloy catalysts supported by activated-carbon (10% AuAg-SiW₉/C) to achieve efficient electrocatalytic conversion of NO_3^- -to- NH_3 under neutral conditions. The highly negative-charged SiW₉ polyoxoanion effectively stabilized and dispersed the ultrafine AgAu alloy nanoparticles (~6 nm) through strong electrostatic repulsion. In 1 M phosphate buffer at pH ~7.4 containing 0.1 M KNO_3 , 10% AuAg-SiW₉/C delivers a Faradaic efficiency (FE) of 95% and an NH_3 yield rate of 1.3963 $\text{mg h}^{-1} \text{cm}^{-2}$ at -0.6 V versus the reversible hydrogen electrode (RHE). The synergistic effect between the SiW₉ polyoxoanions and Au alloying modulates the surface electronic structure of the Ag host via interfacial charge transfer. Density functional theory calculations elucidate that Au doping coupled with SiW₉ incorporation reduces the energy barrier for the $^*\text{NO} \rightarrow ^*\text{NOH}$ step to 0.46 eV, significantly facilitating this rate-determining step during the multistep hydrogenation process. This study confirms an effective electronic modulation strategy by coupling POMs modification and alloying effect for enhancing the NO_3RR performance of metal-based electrocatalysts, providing new insights into the high-value conversion of nitrogen pollutants and the design of materials for electrochemical NH_3 synthesis.

KEYWORDS: polyoxometalate, alloy nanoparticles, electrocatalysis, nitrate reduction, neutral media

1 Introduction

Ammonia (NH_3) is an essential basic chemical feedstock and a prospective carbon-free energy medium, rendering its green synthesis of great significance for constructing a sustainable energy systems[1-3]. Currently, industrial ammonia synthesis is predominantly dominated by the Haber – Bosch route, which typically demands harsh high-temperature and high-pressure environments and depends on fossil-fuel-derived hydrogen(H_2), thereby incurring substantial energy usage and carbon release[1-3]. The electrocatalytic nitrate-to-ammonia reduction reaction (NO_3RR) is regarded as a more feasible and application-promising electrosynthetic strategy to ammonia, enabling the conversion of nitrate into value-added NH_3 under aqueous electrolysis conditions at ambient temperature and pressure[4-6]. Furthermore, NO_3^- exists extensively in nitrogen-containing wastewater systems such as agricultural runoff, industrial effluents, and contaminated groundwater[7-8]. Therefore,

NO_3RR provides a sustainable pathway for nitrate pollution remediation and nitrogen resource recovery[9-10].

Previous studies have demonstrated that NO_3RR typically involves multistep deoxygenation and hydrogenation processes, proceeding via crucial reaction intermediates including $^*\text{NO}_3$, $^*\text{NO}_2$, $^*\text{NO}$, and $^*\text{NOH}$ on the pathway to NH_3 [10-12]. Related studies on electrochemical NO reduction have shown that the further hydrogenation/protonation of $^*\text{NO}$ to $^*\text{NOH}$ or $^*\text{HNO}$ plays a pivotal role in the sequential reduction of NO_x intermediates to NH_3 [13-16]. In some NO_3RR catalytic systems, the $^*\text{NO} \rightarrow ^*\text{NOH}$ conversion has further been identified as one of the rate-determining steps[17]. This step involves proton-coupled electron transfer (PCET) behavior, their kinetics are synergistically determined by interfacial proton (H^+) availability, the local reaction microenvironment, and the adsorption states of key intermediates[18-20]. Although current NO_3RR research has predominantly focused on alkaline electrolyte systems[11], most

natural and contaminated water systems are closer to neutral or near-neutral conditions. Consequently, neutral-pH NO₃RR is more relevant to practical water treatment and nitrogen resource recovery scenarios[21-22]. However, compared with strongly alkaline systems, the more complex interfacial proton transport behavior, local pH regulation, and hydrogen evolution reaction (HER) competitive effects under neutral conditions may limit the occurrence of multistep PCET hydrogenation reactions during the NO₃RR process[21-23]. In experimental studies, phosphate buffer solution (PBS) are commonly employed to provide a stable near-neutral reaction environment for probing the interfacial reaction behavior of NO₃RR under neutral conditions[24]. Developing NO₃RR catalysts that can accelerate multistep hydrogenation while suppressing the competing HER in neutral PBS solutions remains a key challenge for improving the Faradaic efficiency and production rate of NH₃ [22-24].

Owing to the remarkable ability of promoting the initial activation and deoxygenation of NO₃⁻, Silver (Ag)-based electrocatalysts have been received widespread attention[25-26]. For example, Ag nanocubes have shown promising NH₃ production capability[25], while oxide-derived Ag has exhibited adjustable product selectivity between nitrite and ammonia in the electrocatalytic NO₃RR[26]. However, NO₃RR involves multiple deoxygenation and hydrogenation intermediate[9-12]. Although Ag can facilitate the transformation of nitrate to nitrite, the successive deep reduction of nitrite over Ag surfaces remains limited by reaction energy barriers and interfacial hydrogenation kinetics[25-26]. The product distribution of NO₃RR on Ag surfaces is strongly correlated with the surface structure and the capability for intermediate transformation. This suggests that the performance enhancement of Ag-based catalysts should not only consider the initial activation of NO₃⁻, but also pay close attention to the adsorption of NO_x intermediates and their subsequent hydrogenation processes[25-26].

Herein, we design and construct an AgAu nanoalloy electrocatalyst modified with lacunary polyoxometalate (POM) SiW₉ supported on carbon (10% AuAg-SiW₉/C). The AgAu alloy, as the metallic active component, can integrate the advantages of Ag in the initial adsorption and deoxygenation of NO₃⁻, while the Au-Ag bimetallic composition modulates the local reaction environment and intermediate transformation behavior, consequently driving the extensive reduction of NO₃⁻ to NH₃[25-27]. Meanwhile, the lacunary Keggin-type SiW₉ possesses multidentate coordination capability and is expected to act as a POM ligand to stabilize AgAu alloy nanoparticles, while modulating their electronic structure through the metal-POM interface[28-29]. In addition, POMs feature reversible multi-electron redox capability and can serve as electron/proton reservoirs to participate in interfacial charge regulation, providing a reasonable electronic-structure basis for the continuous PCET hydrogenation of NO_x intermediates[30-33]. More importantly, the AgAu-SiW₉ interface is expected to synergistically combine POM-mediated electronic-structure regulation with the anchoring and activation of nitrogen-containing intermediates at alloy sites, thereby accelerating the cascade deoxygenation - hydrogenation pathways for NO₃RR and enhancing the reaction advantage of NO₃RR over the competing HER[23,33-35]. Benefiting from these synergistic effects, the 10% AuAg-SiW₉/C

catalyst delivers a great ammonia yield of 1.3963 mg h⁻¹ cm⁻² and a Faradaic efficiency (FE) of 95% at -0.6 V versus the reversible hydrogen electrode (RHE) in neutral 1 M PBS (containing 0.1 M KNO₃). The ammonia yield rate and Faradaic efficiency achieved over 10% AuAg-SiW₉/C were significantly superior to those of the control samples, including Ag-SiW₉/C (0.5307 mg h⁻¹ cm⁻², FE = 66.8%) and AgAu/C (0.5148 mg h⁻¹ cm⁻², FE = 83.37%). Density functional theory (DFT) calculations elucidate that the AgAu-SiW₉ interface lowers the energy barriers for water dissociation and the *NO-to-*NOH hydrogenation step, which is regarded as the rate-determining step in the proposed NO₃RR pathway. Experiments and theory together suggest that the AgAu alloying effect and SiW₉ modification synergistically facilitate interfacial proton/electron transfer and promote efficient electrocatalytic NO₃RR. This study develops an interface engineering approach for the rational design of high-efficiency NO₃RR electrocatalysts suitable for neutral system.

2 Experimental and Methods

2.1 Reagents and Materials

All reagents were used as received without further purification. Sodium tungstate (Na₂WO₄), sodium metasilicate (Na₂SiO₃), hydrochloric acid (HCl), sodium carbonate (Na₂CO₃), sodium chloride (NaCl), ethanol (CH₃CH₂OH), diethyl ether (C₂H₅OC₂H₅), sodium borohydride (NaBH₄), chloroauric acid (HAuCl₄), and silver nitrate (AgNO₃) were all purchased from Macklin (Shanghai, China) (analytical reagent, AR). Nafion solution (5 wt%) and activated carbon were obtained from Macklin (Shanghai, China). Deionized water was employed throughout all experiments, and all solutions were freshly prepared prior to use to avoid compositional variation or degradation.

2.2 Catalyst Synthesis

2.2.1 Synthesis of AgAu-SiW₉/C catalyst

Na₁₀SiW₉O₃₄ (abbr. SiW₉) was synthesized according to methods described in literature with modifications adapted to the present experimental conditions[36]. The synthetic procedures are provided in the Supporting Information (SI). The structural model of the trivacant Keggin-type [SiW₉O₃₄]¹⁰⁻ is shown in Fig. S1.

SiW₉ (150 mg) was dissolved in 145 mL of low-temperature water (4-6 °C) and dissolved under magnetic stirring. Subsequently, HAuCl₄ solution (50 μL, 0.1 M) and AgNO₃ solutions (450 μL, 0.1 M) were added and stirred for 30 min. Under vigorous stirring, a freshly prepared NaBH₄ solution was slowly dropped into the reaction system. After the completion of the dropping process, the mixture underwent magnetic stirring continuously for another 40 min and the entire process was maintained at 4-6 °C. Activated carbon (97 mg) was then introduced and stirring was continued for an additional 15 min. After rotary evaporation to remove the solvent, the obtained solid was washed sequentially with deionized water three times followed by ethanol once. The resulting product was vacuum-dried 60 °C overnight to afford the AgAu-SiW₉/C catalyst, designated as 10% AuAg-SiW₉/C. A series of AgAu-SiW₉/C catalysts with different nominal Au contents were prepared by adjusting the Au/Ag precursor ratio and are denoted as x% AuAg-SiW₉/C (x = target Au atomic percentage in the feed).

Quantitative EDX analysis (Table S1) of the representative 10% sample reveals an actual Au content of 8.69 ± 1.76 at% (Ag: 91.31 ± 1.76 at%), which is consistent with the nominal target and confirms the reliability of the synthesis.

To investigate the synergistic effects among Au, Ag and SiW₉, a series of Ag-based electrocatalysts was prepared using a single-variable approach. The preparation procedures, reduction conditions, and post-treatment steps for all samples were maintained highly consistent with those of 10% AuAg-SiW₉/C, and only specific adjustments were made to the composition. The as-prepared samples included composition-varied controls and POMs-type-varied controls. Specifically, the composition-varied controls comprised Ag/C, Au/C, AgAu/C, Au-SiW₉/C, and Ag-SiW₉/C. Synthetic details are elaborated in the Supporting Information.

2.2.2 Preparation of the working electrode

The carbon cloth was sequentially cleaned via ultrasonication in acetone, ethanol, and deionized water (10–15 min each), then subjected to reflux condensation in concentrated nitric acid (16 M) at 85 °C in a water bath for 8 h. After natural cooling down to ambient temperature, the carbon cloth was repeatedly washed with deionized water until neutral, followed by further ultrasonication in ethanol for 15 min, and subsequently dried at 60 °C for later use. The dried catalyst powder (10 mg) was dispersed in a mixed solution containing 450 μ L ethanol and 50 μ L of 5 wt% Nafion D-521 dispersion (dissolved in water and 1-propanol). Ultrasonic treatment for 30 min was conducted to obtain a uniform suspension. The suspension (200 μ L) was then uniformly drop-coated onto the surface of the pretreated carbon cloth (1 cm $\times$ 2 cm) and dried naturally at room temperature. The prepared electrode was subsequently used for electrochemical measurements. The catalyst loading on the electrode surface was calculated based on the drop-coating volume and catalyst concentration, and was kept consistent across all experiments.

Detailed experimental methods including material characterizations, electrochemical measurements, product analysis, and DFT calculations are available in the SI.

3 Results and Discussion

3.1 Synthesis and Structural Characterization of the Catalysts

The synthesis process of 10% AuAg-SiW₉/C is depicted in Fig. 1. Specifically, the lacunary-type POM SiW₉, served as a functional coordination unit to anchor Au and Ag precursors. During the subsequent reduction, the POM anions were in situ modified on the surface of AgAu alloy nanoparticles. To ensure high dispersion and long-term structural integrity, the hybrid was further loaded onto a conductive carbon support.

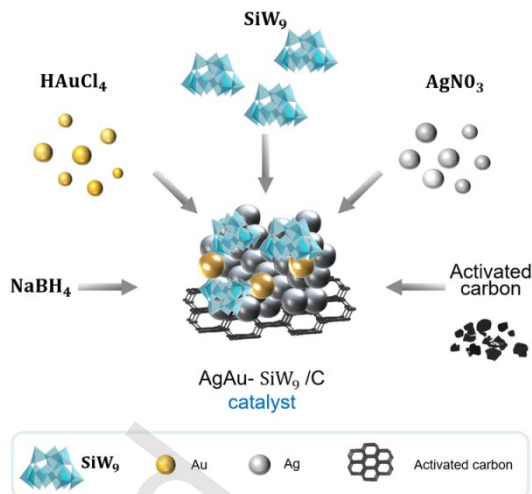


Figure 1 Schematic illustration showing the synthesis process of 10% AuAg-SiW₉/C.

To elucidate the evolution of the crystal structure during material construction, X-ray diffraction (XRD) analysis was performed (Fig. 2(a)). The Au-SiW₉/C and Ag-SiW₉/C exhibit distinct diffraction peaks at $2\theta \approx 38.2^\circ$, 44.4° , 64.6° , and 77.5° , corresponding to the (111), (200), (220), and (311) crystal planes of face-centered cubic (fcc) metallic Au or Ag, respectively, indicating good crystallinity of the monometallic samples. By contrast, 10% AuAg-SiW₉/C only displays a weak Ag (111) diffraction peak at $\sim 38^\circ$, which could be attributed to the smaller size of the AgAu alloy nanoparticles and the low crystallinity owing to the alloying effect. Additionally, the (111) diffraction peak is located between the Au (111) of Au-SiW₉/C and the Ag (111) of Ag-SiW₉/C (inset of Fig. 2(b)), confirming the

formation of a AgAu solid-solution alloy. We present the UV-vis spectra of AuAg-SiW₉, along with those of Ag-SiW₉, Au-SiW₉, and a physical mixture of Ag-SiW₉ + Au-SiW₉ for comparison (Fig. S2). As shown in Fig. S2(a) and S2(b), Ag-SiW₉ and Au-SiW₉ exhibit plasmon resonance absorption peaks at 412 nm and 525.8 nm, respectively. UV-vis shows a single red-shifted plasmon peak for the AgAu alloy, contrasting with the physical mixture that retains two independent peaks of pure Ag and Au (Fig. S2(c) and S2(d)). This result is consistent with the characteristic feature of homogeneous AuAg alloy nanoparticles[37–38]. The alloy nature of AuAg-SiW₉ was further confirmed by single-particle STEM-EDX line-scan analysis (Fig. S3). The well-overlapped Ag and Au profiles across the entire particle, without any detectable segregation, demonstrate a homogeneous Ag-Au solid-solution alloy. Collectively, the UV-vis and STEM-EDX results provide complementary evidence for the formation of a single-phase Ag-Au alloy with POM surface modification. The formation of this alloy is facilitated by the identical crystal structure and similar atomic radii of Au and Ag, which provides a structural basis for solid-solution formation during chemical reduction. In addition, XRD analysis (Fig. S4) provided evidence for differences in nanoparticle size. The AgAu/C without POMs modification presents sharp diffraction peaks, suggesting larger metal particles with good crystallinity. By contrast, the significantly broadened and weakened diffraction peaks of 10% AuAg-SiW₉/C indicates that the strong electrostatic repulsion among SiW₉ anionic clusters effectively suppressed metal particle growth through

spatial confinement, thus forming smaller nanoparticles. To confirm the crystallinity induced by size effects, transmission electron microscopy (TEM) characterization was performed on 10% AuAg-SiW₉/C and AgAu/C. Fig. 2b shows the low-magnification TEM image of 10% AuAg-SiW₉/C, where AgAu nanoparticles uniformly distribute on the carbon support, with mean particle sizes of ~6 nm (Fig. S5(a)(b)), demonstrating near-monodisperse metal nanoparticles and good dispersion. By contrast, the AgAu/C without SiW₉ (Fig. S6) exhibits obvious particle aggregation and irregular particle growth, consistent with the XRD results, confirming that SiW₉ anionic clusters effectively stabilize and disperse metal nanoparticles. Clear lattice fringes with a spacing of ~0.235 nm can be observed in the HRTEM images (inset in Fig. 2(b)), which correspond to the (111) crystal plane of the AgAu alloy, which was similar to the interplanar spacing of Au (111) and Ag (111). This was mainly because the similar crystal dimensions of Ag and Au lead to no lattice distortion upon alloying. No lattice fringes corresponding to POMs were observed, indicating their high dispersion on the metal surface. Elemental mapping (Fig. 2(c)) reveals a uniform distribution of Au, Ag, and W elements, confirming the presence of POMs and their good dispersibility.

To examine the structure of the lacunary POMs in 10% AuAg-SiW₉/C, Fourier transform infrared (FT-IR) and Raman

spectroscopic analyses were performed (Fig. 2(d)(e)). The characteristic vibrational bands in FT-IR, including the terminal W=O_d stretching vibration (~983 cm⁻¹), the Si-O_a vibration (~930 cm⁻¹), and the corner-sharing W-O_b and edge-sharing W-O_c stretching vibrations (~880 cm⁻¹ and ~795 cm⁻¹, respectively), are well preserved. Compared with pristine SiW₉, these framework vibrations contain no obvious peak shifts or band distortions, indicating that the fundamental polyoxoanion skeleton of the lacunary Keggin POM structure is maintained. For the 10% AuAg-SiW₉/C, this peak is significantly weakened and slightly shifted, while the Keggin core remains preserved. In Fig. 2(e), SiW₉ exhibits a prominent peak around 900-1000 cm⁻¹ region, which can be assigned to the terminal W=O stretching vibration of the lacunary Keggin-type silicotungstate framework. After reduction and carbon loading, these characteristic vibrational features are still discernible in 10% AuAg-SiW₉/C, indicating that the SiW₉ polyoxometalate skeleton is largely preserved during the construction of the composite catalyst. To elucidate the alloying effect and POM modification in 10% AuAg-SiW₉/C and the changes in the surface electronic states of Ag induced by POMs modification, X-ray photoelectron spectroscopy (XPS) was conducted. The XPS survey spectrum (Fig. 2(f)) of 10% AuAg-SiW₉/C confirms the coexistence of C, O, Ag, Au, W, and Si elements, consistent with the designed composition of the AgAu-SiW₉/C catalyst. The O 1s spectrum (Fig. S7)

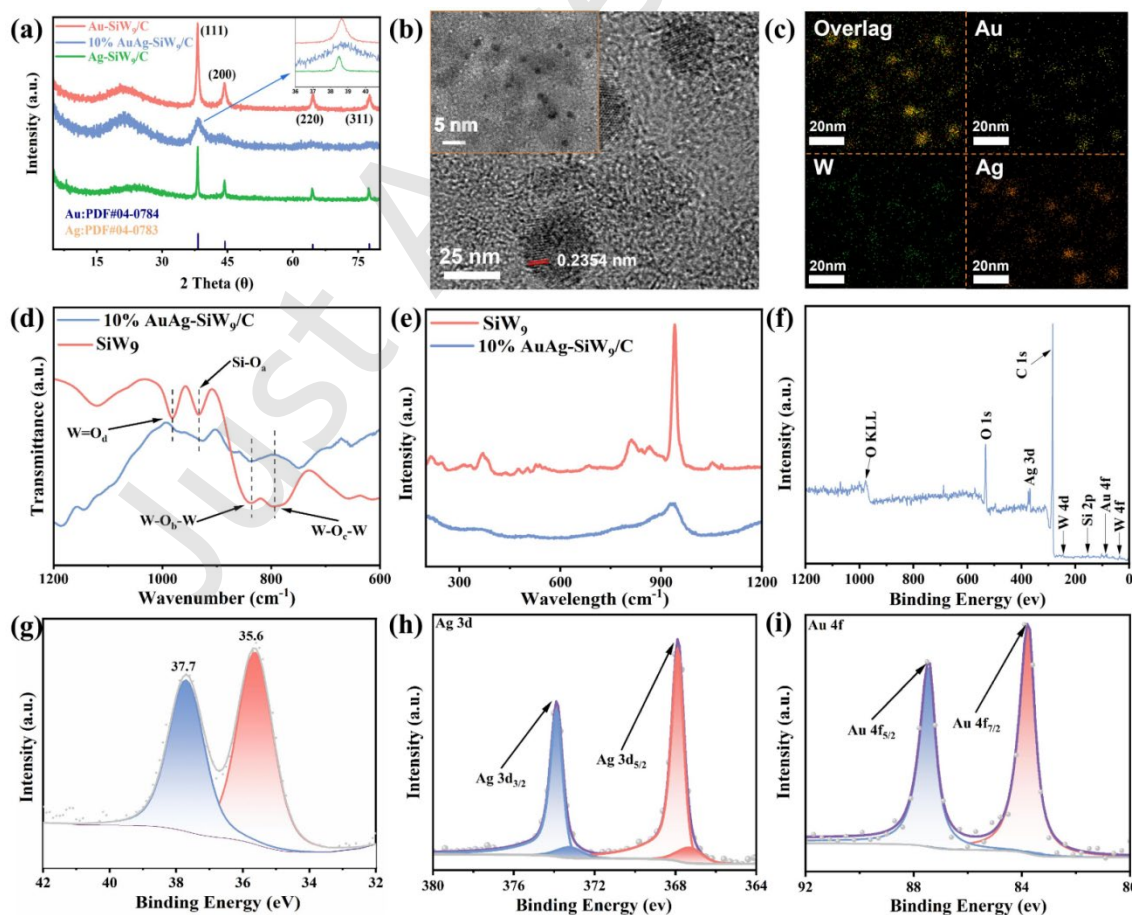


Figure 2 Phase, morphology, and chemical composition characterization of Au-SiW₉/C, Ag-SiW₉/C, and 10% AuAg-SiW₉/C: (a) X-ray diffraction (XRD) patterns of Au-SiW₉/C, Ag-SiW₉/C, and 10% AuAg-SiW₉/C; (b) microstructural characterization of the 10% AuAg-SiW₉/C catalyst; (c) elemental mapping images; (d) Fourier-transform infrared (FT-IR) spectra of SiW₉ and 10% AuAg-SiW₉/C; (e) Raman spectra of SiW₉ and 10% AuAg-SiW₉/C; (f) XPS survey spectrum of 10% AuAg-SiW₉/C; (g) Ag 3d XPS spectra; (h) Ag 3d XPS spectra; (i) Au 4f XPS spectra.

AuAg-SiW₉/C; (g, h, i) X-ray photoelectron spectroscopy (XPS) spectra of W 4f, Ag 3d, and Au 4f, respectively.

can be deconvoluted into five peaks at 530.25, 531.13, 532.36, 533.55, and 535.18 eV, corresponding to Ag-O-W, Si-O-W, W-O, C-O, and the Na KLL Auger peak from trace sodium impurities, respectively. For the typical POM anion composition, the W 4f spectrum was deconvoluted into a set of spin-orbit doublets (Fig. 2g). The peaks at ~35.6 and 37.7 eV show binding energies lower than that of W⁶⁺ (36.1 eV), indicating partial reduction of the W species in the POM anion. This implies that the polyoxometalate is capable of acting as an electron donor, contributing charge to the AgAu alloy. The high-resolution Au 4f and Ag 3d spectra of 10% AuAg-SiW₉/C both exhibit a pair of peaks, corresponding to the metallic state, indicating that Au and Ag predominantly present in the zero-valent state (Fig. 2h and 2i). For Ag, the metallic Ag 3d_{5/2} and Ag 3d_{3/2} peaks of 10% AuAg-SiW₉/C are located at ~367.8 eV and ~373.9 eV, respectively, and the Ag 3d_{5/2} exhibits negative shifts of ~0.4 eV, compared with standard-Ag 3d_{5/2} (~368.2 eV). Auger electron spectroscopy (AES) analysis (Fig. S8) reveals the coexistence of Ag⁰ and Ag⁺ species. The presence of oxidized Ag suggests the formation of interfacial oxygen-bridged linkages between Ag species and the SiW₉ framework, leading to the formation of Ag-O-W coordination bonds rather than simple physical loading. The coexistence of Ag⁰/Ag⁺ indicates clear electronic coupling between the AgAu nanoparticles and SiW₉, which is beneficial for modulating the electronic structure of Ag sites and stabilizing the metal-POM interface. Such an interfacial structure could provide favorable conditions for reactant adsorption and proton-electron transfer during the subsequent NO₃RR process. For Au, the metallic Au 4f_{7/2} and Au 4f_{5/2} peaks of 10% AuAg-SiW₉/C are located at ~83.8 eV and ~87.5 eV, and the Au 4f_{7/2} shows slight negative shifts of ~0.2 eV relative to those of standard-Au (~84.0 eV). After electrolysis, the chemical states of the constituent elements in the catalytic electrode, comprising 10%-AgAu/SiW₉/C loaded on carbon cloth, were investigated by XPS. As shown in Fig. S9, the W 4f spectrum exhibits a pair of peaks at 35.6 and 37.4 eV, which overlap with the K 3s peak arising from the main cation in the electrolyte. In the Ag 3d region (Fig. S10), in addition to the peaks corresponding to metallic silver, additional signals assignable to Ag⁺ are observed at 367.3 eV and 373.2 eV, unambiguously confirming the stable immobilization of POM species on the electrode surface. Meanwhile, no significant change in the chemical state of Au was detected after the reaction (Fig. S11).

3.2 Electrocatalytic NO₃RR Performance

To systematically evaluate the NO₃RR performance of the catalysts and elucidate the influence of structural regulation on the catalytic behavior, a series of electrochemical measurements was conducted in 1 M PBS containing 0.1 M NO₃⁻. First, the reduction behaviors of the catalysts are evaluated by linear sweep voltammetry (LSV) (Fig. 3(a)). Compared with the nitrate-free electrolyte, the current densities of 10% AuAg-SiW₉/C, Ag-SiW₉/C, and Au-SiW₉/C increased significantly in the presence of NO₃⁻, which indicates that the enhanced current response is mainly associated with the occurrence of NO₃RR. Among these, 10% AuAg-SiW₉/C exhibits a higher current response throughout the entire potential range, suggesting faster reaction kinetics and superior catalytic activity toward NO₃RR. To further investigate

the product selectivity during electrocatalytic NO₃RR, chronoamperometric tests were carried out at -0.6 V (Fig. S14(a)). Notably, the 10% AuAg-SiW₉/C catalyst delivers a steady-state current density of ~-17.26 mA/cm², which is significantly higher than those of AgAu/C (~-7.26 mA/cm²), Ag/C (~-3.75 mA/cm²), and Au/C (~-2.26 mA/cm²). Specifically, the current density of 10% AuAg-SiW₉/C is ~2.4 and 4.6 times higher than those of AgAu/C and Ag/C, respectively. The remarkable current density of 10% AuAg-SiW₉/C can be attributed to its high intrinsic activity, which is supported by its low ECSA derived from the C_{dl} measurements (Fig. S12). Liquid-phase products were further quantified, where the indophenol blue colorimetric approach was employed to calculate the ammonia yield. The calibration curve was established using standard solutions prepared from NH₄Cl at various concentrations. The resulting concentrations are expressed as the equivalent NH₃ concentration based on the nitrogen-atom equivalence. For various NH₄Cl standard solutions, their UV-vis spectra (Fig. S15) feature a characteristic absorption signal peaking at roughly 655 nm. Based on the absorbance values at 655 nm, an excellent linear calibration relationship was established (Fig. 3(b), R² = 0.99569). NH₃ was used here as the detectable product to probe the enhancement of electron utilization efficiency by polyoxometalates on alloy catalysts, without examining other byproducts. A more comprehensive reaction network will be established in future studies using in situ DEMS, GC, and complementary spectroscopy to detect volatile intermediates (NO, N₂O) and byproducts (N₂H₄, NH₂OH, N₂). To evaluate whether the detected NH₄⁺ originated from the reduction of NO₃⁻ substrate, control electrolysis experiments were carried out under conditions with and without NO₃⁻. After the colorimetric reaction, the electrolyzed solutions were analyzed by UV-vis spectroscopy. As shown in the Fig. 3(c), a distinct characteristic absorption peak of the indophenol dye (formed via the reaction between the generated NH₃ and the colorimetric reagents) appears at wavelength of λ_{max}=655 nm in the NO₃⁻-containing electrolyte, whereas almost no absorption signal is observed at this wavelength in the NO₃⁻-free blank system. These results indicate that, under identical electrolysis and detection conditions, the background contribution of NH₄⁺ from the electrolyte, catalyst, and testing environment is negligible, and the detected NH₄⁺ signal is mainly associated with the electrocatalytic reduction of NO₃⁻. It should be noted that this control experiment can effectively exclude background interference under NO₃⁻-free conditions.

As shown in Fig. 3(d), the NH₃ yield of 10% AuAg-SiW₉/C is markedly higher than those of monometallic Au/C, Ag/C, and the SiW₉-free AgAu/C, reaching as high as 1.3963 mg h⁻¹ cm⁻². By contrast, the monometallic catalysts Au/C and Ag/C exhibit relatively limited catalytic activity, affording NH₃ yields of only 0.1869 and 0.3055 mg h⁻¹ cm⁻², respectively. After alloying between Au and Ag, the NH₃ yield of AgAu/C increased to 0.5149 mg h⁻¹ cm⁻², but still remain substantially lower than that of 10% AuAg-SiW₉/C. These comparison results demonstrate that the introduction of SiW₉ lead to a significantly more pronounced enhancement in catalytic performance, indicating that the POM

clusters not only serve as structural stabilizer but also actively regulate the interfacial reaction pathway during NO₃RR. Subsequently, SiW₉ modified AgAu alloy catalysts are constructed by tuning the Au/Ag ratio to investigate the effect of bimetallic composition on catalytic performance (Fig. 3(e)). At an applied potential of -0.6 V vs. RHE, the NH₃ yield exhibits a typical volcano-type dependence on Au content, initially increasing and then decreasing. When the Au fraction was 10%, 10% AuAg-SiW₉/C delivers optimal electrocatalytic performance, with an NH₃ yield of 1.3963 mg h⁻¹ cm⁻² and an FE as high as 95%. These results confirm that an appropriate amount of Au introduction could form an optimal alloy synergy with Ag, thereby optimizing the adsorption energies of critical intermediates and lowering reaction energy barriers. By contrast, excessive Au weakened the initial activation of NO₃⁻ on Ag, leading to reduction on catalytic activity. Thus, 10% is identified as the optimal Au loading. Subsequently, the effect of applied potential on NO₃RR performance is examined (Fig. 3(f)). The NH₃ yield gradually increases with more negative potentials, peaking at -0.6 V (vs.

RHE). At more negative potentials, however, competitive HER become increasingly pronounced, resulting in decreased selectivity and no further improvement in NH₃ yield.

To evaluate the stability of the electrocatalyst, cycling tests and chronoamperometric measurements are performed. As shown in Fig. 3(g), neither the Faradaic efficiency nor the ammonia production performance of the catalyst exhibited noticeable decay over 10 consecutive cycles, indicating excellent cycling stability. Furthermore, chronoamperometric measurements are conducted at various applied potentials (Fig. S14(b)). To further investigate the stability of the catalyst during the reaction, phase and structural characterization are performed before and after electrolysis. As illustrated in Fig. S16(a)(b), XRD and Raman spectroscopic confirm that the morphology and structure of the catalyst do not undergo significant changes, confirming the superior structural stability of the catalyst during the electrocatalytic reaction process. Collectively, the above results indicate that the catalyst exhibits

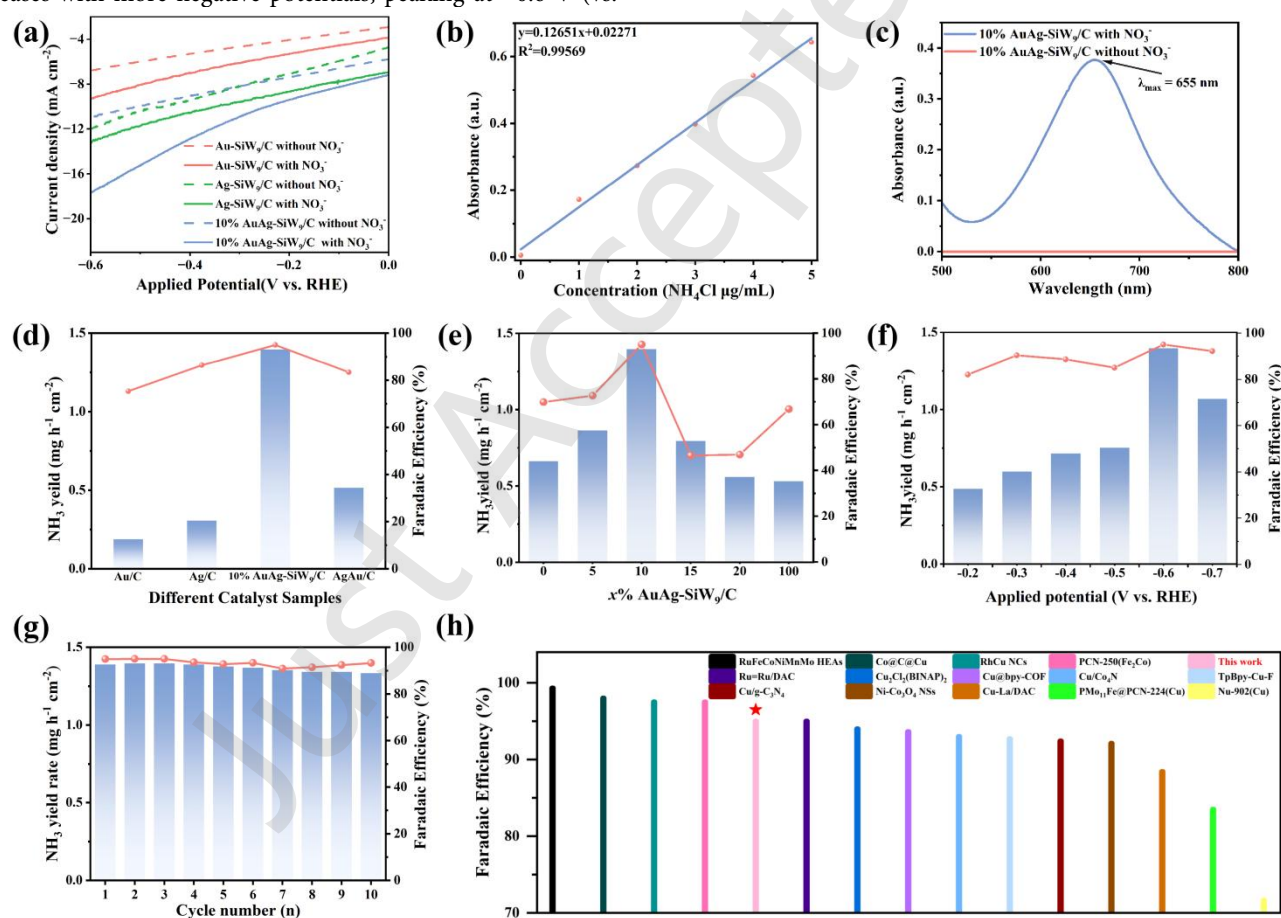


Figure 3. Systematic characterization of NO₃RR catalytic performance: (a) Linear sweep voltammetry curves of the different catalysts; (b) Calibration curve for NH₄⁺ quantification based on the indophenol blue method; (c) UV-vis absorption spectra of the electrolytes after electrolysis with and without NO₃⁻, showing the characteristic NH₄⁺ absorption at 655 nm.; (d) comparison of NH₃ yield rates and FE between 10% AuAg-SiW₉/C and other Au- or Ag-based catalysts, revealing the synergistic effect of the alloy-POM architecture; (e) Volcano-type plot of NH₃ yield rate as a function of Au content, with the optimal performance achieved at an Au content of 10%; (f) Effect of reduction potential on NH₃ yield rate and FE; (g) Variation in NH₃ yield rate of the 10% AuAg-SiW₉/C catalyst over 10 consecutive cycles, demonstrating excellent cycling stability; (h) NH₃ Faradaic efficiency comparison with recently reported carbon-cloth-supported NO₃RR electrocatalysts in neutral electrolyte

outstanding stability in terms of cycling performance and structural integrity, providing strong assurance for its practical

application in the electrocatalytic NO₃RR.

As shown in Fig. 3(h) and Table S2, the NH₃ Faradaic

efficiencies of our catalyst and other reported carbon-cloth-supported NO₃RR catalysts [41–54] are compared under the same nitrate concentration. 10% AuAg-SiW₉/C delivers an NH₃ FE of 95%, which is competitive compared to most reported carbon-cloth-supported electrocatalysts tested in neutral electrolytes.

3.3 DFT Study on the Interfacial Electronic Coupling Mediated NO₃RR Mechanism

To elucidate the catalytic mechanism underlying the enhanced NO₃RR performance of POMs-modified AgAu alloys, systematic density functional theory (DFT) computations were carried out. As presented in Fig. 4(a)–(c) and Fig. S17, structural models were constructed sequentially, beginning with the pristine Ag(111) surface as the baseline, followed by an AgAu alloy model, and finally the AgAu alloy functionalized with a trivacant Keggin-type POMs cluster. The AgAu alloy was modeled using a 6 × 6 supercell consisting of three atomic layers of Ag(111), in which four atomic sites per layer were substituted with Au atoms to simulate a homogeneous doping configuration. To investigate the role of POM, an AgAu-SiW₉ system was further prepared by anchoring charge-compensated neutral species SiW₉O₃₄H₁₀ (SiW₉) onto an optimized AgAu alloy substrate. All models were fully relaxed and served as the foundation for subsequent electronic

structure analysis and reaction pathway exploration.

Fig. 4(d) presents the complete Gibbs free energy profile for the conversion of nitrate to ammonia over the AgAu-SiW₉ catalyst. The overall reaction proceeds via successive PCET steps, involving critical adsorbed intermediates, including ^{*}NO₃, ^{*}NO₂, ^{*}NO, ^{*}NOH, ^{*}N, ^{*}NH, ^{*}NH₂, and ^{*}NH₃. Among these steps, the hydrogenation from ^{*}NO to ^{*}NOH is regarded as the rate-determining step (RDS) with a free energy barrier of 0.46 eV, which is relatively low and suggests favorable thermodynamics for ammonia formation on AgAu-SiW₉. Additionally, we assessed the competing pathway toward hydroxylamine (NH₂OH) formation, with the results presented in Fig. S18. In comparison, the ammonia synthesis pathway is clearly predominant.

To further elucidate the role of Au alloying and POM modification, the reaction energy barriers of the rate-determining step (^{*}NO -to- ^{*}NOH) were calculated for different catalyst systems, as summarized in Fig. 4(e). The obtained barriers are 0.54 eV (Ag), 0.52 eV (Au), 0.51 eV (AgAu), and 0.46 eV (AgAu-SiW₉). The three bare substrates exhibit only minor differences among themselves. However, the addition of SiW₉ considerably reduces the barrier to 0.46 eV, indicating that the POM cluster plays a notable role in accelerating the critical hydrogenation step.

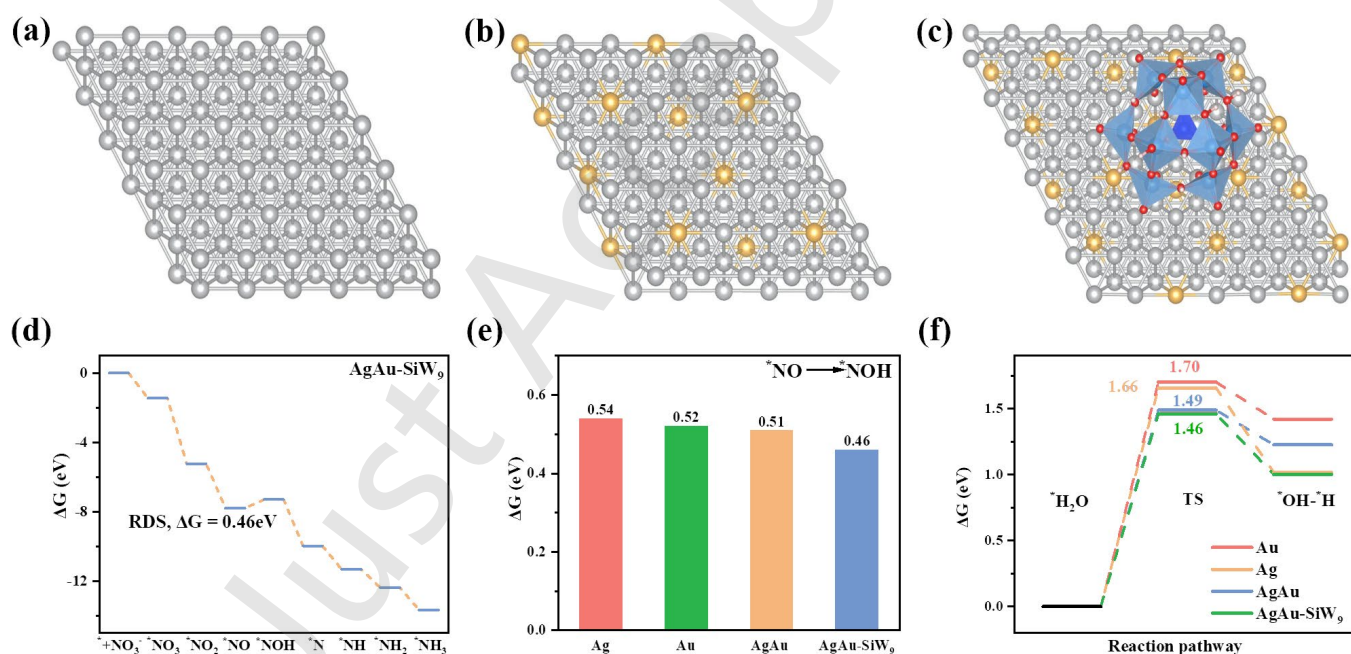


Figure 4. Reaction mechanism and Gibbs free energy pathway analysis based on DFT calculations: (a–c) Optimized Structures of Ag, AgAu and AgAu-SiW₉; (d) The Gibbs free energy diagrams of NO₃RR to ammonia for the AgAu-SiW₉; (e) The reaction energy barrier of rate-determining step (RDS, ^{*}NO-^{*}NOH) for Ag, Au, AgAu and AgAu-SiW₉; (f) The reaction pathway of water splitting for Ag, Au, AgAu and AgAu-SiW₉.

In addition, we further evaluated the hydrolysis capability of each system, as the generation of adsorbed ^{*}H from water dissociation is a prerequisite for the subsequent hydrogenation steps. As shown in Fig. 4(f), the AgAu-SiW₉ catalyst exhibits the lowest energy barrier for ^{*}H production via hydrolysis (1.46 eV), outperforming the Ag, Au, and AgAu counterparts. This enhanced water dissociation ability is consistent with its superior overall NO₃RR performance.

Collectively, these computational results demonstrate that the electronic modulation induced by AgAu alloying and POM

support effectively lower the activation barrier of the RDS while simultaneously promote ^{*}H supply from water dissociation. This dual enhancement synergistically boosts the overall NO₃RR activity toward selective ammonia synthesis.

4 Conclusions

In summary, a SiW₉-modified AgAu nanoalloy electrocatalyst supported on activated carbon (10% AuAg-SiW₉/C), was successfully prepared for efficient NO₃RR under the neutral condition. Structural characterization confirms the formation of highly dispersed AgAu alloys and the preservation of the intact

SiW₉ framework. Electrochemical measurements demonstrated that the catalyst achieved a superior NH₃ yield of 1.3963 mg h⁻¹ cm⁻² with an FE of 95% at -0.6 V vs. RHE. DFT calculations reveal that the synergistic interplay between Au-Ag alloying and SiW₉ modification significantly optimize the reaction kinetics by lowering the free energy barrier of the key *NO→*NOH step to 0.46 eV. This work proves that the coupling of alloy effect with POMs modification could serve as an effective strategy to enhance NO₃RR performance, providing a valuable reference of electrocatalyst design for nitrate remediation and sustainable ammonia synthesis.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article. Author Yangguang Li is the Associate Editor of this journal and one of the guest editors of this special issue, but he is not involved in the peer-review or decision of this article.

Author contribution statement

S.G.: Writing – original draft, investigation, conceptualization. H.D.R.: Writing – original draft, investigation, conceptualization. J.L.Y.: Investigation, conceptualization. R.Q.Y.: Writing – review & Editing. H.Q.T.: Writing – review & editing, investigation, funding acquisition. Y.H.W.: Writing–review&editing, Investigation, conceptualization, funding acquisition. Y.G.L.: investigation, funding acquisition.

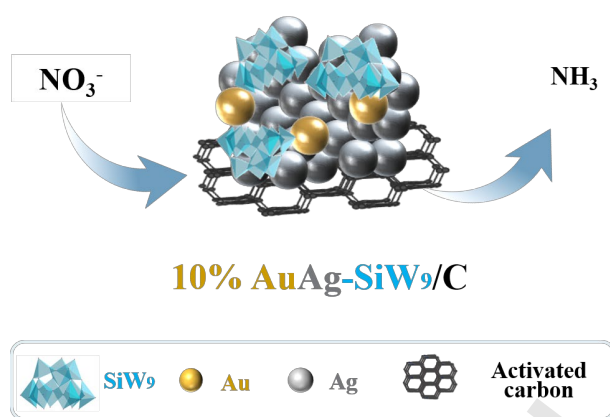
Use of AI statement

During the preparation of this work, the authors used DeepSeek to revise the manuscript. After using this tool, the authors reviewed and edited the content as needed and took full responsibility for the content of the publication.

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Polyoxometalate-modified AgAu nanoalloy electrocatalysts enable efficient nitrate-to-ammonia conversion in neutral media by enhancing the water dissociation and accelerating the rate-determining hydrogenation step.

Electronic Supplementary Material

**Polyoxometalate-modified AgAu nanoalloy
electrocatalysts for highly efficient nitrate-to-ammonia
conversion**

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(Dedicated to Late Prof. M. T. Pope for his pioneering work on polyoxometalates)

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1. Synthesis of SiW₉ and the Control Samples

1.1 Synthesis of SiW₉

First, Na₂WO₄·2H₂O (182 g, 0.55 mol) and Na₂SiO₃·5H₂O (11 g, 0.05 mol) were dissolved in 200 mL of deionized water and magnetically stirred at 80-90 °C until a clear solution was formed. Subsequently, 130 mL of 6 M HCl was added dropwise to the above solution over a period of 30 min under vigorous stirring. The solution was then heated to boiling and concentrated to approximately 300 mL. Then, a Na₂CO₃ solution (50 g of Na₂CO₃ dissolved in 150 mL of deionized water) was slowly introduced into the system under stirring, and stirring was continued for 1 h. After the reaction completed, the precipitate was separated by vacuum filtration. The resulting solid was washed once with 1 L of 4 M NaCl solution, three times with deionized water, and subsequently once each with ethanol (100 mL) and diethyl ether (100 mL). Finally, the product was dried under vacuum at 60 °C overnight to afford the SiW₉.

1.2 Synthesis of the control samples

1.2.1 Preparation of the Ag/C Catalyst

500 µL of 0.1 M AgNO₃ solution was added to 145 mL of supercooled deionized water (4–6 °C) and stirred continuously for 30 min. Subsequently, a freshly prepared NaBH₄ solution was added dropwise as the reducing agent under continuous stirring. After the dropwise addition was complete, stirring was continued for another 40 min to ensure complete reduction of Ag⁺ to Ag nanoparticles. Then, 97 mg of activated carbon was introduced into the reaction system, and stirring was maintained for an additional 15 min to allow the resulting Ag nanoparticles to be uniformly loaded onto the activated carbon surface. Afterward, the solvent was removed by rotary evaporation, and the collected solid product was dried in a vacuum oven at 60 °C, ultimately yielding the Ag/C catalyst powder.

1.2.2 Preparation of the Au/C Catalyst

500 µL of 0.1 M HAuCl₄ solution was added to 145 mL of supercooled deionized water (4–6 °C) and stirred continuously for 30 min. Subsequently, a freshly prepared NaBH₄ solution was added dropwise as the reducing agent under continuous stirring. After the dropwise addition was complete, stirring was continued for another 40 min to ensure complete reduction of Au³⁺ to Au nanoparticles. Then, 97 mg of activated carbon was introduced into the reaction system, and stirring was maintained for an additional 15 min to allow the resulting Au nanoparticles to be uniformly loaded onto the activated carbon surface. Afterward, the solvent was removed by rotary evaporation, and the collected solid product was dried in a vacuum oven at 60 °C, ultimately yielding the Au/C catalyst powder.

1.2.3 Preparation of the AgAu/C Catalyst

HAuCl₄ solution (50 µL, 0.1 M) and AgNO₃ solution (450 µL, 0.1 M) were added to 145 mL of supercooled deionized water (4–6 °C) and stirred continuously for 30 min to ensure thorough mixing of the Ag and Au precursors. Subsequently, a freshly prepared NaBH₄ solution was added dropwise as the reducing agent under continuous stirring. After addition was complete, stirring was continued for another 40 min to ensure the complete reduction of Ag⁺ and Au³⁺ to form AgAu nanoparticles. Activated carbon (97 mg) was then introduced into the reaction system, and stirring was continued for an additional 15 min to allow the resulting AgAu nanoparticles to be uniformly loaded onto the activated carbon surface. Thereafter, the solvent was removed by rotary evaporation, and the solid product was collected and dried in a vacuum oven at 60 °C to finally afford the AgAu/C catalyst powder.

1.2.4 Preparation of Au–SiW₉/C Catalyst

SiW₉ (150 mg) was added to 145 mL of low-temperature deionized water (4–6 °C) and stirred until completely dissolved. Subsequently, HAuCl₄ solution (500 μL, 0.1 M) was introduced and stirring was continued for 30 min to promote sufficient interaction between the Au precursor and the SiW₉ ligand. Freshly prepared NaBH₄ solution was then added dropwise as the reducing agent under stirring. After the addition was complete, stirring was continued for another 40 min to ensure complete reduction of Au³⁺ to form Au nanoparticles and their stable association with the SiW₉ species. Activated carbon (97 mg) was then added to the reaction system, and stirring was continued for an additional 15 min to allow the SiW₉-modified Au nanoparticles to be uniformly loaded onto the activated carbon surface. Upon completion of the reaction, the solvent was removed by rotary evaporation, and the solid product was collected. The resulting product was washed three times with deionized water to remove any unreacted POM residues and once with ethanol to reduce surface-adsorbed water. Finally, the product was dried in a vacuum oven at 60°C to afford the Au–SiW₉/C catalyst powder.

1.2.5 Preparation of the Ag–SiW₉/C Catalyst

First, 150 mg of SiW₉ was added to 145 mL of low-temperature deionized water (4–6 °C) and stirred until completely dissolved. Subsequently, 500 μL of 0.1 M AgNO₃ solution was introduced, and the mixture was continuously stirred for 30 min to promote thorough interaction between the Ag precursor and the SiW₉ ligand. Freshly prepared NaBH₄ solution was then added dropwise under stirring as a reducing agent. After the addition was complete, stirring continued for 40 min to ensure full reduction of Ag⁺ to form Ag nanoparticles and their stable coordination with the SiW₉ species. Next, 97 mg of activated carbon was added to the reaction mixture and stirred for an additional 15 min to achieve uniform loading of the SiW₉-modified Ag nanoparticles onto the carbon surface. Upon completion of the reaction, the solvent was removed by rotary evaporation, and the solid product was collected. The resulting material was washed three times with deionized water to remove residual unreacted POMs, followed by a single ethanol wash to reduce surface-adsorbed water. Finally, the product was dried in a vacuum oven at 60 °C to obtain the Ag–SiW₉/C catalyst powder.

2. Methods

2.1 Materials Characterization

The morphology, structure, and chemical composition of the samples were characterized using various analytical techniques. Powder X-ray diffraction (PXRD) patterns were collected by a Rigaku D/max-BX X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were acquired by an FEI Talos F200X G2 instrument. The surface chemical states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS-Supra+) using a monochromatic Al Kα source (150 W, pass energy 40 eV, spot size 700 × 300 μm). The O 1s spectra were fitted using a Gaussian–Lorentzian function, with the full width at half maximum (FWHM) constrained to a consistent value of 1.62 eV for identical chemical states. Raman spectra were recorded on a Renishaw InVia confocal micro-Raman spectrometer with an excitation wavelength of 532 nm. UV-vis diffuse reflectance spectra (UV-vis DRS) were measured using a Shimadzu UV-2600 spectrophotometer. The characteristic chemical bonds of SiW₉ were verified by Fourier transform infrared (FT-IR) spectroscopy using an Alpha Centauri spectrometer.

2.2 Electrochemical Measurements

Electrochemical performance measurements were conducted on an Imperial Squidstat Plus (CHI760, Chenhua) electrochemical workstation using a standard H-type two-compartment cell separated by a Nafion 117 proton exchange membrane. The Nafion membrane was subjected to standardized pretreatment and subsequently immersed in deionized water. To eliminate any background nitrogen contamination, all glassware, the electrolytic cell, and associated components were rigorously cleaned before use. In addition, a standard three-electrode configuration was employed. Catalyst-loaded carbon cloth (1 cm × 1.6 cm, exposed

geometric area) served as the working electrode, while a platinum sheet served as the counter electrode, and a saturated calomel electrode (SCE, Hg/Hg₂Cl₂) acted as the reference electrode. The cathodic and anodic compartments were both filled with 40 mL of 1 M phosphate-buffered saline (PBS) solution (pH = 7.4-7.45), with the catholyte with/without 0.1 M KNO₃. Prior to testing, the electrolyte was purged with high-purity Ar (99.999%) for 15 min to remove dissolved oxygen. All electrochemical tests were performed at room temperature. All key experiments were independently repeated at least three times, with the results expressed as mean values. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation(Eq.1)[1]:

$$E(\text{vs. RHE})=E(\text{vs. Hg/Hg}_2\text{Cl}_2) + 0.241 + 0.059 \times \text{pH (V)} \quad (1)$$

where, 0.241 V represents the potential of the saturated calomel electrode (SCE, Hg/Hg₂Cl₂/KCl sat.) with respect to the standard hydrogen electrode (SHE).

2.3 Product Analysis

NH₃ was quantified using the indophenol blue method, (i.e., the phenol-hypochlorite colorimetric method)[2]. Ion chromatography (IC) analysis confirmed that the NO₂⁻ concentration in the reaction solution was below the detection limit, ruling out potential interference from NO₂⁻ in the indophenol blue method for NH₃ determination and ensuring the reliability of the quantification. After electrolysis, 1 mL of the catholyte (diluted 20-fold) was mixed with the chromogenic reagent and allowed to react for 150 min at 4 °C in the dark, after which the absorbance was measured at 655 nm. The NH₃ concentration was calculated from an NH₄Cl standard calibration curve (0-4 µg/mL, R² > 0.995).

The calculation equations of NO₃RR are as shown in Equ. 2 and 3.

$$\text{Ammonia yield rate: Yield}_{\text{NH}_3} = (C_{\text{NH}_3} \times V) / (M_{\text{NH}_3} \times t \times A) \quad (2)$$

$$\text{Faradaic efficiency: FE}_{\text{NH}_3} = (8 \times F \times C_{\text{NH}_3} \times V) / (M_{\text{NH}_3} \times Q) \quad (3)$$

where, C_{NH₃} is the measured NH₃ concentration, V is the volume of the electrolyte (40mL), M_{NH₃} is the molar mass of NH₃(17g/mol), t is the reduction reaction time(1h), A is the geometric electrode area, F is the Faraday constant (96485 C/mol), and Q is the charge accumulated via 1 h electrocatalysis.

A piece of carbon cloth (1.0 × 2.0 cm²) was used as the substrate. After being clamped by the electrode holder, the actual working area exposed to the electrolyte was controlled to be 1.6 cm². The catalyst was loaded on carbon cloth with a mass loading of 2.0 mg cm⁻². The calculated NH₃ yield was 1.3963 mg h⁻¹ cm⁻²(0.698 mg h⁻¹ mg_{cat}⁻¹).

2.4 DFT Theoretical Calculations

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP). The exchange correlation functional was treated at the Perdew-Burke-Ernzerhof (PBE) level[3-4]. The electron-ion interaction is described using the projector-augmented plane wave (PAW) scheme [5-6]. The kinetic energy cut off was set to 400 eV. All the atoms in the cell were allowed to relax during the geometric optimizations until the energy convergence threshold and forces were smaller than 10⁻⁵ eV and 0.03 eV Å⁻¹. The Brillouin zone was sampled using the Gamma-centered scheme scheme with a 1 × 1 × 1 k-point mesh. (sufficient for this large 6×6 supercell). A vacuum layer of ~15 Å was applied along the surface normal to avoid interlayer interactions. Additionally, a dipole correction (IDIPOL = 3, LDIPOL = TRUE.) was applied along the surface normally to eliminate the artificial electrostatic field across the vacuum layer due to the asymmetric slab model. The post-processing of energy corrections (zero-point energy and entropy) was performed with the help of the VASPKIT code [7]. A periodic slab model was employed to describe the Ag (111) surface (6×6 supercell, three-layer structure), in which some Ag atoms were substituted by Au atoms for doping. Protons (H⁺) were utilized to compensate for the charge of the polyoxometalate anion. Specifically, the protonated species SiW₉O₃₄H₁₀ is referred to collectively as SiW₉ in the following discussion. SiW₉ molecules were adsorbed onto the metal surface to construct the interface models.

Supplementary Figures

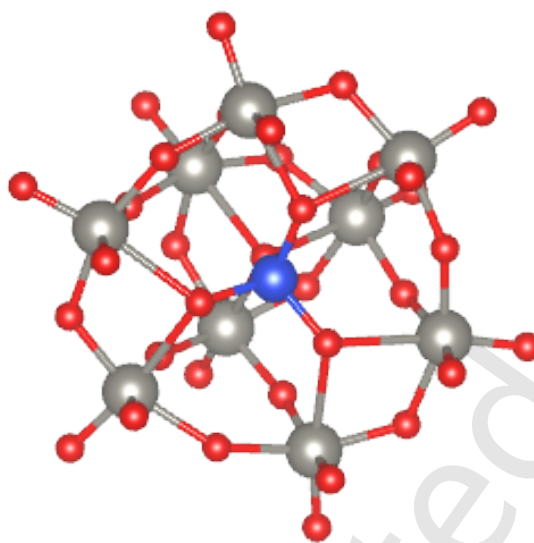


Figure S1 Structural model of the trivacant Keggin-type $[\text{SiW}_9\text{O}_{34}]^{10-}$ unit. Color code: Si, blue; W, gray; O, red.

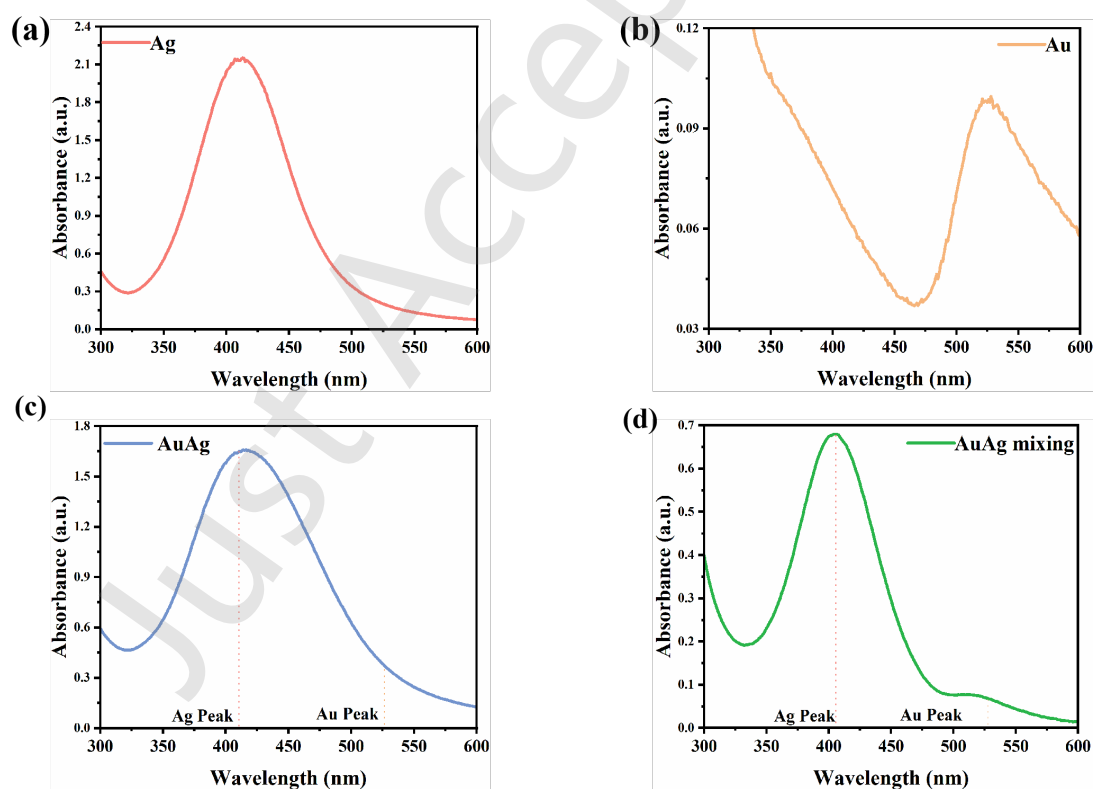


Figure S2 UV-vis DRS spectra of: (a) pure Ag; (b) pure Au; (c) Ag+Au physical mixture; (d) AgAu alloy nanoparticles.

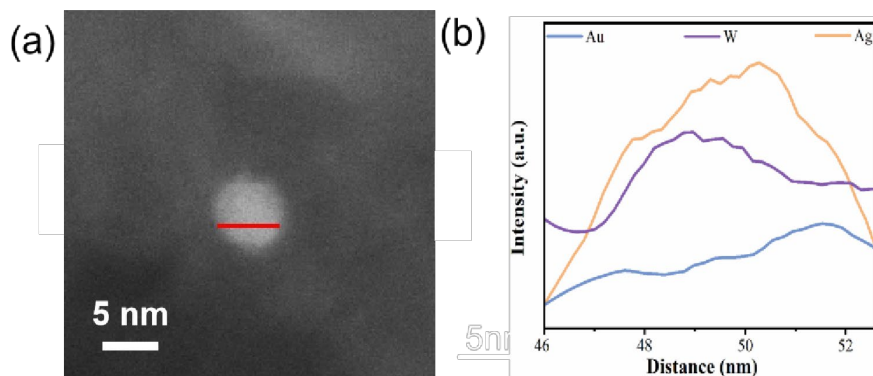


Figure S3 Single-particle (a) STEM image and (b) corresponding EDX line-scan profile of 10% AuAg-SiW₉/C.

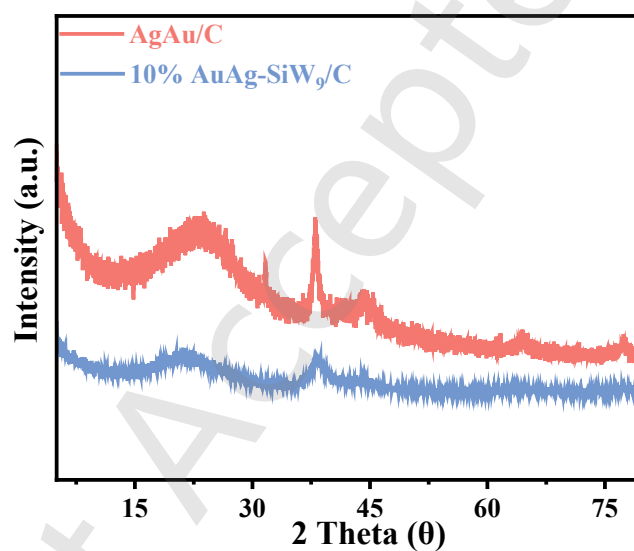


Figure S4 X-ray diffraction (XRD) patterns of the AgAu/C and 10% AuAg-SiW₉/C catalysts, where the red curve represents the AgAu/C catalyst without SiW₉ modification, and the blue curve represents the 10% AuAg-SiW₉/C catalyst with SiW₉ incorporation.

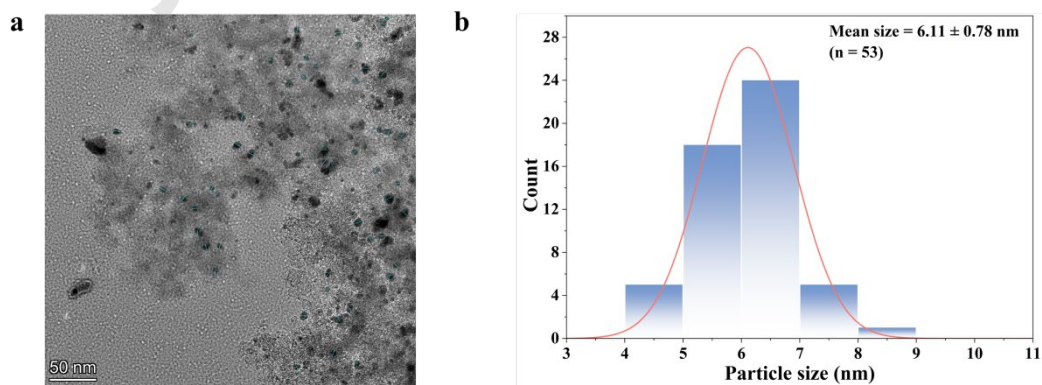


Figure S5 TEM images and particle size distribution of 10%AuAg-SiW₉/C: (a) AgAu nanoparticles disperse uniformly on carbon matrix from TEM observation. (b) Statistical analysis of 53 particles gives mean particle size of 6.11 ± 0.78 nm

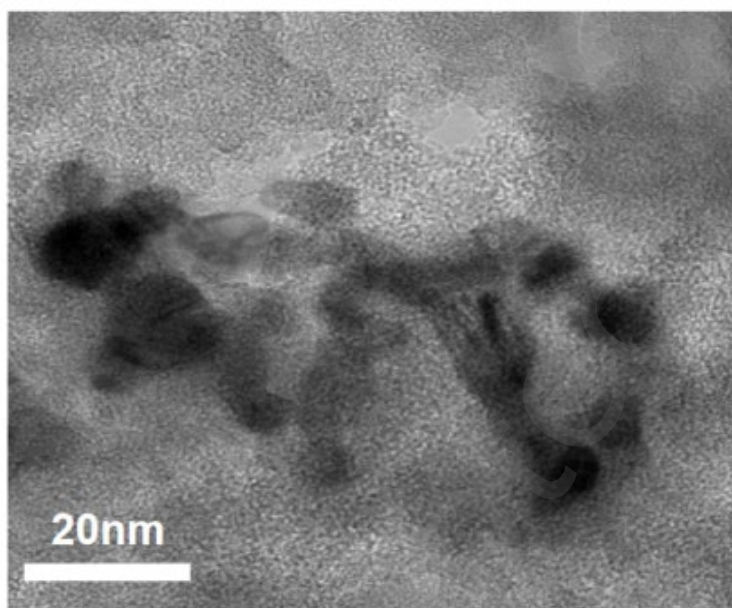


Figure S6 Transmission electron microscopy (TEM) image of the AgAu/C catalyst. In the absence of SiW₉ modification, the AgAu nanoparticles underwent severe aggregation, forming large, irregularly shaped agglomerates without the characteristic features of uniform dispersion.

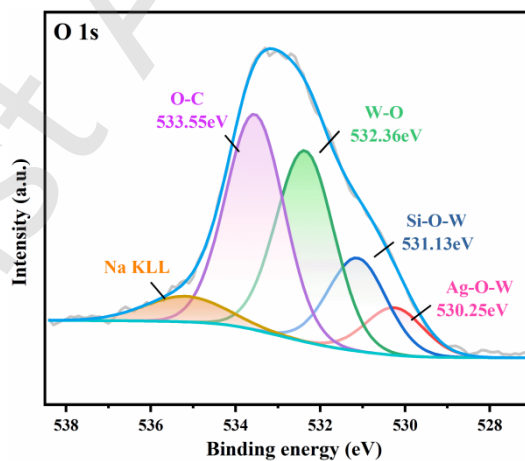


Figure S7 High-resolution O 1s XPS spectrum of 10% AuAg-SiW₉/C, showing the deconvoluted oxygen species associated with Ag-O-W, Si-O-W, W-O, C-O, and Na KLL.

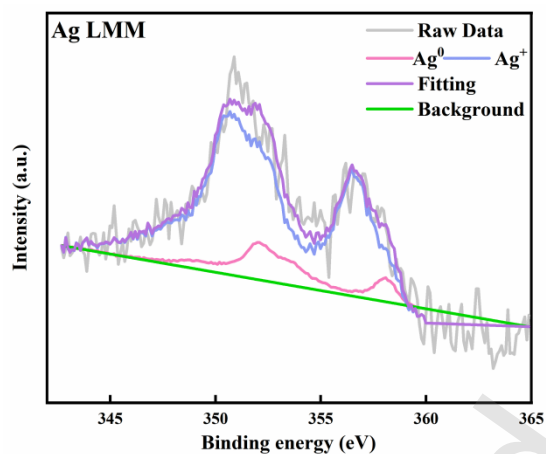


Figure S8 Deconvoluted Ag LMM Auger spectrum of 10% AuAg-SiW₉/C.

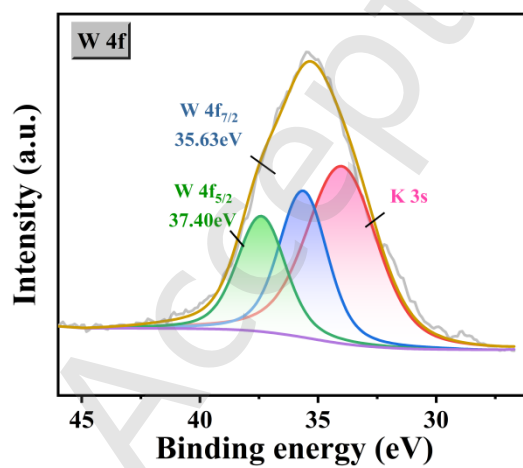


Figure S9 W 4f XPS spectra after reaction.

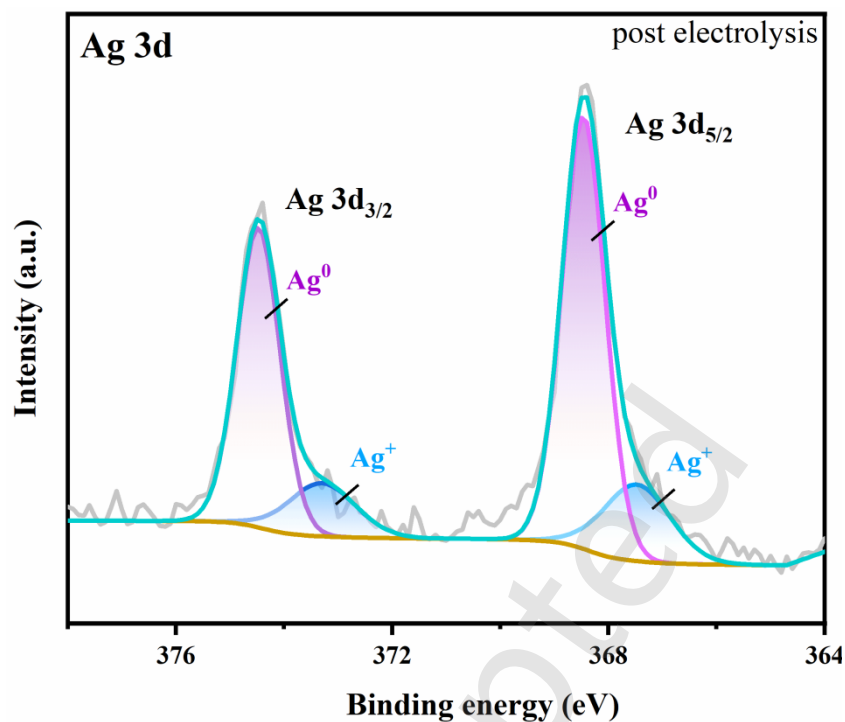


Figure S10 Ag 3d XPS spectra after reaction.

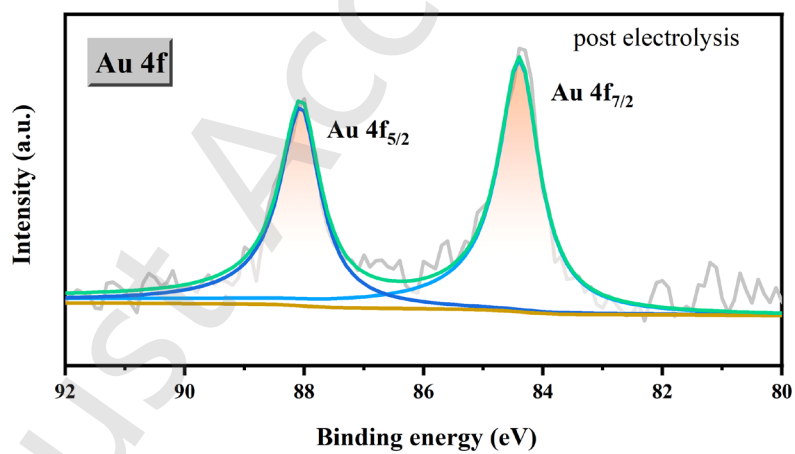


Figure S11 Au 4f XPS spectra after reaction.

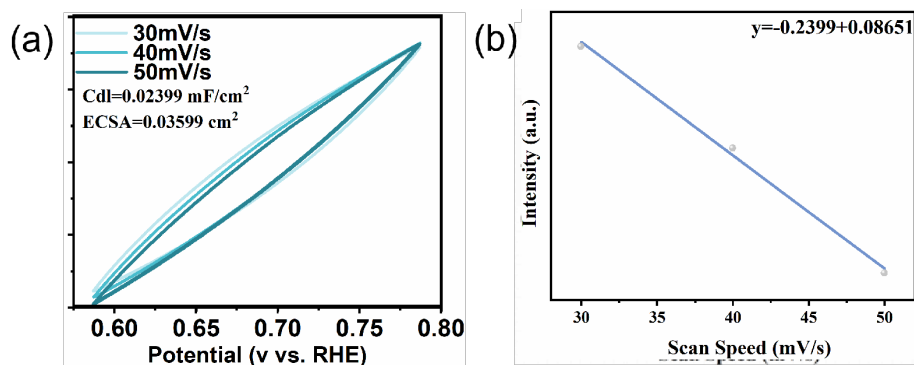


Figure S12(a)(b) CV curves in non-Faradaic region of 10% AuAg-SiW₉/C (0.60–0.80 V vs. RHE, 10–50 mV/s) for Cdl.

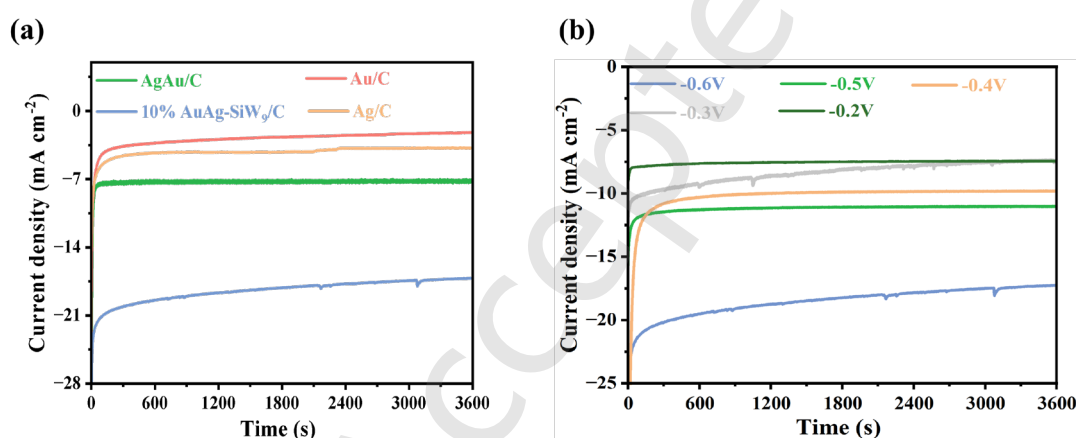


Figure S13 Chronoamperometric curves of different catalysts: (a) chronoamperometric responses of AgAu/C, 10% AuAg-SiW₉/C, Au/C, and Ag/C, where the current densities of all samples remained essentially stable throughout the 3600 s test, indicating favorable electrochemical stability, and among these, 10% AuAg-SiW₉/C exhibited the highest current density; (b) chronoamperometric (i-t) curves of the 10% AuAg-SiW₉/C catalyst at various applied potentials.

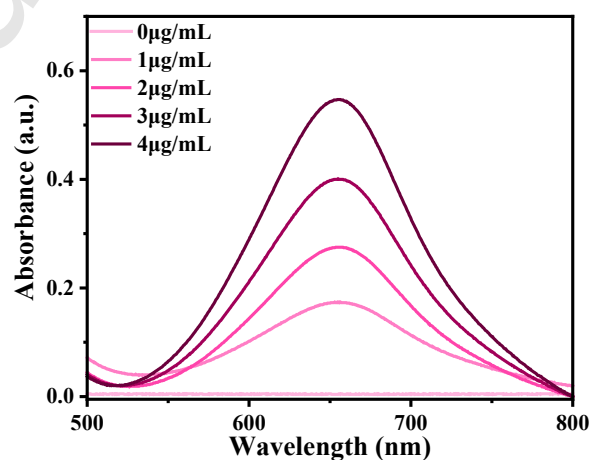


Figure S14 UV-vis absorption spectra of the NH₄Cl standard solutions at different concentrations.

The UV-vis absorption spectra of NH_3 standard solutions at various concentrations for standard curve measurement exhibit a characteristic absorption peak at approximately 655 nm.

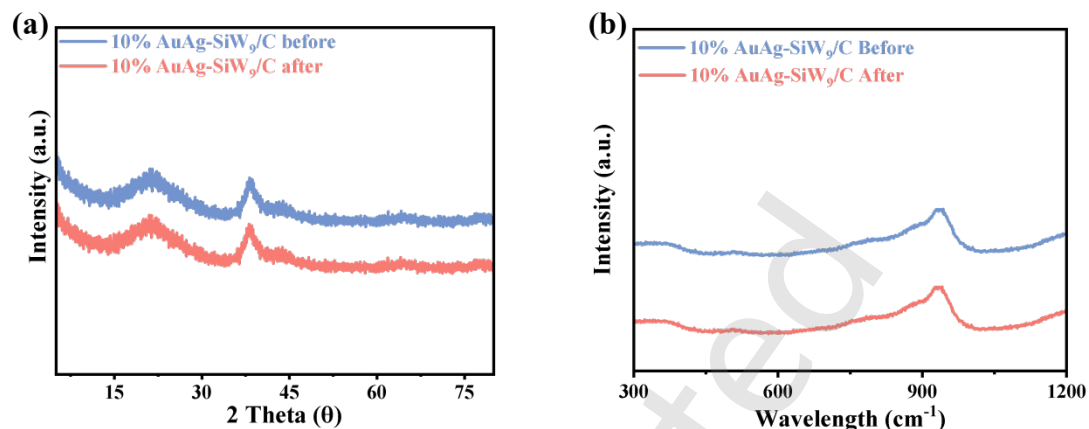


Figure S15 Structural characterization of 10% AuAg-SiW₉/C before and after the NO₃RR stability test: (a) XRD patterns of 10% AuAg-SiW₉/C collected before and after electrolysis, showing that the characteristic diffraction peaks remain essentially unchanged. (b) Raman spectra of 10% AuAg-SiW₉/C before and after electrolysis, where the characteristic vibrational bands are well preserved, indicating the structural integrity of the catalyst during the NO₃RR process.

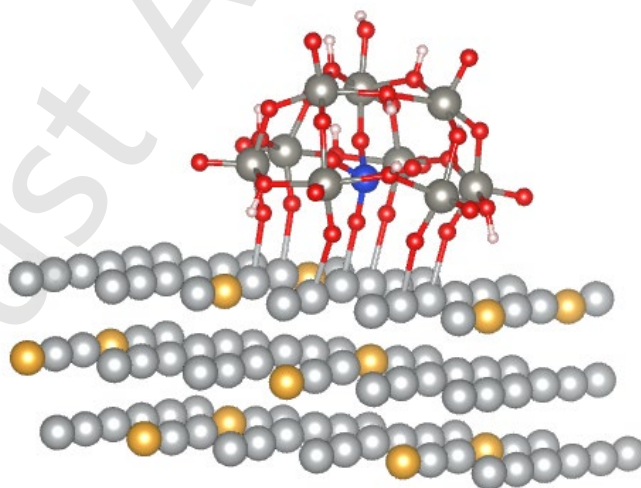


Figure S16 Optimized structural model of the 10% AuAg(111)-H₁₀SiW₉O₃₄ interface.

Color code: Au, gold; Ag, silver; W, gray; Si, blue; O, red.

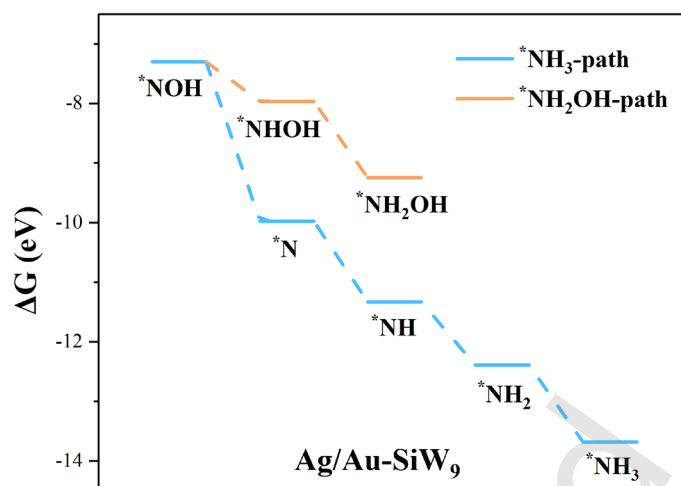


Figure S17 Comparison of the reaction pathways for hydroxylamine (NH₂OH) formation and ammonia (NH₃) synthesis.

Supplementary Tables

Table S1 Quantitative EDX atomic ratio analysis of the catalyst after aqueous washing of the 10% AuAg-

SiW ₉ /C		
Spot	Au(Atom %)	Ag (Atom %)
#1	7.17	92.83
#2	10.61	89.39
#3	8.28	91.72
Average ± SD	8.69 ± 1.76	91.31 ± 1.76

Table S2 Comparison with recently reported carbon-cloth-supported NO₃RR electrocatalysts in neutral electrolyte

Catalyst	Electrolyte	FE	Ref
10% AuAg-SiW₉/C	PBS	95%	This work
RuFeCoNiMnMo HEAs	0.50 M K ₂ SO ₄ + 0.1 M KNO ₃	99.3%	[8]
Co@C@Cu	0.1 M Na ₂ SO ₄ + 0.1 M NaNO ₃	98.0%	[9]
RhCu NCs	0.50 M Na ₂ SO ₄ + 0.1 M NO ₃ ⁻	97.5%	[10]
PCN-250(Fe ₂ Co)	0.1 M Na ₂ SO ₄ + 0.1 M KNO ₃	97.5%	[11]
Ru=Ru/DAC	0.1 M Na ₂ SO ₄ + 0.1 M NaNO ₃	95%	[12]
Cu ₂ Cl ₂ (BINAP) ₂	0.5 M K ₂ SO ₄ + 0.1 M KNO ₃	94.0%	[13]
Cu@bpy-COF	0.5 M K ₂ SO ₄ + 0.1 M KNO ₃	93.63%	[14]
Cu/Co ₄ N	0.5 M K ₂ SO ₄ + 0.1 M KNO ₃	93%	[15]
TpBpy-Cu-F	0.5 M Na ₂ SO ₄ + 0.1 M NaNO ₃	92.7%	[16]
Cu/g-C ₃ N ₄	0.1 M Na ₂ SO ₄ + 0.1 M NaNO ₃	92.4%	[17]
Ni-Co ₃ O ₄ NSs	0.1 M K ₂ SO ₄ + 0.1 M KNO ₃	92.1%	[18]
Cu-La/DAC	0.1 M PBS + 0.1 M NaNO ₃	88.42%	[19]
PMo ₁₁ Fe@PCN-224(Cu)	0.1 M Na ₂ SO ₄ + 0.1 M NaNO ₃	83.5%	[20]
NU-902(Cu)	0.1 M Na ₂ SO ₄ + 0.1 M NaNO ₃	71.65%	[21]

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