

Piezoelectric-induced ligand transformation of metal chlorides in acetonitrile for controllable synthesis of noble metal single-atom catalysts

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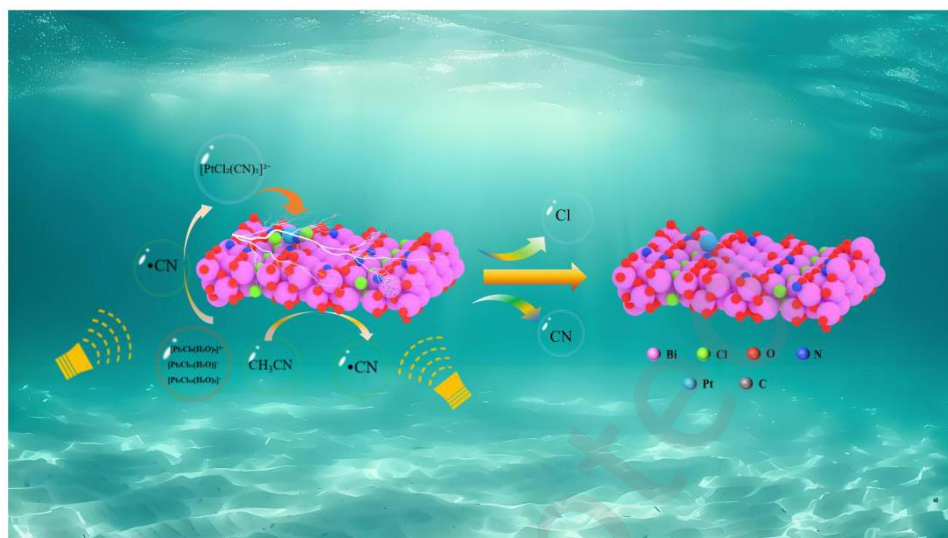
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TOC



Piezoelectrically driven acetonitrile dissociation yields soft-base $\cdot\text{CN}$ radicals, which partially replace borderline-base Cl^- ligands in H_2PtCl_6 to form stable $[\text{PtCl}_2(\text{CN})_2]^{2-}$ intermediates that inhibit uncontrolled Pt species dissociation. Subsequent reduction by piezoelectrically enriched electrons, coupled with the site selectivity of the piezoelectric field, achieves selective Pt single-atom deposition.

Research Article

Piezoelectric-induced ligand transformation of metal chlorides in acetonitrile for controllable synthesis of noble metal single-atom catalysts

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Abstract:

The synthesis of single-atom catalysts (SACs) under mild conditions remains challenging due to the difficulty in controlling precursor dissociation and preventing metal atom aggregation. Here, we present a piezoelectricity-driven "strong-ligand substitution" strategy based on Pearson's hard-soft acid-base principle. By enhancing ligand-metal and ligand-substrate interactions, we precisely regulate metal release kinetics, suppress migration, and achieve accurate anchoring of noble-metal single atoms (Au, Pt, Pd, Ru) on piezoelectric substrates (e.g., BiOCl, Bi₃Ti₄O₁₂) under mild conditions. Herein, the as-prepared SACs show markedly improved TOF values: Pt₁@CdS (photocatalytic H₂ evolution), Pt₁@BOC (piezocatalytic H₂ evolution), and Pd₁@Bi₃Ti₄O₁₂ (ammonia-borane hydrolysis) reach 33.9, 31.4, and 5.2 times those of their respective nanoparticle references, respectively. Using H₂PtCl₆·6H₂O as a model precursor, combined spectroscopic, mass spectrometric, NMR, and computational analyses reveal two distinct transformation pathways during piezoelectric reduction: in water, [PtCl₆]²⁻ is directly reduced to nanoparticles; in acetonitrile, piezoelectric activation induces nitrogen doping of the substrate and generates ·CN radicals that partially replace chloride ligands, forming [PtCl₂(CN)₂]²⁻. The high dissociation energy of CN slows metal release, while strong coordination with the N-doped substrate enhances anchoring stability, synergistically promoting

efficient and stable Pt single-atom dispersion. Moreover, piezocatalysis is shown to critically impact Pt species formation and single-atom deposition site selection. This work provides a mild synthesis route and elucidates the solvent and piezoelectric catalysis synergy in single-atom formation at the molecular level.

Keywords: piezoelectric effect, acetonitrile, solvent effect, single-atom catalysts, ligand transformation

1. INTRODUCTION

Single-atom catalysts (SACs), characterized by their atomically dispersed metal active sites ($M-X$, $X = N, O, S \dots$), achieve theoretical 100% atom utilization efficiency[1, 2]. The isolated metal atoms form uniform $M-X$ active centers through coordination bonds with the support, exhibiting quantum confinement effects, tunable selectivity, and designable coordination environments[3-5]. These properties endow SACs with paradigm-shifting potential in photo-, electro-, and thermal-catalysis, with particular value enhancement for noble metal systems (e.g., Pt, Pd, Au)[6-8]. Since the concept of SACs applied in catalytic reactions was pioneered by Zhang et al. in 2011, SAC synthesis has faced a fundamental challenge: the thermodynamic driving force for metal atom aggregation versus the kinetic disorder of atomic diffusion[9]. Prevailing strategies—including coordination stabilization (e.g., $Fe-N_4$ site anchoring), high-temperature support reconstruction (e.g., Pt incorporation into Al_2O_3 lattice), dynamic trapping techniques (e.g., laser thermal etching), low-temperature inhibition, and reverse thermodynamic regulation—generally require harsh conditions (e.g., extreme temperatures, inert atmospheres), which present substantial barriers to industrial scale-up[10-12]. More critically, such stringent conditions greatly hinder the characterization of SACs formation pathways, impeding mechanistic insight into nucleation and evolution processes. Consequently, the development of mild synthetic approaches coupled with fundamental understanding of formation mechanisms represents an urgent requirement towards practical application of single-atom catalysis technologies.

Among the existing green single-atom synthesis strategies under ambient conditions, photocatalytic synthesis represents a typical approach. This strategy utilises charge carriers generated by photoexcitation of photocatalysts to react with solvent molecules, producing radicals that interact with metal precursors through specific coordination, thereby overcoming the thermodynamic and kinetic barriers in single-atom formation. For instance, Zheng et al. reported a

groundbreaking approach in which glycol radicals generated photocatalytically were combined with specific surface Ti sites on B-TiO₂ and a tailored coordination structure around Pd atoms, achieving stable anchoring of Pd single atoms on the TiO₂ surface[13]. This strategy effectively suppressed Pd atom migration and addressed the aggregation issue commonly encountered during single - atom formation, establishing a pioneering method for SAC synthesis under mild conditions. However, such methods remain limited by their reliance on specific metal-ligand-support combinations-as seen in the glycol-Pd-TiO₂ system—resulting in limited generalisability. Bian et al. reported a strategy using photogenerated holes to induce CH₃CN formation of cyanomethyl radical ($\cdot\text{CH}_2\text{CN}$), enabling SACs preparation in broader systems[14]. They proposed that $\cdot\text{CH}_2\text{CN}$ could inhibit metal-metal bond formation, yet the mechanistic details of single-atom formation remain unexplored. The aforementioned studies demonstrate the use of active radicals generated during photocatalysis to regulate the formation of single atoms offers the distinct advantage of mild reaction conditions. This provides an important insight: utilizing highly reactive radicals for the in-situ substitution of chloride ligands in common noble metal chlorates can effectively enhance the interaction between ligands and central metal atoms. Consequently, this increases the dissociation energy of ligands during the metal atom release stage, thereby enabling precise control over the release rate of metal atoms. Simultaneously, strengthening the adsorption between active species and the support material can further suppress the migration of metal species and regulate their local concentration on the support surface. The synergy of these two effects provides a viable strategy to address the thermodynamic and kinetic challenges associated with the preparation of noble metal single atoms.

In recent years, significant progress has been made in piezoelectric catalysis. Under external mechanical forces such as ultrasound, piezoelectric materials undergo deformation, leading to the separation of their internal positive and negative charge centers and the consequent generation of polarization charges. Functionally similar to photogenerated charge carriers in photocatalysis, these polarization charges can drive redox reactions of substrate molecules, producing corresponding active radicals. Compared to photocatalysis, which is constrained by the Lambert-Beer law-where light intensity decays exponentially with penetration depth in solution, significantly reducing light utilization efficiency in suspension systems-piezoelectric catalysis exhibits notable advantages: ultrasound can establish a uniform acoustic field throughout the

reactor, inducing overall deformation of piezoelectric materials and generating evenly distributed polarization charges [15, 16]. These polarization charges can effectively excite solvent molecules to produce active radicals[17]. This approach overcomes the limitations of mass transfer and spatial distribution inherent in conventional photocatalysis. However, to the best of our knowledge, no studies have yet been reported on the rational design of ligands based on the Hard-Soft Acid-Base principle to modulate the interaction strength between ligands and central metal atoms for the preparation of SACs, nor have there been any reports on utilizing the piezoelectric effect of piezoelectric materials to fabricate SACs.

According to Pearson's Hard- Soft Acid- Base principle, noble metal ions—with their large ionic radii and high polarizability—are typical soft acids that readily coordinate with soft- base radical ligands, enabling precise tuning of metal- ligand interaction strength [18-20]. This offers a promising route to address the thermodynamic and kinetic challenges in noble- metal single- atom catalyst preparation. Previous reports indicate the stability order of noble- metal-anion complexes as $\text{CN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NCS}^- > \text{NCO}^-$, suggesting that cyanide (CN^-) as a ligand provides higher coordination stability and greater potential for efficient single- atom synthesis. Based on this, we propose a “piezoelectric material-noble metal chloride- CH_3CN solvent” strategy for synthesizing single- atom catalysts. Under the piezoelectric effect, CH_3CN generates soft- base cyanide radicals ($\cdot\text{CN}$), which partially replace chloride ligands in noble metal chlorides, strengthening the metal- ligand interaction and facilitating single- atom formation. The resulting monomeric species $[\text{PtCl}_2(\text{CN})_2]^{2-}$ shows high dissociation energy, effectively suppressing rapid Pt release. Moreover, enhanced coordination between this intermediate and the piezoelectric surface raises the adsorption energy of Pt species from -0.1275 eV to -2.1187 eV, inhibiting migration and agglomeration. Together, these effects overcome the thermodynamic aggregation barrier and kinetic migration limitation, enabling atomically dispersed Pt anchoring on the piezoelectric material. Notably, this approach exhibits good dispersion generality across soft- acid noble metals (Pd, Au, Ru) and various piezoelectric substrates ($\text{Bi}_3\text{Ti}_4\text{O}_{12}$, BiOCl , CdS). In summary, this work provides new insights into the controlled synthesis and rational design of single- atom catalysts in ambient liquid- phase environments.

2. MATERIAL AND METHOD

2.1 Chemicals

All chemical reagents employed in this study were without further purification. Bismuth trichloride (BiCl_3), anhydrous ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), sodium hydroxide (NaOH), Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), Ammonium heptamolybdate(IV) tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), ethylenediamine (EDA), thiourea ($\text{CS}(\text{NH}_2)_2$) were purchased from Macklin. Acetonitrile (CH_3CN , HPLC, 99.9%), 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ, AR, 98%), triethanolamine ($\text{C}_6\text{H}_{15}\text{NO}_3$, AR, >99%) were purchased from Sigma Aldrich. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, RG, 99.9%), Tetra-hydrated chloroauric acid ($\text{AuCl}_4(\text{H}_2\text{O})_4$, RG, 99.9%), ruthenium(III) chloride (RuCl_3 , RG, 99.5%), palladium chloride (K_2PdCl_6 , RG, 99.9%) were bought from Sinopharm Reagent Corp.

2.2 Synthesis of catalysts

2.2.1 Synthesis of $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$:

The $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (BOC) nanosheets were synthesized through an optimized hydrothermal protocol involving hydrothermal reactions. Initially, 0.5 g of bismuth trichloride (BiCl_3) precursor was homogeneously dispersed in 40 mL anhydrous ethanol under constant magnetic agitation for 30 min to ensure complete dissolution. The reaction system was then alkalized through controlled addition of 40 mL alkaline solution (0.4 g NaOH dissolved in deionized water) using a burette, which induced gradual formation of a colloidal yellow suspension. After complete phase separation, the intermediate product was hydrothermally treated in a 100 mL PTFE-lined autoclave maintained at 140°C for 12 h under autogenous pressure, followed by three alternating washing cycles with deionized water and ethanol to remove ionic residues. The final product was obtained as a crystalline powder after desiccation in a vacuum oven at 60°C for 8 h. $\text{OV-Bi}_{12}\text{O}_{17}\text{Cl}_2$ was prepared via a modified synthesis route of pristine $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$, involving the introduction of 0.2 g glucose into the precursor solution followed by calcination at 450°C for 2 h.

2.2.2 Synthesis of CdS :

10 mmol $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 30 mL EDA and stirred for 5 min. Next, 30 mmol $\text{CS}(\text{NH}_2)_2$ was added and stirred for another 30 min. Then, the above homogeneous solution was kept at 160°C for 24 h. After cooling, the yellow product was centrifuged with ethanol and

deionized (DI) water in turn for 6 times. Finally, the CdS NRs was obtained after drying at 60 °C for 12 h.

2.2.3 Synthesis of Bi₃Ti₄O₁₂:

Synthesis of Bi₃Ti₄O₁₂ Nanosheets as Templates: Bi₃Ti₄O₁₂ nanosheet templates were prepared using a one-step molten salt synthesis method. First, 3.625 g of NaCl and 4.659 g of KCl were taken as cosolvents, and ground for 10 min in an agate mortar. Next, stoichiometric amounts of Bi₂O₃ and TiO₂ nanopowders were added as starting materials at a molar ratio of NaCl:KCl:Bi₂O₃:TiO₂ = 62.5:62.5:5:7.5. This mixture was ground thoroughly for 1.5 h and transferred to a corundum crucible. Subsequently, the synthesis was performed in a furnace at 700 °C for 2 h (heating rate: 10 °C min⁻¹). After naturally cooling to room temperature, the obtained precipitates were washed with deionized water and ethanol several times and dried at 70 °C overnight.

2.2.4 Synthesis of SACs (Pt₁@BOC, Pd₁@BOC, Pd₁@Bi₃Ti₄O₁₂, Pt₁@CdS, Au₁@BOC, Ru₁@BOC)

M₁/BOC was synthesized through piezoelectric catalytic control. In a typical, 100 mg piezoelectric catalyst (BOC, CdS, Bi₃Ti₄O₁₂) was dispersed in 40 mL CH₃CN with a certain amount of noble metal chlorides salts (K₂PdCl₆, H₂PtCl₆·6H₂O, AuCl₄(H₂O)₄, RuCl₃) and was stirred at room temperature. The well-dispersed solution was subjected to ultrasonic treatment (45 kHz, 350W) for 2 h. Following ultrasonic treatment, the products were collected through centrifugation, washing, and drying. The noble metal (Pt, Pd, Au, Ru) contents in SACs(Pt₁@BOC, Pd₁@BOC, Pd₁@Bi₃Ti₄O₁₂, Pt₁@CdS, Au₁@BOC, Ru₁@BOC) were determined by ICP.

2.2.5 Synthesis of Pt_{nano}@BOC, Pd_{nano}@BOC, Pd_{nano}@Bi₃Ti₄O₁₂, catalysts

In a typical, 100 mg piezoelectric catalyst (BOC, Bi₃Ti₄O₁₂) was dispersed in 40 mL H₂O with a certain amount of noble metal chlorides salts (K₂PdCl₆, H₂PtCl₆·6H₂O) and was stirred at room temperature. The well-dispersed solution was subjected to ultrasonic treatment (45 kHz, 350W) for 2 h. Following ultrasonic treatment, the products were collected through centrifugation, washing, and drying. The noble metal (Pt, Pd) contents in catalysts (Pt_{nano}@BOC, Pd_{nano}@BOC, Pd_{nano}@Bi₃Ti₄O₁₂) were determined by ICP.

2.3 Characterization

The crystallographic characteristics of the synthesized samples were systematically characterized using multiple analytical techniques. Phase identification was performed through X-ray diffraction (XRD) analysis using a Rigaku D/max2550VB/PC diffractometer with Cu K α

radiation and the sweeping speed is 8°/min. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) analysis was performed on ThemisZ transmission electron microscope (accelerating voltage, 300 kV). The X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was used to determine the chemical elements and valence of the samples. The vacancy (Ov) signal and reactive species were analyzed by electron paramagnetic resonance (EPR, Bruker A300-10/12, Germany). The light absorption of the catalysts was measured on UV-visible diffuse reflectance spectra (UV-vis DRS) on a Hitachi UV-3100 UV-Vis spectrophotometer with BaSO₄ as the reference. Electron Paramagnetic Resonance analysis using a Bruker EMXnano and the spin trap reagents 5,5-diethyl-1-pyrroline-N-oxide (DMPO) was used to trap alkyl radicals. ICP Agilent 7700(MS), Powder sample were characterized by fourier transform infrared spectrometer (FTIR, Nicolet Avatar 370). UV-Visible Spectrophotometer, Shimadzu UV-1800. Fluorescence Spectrometer, Shimadzu RF-5301PC. gas chromatography (GC-2014C, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD), where N₂ was used as a carrier gas. The generated H₂ gas was measured by a on line photocatalytic system (Beijing ZhongjiaoJinyuan, China). High-Resolution Mass Spectrometer, Thermo Fisher Scientific Q Exactive Focus.

2.4 Catalytic performance test

2.4.1 The piezoelectric catalytic hydrogen production of Pt₁@BOC and BOC

The piezo-catalytic hydrogen production of the prepared catalyst (Pt₁@BOC and BOC) was evaluated offline. In a typical experiment, 10 mg of the piezoelectric catalyst was dispersed in 20 mL of deionized water and without sacrificial agent. The aqueous suspension sealed in a 25-mL borosilicate tube was evacuated and purged by Ar for about 30 min to completely remove air. Subsequently, the borosilicate tube was then placed in the center of an ultrasonic bath for inducing piezoelectric decomposition to produce hydrogen. To detect the amount of hydrogen production, 1 mL gas component within the borosilicate tube was intermittently extracted and injected into a gas chromatograph (GC-2014C, Shimadzu, Japan) with a thermal conductivity detector. The amount of hydrogen gas produced was calculated using a calibration curve of moles of hydrogen versus peak area.

2.4.2 The photocatalytic hydrogen production from water splitting using Pt₁@CdS and CdS

In a typical experiment, 10 mg of the photocatalyst was dispersed in a mixture of 70 mL of water/ethylenediamine (10 : 1.5 v/v) by 15 min sonication to form a homogeneous suspension. Prior to irradiation, the suspensions were evacuated to remove the dissolved oxygen. The photocatalytic H₂ production experiments were performed at 350 W xenon lamp with a filter (1.5

AM) as the light source (sunlight intensity of 100 mW/cm²) under stirring. The generated H₂ gas was measured by a on line photocatalytic system (Beijing ZhongjiaoJinyuan, China) with gas chromatography (GC-2014C, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD), where N₂ was used as a carrier gas.

2.4.3 Pd₁@BOC and BOC Photocatalytic degradation of TC

The TC was dissolved in deionized water (20 mg/mL) to prepare a solution. Catalysts (Pd₁@BOC and BOC) were added to the solution respectively. Dark adsorption reaction (10 min) was carried out before irradiation with LED lamp (395 nm, 20 W) experiments were carried out. The content of TC was measured by UV-Vis spectrophotometer.

2.4.4 Hydrogen production from ammonia borane (AB) hydrolysis catalyzed by Pd₁@Bi₃Ti₄O₁₂ and Pdnano@Bi₃Ti₄O₁₂

The H₂ activities was evaluated in a three-necked flask. Briefly, 2 mL of catalyst solution (10 mg·mL⁻¹) were added into flask. The reaction temperature was maintained using a water bath. The reactor was purged with Ar gas to completely remove O. Then, 2 mL of AB solution (1 mol·L⁻¹) were injected into the reactor under visible light irradiation. The amount of hydrogen evolved was monitored using a water displacement strategy.

2.5 Catalytic performance calculation.

The TOF value (mol H₂·mol·metal⁻¹·min⁻¹) was calculated based on the number of surface atoms in catalysts. The calculation equation used was as follows:

$$TOF = \frac{n(H_2)}{t \cdot n_{metal} \cdot D_{metal}}$$

wherein, the n_{H₂} represents the molar of the generated hydrogen, n_{metal} represents the total mole of metal Pd in the catalyst determined by the ICP measurement, and *t* is the completion time of the reaction.

2.6 Theoretical calculation details

Based on density functional theory (DFT), the main calculations in this study were carried out in the CASTEP module of Materials Studio software. The OTFG ultrasoft pseudopotential was employed, with the LBFGS optimization algorithm selected for geometry relaxation. The Perdew-Burke-Ernzerhof (PBE) gradient-corrected functional under the generalized gradient approximation (GGA) framework was adopted as the exchange-correlation functional. The energy convergence criterion was set to 2.0×10⁻⁵ eV/atom. A vacuum layer of ≥20 Å along the z-direction was implemented to eliminate periodic image interactions. The Brillouin zone integration utilized

a $1 \times 1 \times 1$ k-point mesh with a plane-wave cutoff energy of 381 eV.

3 RESULTS AND DISCUSSION

3.1 Preparation and Structural Characterization of SAC

Figure S1 illustrates the preparation process of the SACs of $\text{Pt}_1\text{@BOC}$ via a controllable synthesis approach using piezoelectric materials with ultrasonic assistance in an CH_3CN solvent system. The specific experimental steps were as follows: First, the metal chloride precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was evenly dispersed in an CH_3CN solution, followed by the addition of the corresponding piezoelectric material $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ (BOC). The mixture was subjected to continuous ultrasonic treatment for 2 hours at room temperature. After the reaction, the final product was obtained through centrifugation, washing, and drying steps.

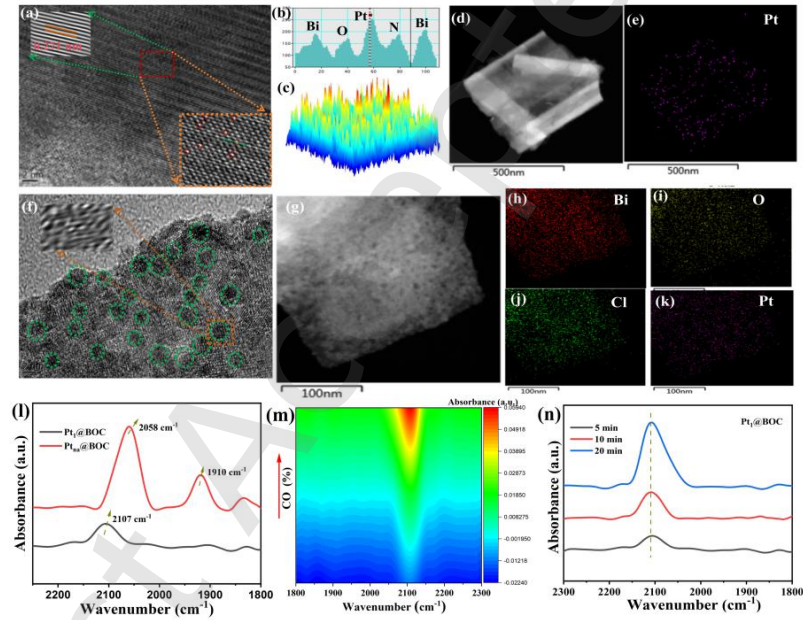


Figure 1 . (a) HAADF-TEM image of $\text{Pt}_1\text{@BOC}$; (b) The local atomic strength distribution on the surface (c) 3D surface intensity profile (top) taken from the yellow dashed rectangle in (a) (bottom); (d) TEM and (e) Pt elemental EDX mapping of $\text{Pt}_1\text{@BOC}$; (f) HAADF-TEM and (g) image of $\text{Pt}_{\text{nano}}\text{@BOC}$; (h~k) EDX elemental mapping of $\text{Pt}_{\text{nano}}\text{@BOC}$; (l) Infrared spectra of CO molecules adsorbed on the surface of $\text{Pt}_1\text{@BOC}$ and $\text{Pt}_{\text{nano}}\text{@BOC}$; (m) Color-coded infrared spectral maps of CO adsorption on the $\text{Pt}_1\text{@BOC}$ surface with concentration dependence, and (n) the corresponding infrared absorption spectra.

According to the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) results (**Fig. 1a–c**), the Pt species in the as-prepared material are present as isolated atoms distributed on the surface of the BOC piezoelectric substrate, with no evidence of metal nanoparticles or clusters. This conclusion is further supported by energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis: the Pt signal exhibits a homogeneous distribution across the substrate surface (**Fig. 1d–e**), confirming the highly dispersed nature of Pt

atoms on the support. In contrast, when the $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ precursor was dispersed in an aqueous solution and subjected to the same ultrasonic treatment, Pt was deposited as nanoparticles (2-5 nm) on the piezoelectric substrate (**Fig. 1f**). Meanwhile, elemental mapping revealed a significantly higher Pt concentration compared to that of the $\text{Pt}_1 @\text{BOC}$ catalyst (**Fig. 1g-k**). These comparative results demonstrate the critical role of the CH_3CN solvent system in regulating the dispersion state of the metal.

To further verify the atomic-level dispersion of Pt, we employed CO as a probe molecule and conducted diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) to characterize the coordination environment of Pt sites on the material surface. As shown in **Fig. 1i**, the sample prepared in the aqueous system of $\text{Pt}_{\text{nano}} @\text{BOC}$ exhibited distinct CO adsorption peaks at 2058 cm^{-1} (linear adsorption) and 1910 cm^{-1} (bridged adsorption)[9, 21]. In contrast, the $\text{Pt}_1 @\text{BOC}$ catalyst synthesized in CH_3CN showed only a single absorption peak at 2107 cm^{-1} corresponding to the linear adsorption mode. This difference is structurally significant: isolated Pt single atoms provide only a single coordination site, allowing CO molecules to adsorb solely in a linear configuration, whereas Pt nanoparticles possess adjacent metal atoms that facilitate μ_2 -bridged adsorption[22, 23]. Further adsorption experiments involving increased CO coverage (**Fig. 1n**) revealed that the intensity of the linear adsorption peak at 2107 cm^{-1} increased proportionally with CO concentration, without any peak shift, indicating no interaction between adsorbed CO molecules and further confirming the single-atom dispersion of Pt species[9]. In summary, combined HAADF-STEM and CO-DRIFTS analyses unequivocally demonstrate that Pt is stabilised as single atoms on the BOC surface in the piezoelectric-assisted $\text{CH}_3\text{CN-H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ system, whereas it exists as nanoparticles in the aqueous system.

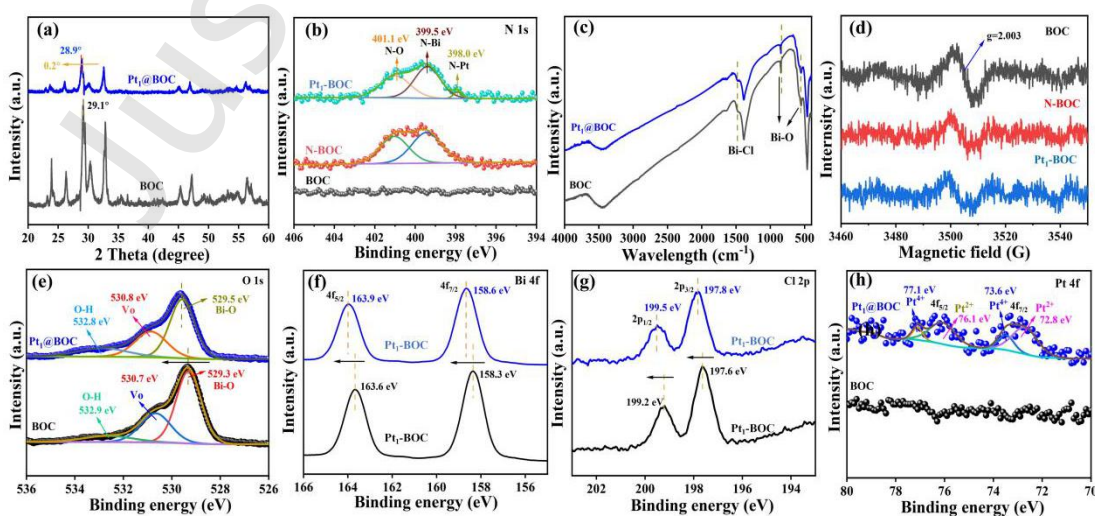


Figure 2. (a) XRD patterns of Pt_1/BOC vs. BOC; (b) N 1s XPS spectra of Pt_1/BOC vs. BOC; (c) IR absorption spectra of Pt_1/BOC vs. BOC; (d) EPR spectra of Pt_1/BOC vs. BOC; (e)-(h) Pt 4f, O 1s, Bi 4f, and Cl 2p XPS spectra of Pt_1/BOC vs. BOC.

Subsequent systematic structural characterization was performed on the as-prepared samples. X-ray diffraction (XRD) results (**Fig. 2a**) indicated that the BOC substrate retained its original crystal structure after Pt single-atom loading. However, the all characteristic diffraction peaks of Pt₁@BOC exhibited a slight low-angle shift (-0.2°), confirming lattice expansion in the crystal structure. Further XPS analysis revealed the presence of N signals on the surface of BOC material after the acetonitrile piezocatalytic reaction (**Fig. 2b**). The binding energy peak observed at 401.1 eV may originate from contributions of N-O or N-Cl bonds. However, considering that the as-prepared BOC predominantly exposes the (200) and (020) crystal planes, with its surface consisting of a [Bi₂O₂] layered structure, this signal is more reasonably attributed to the formation of an N-O bond. Meanwhile, the binding energy peak appearing at 399.5 eV can be assigned to the existence of an N-Bi bond. In addition, EPR results indicated a decrease in the oxygen vacancy concentration ($g=2.003$) of the BOC material after the CH₃CN piezocatalytic reaction (**Fig. 2d**). Based on the comprehensive characterization results from XRD, XPS, and EPR, it can be reasonably inferred that during the piezocatalytic process, N atoms were successfully doped into the BOC structure and occupied the surface oxygen vacancy sites, which may provide anchoring sites for single-atom loading. Based on the N 1s XPS spectrum of the Pt₁-BOC sample, a distinct peak corresponding to the N-Pt bond was clearly observed at a binding energy of 398.0 eV. Meanwhile, comparison of the EPR signals between N-BOC and Pt-BOC samples indicated no significant reduction in oxygen vacancy concentration[24, 25]. These results suggest that the Pt single atoms are predominantly anchored at N sites rather than oxygen vacancy sites[26, 27]. Fourier transform infrared (FTIR) spectroscopy (**Fig. 2c**) showed no characteristic absorption peak for the cyano group ($-\text{C}\equiv\text{N}$) in the 2250-2300 cm^{-1} range, ruling out surface adsorption of cyanide species and thus confirming successful N doping into the BOC lattice and as anchoring sites for Pt single atoms[14, 28]. This phenomenon is consistent with the mechanism reported by Bian et al., wherein N atoms fill oxygen vacancies in TiO₂ to achieve lattice N doping during light-induced CH₃CN radical formation[14]. In addition, the XPS spectra revealed that the binding energies of Bi, O, and Cl elements in Pt₁-BOC shifted toward higher values compared to those in BOC, suggesting the formation of a multi-center electron transfer network involving Bi-O/N-Pt-Cl bonds (**Fig. 2e-g**). Notably, the Pt 4f XPS spectrum (**Fig. 2h**) exhibited characteristic peaks only for the +2 (76.1 eV and 72.8 eV) and +4 (73.6 eV and 77.1 eV) oxidation states[29]. Together with the absence of metallic Pt peaks in the XRD pattern, this further supports the conclusion that Pt atoms exist in a singly dispersed form. Based on these characterization results, it is reasonable to propose that in Pt₁@BOC, Pt single atoms are stabilised via Pt-O/N coordination. Collectively, these analyses demonstrate that Pt SACs can be successfully synthesized on the piezoelectric

material surface via a piezoelectric-induced process in an $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ - CH_3CN precursor solution.

Subsequently, to evaluate the universality of the piezoelectric-catalysed noble metal chloride- CH_3CN system for preparing noble metal SACs, we systematically extended the system to other soft acid systems such as $\text{AuCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and K_2PdCl_6 dissolved in CH_3CN solvent, whilst employing different piezoelectric substrate materials. These mixtures were processed under identical piezoelectric reaction conditions. A series of highly dispersed SACs—including $\text{Au}_1 @ \text{BOC}$, $\text{Ru}_1 @ \text{BOC}$, $\text{Pt}_1 @ \text{CdS}$, $\text{Pd}_1 @ \text{BOC}$, and $\text{Pd}_1 @ \text{Bi}_3\text{Ti}_4\text{O}_{12}$ —were successfully prepared (The single-atom loading ranges between 0.07% ~0.28% **Fig. S6a**). As shown in **Fig. S2–S5**, HAADF-STEM results confirmed that Au, Ru, and Pd were all present as monodisperse species on the surfaces of the piezoelectric substrate catalysts. Furthermore, no diffraction peaks corresponding to metallic phases were detected in the corresponding XRD patterns. Further evidence from CO adsorption infrared spectroscopy shows that $\text{Au}_1 @ \text{BOC}$, $\text{Pd}_1 @ \text{BOC}$, and $\text{Ru}_1 @ \text{BOC}$ exhibit only linear CO adsorption peaks at 2170 cm^{-1} , 2110 cm^{-1} , and 2061 cm^{-1} , respectively, with no corresponding bridged adsorption mode observed (**Fig. S7**). This result confirms that the noble metal species are dispersed on the BOC support in the form of single atoms. These results collectively demonstrate the general applicability of the piezoelectric- CH_3CN -noble metal chloride system for the preparation of SACs.

3.2 Study on Solvent-Dependent Structural Evolution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in H_2O and CH_3CN

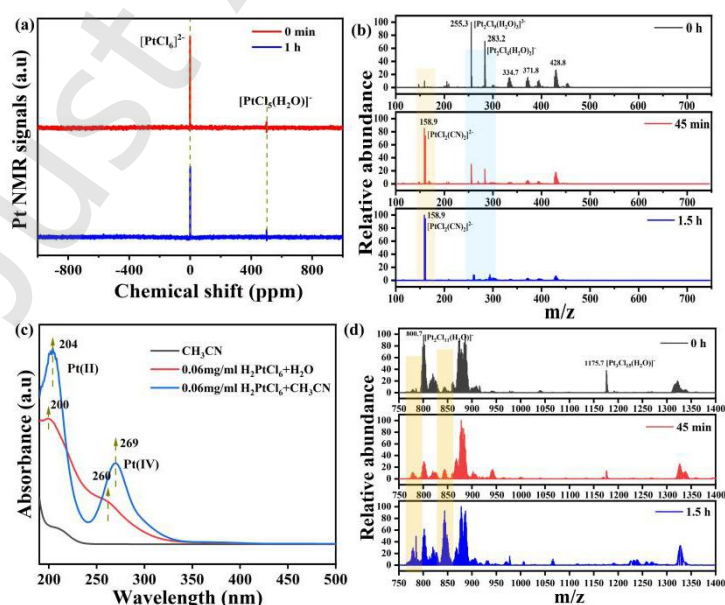


Figure 3. (a) ^{195}Pt NMR spectra of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in aqueous solution before and after reaction; (b) and (d) Mass spectra of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in CH_3CN solution different reaction times; (c) Liquid UV-Vis absorption spectra of CH_3CN and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dispersed in water and CH_3CN .

To further investigate the mechanism of single-atom formation from noble metal chloride precursors in an CH_3CN system under piezoelectric induction, this study systematically analyzed the coordination structure characteristics of the Pt center in $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in both H_2O and CH_3CN solutions, with a focus on the structural evolution induced by piezoelectric catalysis. Using techniques including high-resolution mass spectrometry (HRMS), Pt nuclear magnetic resonance (Pt-NMR), liquid ultraviolet-visible (UV-Vis) spectroscopy, and EPR, the following results were obtained: As shown in **Fig. 3a**, the Pt-NMR spectrum of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in aqueous solution exhibited signals at 501 ppm and 0.5 ppm, corresponding to the species $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_6]^{2-}$, respectively, with $[\text{PtCl}_6]^{2-}$ being the predominant species[30]. In contrast, HRMS analysis of the CH_3CN solution (**Fig. 3b and d 0h**) revealed that $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ primarily existed in polymeric forms, with signals observed at $m/z = 255.3$ ($[\text{Pt}_2\text{Cl}_9(\text{H}_2\text{O})_3]^{3-}$), 800.7 ($[\text{Pt}_2\text{Cl}_{11}(\text{H}_2\text{O})]^-$), and 1175 ($[\text{Pt}_3\text{Cl}_{15}(\text{H}_2\text{O})_2]^-$). Additionally, minor dissociated fragments were detected, such as $m/z = 205.1$ ($[\text{PtCl}_6]^{2-}$), 371.8 ($[\text{PtCl}_5]^-$), and 334.7 ($[\text{PtCl}_4]^-$), but no Pt species coordinated with CH_3CN were observed (Computational details of m/z are provided in the Supplementary Information). These results indicate that $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ exists mainly as trimers and dimers in CH_3CN . The marked difference in speciation is attributed to the distinct polarities of H_2O and CH_3CN . H_2O , being significantly more polar than CH_3CN , promotes a higher degree of dissociation of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. In contrast, the lower polarity of CH_3CN results in limited dissociation, favouring the formation of polymeric species to maintain structural stability.

The UV absorption spectroscopy results further support the aforementioned conclusions. As shown in **Fig. 3c**, a systematic comparison of the UV spectra of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in aqueous and CH_3CN solutions reveals significant differences in their coordination structures. In systems with the same concentration of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.025 mg/mL), characteristic absorption peaks are observed at 200 nm and 260 nm, corresponding to Pt-Cl electronic transitions in Pt(II) and Pt(IV) species, respectively[31, 32]. In CH_3CN system, however, the absorption peaks shift to 204 nm and 269 nm, accompanied by a marked increase in absorption intensity and a red-shift phenomenon. The enhanced UV absorption in CH_3CN is primarily due to its low polarity, which suppresses the dissociation of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, leading to the predominance of polymeric species (as confirmed by HR-MS). This structural distortion partially breaks the Laporte selection rule, increasing the oscillator strength of the electronic transition and thus intensifying the absorption[33]. The red-shift, on the other hand, is mainly attributed to the weaker interaction between bridging Cl^- and Pt in the polymeric aggregates compared to the terminal Cl-Pt bonds in the aqueous system. This results in a decrease in the energy of the $\text{Cl} \rightarrow \text{Pt}$ charge transfer transition, leading to the observed red-shift. Collectively, the results from Pt-NMR, HR-MS, and

UV-Vis absorption spectroscopy confirm that the speciation of Pt in $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ differs fundamentally between CH_3CN and aqueous solutions.

3.3 Mechanistic Study on the Structural Evolution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in H_2O and CH_3CN under a Piezoelectric catalysis

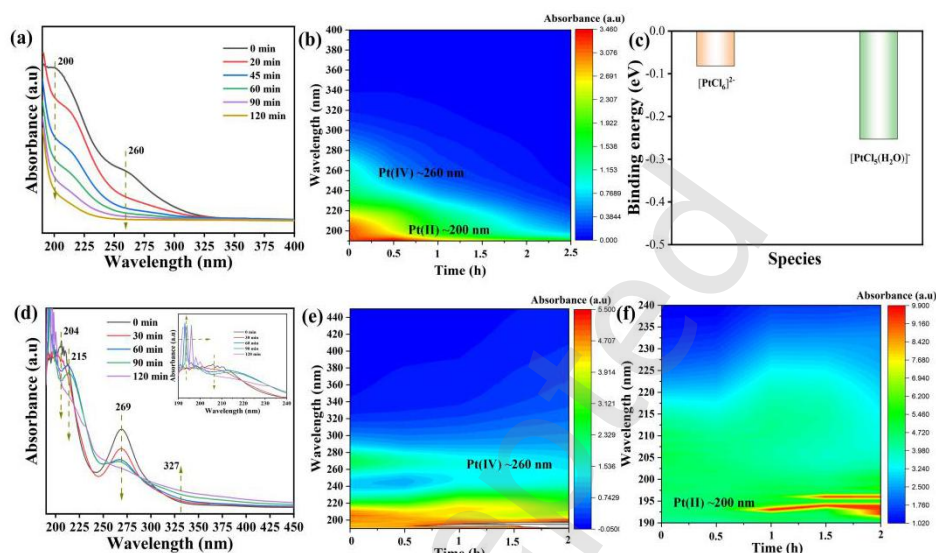


Figure 4. (a) UV-Vis absorption spectra of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in aqueous solution under different piezoelectric treatment times and (b) corresponding color-coded spectral maps; (c) Stabilization energies of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ species in aqueous solution; (d) UV-Vis absorption spectra of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in CH_3CN solution under different piezoelectric treatment times; (e)-(f) Color-coded spectral maps at corresponding time points of (d).

To investigate the structural evolution of Pt species under the piezoelectric effect, we systematically compared their behavior in H_2O and CH_3CN systems. UV-Vis spectroscopy (**Fig. 4a**) revealed that with the progression of piezoelectric treatment, the absorption intensities at 200 nm and 260 nm decreased significantly, indicating the cleavage of Pt-Cl bonds in Pt(II) and Pt(IV) species, which led to a reduction in electron transfer between Cl^- and the Pt centers (**Fig. 4b**). Analysis combining Pt NMR results (**Fig. 3a**) showed that after piezoelectric treatment, the concentration of the $[\text{PtCl}_6]^{2-}$ species decreased markedly, while that of the $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ species remained largely unchanged. This can be attributed to the higher stability of $[\text{PtCl}_5(\text{H}_2\text{O})]^-$ upon solvation (**Fig. 4c**). These results demonstrate that in aqueous solution, the piezoelectric effect primarily promotes the progressive dissociation of Cl ligands from $[\text{PtCl}_6]^{2-}$, and the resulting Pt species eventually deposit onto the surface of the piezoelectric catalyst, forming Pt nanoparticles.

In contrast, significant differences in the species formed were observed in the CH_3CN system after the introduction of BOC and ultrasonic treatment. HR-MS results (**Fig. 3b**) indicated a noticeable decrease in the abundance of polymeric species such as $[\text{Pt}_2\text{Cl}_9(\text{H}_2\text{O})]^{3-}$,

$[\text{Pt}_2\text{Cl}_{11}(\text{H}_2\text{O})]^-$, $[\text{Pt}_3\text{Cl}_{15}(\text{H}_2\text{O})_2]^-$, as well as secondary fragments including $[\text{PtCl}_6]^{2-}$ (m/z 205.1), $[\text{PtCl}_5]^-$ (m/z 371.8), and $[\text{PtCl}_4]^-$ (m/z 334.7). High-resolution mass spectrometry (HR-MS) results (Fig. 3b and 3d) showed that after piezoelectric treatment, the signal intensities of polymeric species such as $m/z = 255.3$ (corresponding to $[\text{Pt}_2\text{Cl}_9(\text{H}_2\text{O})_3]^{3-}$), 205.1 (corresponding to $[\text{PtCl}_6]^{2-}$), 371.8 (corresponding to $[\text{PtCl}_5]^-$), and 334.7 (corresponding to $[\text{PtCl}_4]^-$) decreased significantly. Meanwhile, the signal intensities of species at $m/z = 158.9$ (corresponding to $[\text{PtCl}_2(\text{CN})_2]^{2-}$) and in the m/z range of 800–900 (corresponding to polymeric Pt species) increased markedly. These results indicate that some platinum dimers and monomers were converted into $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species and platinum polymers during the piezocatalytic process. This phenomenon may be attributed to the generation of cyano radicals ($\cdot\text{CN}$) from acetonitrile molecules under piezocatalysis, which coordinate with dissociated platinum species to form $[\text{PtCl}_2(\text{CN})_2]^{2-}$ (as later confirmed). The formation of polymers may result from coupling products such as succinonitrile generated from acetonitrile during catalysis, which further coordinate with platinum species to form polymeric aggregates[34].

Concurrently, the UV-Vis absorption spectrum showed distinct changes (**Fig. 4d**): the absorption peak at 204 nm blue-shifted to 194 nm with increased intensity, the peak at 269 nm showed a significant decrease in intensity, and a new absorption peak emerged at 327 nm. The blue shift and enhancement at 204 nm can be attributed to the dissociation of Pt(IV) species (polymeric aggregates such as $[\text{Pt}_2\text{Cl}_9(\text{H}_2\text{O})]^{3-}$ and $[\text{Pt}_2\text{Cl}_4(\text{H}_2\text{O})_2]^-$ into $[\text{PtCl}_2(\text{CN})_2]^{2-}$ monomers) under ultrasonic treatment, leading to formation of Pt(II) species. The significant decrease of the absorption peak at 269 nm is attributed to the dissociation of some Pt(IV) polymeric species. Notably, the new enhanced absorption at 327 nm can be ascribed to the charge transfer from the π^* antibonding orbital of the CN^- ligand to the vacant d orbital of Pt[35]. Due to the higher energy level of the π^* orbital in cyanide ligands, the transition to the metal orbital requires lower energy, resulting in a longer absorption wavelength compared to the Cl-Pt transition. This observation is consistent with the HR-MS data.

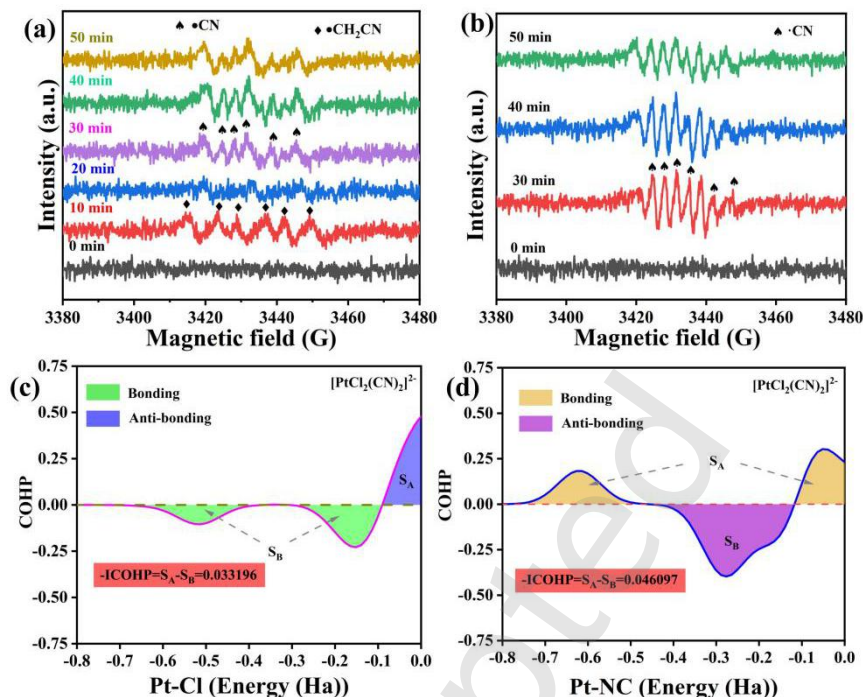


Fig. 5. (a) EPR spectra of the BOC-CH₃CN system under different piezoelectric catalytic conditions; (b) EPR spectra of the BOC-CH₃CN-H₂ PtCl₆ · 6H₂O system under different piezoelectric treatment times; The Crystal Orbital Hamilton Populations (COHP) of Pt-Cl (c), and Pt-CN (d) in $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species, respectively.

Furthermore, EPR spectroscopy was employed to investigate the temporal evolution of radical species in the CH₃CN system under piezoelectric conditions. As shown in **Fig. 5a**, within the 0-50 min time frame, a distinct $\cdot\text{CH}_2\text{CN}$ radical signal emerged after 10 min of piezoelectric reaction. As the reaction progressed to 30 min, the $\cdot\text{CH}_2\text{CN}$ radical signal gradually diminished, while the $\cdot\text{CN}$ radical signal increased correspondingly. This behavior is attributed to the initial oxidation of CH₃CN molecules by piezoelectric-induced charge carriers, generating $\cdot\text{CH}_2\text{CN}$ radicals, which subsequently react with additional CH₃CN molecules to form $\cdot\text{CN}$ radicals[36]. Upon introduction of H₂PtCl₆·6H₂O into the system, the $\cdot\text{CN}$ radical concentration decreased significantly after 40 min of reaction (**Fig. 5b**), indicating the involvement of $\cdot\text{CN}$ radicals in coordination with Pt species, thereby consuming the radicals. This observation is consistent with the formation of the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species detected by HR-MS and UV-Vis spectroscopy, further supporting the critical role of $\cdot\text{CN}$ in the single-atom formation process.

Based on the above findings, the evolution pathways of platinum (Pt) species under piezoelectric catalytic conditions exhibit significant differences between H₂O and CH₃CN systems, with the specific mechanisms summarized as follows: (1) In the H₂O system, H₂PtCl₆·6H₂O primarily exists in the monomeric form of $[\text{PtCl}_6]^{2-}$. Under piezoelectric catalysis, the Pt-Cl bonds in $[\text{PtCl}_6]^{2-}$ undergo progressive cleavage, ultimately leading to the directional deposition

of Pt nanoparticles on the catalyst surface via an atomic assembly mechanism. (2) In the CH_3CN solvent system, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ initially tends to form polynuclear structures such as $[\text{Pt}_2\text{Cl}_9(\text{H}_2\text{O})]^{3-}$, $[\text{Pt}_2\text{Cl}_{11}(\text{H}_2\text{O})]^-$, and $[\text{Pt}_3\text{Cl}_{15}(\text{H}_2\text{O})_2]^-$. Under piezoelectric induction, a part of polynuclear species gradually dissociate and coordinate with in situ generated $\cdot\text{CN}$, forming the monomeric intermediate $[\text{PtCl}_2(\text{CN})_2]^{2-}$. Meanwhile, some of the dissociated Pt species coordinate with the coupling products of acetonitrile to form new polymeric species.

3.4 The Functional of Piezoelectricity in Synthesizing the Single Atom Catalysts

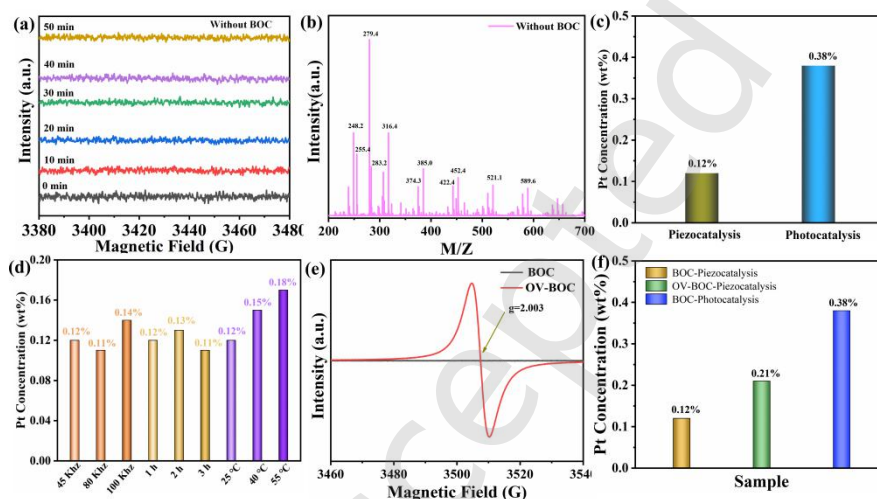


Fig. 6. (a) EPR spectra of $\text{CH}_3\text{CN}-\text{H}_2\text{PtCl}_6$ under ultrasound (45 kHz, 1 h). (b) HR-MS profiles of the same system. (c) Pt loadings (ICP-OES) under piezocatalytic (45 kHz, 1 h) and photocatalytic (350 W Xe lamp, 1 h) conditions. (d) Pt loadings under varied synthesis parameters. (e) Oxygen vacancy signatures in BOC and OV-BOC. (f) Comparative Pt loadings: OV-BOC (piezo) vs. BOC (piezo) vs. BOC (photo).

To elucidate the pivotal role of piezoelectricity in SACs synthesis, this study systematically investigates two key aspects: the formation of reactive Pt species in the solvent and the deposition behavior of Pt single atoms. (1) Regulation of piezocatalysis on reactive species generation in the solvent: Experiments confirmed that the piezoelectric effect plays a deterministic role in the formation of $\cdot\text{CN}$. As shown in **Fig. 6(a)**, EPR spectra revealed no detectable radical signals in the absence of the piezoelectric catalyst BOC, establishing that radical generation is dependent on the piezocatalytic process. Further HR-MS analysis (**Fig. 6b**) demonstrated distinct intermediate profiles between the ultrasound-only system (without BOC) and the piezocatalytic system (with BOC). Specifically, new characteristic peaks emerged at $m/z=279.4$, 316.6 , 385.0 , and 452.4 in the presence of BOC. These peaks are tentatively assigned to coordination complexes formed between chloroplatinic acid species and acetonitrile molecules, substantiating the critical role of BOC piezocatalysis in directing the formation of specific reactive intermediates. (2) Regulation of piezoelectric effects on single-atom deposition behavior: Piezoelectric polarization reconstructs

the local electronic structure of the material, thereby inducing alternating electron-rich and electron-deficient regions on its surface[37]. Consequently, Pt precursors are prone to reduction and deposition at negatively charged, electron-rich sites. Given that the polarization field is a spatial vector with maximal intensity at the crystal termini and weaker effects in the central regions, metal deposition exhibits pronounced site selectivity, thereby limiting the saturation loading of single atoms on the support[17]. In contrast, photogenerated charge carriers, derived from bandgap excitation and separation, distribute relatively uniformly across the semiconductor surface, theoretically offering a greater number of potential deposition sites[38, 39]. To validate this, we compared Pt deposition under piezocatalytic and photocatalytic conditions. TEM characterization (**Fig. S8** and **Fig. S9**) revealed no discernible Pt nanoparticles in the Pt@BOC catalysts synthesized within the BOC-CH₃CN-H₂PtCl₆ system, regardless of the driving force, confirming that Pt exists exclusively as highly dispersed single atoms. However, quantitative ICP-OES analysis as show in **Fig. 6c** demonstrated that the Pt loading under photocatalysis (0.38 wt%) was significantly higher than that under piezocatalysis (0.12 wt%). This quantitative disparity substantiates the precise regulatory effect of piezocatalysis on both the deposition density and spatial distribution of Pt atoms.

To explore the potential for enhancing the Pt single-atom loading, we attempted to optimize the synthesis via adjusting ultrasonic frequency, prolonging the piezocatalytic reaction duration, and raising the reaction temperature. However, as shown in **Fig. 6(d)** (ICP-OES results), with all other parameters held constant: varying solely the ultrasonic frequency yielded Pt loadings of 0.12 wt%, 0.11 wt%, and 0.14 wt% at 45 kHz, 80 kHz, and 100 kHz, respectively; tuning only the reaction time to 1 h, 2 h, and 3 h produced Pt loadings of 0.12 wt%, 0.13 wt%, and 0.11 wt%, respectively. Raising the reaction temperature did result in a measurable increase in Pt loading: the value was 0.12 wt% at 25 °C, rising to 0.18 wt% when the temperature was elevated to 55 °C. This enhancement is likely attributed to the reduced ligand dissociation energy at elevated temperatures, which exposes new active sites for Pt deposition. We conclude that the site selectivity imposed by ultrasound-induced piezoelectric polarization is the primary constraint limiting further increases in Pt loading, a phenomenon stemming from the selective adsorption of reactive species driven by polarization-induced local electron accumulation. Furthermore, as show in **Fig. 6e**, the deliberate introduction of oxygen vacancies onto the BOC surface created additional active sites, boosting the Pt loading to 0.21% (**Fig. 6f**). TEM characterization revealed the complete absence of detectable Pt nanoparticles across the piezocatalytic BOC-CH₃CN-H₂PtCl₆ (**Fig. S8**), piezocatalytic OV-BOC-CH₃CN-H₂PtCl₆ (**Fig. S10**), and photocatalytic BOC-CH₃CN-H₂PtCl₆ (**Fig. S9**) systems, confirming that Pt species remain

exclusively in an atomically dispersed state devoid of aggregation under all synthetic conditions.

Taken together, these comparative results support the central hypothesis: the constrained Pt loading (~0.12 wt%) under piezoelectric conditions is not a consequence of inadequate redox activity of the piezoelectric system, but rather originates from the inherent spatial confinement imposed by the piezoelectric vector field on deposition site accessibility, as further corroborated by the boosted loading upon oxygen vacancy introduction (0.21 wt%) and the substantially higher loading under photocatalysis (0.38 wt%).

3.5 Investigation on the Mechanism of Piezoelectric-induced preparation of SACs

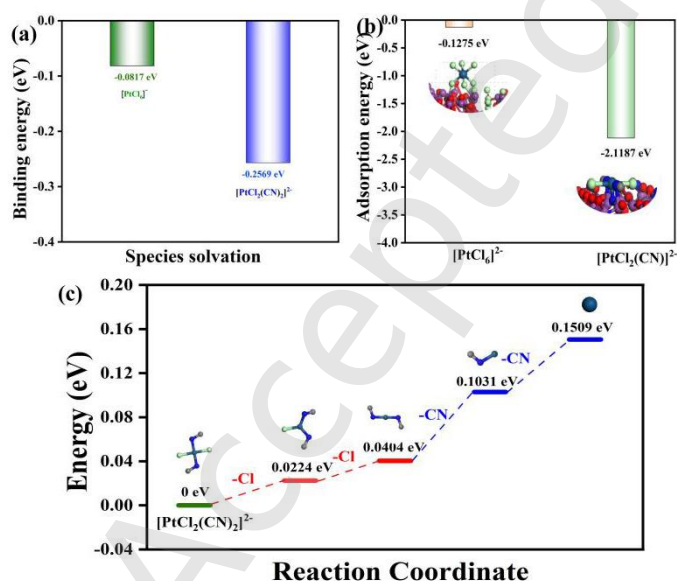


Fig. 7. (a) Solvent stabilization energies of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species; (b) Adsorption energies of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species on the BOC surface; (c) Ligand dissociation energies of $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species in aqueous and CH_3CN systems.

To elucidate the relationship between the aforementioned species transformation pathway and the formation of SACs, this study employed a multi-scale characterization strategy combined with theoretical calculations. Based on the above results, we consider that the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ monomer, compared to polymeric species, is more favorable for forming single atoms. This is because polymeric species possess a more conjugated coordination framework, which tends to be more stable. Therefore, we focus on the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species as the primary precursor for single-atom formation.

To verify that the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species formed via the coordination of $\cdot\text{CN}$ with Pt is crucial for achieving atomically dispersed Pt, methanol was used as a hole scavenger to suppress the generation of $\cdot\text{CN}$, thereby preventing the formation of $[\text{PtCl}_2(\text{CN})_2]^{2-}$. TEM characterization revealed that under this condition, Pt exists as nanoparticles on the BOC surface (**Fig. S11**). This result confirms that the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species plays a decisive role in the formation of Pt single

atoms. Simultaneously, mass spectrometry revealed the absence of characteristic peaks corresponding to the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species after the reaction (**Fig. S12**). Besides, density functional theory (DFT) calculations were systematically conducted to investigate the bond strengths of Pt-Cl and Pt-CN in the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species, the solvation stability in different solvent environments, and the dissociation energy barriers. These calculations, together with kinetic studies and mass spectrometry analysis, provide in-depth insights into the species evolution mechanism. The strength of the Pt-CN and Pt-Cl bonds in the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ complex was assessed using Crystal Orbital Hamilton Population (COHP) analysis. Notably, the Pt-CN bond was found to be markedly stronger, as evidenced by its higher integrated COHP (-ICOHP) value of 0.046097 compared to 0.033196 for the Pt-Cl bond (**Fig. 5c, d**) and this result is in good agreement with the prediction of the acid-base theory.

Subsequently, the stability of the aqueous solvated $[\text{PtCl}_6]^{2-}$ species was compared with that of the CH_3CN -solvated $[\text{PtCl}_2(\text{CN})_2]^{2-}$ complex. As shown in **Fig. 7a**, the $[\text{PtCl}_6]^{2-}$ ion in the aqueous system exhibits the lowest solvation stabilization energy (-0.0817 eV), indicating its tendency to readily dissociate and rapidly release Pt atoms for deposition onto the piezoelectric material surface. In contrast, the stabilization energy of $[\text{PtCl}_2(\text{CN})_2]^{2-}$ in the CH_3CN system (-0.2569 eV) was significantly higher than that of aqueous $[\text{PtCl}_6]^{2-}$, indicating greater stability against dissociation, resulting in a slower Pt atom release rate compared to the aqueous system. Furthermore, based on the dissolution kinetics of Pt species in aqueous and acetonitrile solvents, as shown in **Figs. 4b, 4e, and 4f**, the following insights are obtained: In the aqueous system, during the piezoelectric reaction from 0 to 120 min, the absorption intensity at 260 nm corresponding to the $[\text{PtCl}_4]^{2-}$ species decreases sharply, falling below 50% of its initial value within 20 min. At the same time, the absorption peak at 200 nm assigned to Pt(II) species also diminishes with reaction time. These results indicate that Pt(IV) is not converted into soluble Pt(II) species, but is instead reduced to Pt and deposited on the catalyst surface. In contrast, in the acetonitrile system, although the signal of the Pt(IV) species at 269 nm shows some decrease, the absorption peak intensity of the Pt(II) species at 204 nm increases significantly. This suggests that under piezoelectric conditions, most of the Pt(IV) species is transformed into Pt(II) species that remain dissolved in the solution. Therefore, it is reasonable to speculate that the resulting Pt(II) species is $[\text{PtCl}_2(\text{CN})_2]^{2-}$ which exhibits high stability and is therefore difficult to dissociate rapidly. This conclusion was consistent with ICP-OES results (**Fig. S6a**): under identical piezoelectric treatment conditions, the Pt deposition amount measured by ICP-OES was approximately 1.71 wt% in the aqueous system (Pd: 2.77 wt%), whereas it was only 0.12 wt% for Pt (Pd: 0.24 wt%) on the BOC substrate in the CH_3CN system, significantly lower than in the

aqueous system. Electron scavenger experiments showed that almost no Pt atoms were detected on BOC (only 0.024 wt%, far less than 0.12 wt%; **Fig. S6b**), further supporting that the generation of Pt single atoms originates from the selective reduction mechanism of $[\text{PtCl}_2(\text{CN})_2]^{2-}$. Therefore, the formation mechanism of single atoms can be inferred as follows: the oxidation of acetonitrile molecules by holes generates $\cdot\text{CN}$, which subsequently replace part of the Pt-Cl bonds in the $[\text{PtCl}_4]^{2-}$ species to form the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ complex. The enhanced stability of this complex, along with its slow dissociation driven by the reduction effect of piezoelectrons, provides an opportunity for the formation of single atoms.

Since Pt single atoms can be successfully prepared using various piezoelectric materials in the $\text{CH}_3\text{CN}-\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ system, we propose that the change in dissociation energy of the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ species under the influence of piezoelectrically induced electrons is the dominant factor in single-atom formation, rather than the electronic structure of the carrier surface atoms. To verify this, we further calculated the unrestricted energy changes during the dissociation of $[\text{PtCl}_2(\text{CN})_2]^{2-}$ in the CH_3CN system. As shown in **Fig. 7c**, the energy barriers for the first two steps of Cl^- dissociation are 0.0224 eV and 0.0180 eV, respectively, while the dissociation energies for CN^- are 0.0627 eV and 0.0478 eV, significantly higher than those of Cl^- . These results indicate that the maximum dissociation energy of Cl^- in $[\text{PtCl}_2(\text{CN})_2]^{2-}$ is much lower than that of CN^- , demonstrating that CN^- coordination significantly reduces the release rate of Pt atoms and serves as a key factor promoting single-atom formation. This conclusion is also consistent with the previously mentioned hole scavenger experiment results. Furthermore, the $-\text{CN}$ in $[\text{PtCl}_2(\text{CN})_2]^{2-}$ possesses a lone pair of electrons on the N atom, enabling specific strong adsorption with metal atoms on the substrate surface. As illustrated in **Fig. 7b**, the adsorption energy of $[\text{PtCl}_6]^{2-}$ on the BOC surface was only -0.1275 eV, whereas that of $[\text{PtCl}_2(\text{CN})_2]^{2-}$ reached -2.1187 eV on with N doping BOC surface. This indicates significantly stronger adsorption stability of the latter on the substrate, providing a crucial condition for the stable anchoring of Pt atoms and the formation of a monodispersed state.

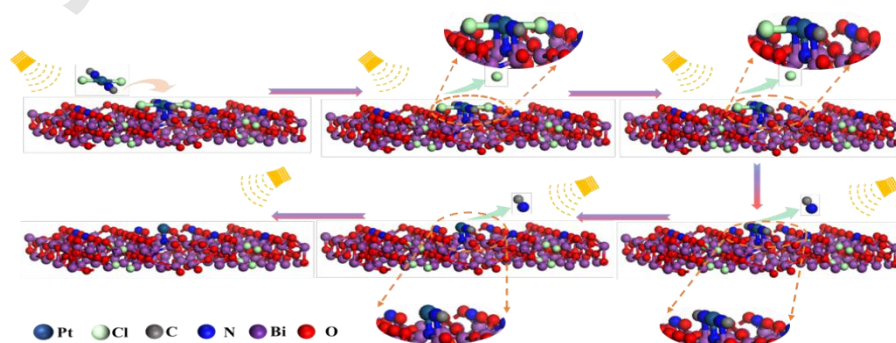


Fig. 8. Formation mechanism of Pt single atoms on the BOC surface.

Based on the aforementioned findings, the formation mechanism of piezoelectric-induced Pt single atoms in the CH₃CN/noble metal chloride system can be systematically elucidated as follows: Under the polarity regulation of the CH₃CN solvent, the initial state of H₂PtCl₆·6H₂O tends to exist stably in the form of polynuclear species. Upon application of the piezoelectric effect, the piezoelectric-induced electron transfer drives the gradual dissociation of the polynuclear structures. Simultaneously, CH₃CN molecules are activated under piezoelectric action to generate ·CN, which coordinate with the Pt monomers produced by dissociation to form the [PtCl₂(CN)₂]²⁻ intermediate. As illustrated in **Fig. 8**, this intermediate undergoes specific chemisorption with the metal sites on the substrate surface via the lone pair electrons of the N atom in the CN group, achieving stable anchoring. Subsequently, driven by the piezoelectric reduction charge, the Cl⁻ and CN⁻ ligands are progressively dissociated, ultimately fixing the Pt atoms on the catalyst surface in a monodispersed state. It is noteworthy that [PtCl₂(CN)₂]²⁻ exhibits a high dissociation energy barrier and strong coordination capability, effectively regulating the release rate of Pt atoms and suppressing their migration and aggregation. Combined with the strong adsorption interaction between the CN group and the substrate surface, these factors collectively ensure the precise single-atom deposition of Pt on the substrate, thereby achieving the controllable construction of Pt SACs.

3.6 Catalytic Performance

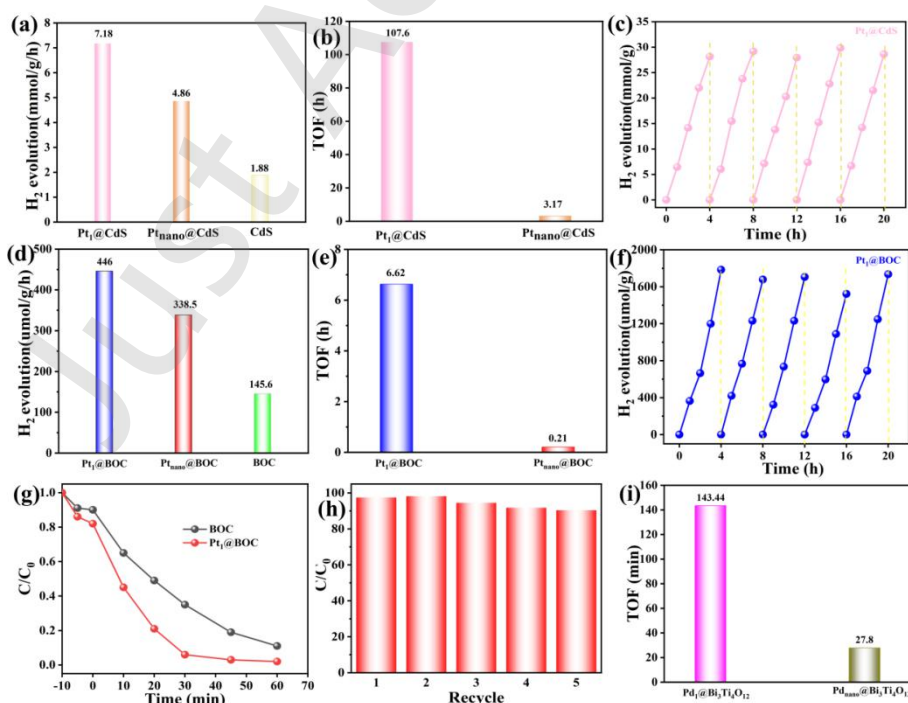


Fig. 9. Catalytic performance of Pt₁@BOC and other catalysts. (a)-(b) Photocatalytic hydrogen evolution kinetic curves and evolution rates (Pt₁@CdS, CdS, Pt₁@CdS); (c) TOF values of Pt sites for hydrogen evolution in Pt₁@CdS and Pt₁@CdS; (d)-(e) Piezoelectric hydrogen evolution kinetic curves and rates (Pt₁@BOC, BOC, Pt₁@BOC); (f) TOF values of Pt sites

for hydrogen evolution in $\text{Pt}_1\text{@BOC}$ and $\text{Pt}_{100}\text{@BOC}$; (g) Photocatalytic pollutant degradation kinetic curves ($\text{Pd}_1\text{@BOC}$, BOC); (h) Photocatalytic degradation stability of $\text{Pt}_1\text{@BOC}$; (i) TOF values of Pd sites for hydrogen evolution in $\text{Pd}_1\text{@Bi}_3\text{Ti}_4\text{O}_{12}$ and $\text{Pd}_{100}\text{@Bi}_3\text{Ti}_4\text{O}_{12}$ during ammonia borane hydrolysis.

To systematically evaluate the catalytic performance advantages of the as-prepared SACs (SACs), four representative SACs ($\text{Pt}_1\text{@BOC}$, $\text{Pt}_1\text{@CdS}$, $\text{Pd}_1\text{@BOC}$, and $\text{Pd}_1\text{@Bi}_3\text{Ti}_4\text{O}_{12}$) were selected and applied to four typical reaction systems: photocatalytic pollutant degradation, piezocatalytic water splitting, photocatalytic hydrogen evolution, and ammonia borane hydrolysis for hydrogen production. As shown in the **fig. 9(a~c)**, In the photocatalytic hydrogen evolution system using triethanolamine as a sacrificial agent, the $\text{Pt}_1\text{@CdS}$ catalyst exhibited a hydrogen production rate of $7.18 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, with a Pt turnover frequency (TOF) of 107.6 h^{-1} . In contrast, $\text{Pt}_{100}\text{@CdS}$ showed a lower hydrogen evolution rate of $4.58 \text{ mmol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and a TOF of only 3.17 h^{-1} . This comparison indicates that the TOF of Pt single atoms in $\text{Pt}_1\text{@CdS}$ is approximately 33.9 times higher than that of Pt nanoparticles in $\text{Pt}_{100}\text{@CdS}$, highlighting the superior catalytic activity of atomically dispersed Pt sites. Meanwhile, after being subjected to five cycles, its photocatalytic hydrogen evolution rate remained unchanged, indicating that the single atoms exhibit good stability on the catalyst surface. In the piezocatalytic hydrogen evolution system, $\text{Pt}_1\text{@BOC}$ demonstrated significantly enhanced activity ($446 \text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), with a Pt TOF of 6.63 h^{-1} , whereas $\text{Pt}_{100}\text{@BOC}$ exhibited a hydrogen evolution rate of $338.5 \text{ }\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and a Pt TOF of only 0.211 h^{-1} . The Pt single atoms in $\text{Pt}_1\text{@BOC}$ thus achieved a TOF approximately 31.4 times higher than that of Pt nanoparticles in $\text{Pt}_{100}\text{@BOC}$ (**fig. 9d~f**). A similar trend was observed in the ammonia borane hydrolysis reaction: the Pt TOF value for $\text{Pd}_1\text{@Bi}_3\text{Ti}_4\text{O}_{12}$ was 143.44 min^{-1} , compared to 27.8 min^{-1} for $\text{Pd}_{100}\text{@Bi}_3\text{Ti}_4\text{O}_{12}$, representing a 5.2-fold enhancement (**fig. 9i**). These results consistently demonstrate the unique structural advantages and outstanding activity of Pt single atoms in hydrogen evolution reactions, with significantly higher TOF values than their nanoparticle counterparts, confirming the critical role of single-atom sites in efficient catalytic processes. In the photocatalytic pollutant degradation reaction, $\text{Pt}_1\text{@BOC}$ achieved 96% degradation of tetracycline (TC) within 30 minutes, compared to 75% degradation by pure BOC. Furthermore, cycling tests revealed that 95% of the initial activity was maintained after five consecutive runs, indicating excellent stability in addition to high catalytic activity (**fig. 9g~h**). The comparative experiments across these three reaction systems—ambient condition catalysis, photocatalysis, and piezocatalysis fully demonstrate that SACs exhibit remarkable activity enhancement and robust structural stability in multiple hydrogen production reactions.

4 Conclusions

In summary, guided by the acid-base theory, this study proposes and demonstrates a mild piezoelectric-induced ligand exchange strategy for the controlled synthesis of noble metal SACs. This approach exhibits excellent universality for soft-acid metal ions such as $\text{AuCl}_3 \cdot 4\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and K_2PdCl_6 , and is compatible with various piezoelectric substrates. Systematic performance evaluation reveals that the as-prepared SACs display outstanding catalytic activity in diverse reactions, including photocatalysis, piezocatalysis, and processes under ambient conditions. The successful construction of atomically dispersed structures was unambiguously confirmed by techniques such as TEM and CO adsorption probe experiments. Furthermore, through a combination of ^{195}Pt NMR spectroscopy, mass spectrometry MS, UV-Vis spectroscopy, and DFT calculations, we systematically elucidated the transformation from Pt polynuclear species to mononuclear Pt species in the CH_3CN -based piezoelectric system, along with the formation of the key $[\text{PtCl}_2(\text{CN})_2]^{2-}$ intermediate via coordination with $\cdot\text{CN}$. The stability of the $[\text{PtCl}_2(\text{CN})_2]^{2-}$ intermediate and its specific adsorption characteristics are identified as the core mechanisms governing the formation of single atoms. Furthermore, this study elucidates the regulatory effect of piezocatalysis on the generation of reactive species in $\text{BOC-CH}_3\text{CN-H}_2\text{PtCl}_6$ system. Crucially, it validates that the piezoelectric field imposes an intrinsic selectivity on deposition sites during the synthesis of single-atom catalysts. These findings not only deepen the scientific understanding of the formation mechanism of SACs but also provide valuable insights for the controllable synthesis of noble metal SACs.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Funding

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Electronic Supplementary Material

Piezoelectric-induced ligand transformation of metal chlorides in acetonitrile for controllable synthesis of noble metal single-atom catalysts

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Method

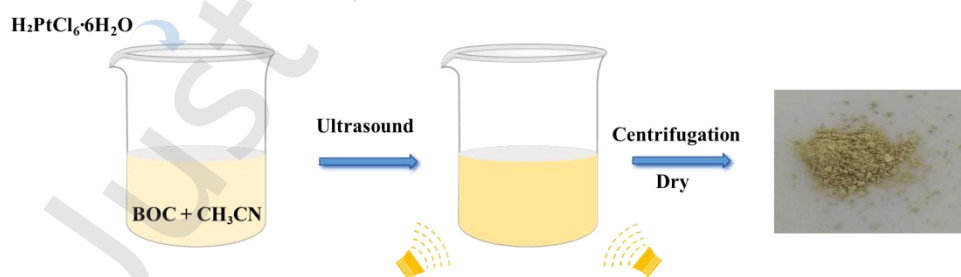


Fig. S1 Flowchart of Single-Atom Catalyst Preparation from H₂ PtCl₆ ·6H₂ O in Acetonitrile System via Piezoelectric Induction

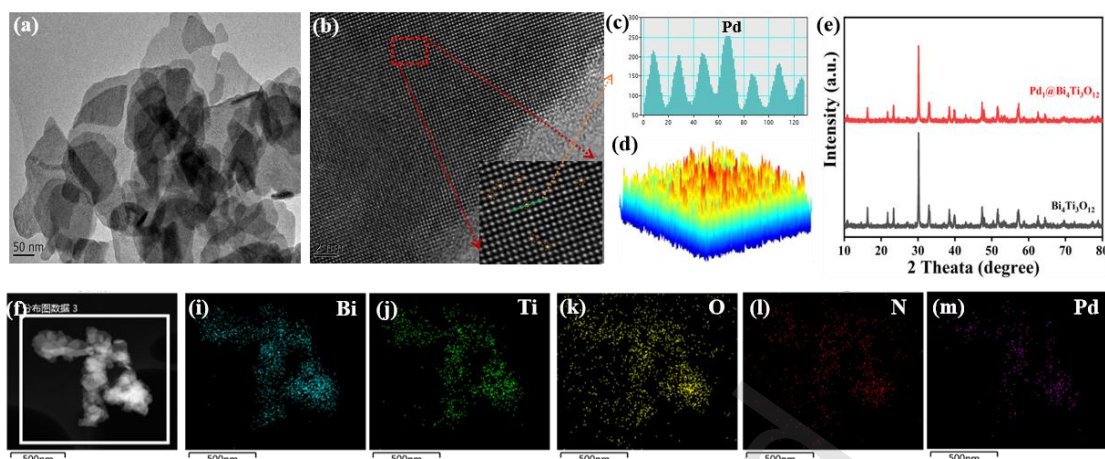


Fig. S2 (a)-(b) TEM and HAADF-TEM image of $\text{Pd}_1@ \text{Bi}_4\text{Ti}_3\text{O}_{12}$; (c) The local atomic strength distribution on the surface (d) 3D surface intensity profile (top) taken from the yellow dashed rectangle in (b) (bottom);(e) XRD of $\text{Pd}_1@ \text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$; (f)~(m) EDX elemental mapping of $\text{Pd}_1@ \text{Bi}_4\text{Ti}_3\text{O}_{12}$.

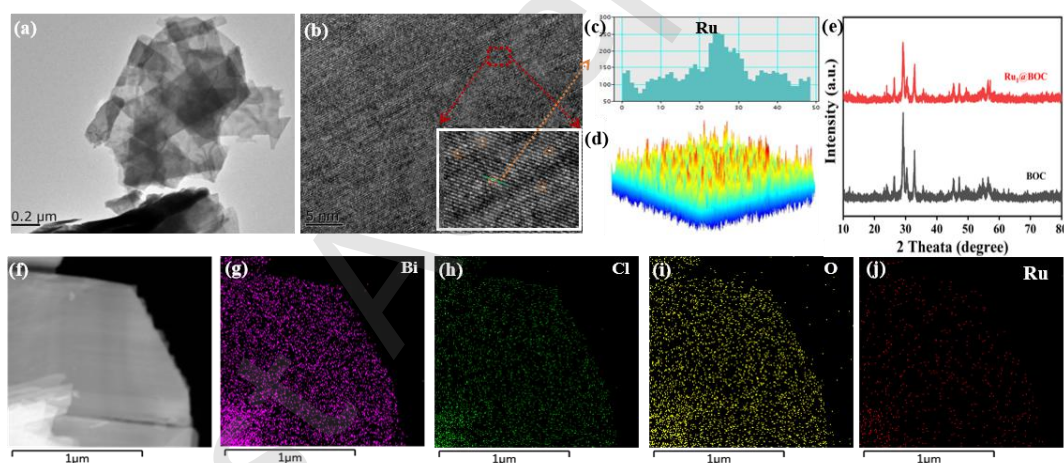


Fig. S3 (a)-(b) TEM and HAADF-TEM image of $\text{Ru}_1@ \text{BOC}$ (c) The local atomic strength distribution on the surface (d) 3D surface intensity profile (top) taken from the yellow dashed rectangle in (b) (bottom);(e) XRD of $\text{Ru}_1@ \text{BOC}$ and BOC; (f)~(i) EDX elemental mapping of $\text{Ru}_1@ \text{BOC}$.

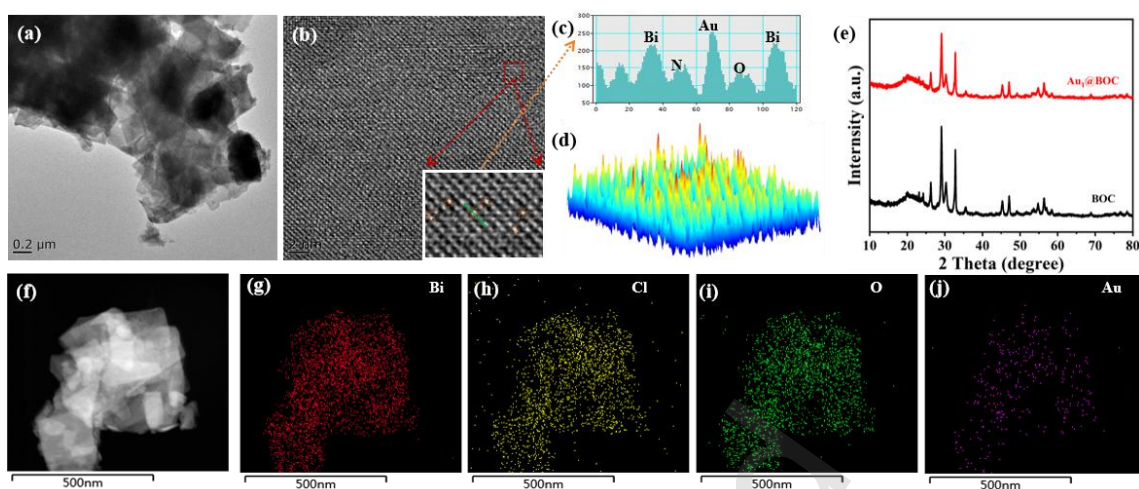


Fig. S4 (a)-(b) TEM and HAADF-TEM image of Au₁@BOC (c) The local atomic strength distribution on the surface (d) 3D surface intensity profile (top) taken from the yellow dashed rectangle in (b) (bottom);(e) XRD of Au₁@BOC and BOC; (f)~(j) EDX elemental mapping of Au₁@BOC.

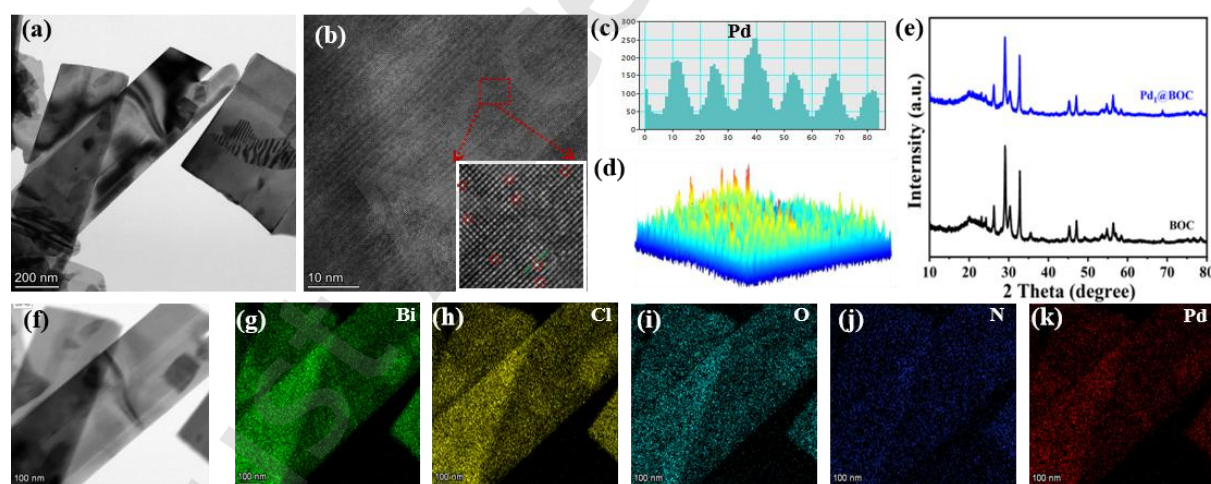


Fig. S5 (a)-(b) TEM and HAADF-TEM image of Pd₁@BOC (c) The local atomic strength distribution on the surface (d) 3D surface intensity profile (top) taken from the yellow dashed rectangle in (b) (bottom);(e) XRD of Pd₁@BOC and BOC; (f)~(k) EDX elemental mapping of Pd₁@BOC.

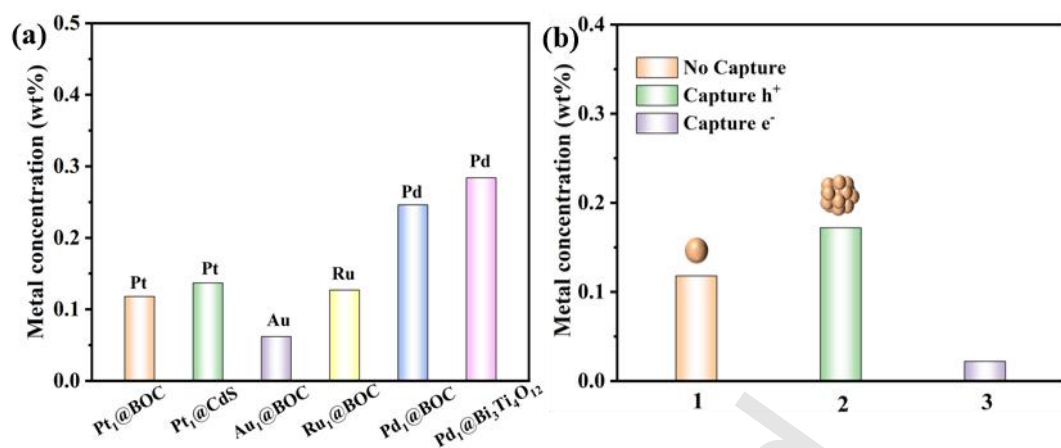


Fig. S6 (a) Loading amounts of noble metals in different single-atom catalysts; (b) The content and morphology of Pt on BOC under the capture of different living species.

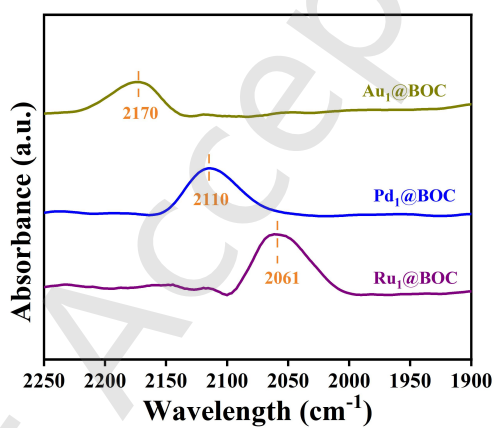


Fig. S7 CO IR absorption spectra of Au₁/BOC, Pd₁/BOC and Ru₁/BOC.

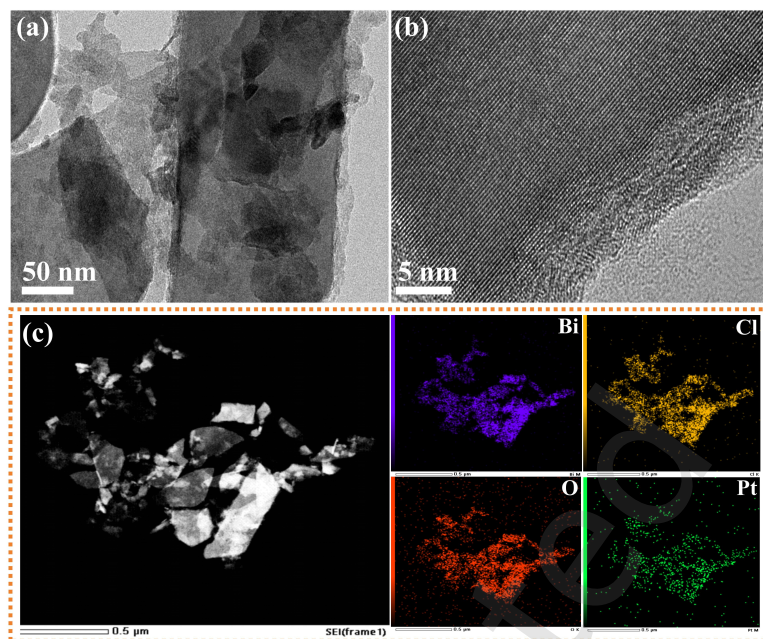


Fig. S8. (a) TEM image of piezocatalytic prepared Pt_1 @BOC; (b) Magnified TEM view of a local area; (c) TEM image and elemental maps (Bi, O, Cl, Pt) of Pt_1 @BOC.

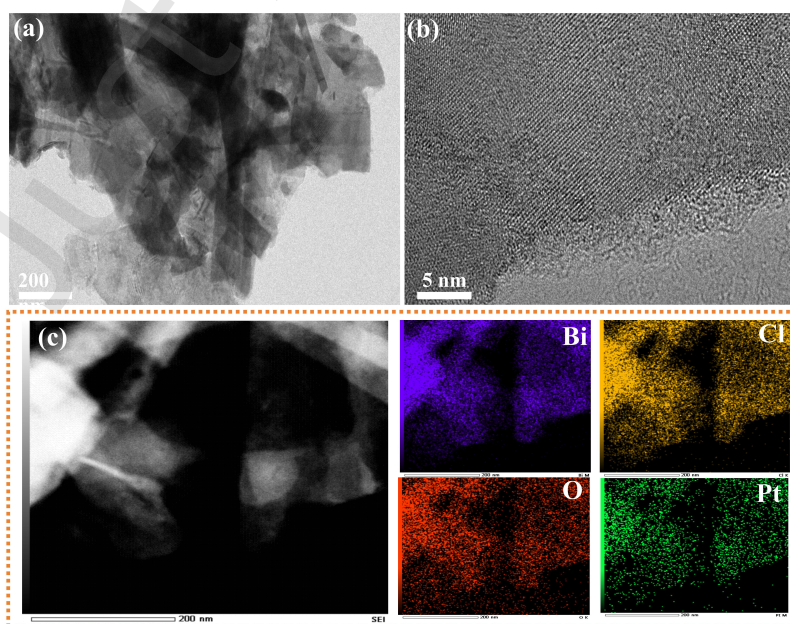


Fig. S9. (a) TEM image of photocatalytic prepared Pt_1 @BOC; (b) Magnified TEM view of a

local area;(c) TEM image and elemental maps (Bi, O, Cl, Pt) of Pt₁@BOC.

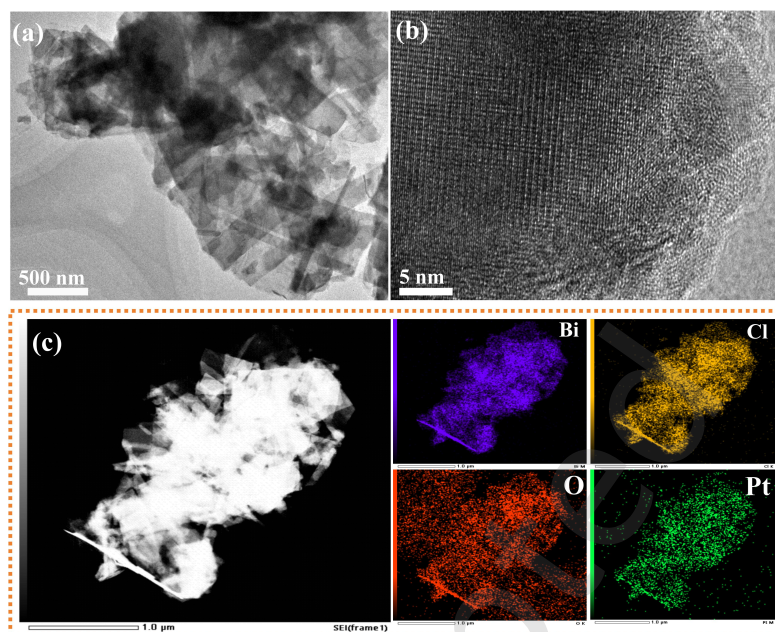


Fig. S10. (a) TEM image of piezocatalytic prepared Pt₁@OV-BOC;(b) Magnified TEM view of a local area;(c) TEM image and elemental maps (Bi, O, Cl, Pt) of Pt₁@BOC.

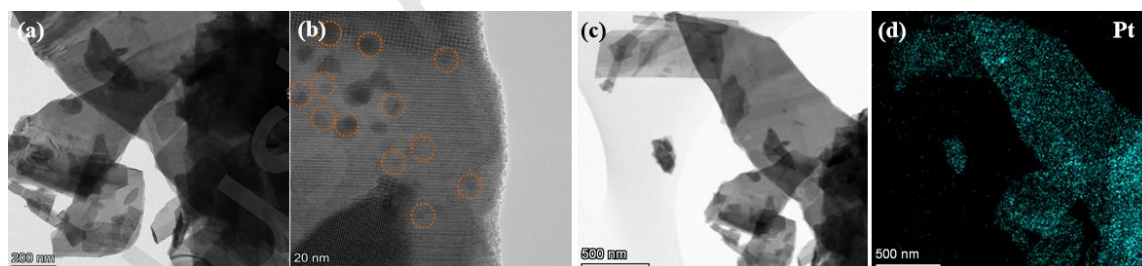


Fig. S11 (a) -(b) TEM images of the sample obtained after adding a hole scavenger to the H₂ PtCl₆ · 6H₂ O acetonitrile system; (c)-(d) Corresponding EDX elemental mapping images.

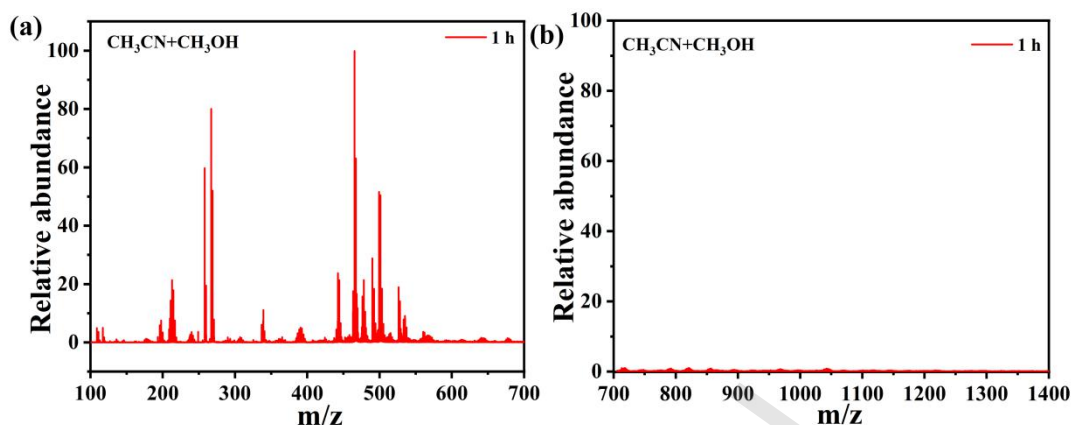


Fig. S12 Mass spectra of $H_2 PtCl_6 \cdot 6H_2 O$ in CH_3CN+CH_3OH solution.

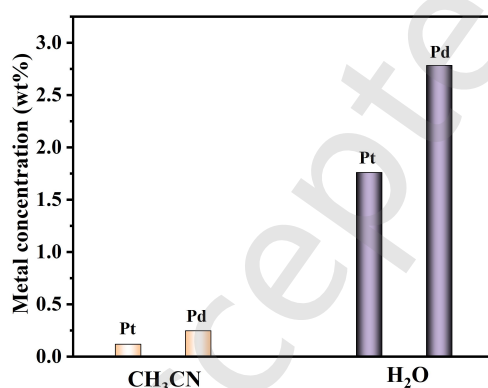


Fig. S13 shows the deposition amounts of Pt and Pd metals on the BOC surface in the aqueous-piezoelectric system and the acetonitrile-piezoelectric system, respectively.

1. Mass spectrometry calculation process:

(1) $[PtCl_2 (CN)_2]^{2-}$:

$$M/Z = \frac{M(Pt) + 2 \times M(Cl) + 2M(CN) + 2M(H)}{2} = \frac{195.08 + 2 \times 35.45 + 2 \times 26.02 + 2}{2} = 159.51$$

(2) $[Pt_2 Cl_9 (H_2 O)_3]^{3-}$:

$$M/Z = \frac{2 \times M(Pt) + 9 \times M(Cl) + 3M(H_2 O) + 3M(H)}{3} = \frac{2 \times 195.08 + 9 \times 35.45 + 2 \times 18.02 + 3 \times 1}{3} = 255.4$$

(3) $[Pt_2 Cl_{11} (H_2 O)]^{-}$:

$$M/Z = \frac{2 \times M(Pt) + 11 \times M(Cl) + 1 \times M(H_2 O) + 1 \times M(H)}{1} = \frac{2 \times 195.08 + 11 \times 35.45 + 2 \times 18.02 + 1 \times 1}{1} = 799.2$$

(4) $[Pt_3 Cl_{15} (H_2 O)_2]^{-}$:

$$M/Z = \frac{3 \times M(Pt) + 15 \times M(Cl) + 2 \times M(H_2O) + 1 \times M(H)}{1} = \frac{3 \times 195.08 + 15 \times 35.45 + 2 \times 18.02 + 1 \times 1}{1} = 1153$$

Considering the presence of some ^{37}Cl isotope, $(37 - 35.45) \times 15 = 23.25$.

$$M/Z = 1153 + 23.25 = 1176.3$$

(5) $[\text{PtCl}_4]^-$:

$$M/Z = \frac{1 \times M(Pt) + 4 \times M(Cl) + 1 \times M(H)}{1} = \frac{1 \times 195.08 + 4 \times 35.45 + 1 \times 1}{1} = 337.8$$

(6) $[\text{PtCl}_5]^-$:

$$M/Z = \frac{1 \times M(Pt) + 5 \times M(Cl) + 1 \times M(H)}{1} = \frac{1 \times 195.08 + 5 \times 35.45 + 1 \times 1}{1} = 372.8$$