Supporting Information

Coexistence of Au Single Atoms and Au Nanoparticles on NiAl-LDH for Selective Electrooxidation of Benzyl Alcohol to Benzaldehyde

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Experimental Detail

Chemicals

Ni(NO₃)₂·6H₂O (99%), Al(NO₃)₃·9H₂O (99%), NaAuCl₄, Na₂CO₃ (99.8%), NaOH (>98%) and C₇H₈O (benzyl alcohol) (99%) were all obtained from Energy Chemical and were used directly without any further purification.

Characterization

Powder X-ray diffraction (XRD) analysis was recorded on a Bruker D8 diffractometer with Cu-Kα radiation. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on a Shimadzu ICPS-7500 instrument. High resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM-2010 electron microscope operating at 200 kV. Ni and Fe K-edge X-ray absorption fine structure (XAFS) measurements were collected at the 1W1B station in Beijing Synchrotron Radiation Facility (BSRF). FT-EXAFS shell fitting was carried out with Artemis Software. WT-EXAFS was analyzed through Continuous Cauchy Wavelet Transform (CCWT). X-ray photoelectron spectroscopy (XPS) measurements were explored with monochromatized Al K exciting X-radiation (PHI Quantera SXM).

Synthesis of NiAl-LDH

The NiAl-LDH was synthesized by using a coprecipitation method according to the reference.¹ A 20.0 ml solution composed 3 mmol Ni(NO₃)₂·6H₂O and 1 mmol Al(NO₃)₃·9H₂O was added drop by drop to a three-necked flask with 20 ml alkaline solution (contained 1 mmol NaOH and 1 mmol Na₂CO₃) by a peristaltic pump under magnetic stirring at 80 °C. The brown precipitates were collected by centrifugation and washed with deionized water for 3 times.

Synthesis of Au_x-NiAl-LDH

For Au_{1+n}-NiAl-LDH, the as-prepared NiAl-LDH was mixed with the solution of 50% H₂O and 50% ethanol, followed by adding NaAuCl₄ solution dropwise into the mixture with 2 hours immersion reduction process, and the size of the loaded Au nanoparticles can be regulated by tuning the reduction time. The obtained product was washed immediately by water and dried by rotary evaporator to avoid further aggregation of Au. The Au_n-NiAl-LDH can be obtained by 4 hours immersion reduction process, while the Au₁-NiAl-LDH was prepared by using 100% H₂O as solution, and 8 hours immersion.

Electrochemical measurements

The electrochemical performances were tested in a three-electrode glass cell by an electrochemical workstation (CHI 660e, CH, Shanghai). A method of preparing a work electrode is as follows: 5 mg catalyst was dispersed in 1 ml water with the assistance of ultrasonication to form a homogeneous solution. Then 200 µL of the solution was dropped onto a carbon paper (1 cm×1cm). Taking the sample loss into consideration, the loading of catalyst can be calculated as 1 mg·cm⁻². A Pt electrode and an Ag/AgCl electrode were used as counter and reference electrode, respectively. In the benzyl alcohol oxidation reaction, the linear sweep voltammetry (LSV) curves were collected at a scan rate of 10 mV s⁻¹ after twenty CV scans. AC impedance measurements were carried out in the same configuration at 0.632 V vs. Ag/AgCl from 0.01 Hz to 100 kHz with an AC voltage of 5 mV. The stability tests were operated through chronopotentiometry measurement with 10 mA anodic current. The current density differences ($\Delta i = ja - jc$) were plotted against scan rates, and the linear slope is twice the double-layer capacitance (C_{dl}). The ECSA can be calculated from the double-layer capacitance (C_{dl}) using the following equation: ECSA = $S_{geo} * C_{dl} / C_s$. Wherein, C_s is specific electrochemical double-layer capacitance and its value in alkaline media is 0.040 mF \cdot cm $^{-2},$ and the S_{geo} represents the geometric surface area of the working electrode.

Product detection

The qualitative analysis was characterized by Gas Chromatography-Mass Spectrometry (GC-MS; GC-SHIMADZU-2010 Plus; GCMS-QP2020).

The quantitative analysis of products (benzyl alcohol, benzaldehyde, benzoic acid in electrolyte) was performed by high performance liquid chromatography (HPLC; Angilent 1200 Infinity Series) equipped with C18 column (Cosmosil C18-MS-II) using MeCN/H₂O (30/70) with 0.02M HCOOH as mobile phase and detected by UV detector at 240 nm. The flow rate was 1.0 mL·min⁻¹.

Computational details

The first principles density functional theory plus Hubbard U (DFT + U) calculation in this work were performed using the CASTEP module in Material Studio software package.² The values of U – J (Ueff) were 3.80 eV for Ni^{2+,3} The Perdew-Burke-Ernzerhof (PBE) functional in generalized gradient approximation (GGA) was used to describe the exchange and correlation⁴ and the ultrasoft pseudopotential were applied to describe the ionic cores to improve transferability and reduce the number of plane waves required in the expansion of the Kohn-Sham orbitals. The potential energy surface was searched with Broyden-letcher-Goldfarb-Shanno (BFGS) algorithm.⁵ The cutoff energy was set as 381.0 eV to balance the cost and effectiveness.⁶ The geometry optimization was based on the following points: (1) an energy tolerance of 1.0 $10^{-5} \times eV/atom$, (2) a maximum displacement tolerance of 5.0 $10^{-3} \times \text{Å}$, and (3) a maximum force tolerance of 0.1 eV/Å.

The Au_{10} nanoparticle with exposed (111) surface was modeled on the basis of HRTEM results according to previously reported work.^{7, 8}

Because of the alkaline reaction condition (1 M KOH electrolyte), the benzyl alcohol was prefer to exist in the form of alkoxide.⁹ In this case, the calculations were conducted by using benzyl alkoxide as substrate.



Figure S1. XRD patterns of Au_{1+n}-NiAl-LDH, Au₁-NiAl-LDH, Au_n-NiAl-LDH and NiAl-LDH.



Figure S2. (a) TEM image of NiAl-LDH; (b) HRTEM image of Au_{1+n} - NiAl-LDH; (c) HAADF-HRTEM image and (d-g) corresponding elemental mappings diagram of Au_{1+n} - NiAl-LDH.

Samples	Mass ratio of Au (wt%)	Mass ratio of Ni (wt%)	Mass ratio of Al (wt%)
Au ₁ -NiAl-LDH	5.28	4.56	6.53
Au _{1+n} -NiAl-LDH	5.48	4.41	6.19
Au _n -NiAl-LDH	4.99	4.44	6.32

Table S1. Mass content of Au, Ni, Al in Au_x-NiAl-LDH samples tested by ICP-OES.



Figure S3. XPS survey results of NiAl-LDH and Au_x-NiAl-LDH.



Figure S4. The R space fitting of Au_x-NiAl-LDH.

Sample	Shell	Nª	$R[\text{\AA}]^{ ext{b}}$	σ2[10 ⁻³ Å ²]°	ΔE_0	R-factor (10 ⁻²)
Au foil	Au-Au	12.00	2.86	7.94	5.49	0.12
Au ₁ -NiAl-LDH	Au-O	3.83	1.99	2.24	9.83	0.71
	Au-Au	/	/	/	/	
Au _n -NiAl-LDH	Au-O	/	/	/	/	10.39
	Au-Au	9.97	2.85	8.83	4.28	
Au _{1+n} -NiAl- LDH	Au-O	1.35	1.99	1.16	14.22	12.41
	Au-Au	9.65	2.86	10.50	4.64	

Table S2. The R space fitting results of Au_x-NiAl-LDH.



Figure S5. The possible locations of single-atom Au and their relative energy with corresponding models.



Figure S6. Conversion of BA and selectivity of BAD during BAOR in 1.0 M KOH for NiAl-LDH and Au_x-NiAl-LDH.



Figure S7. The GC spectrum of the product before and after reaction in Au_{1+n} -NiAl-LDH system.



Figure S8. The Mass spectrum of the product before and after reaction in Au_{1+n} -NiAl-LDH system.



Figure S9. (a) Standard curves of the products detected by HPLC. The HPLC spectrum of the products for Au_{1+n} -NiAl-LDH system.



Figure S10. The evaluation of ECSA. The CV curves of (a) NiAl-LDH, (b) Au₁-NiAl-LDH, (c) Au_n-NiAl-LDH, (d) Au_{1+n}-NiAl-LDH with the scan rate ranging from 10 to 50 mV·s⁻¹ in 1.0 M KOH.

Samples	$C_{dl} (mF \cdot cm^2)$	ECSA (cm ²)
Au _{1+n} -NiAl-LDH	1.54	38.5
Au ₁ -NiAl-LDH	1.33	33.25
Au-NiAl-LDH	0.98	24.5
NiAl-LDH	0.93	23.25

Table S3. The calculated ECSAs of the NiAl-LDH and Au_x -NiAl-LDH.



Figure S11. The stability test of Au_{1+n} -NiAl-LDH.



Figure S12. HRTEM image of Au_{1+n} -NiAl-LDH after reaction.



Figure S13. Optimized geometries of NiAl-LDH and Au_x -NiAl-LDH in top view and side view, respectively. The color for each element is labeled.



Figure S14. Schematic illustrations for the adsorption configurations of benzyl alkoxide on Au_x-NiAl-LDH. The distance between the benzyl alkoxide and Au (111) facet is identified as d_{π} , and that between O atom and bottom Au atom is identified as d_{σ} . The color for each element is labeled.



Figure S15. Multi-potential step curves of NiAl-LDH and Au_x-NiAl-LDH electrode (including 2-s open circuit time).



Figure S16. The corresponding calculation models of dehydrogenation process on Au_1 -NiAl-LDH, Au_{1+n} -NiAl-LDH and Au_n -NiAl-LDH, respectively.



Figure S17. The benzaldehyde adsorption calculation models for Au_1 -NiAl-LDH, Au_{1+n} -NiAl-LDH and Au_n -NiAl-LDH, respectively.

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