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Ultrasmall Ag nanoclusters anchored on NiCo-layered double hydroxide nanoarray for efficient electrooxidation of 5-hydroxymethylfurfural

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ABSTRACT Electrochemical oxidation of 5-hydroxymethylfurfural (HMF) has shown promising prospects in producing highly valuable chemicals. Herein, we report the synthesis of ultrasmall Ag nanoclusters anchored on NiColayered double hydroxide (NiCo-LDH) nanosheet arrays (Ag_n@NiCo-LDH) *via* a facile electrodeposition strategy. The prepared Ag_n@NiCo-LDH nanosheet arrays exhibit excellent electrocatalytic HMF oxidation performance with a current density of 10 mA cm⁻² at 1.29 V_{RHE} and the Faraday efficiency of nearly 100% for 2,5-furandicarboxylic acid production. This study offers an effective approach to rationally design nanoclusters to achieve high catalytic activity for sustainable energy conversion and production.

Keywords: ultrasmall Ag nanoclusters, layered double hydroxides, nanosheet array, electrodeposition, 5-hydroxymethylfurfural electrooxidation

INTRODUCTION

Biomass conversion into value-added chemicals is an important and desirable way to reduce the depletion of fossil fuels and improve energy utilization efficiency [1–4]. 5-Hydroxymethylfurfural (HMF) is one of the most extensively studied biomass-derived platform molecules, serving as a promising candidate for driving numerous high-value chemicals by oxidizing its furan ring, aldehyde, and alcohol groups [5-7]. Of particular importance is the oxidation product 2,5-furandicarboxylic acid (FDCA) [8], acting as a precursor for the production of bio-polymer polyethylene furanoate (PEF) [9] and a large-scale monomer of commercial polyethylene terephthalate [10]. Given the broad demand for FDCA in industry, immense efforts have been made to study the catalytic synthesis of FDCA from HMF [11]. Traditionally, the conversion of HMF to FDCA depends on thermocatalytic processes that require harsh reaction conditions (high temperature and pressure) and expensive catalysts [12,13]. In contrast, the electrochemical synthesis is a thriving alternative method in which the oxidation is driven by the applied potential under mild conditions [14]. However, the electrooxidation of HMF in alkaline media always competes with the oxygen evolution reaction (OER) (4OH⁻ \rightarrow O₂ + 2H₂O + $4e^{-}$) [15–18], resulting in a low Faraday efficiency (FE) for HMF oxidation [19]. Hence, it is crucial to rationally design electrocatalysts to increase the FE and reduce the driven potential, as well as achieve the high yield of FDCA for HMF oxidation.

Currently, most studies on HMF electro-oxidation are focused on heterogeneous electrocatalysts [13,20]. Noble metal-based catalysts, including Pt [21], Pd [22], Au [23], Ru [24], and Agbased [25] catalysts, have been widely studied for HMF electrooxidation because of their unique electron and orbital properties [26]. Considering the metal particle size as a key factor in performance evaluation, downsizing the metal particle is of great importance in introducing more uncoordinated atoms and enhancing the metal-support interaction [27,28]. Once the metal is downsized to nano or sub-nano scale, its catalytic behavior could change dramatically [29]. Particularly, ultrasmall metal nanoclusters with low-nuclearity metal atoms can considerably expose the active centers while retaining the metallic properties [30-32]. As the intermediate states between singleatom catalysts and nanoparticles, supported nanoclusters can provide enough sites for the adsorption and activation of multiple substrates with a relatively high atom utilization efficiency, thus reducing the reaction barrier and increasing the catalytic activity [33-36]. For instance, highly dispersed Pt clusters supported on a metal-organic framework (MOF) displayed high catalytic activity for photocatalytic H₂ production [37]. Gold nanocluster catalyst promoted the electrochemical production of ammonia derived from the electronic interaction between Au nanoclusters and supports [38]. Therefore, such metal nanoclusters could exhibit great potential to improve the HMF electro-oxidation performance. Specifically, Ag has the lowest price among the above mentioned noble-metal catalysts [39]; however, few studies have been done on HMF electro-oxidation by using Ag nanoclusters as the electrocatalyst to date, and the synthesis of Ag nanoclusters also remains a challenge because of the high surface energy of ultrasmall metal nanoclusters.

Herein, we report the rational design and synthesis of Ag nanoclusters anchored on NiCo-layered double hydroxide (LDH) (Ag_n@NiCo-LDH) nanosheet arrays for highly efficient HMF oxidation. LDHs were chosen as the support due to their adjustable components and flexible structures, thus benefiting the performance optimization [40,41]. Particularly, the Ni- and Co-containing LDHs possess variable valence states of metal ions, further enhancing the metal-support interaction [42–44]. The Ag_n@NiCo-LDH nanosheet arrays were prepared *via* a facile electrochemical deposition strategy, which showed great potential in managing the particle size [45]. The obtained Ag_n@NiCo-LDH catalyst exhibited excellent catalytic performance in HMF electro-oxidation reaction, achieving a nearly 100% yield (>98%) and FE (>97%) for FDCA production at the applied potential of 1.39 V *vs.*

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(RHE) without any sacrificial agents. Moreover, the $Ag_n@NiCo-LDH$ catalyst also showed considerable durability and stability, thus demonstrating its potential as a biotransformation catalyst. This work offers an effective approach to rationally design nanoclusters to achieve high catalytic activity for sustainable energy conversion and production.

EXPERIMENTAL SECTION

Synthesis of NiCo-LDH nanosheet array

The NiCo-LDH nanosheet nanoarray was prepared by a facile electrodeposition method. In a typical procedure, a piece of nickel foam (NF, $2 \text{ cm} \times 2 \text{ cm}$) was cleaned with HCl solution $(6 \text{ mol } L^{-1})$ by ultrasonication for 5 min to remove the surface NiO layer and subsequently sonicated in deionized (DI) water and absolute ethanol for 3 min, respectively. Later, the clean NF was used as the working electrode, and the Ag/AgCl electrode and Pt plate were used as the reference and counter electrodes, respectively, for the electrochemical deposition. An aqueous solution containing Ni(NO₃)₂·6H₂O $(0.1 \text{ mol } L^{-1})$ and $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mol L⁻¹) was used as the deposition electrolyte. The NiCo-LDH nanosheet array was obtained on the working electrode under a constant deposition potential of -1.0 V vs. Ag/AgCl electrode for 10 min, and finally rinsed with DI water and ethanol thrice.

Synthesis of Ag_n@NiCo-LDH nanosheet array

The Ag_n@NiCo-LDH nanosheet array was prepared through an electrochemical deposition process in a standard three-electrode system. Typically, the as-prepared NiCo-LDH nanosheet array was used as the working electrode, and the Ag/AgCl electrode and Pt plate were used as the reference and counter electrodes, respectively. A solution containing 100 µmol L⁻¹ AgNO₃ and 1 mol L⁻¹ KOH was used as the electrolyte. The electrochemical deposition was performed *via* cyclic voltammetry (CV) from 0.1 to 0.8 V *vs*. Ag/AgCl electrode with a sweeping rate of 5 mV s⁻¹ for two cycles. After the deposition, the electrode was washed with DI water thrice.

Material characterization

Sample morphology was characterized via field-emission scanning electron microscopy (Zeiss SUPRA 55) and transmission electron microscopy (TEM, Hitachi HT7700). The high-resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a JEOL JEM-2100F. Aberrationcorrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) images were obtained using a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 300 kV. X-ray diffraction (XRD) was performed on an RIGAKU XRD-6000A diffractometer at 40 kV and 100 mA with copper-filtered K α radiation ($\lambda = 1.5406$ Å). X-ray photoelectron spectroscopy (XPS) was performed on a model of ESCALAB 250. The binding energies were calibrated by referring C 1s peak to 284.8 eV. X-ray absorption fine structure (XAFS) measurements were performed at the BL14W1 beamline, Shanghai Synchrotron Radiation Facility (SSRF, energy 3.5 GeV, current 250 mA maximum, Si (311) double crystals as double-crystal monochromator covering the photon energy range of 8.5–50 keV). The loading amount of Ag on the 1 cm \times 1 cm electrode was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES). The catalytic products

were analyzed *via* high-performance liquid chromatography (HPLC, Shimadzu Prominence LC-2030C system) equipped with an ultraviolet (UV)-visible detector.

Electrochemical measurements

All electrochemical measurements were conducted on a CHI 660E electrochemical station (Shanghai Chenhua, China) with a conventional three-electrode configuration at ambient temperature. Saturated Ag/AgCl and platinum plate electrodes served as the reference and counter electrodes, respectively. The Agn@NiCo-LDH nanosheet arrays were directly used as the working electrode. The potentials were referenced to the RHE $(E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.2412 + 0.0591 \text{pH})$. Linear sweep voltammetry (LSV) was measured at a scan rate of 5 mV s⁻¹ with 85% *iR* compensation. Electrochemical impedance spectroscopy (EIS) tests were measured over a frequency range of 10⁵ to 10⁻² Hz with the alternating current (AC) amplitude of 10 mV. A constant potential electrolysis test was conducted in a divided cell separated by the Nafion 117 membrane. The HMF oxidation products were analyzed via HPLC with a UV-visible detector. The UV detector wavelength was set to 265 nm. The mobile phase A of HPLC was methanol, and phase B was 5 mmol L⁻¹ ammonium formate aqueous solution. The ratio of A:B was 3:7, and the flow rate was 0.6 mL min⁻¹. In each measurement, a 20-µL sample was drawn from the electrolyte during the potentiostatic electrolysis and diluted to 1 mL with ultrapure water and analyzed via HPLC. The conversion of HMF, FDCA yield, and FE were calculated according to Equations (1-3), respectively.

HMF conversion (%) =
$$\frac{n(\text{HMF consumed})}{n(\text{HMF initial})} \times 100,$$
 (1)

FDCA yield (%) =
$$\frac{n(\text{FDCA})}{n(\text{HMF initial})} \times 100,$$
 (2)

$$FE (\%) = \frac{n(FDCA)}{Charg e/(6 \times F)} \times 100,$$
(3)

where *F* is the Faraday constant (96,485 C mol⁻¹), and *n* is the mole amount of the reactant calculated from the HPLC concentration analysis.

RESULTS AND DISCUSSION

The fabrication strategy of the Ag_n@NiCo-LDH nanosheet arrays was schematically shown in Scheme 1. The vertically aligned NiCo-LDH nanosheets on NF were first prepared as the support via a facile electrosynthesis method (Fig. S1). Then, Ag species were deposited on the NiCo-LDH nanosheet arrays during the CV cycling process in the electrolyte containing AgNO₃. As shown in Fig. 1a, the obtained Ag_n@NiCo-LDH nanosheets were uniformly distributed on the NF without any morphology change in NiCo-LDH after the loading of Ag species. The TEM image in Fig. 1b confirms the nanosheet characteristic of Ag_n@NiCo-LDH, without an obvious aggregation of silver. The Ag species in Ag_n@NiCo-LDH were further investigated via AC-HAADF-STEM. As shown in Fig. 1c and Fig. S2, after two cycles of CV electrochemical deposition, a significant number of clusters (marked by red circles) were observed, indicating the dispersion of Ag species on NiCo-LDH as about 1.5 nm-sized ultrasmall nanoclusters. However, increasing the CV electrochemical deposition to four or ten cycles, Ag nanoclusters continually grew into larger nanoparticles with a



Scheme 1 Schematic illustration of the fabrication process of Ag_n@NiCo-LDH nanosheet arrays.



Figure 1 Morphology characterizations of the $Ag_n@NiCo-LDH$ nanosheet arrays. (a) Low- and high-magnification (inset) SEM images; (b) TEM; (c) AC-HAADF-STEM, and (d) EDX mapping images of $Ag_n@NiCo-LDH$ nanosheets.

size range of about 4 to 10 nm (Fig. S3). Besides, the lattice plane distances of 2.27 and 2.32 Å were attributed to the (111) crystal plane of Ag and the (012) plane of the LDH phase, respectively. EDX mapping showed that the Ag, O, Ni, and Co elements were homogeneously dispersed over the entire architecture (Fig. 1d).

ICP-AES analysis revealed that the silver content in Ag_n@NiCo-LDH was ~0.3 wt%, consistent with the EDX result (Fig. S4). XRD patterns of Agn@NiCo-LDH and NiCo-LDH exhibited a series of (00l) peaks which matched well with those of NiCo-LDH (JPCDS No. 33-0429) without any impurity peaks (Fig. 2a). No peaks of Ag bulk (JPCDS No. 304-0783) were observed in the patterns of Ag_n@NiCo-LDH, indicating the welldispersed Ag on NiCo-LDH and small-sized Ag nanoclusters. XAFS measurement was further employed to accurately acquire the local structure and coordination environment of Ag species. As shown in the Ag K-edge X-ray absorption near-edge structure (XANES) spectra in Fig. 2b, the Ag absorption edge of Ag_n@NiCo-LDH was located between the Ag foil and Ag₂O, suggesting that the oxidation state of Ag nanoclusters in Ag_n@NiCo-LDH was between 0 and +1. Meanwhile, Fourier transforms of k^2 -weighted extended XAFS (EXAFS) spectra for Ag_n@NiCo-LDH in R space exhibited the main peak at 2.71 Å, corresponding to the Ag-Ag interaction, indicating the predominant metallic Ag feature in Ag_n@NiCo-LDH (Fig. 2c). In addition, a weak peak at 1.67 Å could be assigned to the Ag-O coordination, indicating that the Ag nanoclusters were coordinated with O atoms on NiCo-LDH with partial Ag atoms in a valence state of +1, consistent with the Ag K edge XANES spectrum. To determine the precise atomic structure and explore the interaction between the Ag nanoclusters and NiCo-LDH support, the EXAFS curve fitting of Ag_n@NiCo-LDH was performed (Fig. S5 and Table S1). According to the fitting results, the first coordination shell of Ag-Ag was observed at 2.71 Å with a coordination number of 6, suggesting the formation of Ag clusters. Besides, the Ag-O bond at 1.67 Å with a coordination number of 4 suggested that the Ag nanoclusters were stabilized by the bridging O atoms of NiCo-LDH. XPS was further employed to characterize the chemical composition and electronic properties of Agn@NiCo-LDH. The full XPS spectra of NiCo-LDH revealed signals of Ni, Co, O, and C elements. After the Ag electrodeposition, the signal of the Ag element was observed in the full XPS spectra of Ag_n@NiCo-LDH (Fig. S6). The high-resolution XPS spectra of Ag 3d of Ag_n@NiCo-LDH showed four main peaks (Fig. 2d), where the peaks at 373.3 and 367.3 eV could be assigned to Ag+, and those at 374.8 and 368.8 eV indicated the presence of metallic silver [46-48]. The oxidation state of Ag in Ag_n@NiCO-LDH was higher than zero, which was consistent with the XAFS results [49]. The valence states of Co and Ni in Ag_n@NiCo-LDH and NiCo-LDH were further analyzed to explore the potential interaction between the Ag nanoclusters and support. As shown in Fig. 2e, compared with the prinstine NiCo-LDH, the binding energy of Co 2p_{2/3} in Agn@NiCo-LDH exhibited a positive shift from 780.5 to 780.9 eV, and the atomic ratio of Co^{3+}/Co^{2+} decreased from 1.37 to 1.02 compared with that of pristine NiCo-LDH. Meanwhile, the binding energy of Ni 2p of Ag_n@NiCo-LDH barely changed compared with that of the pristine NiCo-LDH (Fig. 2f). These results suggest an electron transfer from Ag nanoclusters to Co atoms in Ag_n@NiCo-LDH.

The electrocatalytic HMF oxidation performance of the asprepared $Ag_n@NiCo-LDH$ was evaluated in an H-type (proton exchange membrane) electrochemical cell using 1 mol L⁻¹ KOH as the electrolyte at ambient temperature. The electrochemical measurement was performed in a standard three-electrode configuration using a commercial Pt plate and Ag/AgCl as the counter and reference electrodes, respectively (Fig. 3a). A con-



Figure 2 (a) XRD patterns of $Ag_n@NiCo-LDH$ and NiCo-LDH (the sharp diffraction peak at 44.5° belonged to the Ni foam substrate). Ag K-edge (b) XANES profiles and (c) EXAFS spectra in R space for $Ag_n@NiCo-LDH$, Ag_2O , and Ag foil. HR-XPS spectra of (d) Ag 3d, (e) Co 2p, and (f) Ni 2p of $Ag_n@NiCo-LDH$ and NiCo-LDH.



Figure 3 (a) Schematic diagram of the electrochemical system used for HMF oxidation with cathode and anode. (b) LSV curves of electrocatalysts at a scan rate of 5 mV s⁻¹ in 1 mol L⁻¹ KOH with or without adding 10 mmol L⁻¹ HMF. (c) HMF oxidation potentials at current densities of 10 and 100 mA cm⁻² for Ag_n@NiCo-LDH and NiCo-LDH and (d) the corresponding Tafel plots. (e) Capacitive currents at -0.20 V vs. Ag/AgCl electrode as a function of the scan rate for Ag_n@NiCo-LDH and NiCo-LDH. (f) The Nyquist plots of Ag_n@NiCo-LDH and NiCo-LDH in 1 mol L⁻¹ KOH with 10 mmol L⁻¹ HMF.



Figure 4 (a) Schematic illustration of the two possible HMF oxidation pathways to FDCA. (b) HPLC chromatograms at various passed charge states during electrolysis. (c) Plots of concentration *versus* passed charge of HMF, FDCA, and the intermediates during the electrochemical oxidation of HMF over $Ag_n@NiCo-LDH$. (d) Yield and FE (%) of FDCA obtained by $Ag_n@NiCo-LDH$ for eight consecutive cycles in HMF oxidation.

stant potential electrolysis test was conducted in a divided cell separated by the Nafion 117 membrane. Fig. 3b depicts the LSV curves of Agn@NiCo-LDH and NiCo-LDH with or without HMF (10 mmol L^{-1}) in the electrolyte. Notably, OER is the main competing reaction during the HMF oxidation. Without HMF in the electrolyte, the Agn@NiCo-LDH showed an onset potential (at 5 mA cm⁻²) of 1.43 V vs. RHE for OER in 1 mol L^{-1} KOH, slightly lower than that of NiCo-LDH (1.47 V vs. RHE). After adding 10 mmol L⁻¹ HMF into the electrolyte, the onset potential (at 5 mA cm⁻²) of Ag_n@NiCo-LDH reduced to 1.28 V vs. RHE, indicating that the oxidation of HMF on Ag_n@NiCo-LDH was much easier than OER. However, the onset potential of NiCo-LDH showed negligible change on HMF addition, suggesting that the ultrasmall Ag nanoclusters promoted the HMF electro-oxidation process. Moreover, the applied potentials at 10 and 100 mA cm⁻² were tested as important evaluation parameters for this reaction. As shown in Fig. 3c, the Ag_n@NiCo-LDH only needed 1.29 and 1.39 V (vs. RHE) to reach the current densities of 10 and 100 mA cm⁻², respectively, much lower than those of NiCo-LDH (1.46 and 1.54 V vs. RHE) and most developed electrodes (Table S2). The relatively low driving potential at high current density indicates that it is promising for practical applications. In addition, Tafel slope kinetics for OER and HMF oxidation over Ag_n@NiCo-LDH and NiCo-LDH were calculated by the linear fitting of polarization curves. As shown in Fig. 3d, the Tafel slope for HMF oxidation over Ag_n@NiCo-LDH was lower than that for OER (82.4 vs. 87.3 mV dec^{-1}), demonstrating better kinetics of HMF oxidation on Ag_n@NiCo-LDH. In contrast, the Tafel slope for OER was 54.9 mV dec $^{-1}$ and increased to 83.0 mV dec⁻¹ in the presence of HMF over NiCo-LDH, suggesting the inactive nature of NiCo-LDH for HMF oxidation. To investigate the origin of the superior HMF oxidation performance of Ag_n@NiCo-LDH, we further measured the electrochemically active surface area during HMF oxidation, which was linearly proportional to the double-layer capacitance (C_{dl}) . Using the CV method at the non-Faradaic region of -0.22 to -0.18 V vs. Ag/AgCl electrode, the electrochemically active surface area could be calculated from the linear relationship between the current densities at -0.20 vs. Ag/AgCl electrode and scan rates (Fig. S7). Based on these curves, the C_{dl} value of Ag_n@NiCo-LDH was 3.53 mF cm⁻², seven times higher than that of NiCo-LDH (0.55 mF cm⁻²), indicating that Ag_n@NiCo-LDH provided more electrocatalytically active sites for HMF oxidation (Fig. 3e). Moreover, the EIS was also measured. Ag_n@NiCo-LDH showed a smaller charge transfer resistance than NiCo-LDH catalysts, further demonstrating its much higher catalytic activity (Fig. 3f). In addition, the Ag loading on NiCo-LDH was optimized. As shown in Fig. S8, Ag_n@NiCo-LDH with the Ag loading of 0.3 wt% exhibited the highest catalytic activity among other electrocatalysts (Ag_n@NiCo-LDH-1, Ag_n@NiCo-LDH-4 and Ag_n@NiCo-LDH-10).

Generally, there are two possible pathways of HMF oxidation to FDCA owing to the presence of aldehyde and hydroxyl groups in HMF (Fig. 4a). The first step of HMF oxidation is the conversion of HMF to 5-hydroxymethyl-2-furancarboxylic acid (HMFCA, Path 1) or 2,5-diformylfuran (DFF, Path 2). Then, the generated HMFCA and DFF are oxidized to 5-formyl-2-furancarboxylic acid (FFCA) and finally, FDCA. To better understand the kinetics of the catalytic HMF oxidation over $Ag_n@NiCo-LDH$, constant potential oxidation of HMF to FDCA was performed. The oxidation products (HMFCA, DFF, FFCA, and FDCA) in the electrolyte were determined *via* HPLC. The calibration curves were obtained by plotting the peak areas of standard substances with five different concentrations (Fig. S9). Fig. 4b shows the chromatograms of the reactant and product at different charges. The peak attributed to HMF at the retention time of 3.54 min continuously decreased in intensity, while the signal of FDCA at the retention time of 2.16 min gradually increased as the reaction progressed. Moreover, the intermediate product DFF (4.10 min) was not detected, and the concentration of HMFCA increased gradually. The above results implied that the main path of HMF oxidation over Ag_n@NiCo-LDH was Path 1, wherein HMF was preferentially oxidized at the aldehyde groups. Fig. 4c shows the conversion and concentration changes of HMF over different charges. When the passing charge reached 80 C, the peak belonging to HMF in the HPLC spectrum almost disappeared, while that belonging to FDCA increased to the maximum. The corresponding FDCA yield and FE were obtained at 97.5% and 98.8% at this number of electron consumption (80 C), respectively, indicating the high activity and selectivity of Ag_n@NiCo-LDH toward electrocatalytic HMF oxidation. In addition, the Ag_n@NiCo-LDH electrode also showed considerable durability for HMF oxidation. The yield and FE toward FDCA demonstrated no obvious change after eight cycle reactions (Fig. 4d).

CONCLUSIONS

In summary, ultrasmall Ag nanoclusters anchored on NiCo-LDH ($Ag_n@NiCo-LDH$) nanosheet arrays were successfully prepared *via* the electrodeposition method, exhibiting excellent catalytic performance in the electrooxidation of HMF into FDCA, surpassing most developed catalysts. This study demonstrates a promising approach for biomass conversion into high value-added chemicals by using LDH-supported nanoclusters as catalysts, which provides a new platform for the exploration of biotransformation catalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



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NiCo水滑石阵列负载的Ag团簇用于高效电催化氧化 5-羟甲基糠醛

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摘要 将生物质转化为燃料和高附加值化学品具有重要意义. 电催化 氧化5-羟甲基糠醛是将生物质转化为燃料和高附加值化学品的一条重 要途径. 本文通过简便的电沉积方法制备了一种NiCo水滑石纳米阵列 负载的Ag纳米团簇(Ag,@NiCo-LDH)自支撑电极材料. 在碱性介质中, 所制备的Ag,@NiCo-LDH自支撑电极表现出了优异的电催化氧化5-羟 甲基糠醛的活性和循环稳定性. 在电压为1.29 V条件下,电流密度可达 10 mA cm⁻², 2,5-呋喃二甲酸(FDCA)产率高达97.5%, 法拉第效率为 98.8%. 本工作为高效能源转化催化剂的设计提供了新思路。