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Graphical Abstract

Free-standing Ni-Co alloy nanowire arrays are synthesized via a modified template-assisted electrodeposition method. The sample shows excellent electrochemical properties in terms of activity and stability for urea oxidation.

Free-standing Ni-Co Alloy Nanowire Arrays: Efficient and Robust Catalysts toward Urea Electro-Oxidation

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ABSTRACT

Free-standing Ni-Co alloy nanowire arrays are synthesized via a modified template-assisted electrodeposition method. The structure and composition analysis have been performed by employing X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The highly ordered nanowire arrays show a strong adherence to an alloy transition layer. Herein, the alloy nanowire arrays show higher electrocatalytic activity in terms of lower onset potential and higher peak current density compared to the sample synthesized by conventional deposition route for urea electro-oxidation. Moreover, the electrocatalytic activity can be facilely optimized by selecting the length of nanowire arrays (or the deposition time). The best sample deposited with a time of 600 s possesses an onset oxidation potential of 0.372 V (vs. Hg/HgO) and a peak current density of 322.82 mA cm⁻² in 1 M KOH and 0.33 M urea solutions. The sample also shows good stability and activity even after sonication treatment. The excellent electrocatalytic properties of urea oxidation are considered due to the one-dimensional free-standing nanoscale alloy structure, which can largely boost the active sites, facilitate charge transfer, and improve the duration of urea electro-oxidation.

Keywords: Ni-Co alloy; Nanowire arrays; Electrodeposition; Electro-oxidation; Urea.

1. Introduction

Electrochemical oxidation of small or organic molecules, such as hydrogen, alcohols, acids, and glucose, provides an alternative approach to generate green energy from a sustainable resource. This oxidation process serves as a principle for anode reactions in different fuel cells to convert energy stored in chemical bonds into electrical power. Urea is an important organic molecule with wide availability since it is mainly produced from agricultural and industrial procedures and even our daily life. Under natural conditions, urea decomposes into toxic ammonia, resulting in a serious environmental problem [1, 2]. Oxidation of urea via electrochemical route can effectively decompose urea into harmless nitrogen, carbon dioxide, and valuable hydrogen [3], and simultaneously electricity energy can be generated in a more efficient way [4, 5]. However, a suitable catalyst is indispensable to increase the efficiency and rate of the electro-oxidation reaction. Noble metals nanostructures show excellent properties for the oxidation of small biomolecules, but they exhibit poor electrochemical activity to oxidize urea [6]. It would be meaningful to develop highly efficient and durable electrocatalysts toward urea oxidation based on earth-abundant elements. Recent works show that nickel is a promising electrocatalyst for the electro-oxidation of urea under alkaline conditions due to the high activity with low cost [7]. Usually, the onset potential at which the urea electro-oxidation starts is considered as an important factor to evaluate the catalyst performance. The observed onset potential of pure nickel catalysts for urea oxidation is ~0.50 V vs. standard hydrogen electrode (SHE), which is higher than that of the theoretical value of ~-0.46 V vs. SHE [8]. The large overpotential will decrease the efficiency of urea oxidation and cause other side reactions such as oxygen evolution. Further studies demonstrate that nanoscale nickel-based compounds (such as NiO [9, 10], nickel phosphates [11],

and Se-Ni(OH)₂@NiSe NWs/Ni foam [12], Ni-M (M = Pt [13], Mn [14], Co [8]), etc) alloys can reduce the potential of urea electro-oxidation and enhance the current density due to the synergistic effect. Those novel catalysts show better properties compared to the pure nickel catalysts.

It should be pointed that most of the synthesized nickel-based electrocatalysts for urea oxidation are nanoparticles, which suffer several drawbacks for the practical applications. Firstly, the nanoscale particles are prone to agglomerate with each other to reduce the overall surface energy. Although dispersing the nanoparticles with different supporting materials (e.g. graphite, CNTs, graphene, etc) is used to prevent the catalysts aggregation [15-18], the stability of the substrates in the electrolyte and the catalyst-substrate interactions must be carefully considered. Moreover, the substrate addition unavoidably decreases the effective utilization of catalytic material. Secondly, binding agents are used for preparing electrodes with the particle-like catalysts. The addition of binder will decrease the electronic conductivity of the electrode materials, and impede the contact of catalysts with the electrolyte or current collector, thus deteriorating the electrocatalytic properties. Recent works show that constructing self-standing alloy membrane [19] or three-dimensional alloy electrodes on current collectors can overcome the above-mentioned shortcomings [4, 20, 21]. Another promising way is the design of one-dimensional alloy catalysts, which grow from the current collector directly. Specifically, alloy catalysts with one-dimensional morphology such as nanowires have a large aspect ratio and are not easy to agglomerate. Without the addition of any binder, the nanowires together with current collector can be directly used as an electrode for catalyzing. Such configuration makes it possible to use all nanowires with high efficiency since electrons will transfer from the current collector through each individual nanowire

to the reaction sites.

Synthesis of nanowires on conductive substrate can be achieved by a wide range of methods, such as hydrothermal/solvothermal and vapor deposition [22-25]. However, it is still a challenge to form highly order nanowire arrays with a strong adherence to the current collector. Ordered porous template-assisted electrochemical deposition is a facile route to prepare nanowire arrays with well-controlled geometry, dimension, composition, and microstructure. In a conventional growth process, one side of the template must be treated with a conductive layer, which could be metallic film, silver or carbon glue, to facilitate the subsequent electrodeposition in the channels. Those treatments are either complex with high cost (metallic film) or not favorable for the electron transportation (glue).

In this work, we developed a modified template-assisted electrodeposition route to prepare highly ordered Ni-Co alloy nanowire arrays on a current collector with a strong adherence. As shown in Scheme 1, through-hole anodic aluminum oxide (AAO) template without any pretreatment was immobilized between Ti substrate and nickel foam. This sandwich-like structure was used as working electrode to prepare Ni-Co alloy nanowire arrays. After deposition and removing AAO template, the nanowire arrays attached to the substrate were directly used as an electrode to study the catalytic properties of urea electro-oxidation. Electrochemical test results show that the optimized sample possesses an onset oxidation potential of 0.372 V (vs. Hg/HgO) and a peak current density of 322.82 mA cm⁻² in 1 M KOH and 0.33 M urea solutions. Moreover, the sample shows good stability and activity even after sonication treatment. It is concluded that the enhanced electrocatalytic properties of urea oxidation making the adhered Ni-Co alloy nanowire arrays promising for environmental remediation and energy conversion application.

2. Experimental

2.1 Materials Synthesis

Preparation of AAO templates. The AAO templates were prepared using a two-step anodic oxidation method as reported earlier [26, 27]. In a typical process, high purity (99.99%) aluminum sheet with a thickness of ~0.5 mm and metal lead plate (5 cm × 5 cm × 0.3 cm) was used as anode and cathode, respectively. The electrolyte used was an aqueous solution containing 0.3 M oxalic acid. The anodic oxidation reaction was carried out with continuous magnetic stirring at 15 °C. For the first oxidation, the voltage increased from the initial value of 50 V to 100 V with a step of $1/3 \text{ Vs}^{-1}$, and the oxidation voltage was maintained at 100 V for 10 min. The obtained oxidation layer was removed by using an aqueous mixture of H_3PO_4 (6 wt%) and chromic acid (1.8 wt%) at 60 °C for 2 h. The second oxidation was performed in the same electrolyte but with pulse anodization condition [28] ($V = 100 \text{ V}$, $t_{\text{on}} = 3 \text{ s}$, $t_{\text{off}} = 3 \text{ s}$) and the total anodizing time was 15 min. After anodization, Al substrate and barrier layer at the bottom side was removed by chemical etching, resulting in the formation of through-hole AAO templates.

Synthesis of Ni-Co alloy nanowire arrays. The synthesis of alloy nanowire arrays were performed at room temperature by employing electrodeposition method in a three-electrode system. The working electrode was constructed by sequentially assembling a titanium sheet (~150 μm thickness), the through-hole AAO template, and a nickel foam. Platinum foil (2 cm × 2 cm × 0.01 cm) and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The electrolyte was made by dissolving $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (40 g), $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (10 g), NaCl (2 g), and H_3BO_3 (6 g) in de-ionized water (200 mL). The deposition was controlled by a LK2005A electrochemical analyzer at a constant potential of -1.2 V vs. SCE for different

time ($t = 400$ s, 450 s, 500 s, 550 s, 600 s, 650 s, 700 s). After reaction, the nanowire arrays were released by dissolving the AAO template in NaOH solution (5 wt%) for 2 h, followed by rinsing several times with ethanol and deionized water. The final nanowire arrays that attached to the Ti substrate were dried for further characterizations.

2.2 Materials Characterization

Phase structure of the samples was analyzed by using powder X-ray diffractometer (XRD, RigakuD/MAX 2500/PC) with Cu K α radiation ($\lambda = 1.5418$ Å). The morphology and chemical composition were obtained by scanning electron microscopy (SEM, Zeiss Supra 55, 15 keV) and transmission electron microscopy (TEM, FEI Tecnai T20 G², 200 keV) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford equipment).

2.3 Electrochemical Measurements

The electrochemical oxidation of urea was performed at room temperature in a standard three-electrode glass cell on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai). The nanowire arrays attached to the Ti substrate were directly used as catalyst (working electrode) without any further treatment. Platinum foil (1 cm $\times$ 1 cm $\times$ 0.01 cm) and mercury/mercury oxide (Hg/HgO) were used as counter and reference electrodes, respectively. KOH solution (1 M) with or without urea solution (0.33 M) was used as electrolyte. Cyclic voltammetry (CV) was recorded between 0 and 0.65 V vs. Hg/HgO at a scan rate of 10 mVs⁻¹. The chronoamperometry tests were performed at a constant potential of oxidation peak potential vs. Hg/HgO for 2000 s. Electrochemical impedance spectroscopy (EIS) was carried out at the oxidation peak potential over a frequency range of 100 kHz to 1 Hz. All the current densities were normalized using the geometrical area of the working electrodes.

3. Results and Discussion

The AAO templates used in this work were prepared by a modified two-step anodic oxidation method. Fig. S1 shows the morphology of a typical porous AAO template. The pores are circular and ordered with an average diameter of ~180 nm. All the channels are perpendicular to the surface, and the thickness of the template is ~35 μm , which ensure the deposited nanowires are also straight. It should be noted that the deposition time for the following nanowires growth is controlled to keep the nanowires are inside the channels (i.e. length < 35 μm).

The Ni-Co alloy nanowire arrays were then synthesized by template-assisted electrodeposition method, in which the AAO template was directly attached to Ti substrate. The sample deposited with a time of 600 s (NC600/Ti, hereafter the samples are named as NC*t*/Ti, where *t* is the deposition time) was analyzed by XRD to study the phase structure (Fig. 1). Besides the peaks from Ti substrate, the other three characteristic diffraction peaks located at 2θ values of 44.50° , 51.84° and 76.37° corresponded to the (1 1 1), (2 0 0) and (2 2 0) lattice planes of face-centered cubic phase, and the peaks are located between the standard diffraction peaks of bulk Co (JCPDS No. 150806) and Ni (JCPDS No. 04-0805). There is no conclusive evidence for the existence of impurities on the obtained samples. The results indicate the deposited sample is high phase purity with a Ni-Co alloy structure. The relatively high peak intensities also imply that the alloy nanowires are highly crystalline. Based on the positions of the experimental and standard peaks and Vegard's law [29], $a_{\text{Ni}_x\text{Co}_{1-x}} = xa_{\text{Ni}} + (1-x)a_{\text{Co}}$, where $a_{\text{Ni}_x\text{Co}_{1-x}}$ is the lattice parameter of Ni-Co alloy, a_{Ni} and a_{Co} are the lattice parameters of the pure Ni and Co, and x is the molar fraction of Ni in the alloy, the atomic ratio of Ni to Co elements can be roughly estimated as 77.3 : 22.7.

The morphology and chemical composition of NC600/Ti sample were characterized by employing SEM as shown in Fig. 2. The top view and side view SEM images (Fig. 2a and 2b) show that large-scale ordered nanowire arrays are successfully obtained, and the nanowires grow perpendicular to the substrate. The length of nanowires is $\sim 10\ \mu\text{m}$, and diameter is $\sim 180\ \text{nm}$, which is equal to the size of AAO template. The elements in the sample were validated by EDS as shown in the inset of Fig. 2b. Except for titanium and carbon elements from the substrate and carbon paste for SEM sample preparation, only nickel and cobalt elements can be detected. Quantitative EDS calculation indicates the atomic ratio of Ni to Co is $73.5 \pm 3.6 : 26.5 \pm 3.6$, which is very close to the estimation based on XRD analysis. Both values are lower than that in the precursor feed solution (80 : 20), which may induce by the abnormal co-deposition in cobalt containing electrolyte [30, 31]. In the meantime, EDS elemental mapping results reveal the uniform distribution of Ni and Co along the nanowire arrays (Fig. S2). Further observing the morphology (Fig. 2c) and elemental distribution show that an alloy transition layer with a thickness of $\sim 1.5\ \mu\text{m}$ exists between the nanowire arrays and Ti substrate (see the white arrow in Fig. 2c). During the preparing of working electrode for nanowire deposition, the AAO template was directly placed on the top of Ti substrate, inevitably yielding a gap between the template and substrate. Therefore, the alloy layer was initially deposited in the gap area followed by the continuous growth of nanowires in the template channels. This layer plays an important role in firmly contacting the nanowires to avoid the peeling off during repeated using. It is confirmed by intensely sonicating the sample in a water bath for 10 s and after being analysis by SEM (Fig. 2d). Although the nanowires become slightly disordered after the treatment, most of them are still in close contact with the deposited layer without detachment, which is anticipated to show good

electrocatalytic properties in terms of activity and durability. The morphology and composition information of the nanowires were further studied by TEM observations (Fig. 3). Typical TEM images of large-scale nanowires (Fig. 3a) and an individual nanowire (Fig. 3c) show that the sample possesses uniform morphology with a diameter of ~ 180 nm, which is in agreement with the SEM results. The composition and elemental distribution were mapped by displaying the integrated intensity of Ni and Co signals as a function of the beam position that operated in scanning TEM (STEM) mode. Fig. 3b and Fig. 3d show typical high-angle annular dark-field STEM (HAADF-STEM) images of the nanowires. The corresponding elemental mapping results reveal that Ni and Co are distributed homogeneously along each nanowire and no obvious element separation or aggregation is observed, indicating the formation of Ni-Co alloy. In addition, the atomic ratio of Ni to Co show an average ratio of 75.8 : 24.2, which is similar to the EDS analysis from SEM.

It is important to remark that one advantage of template-assisted electrodeposition is the facile control of the dimensions of nanowire arrays, i.e., the diameter and length of nanowires can be determined by the pore size of template [32] and the deposition time. Therefore, the effect of deposition time on the growth of alloy nanowires was studied. Front view (Fig. S3) and side view (Fig. 4a-g) SEM images show that all the nanowire arrays are highly ordered with a uniform diameter (~ 180 nm). As expected, the nanowires become longer by extending the deposition time. Fig. 4h plots the relationship between the average length of nanowires and growth time (t). It can be seen that the deposition of nanowires takes a two-stage ($t < 550$ s and $t > 550$ s) growth mode. The growth rates are calculated to be ~ 18.6 and 91.4 nm s^{-1} , respectively. The faster growth in the second stage may relate to the shorter transportation distance for metal ions (Ni^{2+} and Co^{2+}) in the

electrocrystallization process. For these nanowires deposited with a different time, both Ni and Co also show uniform distribution (Fig. S4). The Ni/Co ratio show a value range of (73.3 - 75.2) : (24.8 - 26.7) (Fig. S4, Fig. 4h). This result indicates that the chemical composition of nanowires keeps unchanged by prolonging the deposition time.

For the evaluation of electrocatalytic oxidation of urea, the as-prepared samples were directly used as electrodes without any further modification, such as catalyst ink preparation and subsequent drop casting on a working electrode, e.g. glassy carbon. Fig. 5a shows the CV curves of NC600/Ti and pure Ti sheet electrodes in the absence and presence of 0.33 M urea in 1 M KOH solution at a scan rate of 10 mV s⁻¹. For the Ti sheet electrode, the scanning (curve #3) is straight with no obvious redox peaks, suggesting the Ti substrate is electrochemically inert on the reaction with urea or KOH. Therefore, the electrocatalytic performance of the Ti substrate can be neglected in the presence of urea. In the absence of urea solution (curve #2), there is a pair of oxidation peak (~0.5 V) and reduction peak (~0.37 V), which are due to the transition from Ni(OH)₂ to NiOOH, and the reduction of NiOOH, respectively. The results are in good agreement with previous studies [33-36]. The process can be described by the following equations:

With the addition of urea into the electrolyte, the CV curve #1 starts to oxidize after the onset potential of ~0.372 V and the curve slope increases significantly after ~0.5 V with a correspondingly higher current density, indicating the Ni-Co alloy nanowire arrays are active for the electro-oxidation of urea.

To optimize the catalytic performance, the electrochemical measurements on the alloy nanowire arrays with different length were performed. The CV curves are displayed in Fig. S5 and the main results are illustrated in Fig. 5b. It is clearly seen that the current densities corresponding to the oxidation peak increase and the onset potentials decrease with increasing the nanowire arrays deposition time (or nanowire length) until it reaches 600 s. It means that the NC600/Ti sample possesses the optimum electrocatalytic performance in terms of the highest oxidation peak current density and the lowest onset potential. For example, the peak current density of NC600/Ti is 322.8 mA cm^{-2} , which is 4.1, 2.0, and 1.4 times higher than that of NC450/Ti, NC550/Ti, and NC650/Ti, while the onset potential of NC600/Ti (0.372 V) is lower than that of NC450/Ti (0.432 V), NC550/Ti (0.412 V), and NC650/Ti (0.433 V). The oxidation peak current density is related to the active contact of nanowire arrays to the electrolyte. With the prolonging deposition time (or the length of nanowire arrays), the exposed area of the nanowires is increased, which facilitates the entry of the electrocatalytic reactants and the emission of the gaseous products [37-41]. However, with a further extension of the deposition time (over 600 s in this work), the nanowire tips tend to agglomerate together during the capillary force-induced closure process [42], which blocks the entry of reactants and the exhaust of the products, and reduces the active reaction area. The onset potential of the alloy nanowire arrays is dependent on the structural defects and oxidation state of Ni-induced by Co addition [8, 43-45]. Since all samples were deposited by using the same electrolyte, the chemical composition of the nanowire arrays is supposed to be the same (see Fig. S4). In this way, the active catalytic sites for urea oxidation, which correlate with the exposed surface area of the nanowires, determine the onset potential. Considering the above aspects, we can understand the NC600/Ti sample possesses optimized electrochemical properties

for oxidation of urea. It should be noted here that the composition of Ni-Co nanowire arrays, which can be determined by the electrolyte and deposition conditions, is also an important parameter that may affect the electro-oxidation properties. Further studies of this composition effect are still on-going in order to get a better understanding. The effect of scan rate on the electrocatalytic oxidation of urea on NCt/Ti electrodes was studied as shown in Fig. S6 (a1-g1). It can be seen that the current density increases rapidly with increasing the scan rate. At lower scan rates from 10 to 100 mVs^{-1} , the change of oxidation peak current density (I_{pa}) shows a liner relationship with scan rate (the insets of Fig. S6 (a2-g2)). While the I_{pa} is linearly scaled with the square root of scan rates at higher values (200 - 1000 mVs^{-1} , Fig. S6 (a2-g2)). The studies indicate the prevalence of diffusion-controlled process during the oxidation of urea at the electrode surfaces [7, 19]. Similar results were also reported by Abdel Hameed *et al* [9].

To further exploration of the free-standing Ni-Co alloy nanowire arrays deposited by the modified electrode configuration, we measured electrochemical properties of two control samples for better comparison. First, the NC600/Ti sample that sonicated in a water bath for 10 s shows a peak current density and onset potential of 228.0 mA cm^{-2} and 0.380 V (Fig. S7a, the triangles in Fig. 5b), which are 29.2% decrease and 2.7% increase compared to the pristine NC600/Ti sample. The performance results also confirm the strong adherence of nanowires and deposition layer, which is consistent with the morphology observations (Fig. 2d). Second, NC600 nanowire arrays were deposited by a conventional method, where the growth electrode was prepared by stabilizing AAO template on Ti substrate with carbon conductive glue. The obtained sample was respectively denoted as NC600/Ti-C. Fig. S8 shows the CV curves of NC600/Ti-C and Ti-C electrodes in the absence and presence of 0.33 M urea in 1 M KOH solution at a scan rate of 10 mV s^{-1} . Since the

Ti-C electrode has no electrocatalytic activity for urea oxidation (curve #3), the electrochemical response mainly comes from the Ni-Co alloy nanowire arrays (curves #1, #2). The peak current density and onset potential of NC600/Ti-C sample are 64.3 mA cm^{-2} and 0.440 V (see the circles in Fig. 5b), respectively. Obviously, the performance of NC600/Ti-C is much inferior to the nanowire arrays synthesized by the modified deposition method and even the sample after sonication treatment. EIS technique was employed to reveal the origin of different electrochemical properties in NC600/Ti and NC600/Ti-C samples. Fig. S9 shows typical Nyquist plots of the two samples, which were operated at the oxidation peak potentials (0.61 V for NC600/Ti and 0.63 V for NC600/Ti-C) in 1 M KOH and 0.33 M urea . The detailed kinetic parameters can be obtained by fitting the plots with equivalent circuit (inset of Fig. S9) [46,47]. Here the values of charge transfer resistance (R_{ct}) can be determined to be $4.07 \text{ } \Omega$ and $18.81 \text{ } \Omega$ for NC600/Ti and NC600/Ti-C, respectively. The higher R_{ct} in NC600/Ti-C sample may induce by the non-conductive components such as epoxy resin in the carbon conductive paste, which increases the charge transfer resistance. While in NC600/Ti sample, each nanowire is firmly attached to the substrate. Therefore, efficient electron transfers and better catalytic activity and durability toward urea oxidation are achieved.

The present freestanding Ni-Co alloy nanowire arrays show excellent electrocatalytic activities toward urea oxidation in terms of low onset potential and high peak current density, which is superior to other nickel-based nanocatalysts (Fig. S10 and Table S1), such as electrodeposited Ni film and nanowire arrays, Ni or NiO nanoparticles decorated carbon nanostructures, and Ni-M ($M = \text{Pt, Mn, Co, etc}$) alloys. The activity of NC600/Ti sample is also comparable with that of Ni/MWCNTs and $\text{Se-Ni(OH)}_2\text{@NiSe NWs/Ni foam}$ despite complex

processes (thermal decomposition of metal-organic compounds at high temperature or multi-step preparation) are involved in the materials synthesis. The activities of the freestanding Ni-Co alloy nanowire arrays were also evaluated by considering the nanowire surface area (specific activity). As shown in Fig. S11, the NC600/Ti sample shows the highest intrinsic activity (1.55 mA cm^{-2}) compared to the other samples.

Besides activity, stability is another important factor for catalysts applications. We investigated the current density-time response of NC600/Ti by chronoamperometric measurements, which were performed at a potential of 0.61 V vs. Hg/HgO electrode (Fig. 6a). Without the addition of urea (curve #2), the current measured is negligible. While in the electrolyte containing urea and KOH (curve #1), the electrode delivers a current density of 204.3 mA cm^{-2} . The current density then shows slight decrease, which may be induced by the continuous consumption of urea near the electrode surface and surface coverage by reaction intermediates or gaseous products. After 2000 seconds operation, the electrode maintains a current density of 93.5 mA cm^{-2} , which is 45.8% retention of the initial value. The morphology the NC600/Ti sample after the duration test (2000 s) was also characterized by SEM observations (Fig. 6b). The nanowire arrays are still freestanding and no obvious change can be found, demonstrating the good morphology stability during operation. Even after sonication treatment, the NC600/Ti sample also shows good stability during the 2000 s' period (Fig. S7b). The current density decreases from the initial value of 198.9 mA cm^{-2} to 81.5 mA cm^{-2} with a retention of 40.9%. To further study the chemical composition and structural stability, XRD patterns of NC600/Ti sample before and after urea electro-oxidation test were compared as illustrated in Fig. S12. After the duration operation, no significant diffraction peaks from impurities are detected, and the peak position related to Ni-Co is almost

unchanged. Consequently, the good stability of NC600/Ti sample as a catalyst for urea electro-oxidation is demonstrated.

4. Conclusions

In conclusion, highly ordered Ni-Co alloy nanowire arrays were successfully synthesized by a modified AAO template-assisted electrodeposition method. Compared to the conventional sample, the obtained free-standing nanowire arrays show a strong adherence to an alloy transition layer, which is favorable for boosting the active sites, decreasing the charge transfer resistance, and improving the duration for urea electro-oxidation. The optimized sample (NC600/Ti) shows an onset oxidation potential of 0.372 V (vs. Hg/HgO) and a peak current density of 322.82 mA cm⁻² in 1M KOH and 0.33 M urea solutions with considerable stability, which this result is comparable with previously reported electrocatalysts results. The excellent electrocatalytic properties combined with the low-cost elements endows the free-standing Ni-Co alloy nanowire arrays with high potential in energy conversion fields. As there is enormous interest in electrocatalysis, the current modified template-assisted electrodeposition strategy can be applied to synthesize other nanowire arrays with unique designed composition for diverse applications.

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Figure Captions

Scheme 1. Schematic illustration of the modified AAO template-assisted electrodeposition of free-standing Ni-Co alloy nanowire arrays.

Fig. 1. XRD pattern of NC600/Ti sample. The pattern of Ti substrate and the standard diffraction of metals Co and Ni are also shown for comparison. The inset indicates the enlarged (111) peak.

Fig. 2. Morphology and chemical composition of NC600/Ti sample (a) top-view, (b) side-view SEM images, the inset in (b) is the EDS spectrum and quantitative element analysis result, (c) SEM image of the contact area between nanowire arrays and substrate, and (d) SEM image of the nanowire arrays after intense ultra-sonication treatment for 10 s.

Fig. 3. (a, c) TEM and (b, d) HAADF-STEM images of large-scale nanowires and an individual nanowire. Panels labeled as Ni and Co are intensity maps for the respective characteristic X-rays, which show uniform distributions of the elements and demonstrate the formation of Ni-Co alloy.

Fig. 4. Side view SEM images of Ni-Co alloy nanowire arrays synthesized at different deposition time. (a) 400 s, (b) 450 s, (c) 500 s, (d) 550 s, (e) 600 s, (f) 650 s, (g) 700 s, and (h) deposition time-dependent average length of Ni-Co alloy nanowire arrays.

Fig. 5. (a) CV curves of the NC600/Ti electrode in the presence (curve #1) and absence (curve #2) of 0.33 M urea in 1 M KOH solution at a scan rate of 10 mV s^{-1} . The scanning for the bare Ti sheet in the electrolyte containing 0.33 M urea and 1 M KOH solution is displayed for comparison (curve #3), and (b) The plot of oxidation peak current density (left axis) and onset oxidation potential (right axis) vs. deposition time (square, length of nanowire arrays).

The results for the electrodes of NC600/Ti-C (triangle) and NC600/Ti after 10 s sonication treatments (circle) are also shown.

Fig. 6. (a) Chronoamperometric curves of NC600/Ti electrode for urea electro-oxidation at the potential of 0.61 V vs. Hg/HgO in the presence (curve #1) and absence (curve #2) of 0.33 M urea in 1 M KOH solution, and (b) SEM image of NC600/Ti electrode after the chronoamperometric test.

Highlights

- Free-standing Ni-Co alloy nanowire arrays are synthesized.
- The sample shows good activity and stability for urea electro-oxidation.
- The good properties are due to the unique free-standing alloy structure.