**NiCo₂O₄ nanosheets grown on current collectors as binder-free
electrodes for hydrogen production via urea electrolysis**

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Abstract

As a novel solid hydrogen carrier, urea ($\text{CO}(\text{NH}_2)_2$) has shown great promise in hydrogen production, hydrogen storage and transportation. Mesoporous NiCo_2O_4 nanosheets were synthesized on current collectors and evaluated as binder free electrodes for hydrogen production via urea electrolysis. The as-grown NiCo_2O_4 nanosheet electrodes with $0.6 \text{ mg}\cdot\text{cm}^{-2}$ catalyst loading exhibit ca. 80 mV decreasing in the onset potential of urea oxidation in alkaline solution comparing to those of bulk nickel hydroxide modified electrodes. The NiCo_2O_4 nanosheet electrodes also improved the urea oxidation current density by at least 28 times at a constant potential of 0.50 V vs. Hg/HgO compared to that of bulk $\text{Ni}(\text{OH})_2$ electrodes. The enhanced electrocatalytic performances of the binder free NiCo_2O_4 nanosheet electrodes may bring new opportunities for the scale-up of the urea electrolysis technology, which will benefit energy and environmental issues, such as urea-rich wastewater treatment, hydrogen production, and fuel cells.

Keywords: Hydrogen production, urea electrolysis, NiCo_2O_4 nanosheet, wastewater treatment, binder free electrodes

1. Introduction

To alleviate the requirement of non-renewable fossil fuels and satisfy the increasing global energy demands, it is important to seek and develop sustainable and environmentally friendly energy sources. Urea ($\text{CO}(\text{NH}_2)_2$) has been demonstrated as a novel solid hydrogen carrier for long-term sustainable energy supply due to its intrinsic properties, such as non-toxicity, non-flammability, easy storage, and convenient transportation, as well as being a widely available commodity.[1-5] In addition, the utilization of urea from waste, such as urea-rich wastewater produced from industrial synthesis of urea, human/animal urine, etc., will benefit the environment while providing energy savings and recovery from waste.[6-10] Compared to traditional electro-oxidation of urea using noble metal catalysts, urea electrolysis with an inexpensive bulk nickel catalyst showed great promise in directly converting urea into a valuable energy product (H_2) and a non-toxic product (N_2) (reaction 1~3).[1, 11]

The incorporation of cobalt into the nickel catalysts has been demonstrated to decrease the overpotential of urea oxidation and improve the reaction rate considerably.[12-15] In addition, nanostructured nickel catalysts enhanced the electrocatalytic oxidation of urea due to their large surface areas and controlled low

dimensional structures.[16-18] However, the electrode preparation of nickel powder based catalysts requires the introduction of polymer binders, which unavoidably decrease the conductivity of catalysts and weaken their electrocatalytic performance for urea electrolysis. Therefore, it is important to develop nanostructured nickel-cobalt based catalysts and eliminate the dependence on polymer binders during the electrode preparation for urea electrolysis.

Nickel cobaltite (NiCo_2O_4) is a promising electrode material for supercapacitors, batteries, and electrocatalysis due to its low cost, good redox behavior, high conductivity, abundant resources, and environmental benignity.[19-26] Nanostructured NiCo_2O_4 on conductive substrates has exhibited improved specific capacitance and cycling performance.[20, 27] Therefore, it is interesting to extend the applications of nanostructured NiCo_2O_4 to urea electrolysis for hydrogen production. Within this context, this work focuses on directly synthesizing mesoporous NiCo_2O_4 nanosheets on current collectors (stainless steel gauzes) as binder free electrodes for urea electrolysis, with the intention of enhancing the oxidation current density and reducing the oxidation potential of urea electrolysis.

2. Materials and methods

2.1 Chemicals and materials

Nickel (II) nitrate hexahydrate (99%) and ethanol (HPLC grade) were purchased from Acros Organics. Hexamethylenetetramine (HMT) (99+%) and polytetrafluoroethylene (PTFE) (60 wt.%) were obtained from Sigma-Aldrich. Cobalt (II) nitrate hexahydrate (ACS, 98.0-102.0%), nickel (II) hydroxide powder (Ni 61%),

and stainless steel gauze (325 mesh woven from 0.036mm diameter wire, LOT #: Q29A042) were purchased from Alfa Aesar. Potassium hydroxide (85.0+%), urea (99.7%), acetone (99+%), and hydrochloric acid (37.4%) were obtained from Fisher Scientific.

2.2 Synthesis of NiCo_2O_4 nanosheets on stainless steel gauze

NiCo_2O_4 nanosheets were synthesized through a hydrothermal method and subsequent annealing treatment. In a typical experiment, 0.5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a solution containing 40 ml of dionized water and 20 ml of ethanol. 3 mmol of HMT was then added into the solution. After dissolving HMT, the mixture was transferred to a Teflon-lined autoclave. Stainless steel gauzes (1 cm x 3 cm) were first cleaned by sonication (Zenith Ultrasonicator at 40 kHz) in acetone, 3M HCl, and dionized water for 10 min each, and then immersed in the solution in the Teflon-lined autoclave. The autoclave was then sealed and heated at 120 °C for 18 hours (Isotemp muffle furnace, Fisher scientific), followed by cooling down to room temperature. The gauzes with reaction products were collected, rinsed with dionized water, dried at 70° C overnight (Isotemp muffle furnace, Fisher scientific), and then annealed at 350 °C (EQ-OTF-1200X split tube furnace, MTI corporation) in air for 2 hours to obtain the NiCo_2O_4 nanosheets. The loading of the NiCo_2O_4 nanosheets on stainless steel gauze was $0.6 \text{ mg} \cdot \text{cm}^{-2}$, carefully weighted after the annealing step of the synthesis.

2.3 Characterization

The morphology of the NiCo_2O_4 nanosheets was characterized by a

transmission electron microscopy (TEM) using a JEM 2100 F (JEOL) and a scanning electron microscopy (SEM) using a JEOL-JSM-639OLV. The crystal structure of the products was analyzed by a Rigaku Ultima IV X-ray Diffractometer with monochromatic Cu K α radiation ($\lambda=0.15405$ nm) at a scanning rate of 1° min^{-1} . The NiCo₂O₄ sample was carefully scratched from the gauze using a blade and mixed well with a mortar and pestle. The scratched NiCo₂O₄ powder was then added in the sample holder for XRD measurements. As for the TEM sample preparation, the NiCo₂O₄ powder was first dispersed in ethanol solution by 10 minutes of sonication. Then the NiCo₂O₄ dispersion was dropped on TEM grid and dried in air for TEM measurements. The stainless steel gauzes before and after NiCo₂O₄ growth were directly mounted on the sample holder through carbon conductive tape for SEM measurements. The surface area, nitrogen adsorption-desorption isotherms, and the pore size of the NiCo₂O₄ nanosheets were measured using a TriStar II 3020 surface area analyzer (Micromeritics). The NiCo₂O₄ nanosheets were degasified overnight at 80° C using nitrogen gas (99.999% purity, Praxair) prior to the measurements.

2.4 Electrochemical measurements

All of the cyclic voltammograms and chronoamperograms were carried out in 5 M KOH solution in the absence and presence of 0.33M urea using a Solartron 1470E potentiostat. NiCo₂O₄ nanosheets on stainless steel gauzes were directly used as working electrodes for all the electrochemical measurements. A Hg/HgO electrode and a platinum foil (5 cm x 5 cm, 99.99% purity, ESPI metals) were chosen as the reference and counter electrodes, respectively. The cyclic voltammograms (CVs) were

obtained between 0 V to 0.7 V vs. Hg/HgO at a scan rate of 10 mVs⁻¹. All the voltammograms reported are the sustained periodic state achieved after 20 sweeps. The chronoamperograms were carried out a constant potential of 0.50 V vs. Hg/HgO.

In order to have the same loading (0.6 mg·cm⁻²) with NiCo₂O₄ nanosheet electrodes, the Ni(OH)₂ electrodes were prepared as follows: the bulk nickel hydroxide powder was first mixed with PTFE binder in a ratio of 75:25 by weight, and dispersed in isopropanol by sonication; the suspension was then immediately drop-dried onto the stainless steel gauzes at 60°C. The Ni(OH)₂ suspension was continually dropped onto the gauze until the loading of Ni(OH)₂ content reached 0.6 mg·cm⁻². The stainless steel gauzes with loaded sample were finally hand pressed and used as the working electrodes in the control experiments. All of the electrochemical test conditions of control experiments are the same as those of NiCo₂O₄ nanosheet electrodes.

2.5 Gas product analysis

A Hoffman electrolysis cell was used for collecting the gases generated at both the cathode and the anode electrodes. The electrolysis was performed in 5 M KOH in the presence of 0.33 M urea with NiCo₂O₄ nanosheet anode and Pt foil cathode at a constant voltage of 1.4 V for 24 hours. The composition of the gases evolved was analyzed using an Agilent Technologies customized 7890B Gas Chromatograph system equipped with a thermal conductivity detector, two Hayesep Q packed columns, and a molsieve 13X column. Helium was used as the carrier gas with a flow rate of 28mL·min⁻¹. The oven was held at 60°C for 11 minutes and increased to 200°C,

and then held for 5 minutes to finish the 20 minutes analysis time.

3. Results and discussion

3.1 Morphology and structure analyses of NiCo₂O₄ nanosheets

The low magnification TEM image (Figure 1 a) shows a continuous planar thin film over a large area on the TEM grid. The formation of the wrinkles is due to the back-folding or overlapping of the nanosheet during TEM sample preparation. The high magnification TEM image (Figure 1 b) further reveals the nanosheets consist of randomly arranged NiCo₂O₄ nanoparticles and mesopores are distributed over the whole nanosheets. The lattice fringes in the HRTEM image (Figure 1 c) correspond to (111), (311), (400), and (440) crystal planes, which confirmed the polycrystalline structure of the synthesized NiCo₂O₄. Figure 2 (a-b) shows the comparison of bare surface of stainless steel wire and the clusters of planar sheet-structure materials after NiCo₂O₄ growth on the gauze. The photograph (Figure 2 c) shows the whole surface of the gauze was covered by a dark material after the synthesis, indicating that the nanosheets grew on a large area.

The crystallographic structure of the synthesized products was identified by X-ray diffraction (XRD). The XRD patterns are shown in Figure 3 and Figure S1. All the diffraction peaks can be indexed to nickel cobaltite (NiCo₂O₄) and are consistent with the standard card JCPDS 01–073–1702 provided by the international center for diffraction data (ICDD). The nitrogen adsorption and desorption isotherms were measured to investigate the porosity of nickel cobaltite nanosheets. It can be seen from Figure 4 a, that the isotherms exhibit hysteresis loops at a relative pressure

above 0.4, suggesting the porous structure of the nickel cobaltite nanosheets.[21, 28] The pore size distribution was determined by the desorption isotherm through the Barret-Joyner-Halenda (BJH) method. As shown in Figure 4 b, the pore size distribution is centered at ~ 3.6 nm, which further confirmed the mesoporous nature of the NiCo₂O₄ nanosheets. The surface area of the nickel cobaltite nanosheets was determined by the Brunauer-Emmer-Teller (BET) method and the BET surface area was found to be $65.6 \pm 4.5 \text{ m}^2\text{g}^{-1}$. As a comparison, the BET surface area of the bulk nickel hydroxide powder was measured to be $5.1 \pm 0.7 \text{ m}^2\text{g}^{-1}$ under the same conditions.

3.2 Electrochemical analyses of binder free NiCo₂O₄ nanosheet electrode for urea electrolysis

To evaluate the electrochemical performance of the as-grown NiCo₂O₄ nanosheet electrodes for urea electrolysis, cyclic voltammograms (CVs) and chronoamperograms were performed with a standard three-electrode system in 5 M KOH solution in the absence and presence of 0.33 M Urea. A pair of redox peaks is shown in curve 1 in Figure 5 a, which is due to the reversible transformation between Ni(II) and Ni(III).[1, 11] When urea is present in the KOH solution, a strong oxidation starting at ca. 0.38 V is observed in curve 2 (Figure 5 a), suggesting that the urea electrooxidation is catalyzed by the NiCo₂O₄ nanosheets in alkaline media. As a comparison, bulk nickel hydroxide powder modified electrodes were tested under the same conditions. As shown in Figure 5 b, the Ni(OH)₂ electrodes can also catalyze the urea electrooxidation. However, the urea oxidation potential starts at ca. 0.46 V on the

anodic sweep of the CV, which is 80 mV higher than that of the NiCo_2O_4 nanosheets electrode. In the reverse cathodic sweep, the oxidation current of the $\text{Ni}(\text{OH})_2$ electrode crosses over the anodic sweep around 0.4 V to 0.6 V, which may be attributed to local convection induced by oxygen evolution reaction on $\text{Ni}(\text{OH})_2$ electrodes in alkaline solution.[29-31] Interestingly, the crossing loop does not occur in the cathodic sweep of NiCo_2O_4 nanosheets electrode. The same phenomenon was observed for urea electrooxidation on other cobalt-contained electrodes.[12, 14] This may be due to the cobalt-contained catalysts promoting urea electro-oxidation, reduce the interference of the oxygen evolution reaction,[12, 13, 32] and thus avoiding the local convection around the region of 0.4 V to 0.6 V.

Chronoamperometry experiments were carried out to further evaluate the electrocatalytic activity of the NiCo_2O_4 nanosheet electrodes for urea electrolysis. As shown in Figure 6 a, a stable and higher current density is produced when urea is present in the KOH solution, indicating that the NiCo_2O_4 nanosheets are stable and effective catalysts for urea electrolysis. Although the electrooxidation of urea also occurred on $\text{Ni}(\text{OH})_2$ electrodes (Figure 6 b), the as-grown NiCo_2O_4 nanosheet electrodes improved the urea oxidation current density for at least 28 times compared to that of the bulk $\text{Ni}(\text{OH})_2$ electrodes. Figure S2 further shows the NiCo_2O_4 nanosheets are stable and effective catalysts for at least 24 hours, although the oxidation current slightly decreases with time due to the consumption of urea from the electrolyte.

The enhanced electrocatalytic performance of NiCo_2O_4 nanosheet electrodes for urea electrolysis, such as higher current density and lower oxidation potential, may be due to the following reasons: first, the large surface area of the NiCo_2O_4 nanosheet provides more electroactive sites for the reaction to proceed. Second, the mesoporous

structure of the NiCo_2O_4 nanosheet facilitates the electrolyte transport.[20] Third, the cobalt content inhibits water electrolysis of the urea containing electrolyte, thereby promoting urea electrolysis.[12, 33, 34] Fourth, directly growing the NiCo_2O_4 nanosheet catalyst on current collector eliminates the need of isolating polymer binders for electrode preparation, and thus enhances urea electrolysis.

3.3 Gas product analyses

The gas chromatogram (Figure 7 a) shows hydrogen is the gas product of the cathodic compartment of the electrolysis cell, which agrees with the state reaction in Equation (2). The signals of nitrogen and oxygen (Ratio: 79: 21) in Figure 7 a are due to the air contamination during the sample injection, which was further examined by the gas chromatogram of He carrier gas only ($\text{N}_2:\text{O}_2 = 79:21$) (Figure 7 c). Nitrogen and oxygen (Ratio: 89: 11) (Figure 7 b) were detected at the anodic compartment. The obvious increase of nitrogen component in anodic compartment indicates nitrogen is the gas product of the anode, which confirms the state reaction in Equation (1). The generated carbon dioxide was dissolved in the alkaline electrolyte (5M KOH) as carbonate salt, and thus cannot be found in the gas chromatogram of the anode.

4. Conclusions

Mesoporous NiCo_2O_4 nanosheets were directly synthesized on current collectors through a simple hydrothermal method, and used as binder free electrodes for hydrogen production via urea electrolysis. SEM, TEM, XRD, nitrogen adsorption-desorption isotherms measurements, and electrochemical measurements

were used to characterize the synthesized NiCo_2O_4 nanosheet electrodes. The NiCo_2O_4 nanosheets catalyzed urea electrolysis and directly converted urea into hydrogen and nitrogen. Due to their intrinsic properties, such as large surface area, mesoporous structure, the incorporation of Co, and binder free, the as-grown NiCo_2O_4 nanosheet electrodes were found to promote urea electrolysis by increasing the current density and decreasing the onset potential of urea oxidation, and thus show promise in the applications of urea-rich wastewater treatment, hydrogen production, and fuel cells.

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Figure captions:

Figure 1. The low (a) and high (b) magnification TEM images of the NiCo_2O_4 nanosheets. The planar structure of the NiCo_2O_4 nanosheets and porous feature are confirmed. (c) HRTEM image of the NiCo_2O_4 nanosheets

Figure 2. The SEM images of the stainless steel gauzes before (a) and after (b) the NiCo_2O_4 nanosheets growth. The SEM images show the comparison of bare surface of stainless steel wire and the clusters of planar sheet-structure materials after NiCo_2O_4 growth on the gauze. (c) the photograph of stainless steel gauzes before (left) and after (right) NiCo_2O_4 nanosheets growth.

Figure 3. XRD pattern of synthesized NiCo_2O_4 nanosheets. All the diffraction peaks can be indexed to NiCo_2O_4 (JCPDS 01–073–1702).

Figure 4. (a) Nitrogen adsorption and desorption isotherms (b) pore size distribution of NiCo_2O_4 nanosheets. The pore size distribution is centered at ~ 3.6 nm, which further confirms the mesoporous nature of the NiCo_2O_4 nanosheets.

Figure 5. CVs of (a) as-grown NiCo_2O_4 nanosheets electrode (b) and bulk Ni(OH)_2 modified electrodes in 5 M KOH in the absence (curve 1) and presence (curve 2) of 0.33 M urea. Scan rate: 10 mVs^{-1} . The as-grown NiCo_2O_4 nanosheet electrodes exhibit ca. 80 mV decrease in the onset potential of urea oxidation in alkaline solution in comparison to those of bulk nickel hydroxide powder modified electrodes.

Figure 6. Chronoamperograms of (a) as-grown NiCo_2O_4 nanosheets electrode and (b) bulk $\text{Ni}(\text{OH})_2$ modified electrodes in 5 M KOH in the absence (curve 1) and presence (curve 2) of 0.33 M urea at a constant potential of 0.50 V vs. Hg/HgO. A continuous, stable, and higher current density is shown in the presence of urea, indicating the NiCo_2O_4 nanosheets are stable and active catalysts for urea electro-oxidation in alkaline media.

Figure 7. Gas chromatograms (GC) of the gas products of urea electrolysis in 5 M KOH in the presence of 0.33 M urea from (a) cathode, (b) anode, (c) gas chromatograms of He carrier gas only. Oxygen observed is due to air contamination during the injection of the gas, as demonstrated by the chromatogram in (c).

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Figure 1.

Figure 2.

Figure 3

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Figure 7