Research Article

Exploring the effect of Ni/Cr contents on the sheet-like NiCr-oxide-decorated CNT composites as highly active and stable catalysts for urea electrooxidation

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Abstract

The developing high-efficiency urea fuel cells have an irreplaceable role in solving the increasingly severe environmental crisis and energy shortages. The sluggish six-electron dynamic anodic oxidation reaction is the bottleneck of the rapid progress of urea fuel-cell technology. To tackle this challenge, we select the NiCr bimetallic system due to the unique synergic effect between the Ni and the Cr. Moreover, better conductivity is assured using carbon nanotubes (CNTs) as the support. Most importantly, we use a simple hydrothermal method in catalyst preparation for easy scale-up at a low cost. The results show that the hybrid catalysts of NiCrx-oxide-CNTs with different Ni/Cr ratios show much better catalytic performance in terms of active surface area and current density as compared to that of Ni-hydro-CNTs. The optimized NiCr2-oxide-CNTs catalyst exhibits not only the largest electrochemically active surface area (ESA, 50.7 m² g⁻¹) and the highest urea electrocatalytic current density (115.6 mA cm⁻²), but also outstanding long-term stability. The prominent performance of the NiCr2-oxide-CNTs catalyst is due to the combined effect of the improved charge transfer between Ni and Cr species, the large ESA, along with an elegant balance between the oxygen-defect sites and hydrophilicity. Moreover, we have proposed a synergistically enhanced urea catalytic mechanism.
Introduction

Growing energy demand and serious pollution issues have prompted the development of alternative environmentally friendly and sustainable energy sources [1], such as hydrogen fuel, which is an ideal replacement for conventional energy sources due to its high energy density and pollution-free products [2, 3]. Urea [CO(NH$_2$)$_2$] has proven to be an effective H$_2$ carrier and CO$_2$-storage medium for continuous energy supply due to its inherent characteristics, such as high energy density (16.9 MJ L$^{-1}$, 10.1 wt% of H$_2$), non-flammability, non-toxicity, ease of transportation and low storage cost [4, 5]. As an essential intermediate in nitrogen and carbon cycling in nature, urea is formed by combining NH$_3$ and CO$_2$; thereby, it can efficiently stabilize NH$_3$ and fix CO$_2$ while storing H$_2$ with high density. The stored energy in urea can be retrieved either by releasing H$_2$ thermally and catalytically or via a direct urea fuel cell (DUF). The DUF can also be used to oxidize urea-based organics from the wastewater stream to generate energy as well as pretreat the wastewater. Developing a high-performance anode catalyst is a crucial step towards achieving an efficient DUF system.

A series of studies have shown that noble metal catalysts such as Pt- and Pd-based composites as anode materials have the high catalytic activity of the urea-oxidation reaction (UOR) [6–8]. Nevertheless, its industrial application is limited by cost and scarcity. Therefore, continued efforts are being made to find affordable, earth-abundant and non-precious-metal catalysts for UOR.

In the past few decades, researchers have discovered that Ni-based transition metal catalysts have comparable catalytic performance and stability to these of noble-metal-based catalyst for UOR. However, most Ni-based catalysts are often limited by high UOR overpotentials [9]. Moreover, two types of UOR mechanisms were reported on Ni-based catalysts. The first one is a direct mechanism in which the intermediate nickel oxyhydroxide (NiOOH) initiates urea oxidation in a series of electrochemical steps [10]. The other, which is an indirect mechanism proposed through density functional theory (DFT), suggests that the indirect route of urea oxidation is that the urea reacts with NiOOH to form the final product in a chemical step [11]. To address the high UOR overpotential challenge, bimetallic catalysts composed of Ni and other transition metals have been developed such as NiCo$_2$O$_4$ nanowire array/Ni foam [12], NiMoO$_4$ nanosheets [13], NiMn/carbon nanofibres [14], Ni-Mo/graphene [15], Ni&Mn/carbon nanofibres [16], etc. The studies suggest that the bimetallic catalyst-based UOR follows both the direct- and the indirect-mechanism paths [17, 18].

Special attention needs to be paid to the NiCr bimetallic system in which Cr modifies the d-band electronic structure by weakening the Ni–O interaction, thereby improving the UOR rate [19]. Furthermore, Cr shows strong resistance towards the quaternary ammonium functional group-initiated reaction inhibition [20]. Moreover, NiCr bimetallic catalysts also show enhanced methanol oxidation and hydrogen evolution under alkaline medium [20, 21]. However, Cr-based materials have been rarely reported as catalysts for urea oxidation. A recent study revealed that 40% Cr of NiCr on carbon support exhibits a high current density of 2933 mA mg$^{-1}$Ni for urea oxidation at a potential of 0.55 V, which is 3.6-fold higher than that of Ni/C [22]. However, the interaction between Ni and Cr is still unclear and the poor catalytic stability needs to be further improved.

Herein, we take a simple hydrothermal approach to synthesize NiCr$_x$-oxide-carbon nanotubes (CNTs). The catalysts were characterized extensively using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman,
X-ray photoelectron spectroscopy (XPS) and electrochemical methods to achieve the best-performing catalyst in terms of electrocatalytic active surface area and electrocatalytic current density by varying the Ni/Cr ratio. The results demonstrate that NiCr₂-oxide-CNTs show superior performance that gives the highest electrochemically active surface area (ESA) (50.7 m² g⁻¹) and the highest electrocatalytic current density (115.6 mA cm⁻²). Moreover, the optimized catalyst reveals long-term stability for UOR in 1.0 M KOH + 0.33 M urea solution. The exceptional catalytic performance is ascribed to the fast charge-transfer kinetics, large active surface area and better dispersion of Ni nuclei [22].

1 Experimental
1.1 Materials
Chromic chloride hexahydrate (CrCl₃·6H₂O, ≥99%, Aladdin), nickel chloride hexahydrate (NiCl₂·6H₂O, ≥98%, Aladdin), ammonium fluoride (NH₄F, ≥96%, Xilong), urea (CO(NH₂)₂, ≥99%, Aladdin), Nafion solution (~5%, Alfa Aesar), ethylene glycol (≥99%, Aladdin), polyvinylpyrrolidone (PVP, M = 58 000, ≥99.6%, Xilong). All reagents were of analytical grade and could be used without further purification. CNTs (>95%) were purchased from Aladdin.

1.2 Synthesis of NiCrₓ-oxide-CNTs composites
The NiCr₂-oxide-CNTs hybrid composites were obtained through the hydrothermal method as follows: 73.3 mg CrCl₃·6H₂O, 163.5 mg NiCl₂·6H₂O, 0.277 8 g NH₄F, 0.225 2 g CO(NH₂)₂, 100 mg PVP and 100 mg CNTs were added to a continuous sonication solution of 20 mL H₂O/ethylene glycol (ν/v = 1/1). After 30 min, the resulting suspension was transferred to Teflon-lined stainless steel and autoclaved for 9 h at 120°C. The resulting products were centrifuged at 6000 rpm for 10 min, rinsed with excess H₂O/ethanol and freeze-dried over 12 h. The obtained products were nominated as NiCr₂-oxide-CNTs. As a comparison, a series of NiCrₓ-oxide-CNTs composites with different Ni/Cr molar ratios (1/1, 1/3, 2/1 and 3/1) were further prepared using a similar approach, as mentioned above. Meanwhile, the best-performing catalyst was also made using direct hydrothermal methods for comparison purposes.

1.3 Characterizations
The morphology and microstructure of the catalyst were investigated in detail by SEM (FEI Quanta 200 FEG) and TEM (JEM-2100F) with X-ray energy dispersive spectroscopy (EDS). The crystal structure of the material was characterized by XRD (Rigaku D/Max 2 500 V/PC) at a scan speed of 2.0 degree min⁻¹. Thermal gravimetric measurement was made on a TGA/STA409 PC module with a rising temperature rate of 2.5°C min⁻¹ from 20 to 800°C under continuous O₂ flow. The true ratio of the different metals in the catalyst was examined by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP). The chemical states of the different elements were probed by XPS (JPS-9 010 Mg Ka). The binding energy was calibrated based on a 284.8-eV (C–C bond) of the C 1s peak and a standard deviation of approximately ±0.05 eV. The true ratios of Ni and Cr for different materials were determined by inductively coupled plasma (ICP, PekinElmer FLexar-NexION300X).

1.4 Electrochemical measurements
All electrochemical measurements were performed in a standard three-electrode cell with a multi-channel Biologic VMP3 as an electrochemical workstation, in which a glassy carbon electrode (GCE), graphite plate and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. Before the experiment, several GCEs were polished with Al₂O₃ fine powder, then washed with H₂SO₄, ethanol and H₂O three times. The working electrode was prepared as follows: 4.0 mg of the catalytic material was ultrasonically dispersed in 1.0 mL mixed solvent (32 μL of 5% Nafion + 200 μL of ethanol + 768 μL of H₂O) for 30 min to form a homogeneous solution. Then, 10 μL of the above catalyst inks was pipetted onto the surface of the GCE (φ = 3 mm) and naturally dried for use. The loading of the catalyst was about 0.566 mg cm⁻². Cyclic voltammetry (CV) was analysed in the potential range of 0.0 to 0.8 V (vs. SCE) with a scan rate of 50 mV s⁻¹ in 1.0 M KOH saturated with N₂ with and without 0.33 M urea electrolyte. Since the concentration of urea in human urine is approximately 0.33 M and most previous reports on the electrocatalysis of urea were carried out in 1.0 M KOH solution, the urea concentration of 0.33 M was used for comparison purposes in this work [23–25]. The stability of the catalyst was tested by chronoamperometry at a fixed potential of 0.45 V (vs. SCE) for 2.0 h in a 1.0 M KOH + 0.33 M urea solution. All electrochemical studies were conducted at room temperature (25 ± 1°C).

2 Results and discussion
2.1 Crystal structure and thermogravimetric analysis
The sheet-like NiCr₂-oxide-CNTs was synthesized by a facile one-step method, in which the precursors of NiCl₂, CrCl₃, CNTs, NH₄F, PVP and urea were ultrasonically dispersed in a mixed solution of H₂O-ethylene glycol and then heated to 120°C for 9 h to achieve the final composite (Fig. 1a). Studies have shown that urea provides an alkaline environment, PVP and ethylene glycol manipulate microstructures as ligands, while NH₄F regulates the directional growth.
The XRD patterns of the optimized catalyst NiCr$_2$-oxide-CNTs with the two catalysts prepared using hydrothermal methods in the absence of either Ni (Cr-hydro-CNTs) or Cr (Ni-hydro-CNTs) are shown in Fig. 1b. The rest of the NiCrx-oxide-CNTs catalysts show similar XRD patterns [Fig. S1 in the online Supplementary Data (see the online Supplementary Data)]. Fig. 1b indicates that the crystal structures of NiCr$_2$-oxide-CNTs are consistent with the standard model of NiCr$_2$O$_4$ (JCPDS: 65–3105) [26], including the typical peak of the crystal plane (002) of CNTs at 25.8°. Notably, the Cr-hydro-CNTs exhibits four characteristic diffraction peaks at 18.2, 19.4, 26.6 and 43.7° corresponding to the (001), (100), (101) and (201) crystal planes of Cr(OH)$_3$·3H$_2$O (JCPDS: 16–0817) [27]. Simultaneously, the XRD pattern of Ni-hydro-CNTs matches well with the standard models of NiOOH (JCPDS: 27–0956) and Ni$_3$O$_2$(OH)$_4$ (JCPDS: 06–0 114) as well, suggesting the co-existence of these two species in Ni-hydro-CNTs composite. The ICP test results of NiCr$_x$-oxide-CNTs samples with different molar ratios of Ni/Cr indicate a high level of consistency between the experimental values and the theoretical values [Table S1 in the online Supplementary Data (see the online Supplementary Data)].

2.2 Morphology analysis

The morphology and microstructure of NiCr$_2$-oxide-CNTs were further investigated by SEM image, TEM images and EDS mappings. Fig. 2a is an SEM image which shows that some spherical structural species are intertwined with CNTs. The TEM image of Fig. 2b further discloses the spherical species composed of sheet-like species containing two types of clear lattice stripes with the lattice spacings of about 0.25 and 0.32 nm (Fig. 2c), which are consistent with the (311) facet of NiCr$_2$O$_4$ and (002) facet of CNTs, respectively [31]. Moreover, the EDS mappings manifest that the elements of Ni, Cr and O are evenly distributed throughout the entire skeleton of the NiCr$_2$-oxide-CNTs composite (Fig. 2d).

2.3 XPS analysis

XPS analysis was adopted to probe the chemical states of Ni and Cr elements in NiCr$_2$-oxide-CNTs (Fig. 3). As shown in Fig. S3a in the online Supplementary Data (see the online Supplementary Data), the survey XPS spectra showed...
that NiCr$_x$-oxide-CNTs with different Ni/Cr ratios contained Ni, Cr, C and O elements. The high-resolution C 1s ([Fig. S3b in the online Supplementary Data (see the online Supplementary Data)]) of each catalyst consists of four peaks at C=C (284.0 eV), C–C (284.8 eV), C–O (286.0 eV) and C=O (288.8 eV) [32], which are used as calibration standards. As shown in Fig. 3a, the high-resolution Ni 2p spectrum of NiCr$_2$-oxide-CNTs has been deconvoluted into four peaks, in which the binding energies at 854.9 and 872.7 eV are ascribed to Ni 2P$_{3/2}$ and Ni 2P$_{1/2}$, respectively, and the other two peaks are attributed to satellite peaks [33, 34]. All of these characteristics indicate that the Ni species in the composite is mainly present as Ni$^{2+}$. It is worth noting that the binding energy of Ni 2P$_{3/2}$ in the NiCr$_2$-oxide-CNTs composite has a negative shift of 0.25 eV compared to that of Ni-hydro-CNTs. Meanwhile, the high-resolution Cr 2p region of the NiCr$_x$-oxide-CNTs composite was fitted to two peaks corresponding to Cr 2P$_{3/2}$ (576.4 eV) and Cr 2P$_{1/2}$ (586.2 eV) of Cr$^{3+}$ [33], respectively ([Fig. 3b]). The binding energy of Cr 2P$_{3/2}$ for NiCr$_x$-oxide-CNTs exhibits a positive shift of 0.18 eV as compared to that of Cr-hydro-CNTs. The binding-energy changes indicate the presence of electronic-coupling and electron-transfer effects between the components of NiCr$_x$-oxide-CNTs [35, 36]. The electron migration between Ni and Cr is believed to promote the electrooxidation of urea synergistically [37]. The high-resolution Ni 2p and Cr 2p of the rest of the NiCr$_x$-oxide-CNTs composites were also analysed for comparison ([Fig. S3c and d in the online Supplementary Data (see the online Supplementary Data)]), which show a similar electronic structure. In addition, the high-resolution O 1s of all composites are fitted to four peaks representing metal-oxide, vacancies, C–O and adsorbed H$_2$O (Fig. 3c), respectively [38]. The results reveal that the Cr species has a positive effect on the oxygen-defect sites, while the Ni species increase the hydrophilicity of the composite. As a result, the excellent urea electrocatalytic activity of the optimized NiCr$_2$-oxide-CNTs is the fruit of an elegant balance between the oxygen-defect sites and hydrophilicity.

2.4 Electrochemical performance analysis

The CV curves of NiCr$_x$-oxide-CNTs, Ni-hydro-CNTs and Cr-hydro-CNTs performed in 1.0 M KOH solution were used to evaluate their ESA ([Fig. 4a]). The figures indicate that all catalysts except Cr-hydro-CNTs present a pair of redox peaks in the potential range of 0.0 to 0.8 V. The anode peak in the forward scan is consistent with the Ni(OH)$_2$ species oxidized to NiOOH and the cathode peak in the reverse scan is ascribed to the reduction of NiOOH to Ni(OH)$_2$ [11, 39]. Generally, the ESA was calculated by the required reduction charge in the reverse scan, which is directly proportional to the number of active sites for urea electrooxidation. The ESA values of all catalysts can be estimated from the equation $ESA = \frac{Q}{mq}$ [38, 40], where Q is the total charge used for the reduction.

![Fig. 2: (a) SEM, (b) TEM and (c) high-resolution TEM images of NiCr$_2$-oxide-CNTs. (d) EDS mappings of NiCr$_2$-oxide-CNTs with Ni, Cr and O elements](image1)

![Fig. 3: High-resolution XPS regions of (a) Ni 2p, (b) Cr 2p and (c) O 1s from NiCr$_x$-oxide-CNTs, Ni-hydro-CNTs and Cr-hydro-CNTs](image2)
of NiOOH species to Ni(OH)₂, m is the mass of Ni in the supported catalyst and q is 257 μC cm⁻² as only one electron for NiOOH converted to Ni(OH)₂. As shown in Fig. 4b, the NiCr₂-oxide-CNTs shows the highest ESA of 50.7 m² g⁻¹, which is 1.44-, 3.70-, 1.23-, 1.37- and 46-fold higher than NiCr-oxide-CNTs (35.3 m² g⁻¹), NiCr₃-oxide-CNTs (13.7 m² g⁻¹), Ni₂Cr-oxide-CNTs (41.3 m² g⁻¹), Ni₃Cr-oxide-CNTs (36.8 m² g⁻¹) and Ni-hydro-CNTs (1.1 m² g⁻¹). Studies have found that the introduction of a certain amount of Cr species can expose more active sites through synergistic interactions of Ni and Cr species [41]. Moreover, the various Ni/Cr ratios result in different morphology in NiCrₓ-oxide-CNTs composites, which also have a significant effect on ESA values [21]. Therefore, the optimal value of the Ni/Cr ratio is required to obtain the highest ESA. Thereafter, the electrocatalytic tests of all catalysts were performed in 1.0 M KOH + 0.33 M urea (Fig. 4c). Although all catalysts show a similar onset potential at ~0.32 V except for Cr-hydro-CNTs (0.56 V), the NiCr₂-oxide-CNTs catalyst has the largest current density (115.6 mA cm⁻²), which is about 1.36-, 2.71-, 1.20-, 1.22- and 7.2-fold higher than those of NiCr-oxide-CNTs, NiCr₃-oxide-CNTs, Ni₂Cr-oxide-CNTs, Ni₃Cr-oxide-CNTs and Ni-hydro-CNTs, respectively (Fig. 4d). Here, the higher onset potential of the Cr-hydro-CNTs catalyst than others may be due to the fact that the catalyst lacks effective active sites to adsorb urea molecules, thereby requiring a higher polarization potential to drive the reaction. It is also worth noting that Cr-hydro-CNTs has almost no catalytic activity for urea, but the composite catalysts including Ni and Cr possess higher catalytic performance as compared to both Ni and Cr single-component catalysts for urea oxidation, once again indicating the synergistic effect between Ni and Cr species. In addition, we also studied the electrochemical performance of NiCrₓ-oxide, CoCrₓ-oxide-CNTs and FeCrₓ-oxide-CNTs in 1.0 M KOH and 1.0 M KOH + 0.33 M urea [Fig. S4 in the online Supplementary Data (see the online Supplementary Data)]. The results show that the catalytic performances of these control catalysts are much lower than that of NiCr₂-oxide-CNTs, which indicates not only the importance of the CNTs, but also the unique effect of synergy between Ni and Cr towards the catalytic performance of urea oxidation.

In the initial stage of electrocatalysis, studies found that the Ni(OH)₂ species first lose one electron to form NiOOH on the catalyst surface [Ni(OH)₂+OH⁻ → NiOOH+H₂O+e⁻] [42, 43]. Subsequently, the produced NiOOH intermediates could adsorb hydroxyl ions and urea molecules from the electrolyte. After undergoing a complex multi-electron-transfer process, the urea molecules are finally oxidized to N₂, CO₂ and H₂O on the active sites [CO(NH₂)₂+6OH⁻ → CO₂+N₂+5H₂O+6e⁻] [38, 44] while the NiOOH species is reduced back to Ni(OH)₂ species [45]. The summarized forward current densities of NiCrₓ-oxide-CNTs are shown in Fig. 4d; the NiCr₂-oxide-CNTs shows the highest current density. Furthermore, it is also among the top-performing urea-oxidation catalysts reported in the literature because of the low onset potentials and high peak current densities [Table S2 in the online Supplementary Data (see the online Supplementary Data)].

Fig. 4: (a) CV curves of NiCrₓ-oxide-CNTs with different Ni/Cr ratios, Ni-hydro-CNTs and Cr-hydro-CNTs in 1.0 M KOH. (b) The summarized ESA values from (a). (c) CV curves of different catalysts in 1.0 M KOH + 0.33 M urea. (d) The summarized forward current densities from (c).
The stabilities of NiCr\textsubscript{x}-oxide-CNTs catalysts with different Ni/Cr ratios were tested by chronoamperometry at a constant potential of 0.45 V in 1.0 M KOH + 0.33 M urea electrolyte. As shown in Fig. 5, the NiCr\textsubscript{2}-oxide-CNTs catalyst shows the highest initial current density (85.0 mA cm\textsuperscript{−2}) and limiting current density (38.6 mA cm\textsuperscript{−2}). The initial spike can be attributed to the higher urea concentration on the surface of the catalysts at the beginning and the current stabilizes after some time where the system reaches the equilibrium [46].

2.5 Catalytic-mechanism analysis

As discussed above, the NiCr\textsubscript{2}-oxide-CNTs catalyst exhibits excellent electrocatalytic performance for urea oxidation. Electrochemical studies show that the Ni\textsuperscript{2+} species on the surface of the NiCr\textsubscript{2}-oxide-CNTs catalyst is first oxidized to NiOOH species (lose 1 e\textsuperscript{−}) as the active sites (M) (Fig. 6, Step I). Then, the urea molecules in the solution are adsorbed into the active sites of the NiOOH surface and the partially positively charged H atoms of the urea molecules are adsorbed onto the surface of the negatively charged Cr species (due to a higher electron density than Ni species) through electrostatic interaction (Step II). After the attack of OH\textsuperscript{−} ions and the combination of electrooxidation (loss of 1 e\textsuperscript{−}), one H atom is removed to form a free H\textsubscript{2}O molecule (Step III). After three consecutive dehydrations, an intermediate state of M-CO-N\textsubscript{2} is formed. Similarly, after an OH\textsuperscript{−} attack and the electrooxidation (loss of 1 e\textsuperscript{−}) followed by losing of a N\textsubscript{2}, another intermediate state of M-CO-OH is formed (Step IV). Along with the further attack of OH\textsuperscript{−} ions and one more electrooxidation process (loss of 1 e\textsuperscript{−}), the last intermediate state of M-CO\textsubscript{2} is formed while releasing one molecule of H\textsubscript{2}O (Step V). Finally, the active site M is recovered by releasing CO\textsubscript{2} (Step VI) [11, 43].

3 Conclusion

In summary, the NiCr\textsubscript{x}-oxide-CNTs with different Ni/Cr ratio catalysts were prepared by a facile hydrothermal method. Various techniques were applied to investigate the crystal structures, morphologies and chemical states. The results indicate that the NiCr\textsubscript{2}-oxide-CNTs composite is composed of the sheet-like structure of NiCr\textsubscript{2}-oxide and CNTs. There is a visible synergistic effect between Ni and Cr. The electrochemical studies show that the NiCr\textsubscript{2}-oxide-CNTs catalyst exhibits the immense ESA value (50.7 m\textsuperscript{2} g\textsuperscript{−1}), highest current density (115.6 mA cm\textsuperscript{−2}) and permanent stability for urea electrooxidation in alkaline medium. The prominent performance of the NiCr\textsubscript{x}-oxide-CNTs catalyst is mainly ascribed to its improved charge-transfer kinetics, the larger ESA, along with an elegant balance between the oxygen-defect sites and hydrophilicity. Moreover, the results also demonstrate a promising application of the non-noble-metal catalysts in water splitting, hydrogen production, fuel cells, etc.

Supplementary data

Supplementary data is available at Clean Energy online.

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Conflict of Interest

None declared.
Reference

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