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Temperature effect on crystallinity and chemical states of nickel hydroxide as alternative superior catalyst for urea electrooxidation

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Developing a highly ef cient and stable catalyst, composited by inexpensive, earth-abundant and non-toxic materials, is the critical issue for electrochemical urea oxidation. Among the all other physical parameters, the reaction temperature plays the key role in catalyst performance. Herein, we have studied the effect of temperatures on the synthesis of nickel hydroxide-carbon nanotubes composites via a facile hydrothermal method and the catalytic performance towards urea electro-oxidation in detail. Our studies indicate that the higher temperature enhances the crystallinity of b-Ni(OH)$_2$ species. Furthermore, the Ni(III) species in Ni(OH)$_2$-CNTs composites show an optimal point upon the changes of the reaction temperature, and the highest Ni(III) content appears at 80 C of b-Ni(OH)$_2$-CNTs. Meanwhile, electrochemical studies show that the electrochemically active surface areas (ESA) of the optimized b-Ni(OH)$_2$-CNTs (80 C, 95.6 m^2 g^{-1}) catalyst is 4.51- and 2.76-fold higher than that of b-Ni(OH)$_2$-CNTs synthesized at 20 and 140 C, respectively. The higher ESA of b-Ni(OH)$_2$-CNTs (80 C) also accompanies a superior electrochemical urea oxidation with a peak current density of 98.5 mA cm^{-2}, signi cantly higher than all the other studied catalysts. Additionally, the optimal b-Ni(OH)$_2$-CNTs (80 C) also demonstrates the highest initial and limiting current densities after uninterrupted long-term operation. These excellent performance of b-Ni(OH)$_2$-CNTs (80 C) catalyst indicates the positive effect of Ni(III) content which provides more catalytically active species along with the unique lamellar structures of CNTs as the support to facilitate electron/mass transfer and gas emission.

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1. Introduction

With the increase in energy demand and environmental pollution, the development of renewable energy (wind, solar, biomass, etc.) has gradually become the main theme in replacing fossil fuel [1,2]. Hydrogen, as a fuel with high speci c energy density, has captured a lot of attentions due to its clean and sustainable features [3,4]. With the rising enthusiasm on hydrogen energy research, urea electrooxidation has evolved into a hotspot because the reaction can provide fuel energy directly at the anode, meanwhile hydrogen can be released at the cathode during the electrolysis [5,6]. Studies have found that the urea catalytic system consumes less electrical energy than the water electrolysis in the case of producing the same hydrogen [7]. In addition, the consumption of urea is of great signi cance in eliminating environmental pollution because there is an approximately 2 e 2.5% of urea discharged in wastewater from various industrial streams [8]. Most of studies found that noble metal catalysts such as Ru-based composites and platinum group metals can improve the catalytic performance of urea oxidation [9,10]. Nevertheless, high cost and scarcity limit their large-scale applications. Therefore, searching low-cost and earth abundant catalysts to replace the precious metal catalysts for urea electrooxidation is still an urgent problem until now.

Previous studies have shown that non-precious metals also have catalytic performance for urea electrooxidation, such as Ni-M double hydroxides on carbon ber and Ni foam [11], nickel nanowire arrays on polycarbonate [12], nickel manganese oxide [13],

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porous Ni_3N nanosheet array on carbon cloth [14], carbon-encapsulated nickel-iron [15], CoS_2 nanoneedle array on Ti mesh [16], multi-layers graphene/nickel [6], sodium nickel fluoride on carbon nanotubes [17], mesoporous nickel phosphide [18], Ni-decorated graphene sheets [19], mesoporous $NiCo_2O_4$ nanosheets [20], NiO-Fe_2O_3 based graphene aerogel [21], hierarchical coral-like Ni-Mo sulfides on Ti mesh [22], three-dimensional MnO_2/$MnCo_2O_4$/Ni [23], two-dimensional metal-organic framework [24], *etc*. Among them, nickel-based catalysts has been extensively explored, but there are still many shortages on catalytic activity, stability, mechanism analysis, *etc*. To further explore and clarify reaction mechanism, many $Ni(OH)_2$-based catalysts are investigated, *e.g.*, exfoliated $Ni(OH)_2$ nanosheets [25], $Ni(OH)_2$ nanoflakes

3.1. Crystal structure analysis

The crystal structures and crystallinity of the synthesized series of $Ni(OH)_2$ with and without coexisting CNTs are initially investigated. Fig. 1 shows that the crystal structures of $Ni(OH)_2$ synthesized at 20, 80 and 140 °C are perfectly consistent with the standard model of hexagonal β-$Ni(OH)_2$ (JCPDS: 14–0117) [35], and the distinct peaks at 19.3, 33.1, 38.4, 52.0, 59.1, 62.6, 69.3, 72.7 and 82.6° are corresponding to (001), (100), (101), (102), (110), (111), (200), (201) and (202) crystal planes, respectively [36]. After incorporation of CNTs, there are two additional peaks appearance at 25.8 and 43.5° corresponding to (002) and (101) crystal planes of CNTs, respectively [37]. In addition, one should note that the diffraction peaks position of NiOOH are very close to these of β-$Ni(OH)_2$ as shown in Fig. S1, so the both species may coexist in the samples. Moreover, we can observe that the β-$Ni(OH)_2$ synthesized at low temperatures (*e.g.*, 20 and 80 °C) exhibit a wider half-width and weaker peak intensity compared to the sample prepared at high temperature (*e.g.*, 140 °C), indicating that β-$Ni(OH)_2$ synthesized at low temperatures have a smaller crystallite sizes, and low crystallinity which increases gradually with increasing the reaction temperatures [38].

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3.2. Morphology and microstructure analysis

The morphologies and compositions of $Ni(OH)_2$-CNTs synthesized at 20, 80 and 140 °C are further explored by SEM images and EDS mappings. The SEM image of β-$Ni(OH)_2$-CNTs (20 °C) is composited of continuous wavy-like structures (Fig. 2a). The β-$Ni(OH)_2$-CNTs (80 °C) exhibits a layered structures with the fish scales diameter of around 2 μm (Fig. 2b–c). As for comparison, we also carried out the experiment using water bath instead of an oil bath. The resulted sample in a water bath shows a honeycomb structure (Fig. S2) due to the no uniform heating. Notably, the high surface roughness of β-$Ni(OH)_2$-CNTs (80 °C) compare to that of the β-$Ni(OH)_2$-CNTs (20 °C) results larger surface area that is beneficial for facilitating mass transfer as well as gas emission through the layered spacing. When the reaction temperature reaches to 140 °C (Fig. 2d–e), the layered β-$Ni(OH)_2$-CNTs becomes much thicker and larger than that of prepared at 80 °C together with the narrower layered spacing as a result of the higher crystallinity as observed in XRD patterns. Additionally, the EDS mappings indicate that the Ni, O, and C elements are all uniformly distributed on the surface of the β-$Ni(OH)_2$-CNTs (80 °C).

The microstructures of the synthesized β-$Ni(OH)_2$-CNTs (80 °C) are also observed by TEM. The β-$Ni(OH)_2$ species exists in the form of layered structures and evenly intertwined with CNTs in the composites (Fig. 3a) which enhances the electrical conductivity of the composite. High-resolution TEM image (Fig. 3b) shows two

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