N-doped carbon encapsulated nickel nanoparticles: rational fabrication and ultra-high performance for ethanol oxidation

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ABSTRACT

N-doped carbon encapsulated nickel nanoparticles (NiNC) are prepared from mixtures of nickel salt, glucose and urea by a simple heating protocol. A higher viscosity of the mixture inhibits the migration of Ni species such that highly dispersed and very small Ni nanoparticles form during heat treatment. The sizes of the Ni nanoparticles can be controlled by adjusting the composition of the raw mixtures. The optimized sample of NiNC-4 contains Ni nanoparticles of 2.02 nm in size which afford a large metal surface area of $400.7 \, m^2 \, g^{-1}$ and a high nitrogen content of 7.21 at%. An ultra-high current density of $327 \, mA \, cm^{-2}$ is achieved in 0.1 M NaOH electrolyte containing 1 M ethanol using NiNC–4 as the electrocatalyst. NiNC-4 electrodes also exhibit a good long-term cycling stability. After 500 cycles, 89% of the initial current density is sustained in 0.1 M NaOH electrolyte containing 0.5 M ethanol. 96.8% of the initial current density is retained by moving the NiNC–4 electrode into fresh 0.1 M NaOH solution with 0.5 M ethanol after 500 cycles. The excellent electrocatalytic properties of NiNC–4 for ethanol oxidation stem from the synergistic effect of the porous carbon substrate, abundant N-containing groups and the small nickel nanoparticle size.

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1. Introduction

The direct ethanol fuel cell (DEFC) is a promising alternative energy transducer because of its high energy conversion efficiency, low level of pollutant emission and good stability as well as the ready availability of ethanol [1–4]. However, expensive catalysts such as Pt, Pd and their alloys, inhibit its large scale application [5,6]. Designing novel, effective and cheap catalysts is of paramount importance in order to replace the expensive noble metal catalysts. Numerous non-noble metal electrocatalysts, including transition metals [7–9], metal oxides [10,11] and metal complexes [12,13], have been investigated as alternative catalysts to enhance the kinetics of electrocatalytic alcohol oxidation.

Among transition metals, nickel-based catalysts have been shown to exhibit good electrocatalytic performance for ethanol oxidation. Notably, nanostructured nickel-based catalysts have afforded greatly improved electrocatalytic activities for oxidizing ethanol relative to bulk nickel due to their higher specific surface area. Much effort has been spent in fabricating nanostructured nickel-based catalysts with versatile morphologies and micro-structures. Mesoporous $Ni/Ni(OH)_2$ catalysts provide a large active surface area which promotes mass transport in the catalyst layers, effectively enhancing the electrocatalytic performance for ethanol oxidation reaction [14]. Also, Ni/4-nitroaniline/multi-walled carbon nanotube composites with electrodeposited 7.2 nm Ni nanoparticles exhibit a significantly improved electrocatalytic activity for ethanol oxidation [15]. By using reduced graphene oxide sheets as the support, three dimensional networks of 5 nm Ni-P nanowires were shown to provide more catalytic sites and afford a high current density of $16.4 \, mA \, cm^{-2}$, which is nearly twice as high as that of Ni-P microspheres ($8.5 \, mA \, cm^{-2}$) [16]. These results demonstrate that fabricating metallic nickel into nanostructures with high surface areas, controllable morphologies and particle sizes is an effective strategy to enhance electrocatalytic properties.

Furthermore, utilization of proper supports is another key factor to improve the electrocatalytic performances of nanostructure nickel catalysts. Various carbon materials have been used widely as supports including carbon black [17], carbon nanofibers (CNFs) [18], carbon nanotubes [19], graphenes [20] and graphene

foams [21]. For example, PdNi/C composites [22] and Ni@PbPt supported on graphene catalysts [23] exhibit high catalytic activity for fuel cells which stems from the carbon matrix structure. Materials with designed microstructures or unique morphologies, such as Ni-B amorphous alloy nanoparticles modified nanoporous Cu [24], ball-flower-shaped Ni nanoparticles and Cu modified TiO_2 nanotube arrays [25] have also been studied as catalysts towards direct ethanol or methanol oxidation.

Recently, doping heteroatoms into the carbon support, including nitrogen [26], sulfur [27] or fluorine [28], has demonstrated a remarkable improvement of the physical and chemical properties. Various doped carbon composite materials, such as nitrogen/sulfur dual-doped mesoporous carbon with controllable morphology [29], honeycomb-like mesoporous nitrogen-doped carbon [30], and N-doped CNFs supported on graphite [31] have been fabricated as the support for Ni or Pt catalysts for methanol electrooxidation.

As is well-known, glucose is a cheap, readily purified and accessible carbon resource. N-doped carbon is easily obtained via pyrolysis of N-containing organic molecules. Heat treatment will increase the viscosity of glucose to inhibit the migration of added metal cations and produce tiny nanoparticles upon reduction. These considerations imply that porous N-doped carbon with embedded small metal nanoparticles fabricated from glucose by a one-pot method is feasible. The synergistic effects of porous structure, small size of Ni nanocrystals and abundant N-containing groups are therefore postulated to enhance the electrocatalytic performance for electrochemical ethanol oxidation.

2. Experimental

2.1. Catalysts

All reagents were of analytical grade and used without further purification. Distilled water was used in all experiments. In a typical synthesis of NiNC samples, 2 g glucose, a certain amount of urea (0.8, 1.3, 2.3, 3.3, or 3.8 g) and 0.5 g of nickel acetate were successively dissolved in 50 mL of distilled water and vigorously stirred for 20 min to form a homogeneous solution. Subsequently, gelatinous mixture was obtained by drying the solution at 100 °C for 10 h. The gelatinous precursors were then heated to 800 °C at a heating rate of 3 °C/min under a N_2 atmosphere and kept at 800 °C for 2 h to obtain the catalysts. Samples with urea additions of 0.8, 1.3, 2.3, 3.3 and 3.8 g were sequentially denoted as NiNC–1, NiNC–2, NiNC–3, NiNC–4 and NiNC–5. By using the analogous synthetic route, reference catalysts without nitrogen doping were also fabricated from various nickel acetate loadings (0.3, 0.5, 0.7, or 0.9 g) and labelled as NiC–1, NiC–2, NiC–3 and NiC–4, respectively.

2.2. Methods

The morphology of the samples was studied using a field-emission scanning electron microscope (FESEM, Hitachi S-4800) with an energy-dispersive X-ray spectrometer (EDX) for elemental mapping. A Hitachi H-7650 transmission electron microscope (TEM, operating voltage 100 kV), and JEOL JEM 2010 field emission transmission electron microscope (HRTEM, operating voltage 200 KV) were used to characterize the microstructures of the samples. The samples for TEM and HRTEM observations were prepared by dipping sonicated ethanol suspensions of powdery samples onto copper grids. The size distributions of embedded Ni nanoparticles were evaluated by the TEM images of each sample to obtain statistically significant results. The phase identification was carried out with powder X-ray diffraction (XRD) using a Bruker D8 Discover with Cu Kα radiation (λ = 1.5418 Å). The diffraction patterns were collected in a two theta range of 10°–80° in

0.02°steps at a rate of 8° min^{-1}. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 X-ray photoelectron spectrometer) was used to investigate the surface elemental composition and chemical oxidation states. The nitrogen adsorption-desorption isotherms and the Brunauer-Emmett-Teller (BET) surface area were measured at 77 K on a Micromeritics ASAP 2020 M system. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PG/PC under an air flow with a heating rate of 10 °C min^{-1}. As shown in Fig. S1 and Table S1, the Ni contents were determined to be 27.5 wt % for NiC–1, 37.2 wt% for NiC–2, 47.1 wt% for NiC–3, 62.9 wt% for NiC–4, 38.1 wt% for NiNC–1, 32.1 wt% for NiNC–2, 28.2 wt% for NiNC–3, 24.2 wt% for NiNC–4, and 22.9 wt% for NiNC–5, respectively.

2.3. Catalytic tests

A CHI660D electrochemical workstation (Shanghai Chenhua, China) was employed for the electrochemical measurements, which were carried out in a conventional three-electrode electrochemical cell. A Pt wire, a saturated calomel electrode (SCE) and a glassy carbon electrode (GCE) were used as the counter, reference and working electrodes, respectively. All potential values were referred to the SCE reference scale. Cyclic voltammetry (CV) and chronoamperometry (CA) were used to study the activity and stability of the catalysts for ethanol oxidation. The current densities were calculated on the basis of the geometrical area of the electrode. The glassy carbon electrode was mechanically polished with 50 nm gamma alumina powders, rinsed thoroughly with distilled water, and dried at room temperature. To fabricate a working electrode, a slurry was prepared by mixing 0.78 mg NiNC or NiC powders, 30 μL Nafion solution, 270 μL water and 90 μL isopropyl alcohol. After sonicated for 30 min at room temperature, 10 μL of slurry was deposited on the active area of the glassy carbon electrode to form a homogeneous coating and dried.

3. Results and discussion

Figs. S2 and 1a shows XRD patterns of all samples. All the samples exhibit diffraction peaks at 44.51°, 51.85° and 76.37° that are readily indexed into (111), (200) and (220) planes of nickel with the face-centered cubic (fcc) structure [32] (JCPDS card No. 04-0850), respectively, revealing the presence of metallic nickel. The calculated particle sizes for NiNC–n (n = 1–5) are 3.20, 2.99, 2.74, 2.26 and 1.98 nm, respectively, indicating that the particle size is gradually reduced with the increase of urea content in the starting mixtures. Comparing the NiNC with the NiC samples, nitrogen species introduced into the carbon matrix can obviously decrease the size of Ni nanoparticles, as shown in Table S2. As is also well-known, urea molecules may interact with glucose molecules to increase the viscosity of the precursor. A higher viscosity greatly inhibits the migration of Ni cations [31]. N_2 adsorption-desorption measurements (Fig. S3 and Table S3) reveal that NiC–2 has the largest BET surface area of 223.7 m^2 g^{-1} with an average pore size of 5.03 nm. However, NiNC samples exhibit improved BET surface areas due to nitrogen doping. The BET surface areas for NiNC–1, NiNC–2, NiNC–3, NiNC–4 and NiNC–5 are 226.9, 314.0, 336.2, 400.7, and 336.1 m^2 g^{-1}, respectively. The large surface areas of NiNC–4 originate from the abundant micropores with an average pore size of 1.98 nm. The pores sizes of other NiNC samples locate in the mesoporous range of 2.61–4.57 nm.

XPS spectra in Fig. 1b and Fig. S4 confirm the presence of elemental nitrogen in NiNC nanocomposites. N$_{1s}$ spectrum (Fig. 1b) of NiNC–4 is readily fitted with four peaks at 398.3, 400.2, 401.1 and 402.3 eV, which are sequentially attributed to N–6 (pyridinic N), N–5 (pyrrolic N), N–Q (graphitic N) and N—O (oxidized N). N–5 and N–6 components can provide additional