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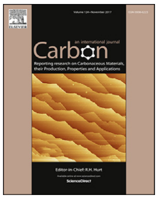

# Molecularly dispersed nickel-containing species on the carbon nitride network as electrocatalysts for the oxygen evolution reaction

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## ABSTRACT

Hybrid materials containing single atoms or molecule-based active species immobilized on nanomaterials have been suggested as new, efficient catalytic systems for various reactions. In this study, novel hybrid materials consisting of molecularly dispersed Ni-based species on a graphitic carbon nitride (g-$C_3N_4$) framework are prepared, and their excellent electrocatalytic performance for the oxygen evolution reaction (OER) is discussed. Extensive chemical and structural characterizations confirm that the Ni-based species are attached and well-dispersed on the $C_3N_4$ network without agglomeration. In addition, results obtained from electrochemical characterization suggest that Ni-containing molecular entities dispersed on the $C_3N_4$ network are active species for the OER.

## 1. Introduction

Transition metal-containing inorganic species as molecular catalysts often exhibit great performance in various reactions [1–3]. Their catalytic performance depends on the electronic, chemical, and steric environment around the metal center [1,4]. Recently, the anchoring of transition metal-based molecular species on the surface as well as defect sites, of carbon-based nanomaterials has been increasingly reported as a new route to create efficient catalytic systems for various reactions [2,5–9]. As carbon-based nanomaterials, such as graphene-based materials, carbon nanotubes, and carbon nitrides, are sterically bulky, and they exhibit a wide spectrum of electrical properties, they can dramatically tune the catalytic behavior of transition metal-based active species [6–8]. In this study, we applied the aforementioned concept to the creation of electrocatalysts for the oxygen evolution reaction (OER).

The splitting of water, which results in the generation of $H_2$ and $O_2$, is a process crucial for various energy storage systems in renewable and environment-friendly ways [10,11]. Electrocatalysts are required for the OER, representing the oxidation step of water, to achieve high efficiency and low overpotential [11–15]. Precious metal oxides such as $IrO_2$ and $RuO_2$, show great electrocatalytic activity and stability for OER in acidic and alkaline conditions [16–20]. Generating their hybrids with other metallic and carbon-based materials or heterostructures consisting of $IrO_x$ generated on the surface of $SrIrO_3$ or metallic Ir can further boost their activity for the OER [19,21]. However, because of high cost and scarcity of the precious metal elements, it is required to develop new OER catalysts using cost-effective and Earth-abundant metals, such as Fe, Co, and Ni [22–26]. Among them, Ni-containing materials, such as $NiP_2$, Ni chalcogenides, and nickel oxides [25,27–29], show excellent electrocatalytic performances in alkaline medium. Furthermore, through experimental comparisons of OER performances of a number of electrocatalysts revealed that many Ni-containing materials have low overpotentials comparable to other efficient catalysts [30]. In this context, we prepared novel hybrid materials consisting of molecularly dispersed Ni-based species on a graphitic carbon nitride (g-$C_3N_4$) framework, which exhibited excellent electrocatalytic performance for the OER.

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## 2. Experimental

### 2.1. Preparation of Ni–CN samples

The method for preparing Ni-CN-10 is described as follows. First, melamine (99%, Sigma-Aldrich, 1 g) and 10 mg of Ni(II) chloride hexahydrate (99.999%, Sigma-Aldrich) were added in a vial filled with 10 mL of ethanol, and the slurry was stirred for 12 h at 80 °C in an oil bath for removing ethanol. Second, the resulting mixture was dried under vacuum for completely removing ethanol. Third, the dried powder was then added to an alumina crucible, followed by heating the crucible in a quartz tube furnace (TFP-80-3, Dongseo Science Co., Ltd., Korea). Next, the furnace was filled with $N_2$ gas (99.99%), and the temperature was increased to 520 °C at a heating rate of 10 °C/min, followed by maintaining the temperature at 520 °C for 4 h under $N_2$.

After cooling to room temperature, the resulting product was filtered using a membrane filter (Anodisc membrane filter, diameter of 47 mm, pore size of 0.2 μm, Whatman, UK), followed by washing several times with ethanol for removing unreacted nickel-containing species. The resultant powder was dried under vacuum at room temperature for 12 h, affording Ni–CN-10. The same procedure was used for preparing Ni–CN-30, Ni–CN-50, Ni–CN-70, Ni–CN-100, and Ni–CN-200 using 30, 50, 70, 100, and 200 mg of Ni(II) chloride hexahydrate, respectively.

### 2.2. Electrochemical measurements

A glassy carbon electrode (GCE) (diameter of 3 μm, ALS Co., Ltd, Tokyo, Japan) was used as the support for samples. GCE was prepared by polishing with 1.0 and 0.3 μm alumina powder on a polishing cloth (Buehler, Lake Bluff, Illinois), followed by sonication in water for 15 min. Then, the electrodes were rinsed with water and dried. The loading sample solution was prepared by dissolving 2.0 mg of each sample powder and 20 μL of a Nafion® perfluorinated ion-exchange resin solution (5% (w/w) in lower aliphatic alcohols/water mixture, Aldrich) and 1.98 mL of a water/ethanol (1:1 (v/v)) solution, respectively.

Next, 10 μL of the loading sample solution was dropped on the cleaned GCE and dried for 1.5 h. Then, the loading sample solution was spread out not only on the electrode but also on the insulator part surrounding the electrode. Considering the spreading pattern of the loading sample solution on the electrode surface and insulator sides, the amount of loaded sample on the electrode surface was estimated as 79 $\mu g/cm^2$.

An electrochemical cell was constructed in the three-electrode configuration, consisting of a sample-modified GC working electrode, a Pt wire counter electrode, and a $Hg/Hg_2SO_4$, $K_2SO_4$ (saturated) reference electrode (0.64 V vs. NHE) was used. Nevertheless, all potentials were reported vs. reversible hydrogen electrode (RHE) for the convenience of comparison. Potentials were changed to the RHE scale according to the following equation [31]:

$$\text{RHE} = \text{E (vs. MSE)} + 0.059\ \text{pH} + 0.64$$

A 1 M Ar-saturated KOH electrolyte solution was used in OER experiments at a scan rate of 5 mV/s and a rotating rate of 1600 rpm [32].

The electrochemical impedance spectra (EIS) were also obtained using CHI 750 E instrument. Prior to the impedance measurements, linear sweep voltammograms (LSVs) was conducted from 1.2 to 1.7 V for checking the surface condition and ensuring a stable state of electrode surface. A 10 mV ac perturbation voltage was applied on top of a given dc overpotential (here, 1.7 V), and the frequency was scanned from 1 MHz to 0.01 Hz.

### 2.3. Instruments and measurements

X-ray photoelectron spectroscopy (XPS) measurements of each powder sample were performed using an angle-resolved XPS instrument (Theta Probe AR-XPS, Thermo Fisher Scientific, U.K.) equipped with an MXR1 Gun 400-μm 15 keV spectrometer. X-ray diffraction (XRD) patterns were recorded on a micro-area X-ray diffractometer (DMAX-2500, Rigaku, Japan). Scanning electron microscopy (SEM) images were recorded on a field-emission SEM system (S-4300SE, Hitachi, Tokyo) at an accelerating voltage of 15 kV. Fourier-transform infrared (FT-IR) spectra were obtained with KBr pellets containing powder samples using an FT-IR Vacuum Spectrometer (Bruker VERTEX 80 V, Bruker, Germany). Field emission transmission electron microscopy (FE-TEM) analyses were conducted on a JEM2100F system (JEOL, Japan) at 200 kV with samples on a carbon film supported on a 200 mesh copper grid (CF200-CU, EMS, USA). Energy dispersive X-ray spectroscopy (EDX) spectra were recorded using JEM-2100 F (JEOL) at 200 kV. SEM images were recorded on a high-resolution SEM instrument (HR-SEM, SU 8010, Hitachi, Japan). Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method using a Tristar ASAP 2020 (Micromeritics, USA). All electrochemical measurements were conducted on a CHI 750 E potentiostat (CH Instruments, Austin, TX). RRDE-3A (ALS Co., Ltd, Tokyo, Japan) was used for the rotating disk electrode (RDE) experiments. Inductively coupled plasma mass spectrometer (ICP-MS) measurements of the electrolyte for the dissolved Ni were performed using an ELAN 6100 (Perkin Elmer).

XPS measurement at Ni K-edge was carried out at a beamline 6D of Pohang Accelerator Laboratory (PAL). The incident beam energy and current were 3 GeV and 350 mA, respectively. Si(111) double crystal monochromator was used to filter the incident beam and was detuned by 15% to suppress spectroscopic contamination from high-order harmonics. Pelletized sample was used for the measurement in transmission detection mode. Background removal, normalization of the raw spectra, and extended X-ray absorption fine structure (EXAFS) fitting were performed using Athena and Artemis software [33].

## 3. Results and discussion

### 3.1. Preparation of Ni–CN samples

Among various $C_3N_4$-based materials, g-$C_3N_4$ is the most stable form, which is composed of triazine or tri-*s*-triazine building units; these units contain alternating $sp^2$ hybrid C and N atoms [34]. The g-$C_3N_4$ can be produced by the solid-state poly-condensation of monomers, such as melamine, dicyandiamide, and urea at high temperature [34–38]. Typically, the mutual dispersion of each component in the hybrid system is a critical factor for achieving the best performance [39,40]. For achieving good dispersion in our hybrid system, two precursors (melamine and $NiCl_2(H_2O)_6$) were uniformly mixed in ethanol (Fig. 1). The subsequent thermal treatment of this mixture in a furnace afforded hybrid materials as a light brown powder.

Herein, a series of hybrid materials containing different amounts of Ni (hereafter referred to as Ni–CN-($NiCl_2(H_2O)_6$ amount)) were prepared by thermal treatment. As a control sample, g-$C_3N_4$ was prepared using the same procedure without $NiCl_2(H_2O)_6$. The discussion will be focused on Ni–CN-200, among the samples prepared, because it exhibits the best catalytic performance for the OER, as will be discussed later (Supporting Information (SI) for characterization data of other Ni–CN samples).