Nitrogen-doped graphene/CoNi alloy encased within bamboo-like carbon nanotube hybrids as cathode catalysts in microbial fuel cells

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Abstract

Cost-effective catalysts are of key importance to the successful deployment of microbial fuel cells (MFCs) for electricity generation from organic wastes. Herein, a novel catalyst prepared by one-step synthesis strategy is reported. The catalyst features N-doped bamboo-like carbon nanotube (BCNT) in which CoNi-alloy is encapsulated at the end and/or the middle section of the tube with many graphene layers inside inner cavities of BCNT (N-G@CoNi/BCNT). The prepared N-G@CoNi/BCNT exhibits a high oxygen reduction reaction (ORR) activity with an early onset potential of 0.06 V vs. Ag/AgCl and a comparable exchange current density to that of commercial Pt/C. The excellent catalytic activity is further evidenced by a high electron transfer number of 3.63. When being applied in MFCs, the N-G@CoNi/BCNT yields an average current density of 6.7 A m^{-2} , slightly lower than that of Pt/C but with a less mass transfer potential loss. The cost of the N-G@CoNi/BCNT for constructing a 1-m^2 cathode is 200 times lower than that of Pt/C. With such a competitive price and excellent electrocatalytic-activity resulting from its unique morphology, CoNi-alloy/nitrogen dopants, considerable surface area, and carbon-coated alloy/graphene hybridization, the present catalyst is a promising candidate for ORR catalysts in MFCs for energy recovery from wastes.

Keywords: Graphene; Bamboo-like carbon nanotube; Defect structures; Oxygen reduction reaction; Microbial fuel cells

Graphic abstract

1. Introduction

Microbial fuel cells (MFCs) as an evolving wastewater treatment technology have attracted much attention in the past decade [1-4]. In a typical MFC, organic energy (e.g., organic compounds in wastewater) is directly converted to electricity by taking advantage of microbial extracellular respiration with an electrode [5, 6]. As such, organic removal and electricity generation can be accomplished simultaneously at low energy consumption. Oxygen is widely used as an electron acceptor in MFCs because of its availability and high reduction potential. However, oxygen reduction reaction (ORR) is sluggish and thus often requires the presence of catalysts. Platinum is a common ORR catalyst in bench-scale experiments due to its superior ORR catalytic activity, but is not economically viable in practice and accounts for the major hindrance for the large-scale application of MFCs [7, 8].

To make MFCs more practical, great efforts have been devoted to developing non-precious alternatives such as carbon/graphite materials [9, 10], earth-abundant metal alloys [11], and transition metal oxides [12, 13], among which graphene and its derivatives-based catalysts are of great interest due to their excellent electrical conductivity, abundant active sites, large specific surface area, and high stability [14-19]. Electrodes decorated with modified graphene-based materials have been reported to substantially decrease the loss of electrical potential and enhance the MFC performance (SI Table S1) [18]. For instance, it was found that nanotubular MnO₂/graphene oxide composites exhibited a maximum power density of 3,359 mW

m^{-2} that outperformed the unmodified electrode and achieved a comparable performance to the Pt/C electrode [12]. Liu *et al.* reported the nitrogen-doped graphene as a new cathode catalyst for MFCs, which displayed a high catalytic activity with the maximum power density of $776 \pm 12 \text{ mW m}^{-2}$ [20]. The carbon cloth cathode was modified with Fe- and N-functionalized graphene and exhibited a maximum power density of 885 mW m^{-2} [19]. Despite some progress, it is still highly challenging but extremely desirable to develop low-cost graphene catalysts with high activity for MFCs.

In this work, we have demonstrated for the first time the use of a one-step strategy to prepare a novel N-doped graphene/CoNi-alloy encased within bamboo-like carbon nanotube hybrid (N-G@CoNi/BCNT) in which CoNi alloy particles were encapsulated at the end and/or the middle section of tubes, with many graphene layers inside inner cavities of the BCNT. The synthesized hybrid was applied on carbon cloth serving as an electrode for the investigation of ORR catalysis by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The durability of the prepared electrode was examined by cyclic voltammetry for continuous 3,000 and 6,000 cycles. To better understand the catalysis performance, the electrode was further examined in an MFC and its superior performance was confirmed. The present work is expected to provide insights into the simplification of the N-G@CoNi/BCNT synthesis and the application of this material in MFCs and/or other biological systems for energy-efficient water and wastewater treatment.

2. Experimental section

Synthesis of N-G@CoNi/BCNT: In a typical procedure, 5 g of urea was mixed with 10 mL ethanol that contained 0.12 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.10 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under stirring and heating at 80 °C until completely dry. The mixture powder was then transferred to a furnace and heated at 900 °C at a rate of 2 °C min⁻¹ and maintained at 900 °C for 1 h under Ar atmosphere. The resulting product was further dispersed in 0.5 M H_2SO_4 solution and stirred overnight to remove any accessible cobalt and nickel species present on it. About 1.0 g black products (N-G@CoNi/BCNT) were obtained for further experiments. Controlled synthesis experiments were carried out by tuning the ratio of urea to $\text{Co}^{2+}/\text{Ni}^{2+}$ ions (See Supporting Information for experimental details, SI).

Characterization: The N-G@CoNi/BCNT morphology was examined using a Hitachi H-9000 NAR transmission electron microscope (TEM) and a field emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with an energy-dispersive X-ray (EDX) analytical system. Powder analysis was performed using an X-ray powder diffractometer operating at 40 kV, 40 mA for Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, Scintag XDS 2000). Raman characterization was carried out using a Renishaw 1000B with a 633 nm laser excitation. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector Fourier transform spectrophotometer. X-ray photoelectron spectroscopy (XPS) was obtained using an HP 5950A equipped with Mg K α source and the C 1s peak at 284.6 eV as an internal standard. Thermogravimetric analysis (TGA) was carried out on a thermoanalyzer (TA SDT 2960) with a heating rate of 5 °C min⁻¹ in air atmosphere. BET surface area was

measured with a Micromeritics ASAP 2020. The inductively coupled plasma–optic emission spectrometry (ICP-OES) tests were performed using a Perkin Elmer Optima 7000DV.

Electrode preparation: The synthesized catalysts were mixed with 40 μL Nafion® perfluorinated ion-exchange resin (Sigma-Aldrich, MO, USA) and 60 μL deionized (DI) water and applied to a carbon cloth (PANEX®30PW03, Zoltek Corporation, MO, USA), yielding a loading rate of 5 mg cm^{-2} . After coating, the carbon cloth was dried in a fume hood for 24 h, cut to 1 cm^2 and ready for use [21]. A carbon cloth coated with 5 mg cm^{-2} of Pt/C (10% wt. Platinum on Carbon Vulcan, Fuel Cell Earth LLC, Ma, USA) was prepared with the same method and served as control.

Electrochemical analysis: Electrochemical experiments were conducted in a three-electrode cell containing 120 mL of 1.0 M PBS (phosphate buffer saline, 53 g L^{-1} KH_2PO_4 and 107 g L^{-1} K_2HPO_4), where the modified electrodes served as the working electrode, platinum wire (CH Instruments, Inc., TX, USA) acted as the counter electrode, and Ag/AgCl electrode (CH Instruments, Inc., TX, USA) worked as the reference. LSV was measured with a potentiostat (Reference 600, Gamry Instruments, Warminster, PA, USA) at a scan rate of 5 mV s^{-1} (-0.6 to 0.4 V vs. Ag/AgCl). Tafel slope was derived from the LSV curve. Rotation ring disk electrode (RRDE) was conducted to study the mechanism of ORR. The electron transfer number (n) and H_2O_2 yield ($\text{H}_2\text{O}_2\%$) were calculated as follows [22]:

$$n = 4 \times \frac{I_d}{I_d + I_r / N} \quad (1)$$

$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_r / N}{I_d + I_r / N} \quad (2)$$

where I_d is the disk current, I_r is the ring current, and $N = 0.424$ is the collection efficiency determined with $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$. Cyclic voltammetry was conducted at 100 mV s^{-1} to examine the durability of the prepared electrode (-0.6 to 0.4 V vs. Ag/AgCl). The EIS was carried out at the open circuit voltage with a frequency ranging from 10^{-2} to 10^5 Hz and a sinusoidal perturbation of 10 mV and the equivalent circuit is shown in Scheme S1. The PBS solution was aerated for 15 min prior to each experiment, and kept aerating in the headspace during the course of experiments. Electrodes were air dried before each test. All electrochemical experiments were conducted at room temperature for three times.

MFC construction and operation: A two-chamber MFC was built by connecting two glass bottles with a cation exchange membrane (CEM) as a separator (UltexCMI7000, Membranes International, Inc., NJ, USA) (SI Scheme 2). The liquid volume of the anodic chamber and the cathodic chamber was 130 and 140 mL, respectively. The anode electrode was a carbon brush (length 5 cm, diameter 5.1 cm, Gordon Brush Mfg.Co., Inc., CA, USA) that had been cultivated in the MFC for one month. The anolyte contained (per liter of DI water): sodium acetate, 1.0 g; NaCl, 0.5 g; MgSO_4 , 0.015 g; CaCl_2 , 0.02 g; KH_2PO_4 , 0.53 g; K_2HPO_4 , 1.07 g; NaHCO_3 , 1.0 g; and trace element, 1.0 mL [23]. The cathode electrode was carbon cloth (1 cm $\times$ 1 cm) coated with catalysts. PBS solution (50 mM) was used as the catholyte. The anode and cathode electrodes were connected through a 1- Ω resistor. The voltage on the 1- Ω resistor was recorded by a digital multimeter (2700, Keithley Instruments, Inc., OH, USA) at a time interval of 5 min. The current of the MFC was calculated according to Ohm's law. Polarization curve and power density were measured using the potentiostat. To study the

performance of the catalysts under different conductivity and pH, NaCl solution (35 g L^{-1}), tap water, and buffer solutions were prepared and used as catholyte. The initial pH of NaCl solution and tap water was controlled at 7.0 using HCl and NaOH. Acid buffer (pH = 4.0) was prepared by mixing 0.2 M sodium acetate and 0.2 M acetic acid at a volume ratio of 9:41. Neutral buffer (pH = 7.0) was PBS solution, and alkaline buffer (pH = 10.0) was purchased from Fisher Scientific (PA, USA). The conductivity of the buffer solutions was controlled at 10.0 mS cm^{-1} using DI water and NaCl solution. The MFC was operated under a batch mode at room temperature. The electrolyte was changed every 24 h. The cathode chamber was stirred and aerated during the course of experiments. All cathode electrodes were examined at room temperature for two cycles.

3. Results and discussion

3.1. Material Characterization.

The synthesis of N-G@CoNi/BCNT was accomplished by pyrolysis of urea, $\text{Co}(\text{NO}_3)_2$, and NiCl_2 , followed by acid treatment of the resulting material. During the process, the $\text{Co}^{2+}/\text{Ni}^{2+}$ ions were reduced to CoNi alloy nano-catalysts to assist the evolution of gases released from the decomposition of urea into the hybrid (Figure 1a). Figure 1b shows typical field-emission scanning electron microscopy (FESEM) image of the N-G@CoNi/BCNT, indicating that the sample is dominated by 1D tubular nanostructures. The diameter of the nanotube is estimated to be in the range of 100-200 nm with several μm in length (Figure 1b-1c). From an open end of the nanotube shown in Figure 1d, an interesting tube-in-tube structure can be clearly

observed. Solid dots observed at the tip of the nanotube in Figure 1e are determined to be CoNi nanoparticles based on transmission electron microscopy (TEM) images (SI Figure S1). TEM images and energy dispersive X-ray (EDX) analysis reveal a bamboo-like structure of the individual nanotube in which CoNi nanoparticles are sparsely encapsulated at the end and/or the middle section of the tube (Figure 2a-2b and SI Figure S1), as well as many crumpled stripes composed of random graphene layers formed inside inner cavities of the BCNT (Figure 2c-2e). The graphene layers are easily identified with an interlayer spacing of around 0.34 nm (Figure 2f). Notably, the named herein bamboo-like structure did not form closed “knots”, which is different with those of traditional well-defined bamboo-like CNT structures with a diameter ranging from 20 to 60 nm [24, 25]. The main reason is that the diameter of N-G@CoNi/BCNT is so large (over 100 nm) that the graphene nanosheets can only grow into small nanosheets rather than form “knots”. Focusing on the inner part of these nanotubes, one can also distinguish some tube-in-tube structures besides crumpled graphene layers, which is consistent with FESEM observations (Figure 2d-2e). The diameter of inner tubes is about 50 nm. In this hybrid structure, an effective-conducting network can be formed among inner tubes, graphene layers, and outer tubes. In this case, both inner BCNT and crumpled graphene layers may serve not only as conduction paths for shuttling electrons but also as additional active sites for the electrocatalytic process [26].

Based on the experimental results, a plausible mechanism for the growth of the N-G@CoNi/BCNT hybrid structure is proposed. During the heat treatment, the nitrogen-containing polymer (e.g., polymeric carbon nitride) [27] evolved from urea can be

decomposed and a large number of nitrogen-containing gases (e.g., $C_2N_2^+$, $C_3N_2^+$, $C_3N_3^+$) are released simultaneously [28], which can serve as carbon and nitrogen sources for BCNT growth and nitrogen-doping reactions (SI Figure S2). As a result, the BCNT appears with visible metal nanoparticles at the end and/or the middle section by a well-known "tip-growth mechanism" [29], suggesting that the growth of such carbon nanotubes is catalyzed by the CoNi alloy [16]. Previous report revealed the existence of N-doping is necessary to catalyze the formation of the BCNT structures [25]. At a low concentration of the Co/Ni source, the resulting CoNi alloy nanoparticles are small, thus leading to the formation of nanotubes with a relatively small diameter (SI Figure S3). With an increasing concentration of Co/Ni, the obtained carbon nanotubes have a much larger diameter than nanotubes with a low concentration of the Co/Ni as the size of CoNi alloy catalyst becomes larger accordingly (Figure 2). Besides the large inner cavities of as-formed BCNT, the structural defects and broken sites formed inside the BCNT due to N-doping could contribute to the formation of graphene nanosheets [30-32], leading to the formation of the unique nanostructure where N-doped graphene/CoNi-alloy is encased within the BCNT. It is worth noting that when only Co or Ni salt instead of Co/Ni composite salt was used as precursor, the diameters of the resulting nanotubes were still less than 100 nm (SI Figure S4) and no such N-G@CoNi/BCNT hybrid nanostructures were obtained. In other words, the co-existence of Co and Ni with proper concentrations and urea are important for the formation of N-G@CoNi/BCNT hybrids. Of course, the detailed mechanisms need to be further clarified in the future work.

The crystal structure of the N-G@CoNi/BCNT was examined by XRD (Figure 3a). The feature peaks at 44.38° and 51.69° match well with the (111) and (200) planes of the face-centered cubic (fcc) phase of the CoNi alloy [33, 34], respectively. The broad peak at 26.35° is attributed to the graphitic carbon [16]; no other phases are present in the N-G@CoNi/BCNT. The Raman spectrum of N-G@CoNi/BCNT (Figure 3b) shows that the hybrid exhibits intense D ($1,332\text{ cm}^{-1}$) and G ($1,581\text{ cm}^{-1}$) bands as well as a weak 2D ($2,656\text{ cm}^{-1}$) band. The intensity ratio of D to G band is about 1.08, indicating the existence of substantial defects or disordered sites in the structure of N-G@CoNi/BCNT [35], presumably stemming from the presence of N dopants and concomitant absence of C atoms in the hybrid structure [36]. X-ray photoelectron spectroscopy (XPS) analysis (SI Figure S5) reveals that the N-G@CoNi/BCNT is mainly composed of C, N, and O with a nitrogen content of 4.1 %, confirming that nitrogen has been successfully doped into the nanocarbon. Although no obvious CoNi signals were detectable because the formed carbon shells in the hybrid hindered the CoNi alloy [37], the presence of CoNi alloy was confirmed by EDX analysis and high-resolution Co 2p and Ni 2p XPS spectra (SI Figure S1, Figure S5, and Figure 2). The atomic ratio of Co/Ni in the N-G@CoNi/BCNT hybrid was found to be $\sim 1:1$ from ICP-OES measurements. Further, based on TGA analysis, the wt.% of CoNi alloy in the N-G@CoNi/BCNT was calculated to be 3.95% (SI Figure S6). A high-resolution N 1s XPS spectrum (Figure 3c) of N-G@CoNi/BCNT shows that there exists pyridinic (398.7 eV), pyrrolic (400.6 eV), graphitic (402.2 eV), and oxidated N (404.1 eV) [38, 39]. The evidence of N-doping in the hybrid is also provided by Fourier transform infrared spectroscopy (FTIR,

SI Figure S7), which reveals a new band around 1,619-1,363 cm^{-1} that matches well with the stretching of the carbonyl aromatic C=C bond and the formed C–N bond [40]. As determined by N_2 sorption measurements (Figure 3d), the N-G@CoNi/BCNT sample possesses a high Brunauer–Emmett–Teller specific surface area of 114.3 $\text{m}^2 \text{g}^{-1}$ with a pore volume of 0.22 $\text{cm}^3 \text{g}^{-1}$.

3.2. Electrochemical Analysis.

It has been reported that N-doped carbon can efficiently catalyze ORR due to the high specific surface area and good electrical conductivity [41, 42]. The catalytic activity of the synthesized N-G@CoNi/BCNT in the present study was thus evaluated with LSV in 1.0 M PBS. Compared to the early onset potential of the Pt/C electrode (0.2 V vs. Ag/AgCl), N-G@CoNi/BCNT started to catalyze ORR at ~ 0.06 V vs. Ag/AgCl (Figure 4a). This onset potential is significantly more positive than that of bare Co and Ni, indicating an enhanced ORR catalysis of the hybrid. The difference of onset potentials between Pt/C and N-G@CoNi/BCNT (0.14 V) is consistent with the previous study on N-doped graphene [20]. The catalytic activity was further confirmed by the exchange current density calculated from the corresponding Tafel slope (the exchange current was obtained as the intercept of the y-axis from the Tafel plot after the Tafel slope was determined, SI Table S2). According to the Butler-Volmer model, exchange current density is proportional to standard rate constant at equilibrium, and thus is an important kinetic parameter reflecting the reaction rate [43]. The highest exchange current density was obtained from Pt/C ($2.59 \times 10^{-3} \text{ A m}^{-2}$), followed by N-G@CoNi/BCNT ($1.73 \times 10^{-3} \text{ A m}^{-2}$), which is several folds higher than that of the

pristine Co and Ni. This suggests that the hybrid could catalyze ORR faster than Co and Ni. A similar trend was observed in the EIS results (SI Figure S8), in which the charge transfer resistance, characterized by the diameter of the semicircle [12, 44], was 5 Ω for Pt/C and ~ 10 Ω for N-G@CoNi/BCNT, while those for Co and Ni were noticeably higher. Because the three-electrode cell was purged with air in the headspace, the early occurrence of Warburg impedance could be attributed to the low oxygen concentration in the PBS solution.

In principle, oxygen can be reduced through two mechanisms: 1) one-step four-electron pathway or 2) two-electron pathway in which O_2 is reduced to HO_2^- followed by the disproportionation of HO_2^- [45]. While the 2-e pathway generates highly reactive hydrogen peroxide that may lead to damage of membranes and electrodes, the 4-e pathway is more favorable in fuel cells applications because of the higher reduction potential. The ORR pathway was investigated with RRDE measurements in 1.0 M PBS solution (SI Figure S9). Calculated from Figure S9, the H_2O_2 yield at N-G@CoNi/BCNT is potential dependent, and drops from 100% at a low overpotential to 18.2% at a high overpotential (Figure 4b), suggesting that ORR catalyzed by N-G@CoNi/BCNT proceeds initially through the 2-e pathway, and shifts to the 4-e pathway with increasing potentials. The electron transfer number of N-G@CoNi/BCNT reached the plateau of 3.63 at -0.46 V vs. Ag/AgCl, close to the 3.9 of Pt/C, showing an efficient 4-e process. This value is also comparable to that obtained by polyelectrolyte-functionalized CNT (3.72) and N-doped graphene (3.69) [46, 47]. The ORR catalysis of the N-G@CoNi/BCNT can mainly be attributed to the introduction of three nitrogen species shown in Figure 3c: graphitic N can adsorb OOH and reduce O_2 to

H₂O₂ via 2-e pathway, while pyridinic and pyrrolic N are responsible for the catalysis of 4-e pathway [17, 48]. Besides, the CoNi alloy can be stripped by nitrogen atoms to form the enclosed Co-coordinated nitrogen complex that reduced the oxygen adsorption energy of carbon surfaces and made the reduction of oxygen more easily [49, 50]. Finally, the presence of O species (SI Figure S5a) may help decrease active energy carrier of ORR and protects catalytic C-N groups from being degenerated by protons [20]. In a recent study, a N-doped graphene/CNT nanocomposite achieved an electron transfer number up to 3.7 at a large overpotential [51]. The synthesis of this nanocomposite started from the pre-oxidation of multiwalled CNTs and the reduction of graphene oxide with the Hummer's method, followed by the hydrothermal treatment in the presence of ammonium for 12 h. Compared to the modified Hummer's method that is complicated and secondary reduction to graphene reported in the previous works (SI Table S1), the decomposition of urea with the assistance of CoNi alloy demonstrated in the present study greatly simplifies the synthesis of N-doped nanocarbon. Another relevant parameter for practical applications is the durability of the electrode. Although the current density showed slight fluctuation possibly due to the operational error during aeration, the onset potential of N-G@CoNi/BCNT after continuous 3,000 and 6,000 cycles remained the same as in the first cycle (Figure 4c), indicating that the N-G@CoNi/BCNT is stable as an ORR catalyst.

3.3 MFC Performance.

It should be noted that the electrochemical analysis in a well-defined system (i.e., a three-electrode cell) may yield results different from those in real situations, where various

factors such as mass transfer and adsorption/desorption may play a dominant role in the ORR catalysis. Therefore, the prepared N-G@CoNi/BCNT was examined in an MFC to mimic real applications. It can be seen from Figure 5a that the current density for all testing groups gradually decreases over time due to the consumption of substrates. The sudden drop of current density at 24 h indicates the renewal of electrolyte, and the rapid recovery implies that the MFC anode is well cultivated and exerts little effects on the investigation of cathode electrode. The MFC equipped with N-G@CoNi/BCNT yielded an average current density of 6.7 A m^{-2} , slightly lower than that with Pt/C (7.5 A m^{-2}). In comparison, the maximum current densities obtained from pristine Co and Ni were only 64.2 % and 44.8 % that of N-G@CoNi/BCNT, respectively.

The maximum power density calculated from the polarization curve (Figure 5b) is $2.0 \pm 0.1 \text{ W m}^{-2}$ for N-G@CoNi/BCNT and $2.6 \pm 0.2 \text{ W m}^{-2}$ for Pt/C, implying that the power density of N-G@CoNi/BCNT is only about 71.4% that of Pt/C. Nevertheless, to the best of our knowledge, this value of the power density for N-G@CoNi/BCNT is one of the highest reported compared to those of other top doped nanocarbons as MFC catalysts (SI Table S1). Interestingly, the current density of N-G@CoNi/BCNT is calculated to be 89.3% that of Pt/C. Such a discrepancy in power and current is a complicated result of catalytic activity and mass transfer [52]. It can be seen from the polarization curve that the open circuit voltage (i.e., the intercept of y-axis) of N-G@CoNi/BCNT is 0.1 V lower than that of Pt/C, agreeing well with the findings in the electrochemical measurements. Furthermore, the polarization curve shows three typical regions representing different types of potential losses [53]. The sudden

potential drop at a low current ($< 0.5 \text{ A m}^{-2}$) indicates a high activation potential loss of N-G@CoNi/BCNT. At a high current ($> 5.5 \text{ A m}^{-2}$) where the mass transfer potential loss is located, the drop of N-G@CoNi/BCNT is less drastic than that of Pt/C. This implies a more efficient interaction between O_2 and the catalyst, which could be ascribed to the unique morphology and considerable specific surface area ($114.3 \text{ m}^2 \text{ g}^{-1}$) of the synthesized N-G@CoNi/BCNT [18, 54]. Collectively, the N-G@CoNi/BCNT exhibits a relatively high current density (it means a rapid oxidation reaction in the anode and thus fast degradation of organic matters and short hydraulic retention time) but a low power density, suggesting that this material is more suitable for applications in which a high current is desired. For example, the MFCs equipped with the N-G@CoNi/BCNT may be a competitive approach for treating domestic wastewater compared to the energy-consuming activated sludge process. Previous studies of microbial desalination cells have reported enhanced desalination performance and energy efficiency at the high-current mode [55]. These results imply that the hybrid may hold great promise not only in wastewater treatment, but also for fresh water recovery.

Because N-G@CoNi/BCNT exhibited comparable performance to Pt/C in both electrochemical and MFC experiments, it was further studied using catholyte with different conductivity and pH. The current density of Pt/C and N-G@CoNi/BCNT with 35 g L^{-1} NaCl solution reached up to 12.7 and 11.2 A m^{-2} , respectively, but dropped below 4 A m^{-2} with tap water (Figure 5c), indicating that high conductivity was favorable for current generation. This was confirmed with neutral buffer ($\text{pH} = 7.0$, 10.0 mS cm^{-1}), whose current density was higher than that with 50 mM PBS (Figure 5a, $\text{pH} = 7$, 6.4 mS cm^{-1}) due to the increased

conductivity. On the other hand, the current density of both Pt/C and N-G@CoNi/BCNT decreased with increased pH (Figure 5c). This is because, according to the Nernst equation, high pH (i.e., low proton concentration) leads to a low reduction potential of ORR, and thus low cell voltage and current. It is worth noting that the MFC equipped with N-G@CoNi/BCNT was less susceptible to pH change and yielded comparable current density to Pt/C at the pH of 10.0, which could be attributed to the ORR mechanisms of Co and Ni under alkaline condition. A previous study on carbon supported palladium–nickel alloys showed that the alloy with high Ni content had a higher electron transfer number than commercial Pt did in alkaline media [56]. In another study, cobalt-polypyrrole catalysts were synthesized and it was proposed that the materials possessed two types of active sites: the Co-N sites adsorbed O_2 molecules and converted them via $2 e^-$ process to HO_2^- , which were then converted to OH^- at the decorating cobalt oxides/Co nanoparticle sites [57]. Given that the N-G@CoNi/BCNT synthesized here is composed of different nitrogen species, Ni and Co, it may catalyze ORR individually or interact with each other and exert effects to catalysis. While the outstanding performance of N-G@CoNi/BCN at high pH remains to be understood by further studies, it is highly desirable as it can reduce the cost of pH control (e.g., buffer addition).

3.4. Cost Studies.

Finally, the N-G@CoNi/BCNT is significantly advantageous over catalysts based on noble metals in terms of material cost. Given that 1 g of N-G@CoNi/BCNT can be produced from 5 g of urea, 0.12 g of Co salt, and 0.10 g of Ni salt with the synthesis method demonstrated in

this study, the cost for synthesizing 50 g N-G@CoNi/BCNT to construct an 1-m² electrode is \$ 13.3, which is 200 times less expensive than using the 10% Pt/C (\$2,750 for 59 g).

4. Conclusions

We have reported the synthesis of a novel N-G@CoNi/BCN hybrid that is proven to be a highly efficient non-noble metal based electrocatalyst for ORR in MFCs, thanks to the unique morphology and defect structures, such as CoNi/N-doping effect, carbon-coated alloy/graphene hybridization, considerable specific surface area, and high electron conductivity. It can be seen from the electrochemical experiments that ORR catalysis of the hybrid is comparable to that of commercial Pt/C catalyst, and the MFC experiments reveal a high current density possibly due to the synergy between effective catalysis and enhanced mass transfer. The novel hybrid holds great promise for practical applications due to its simple synthesis procedure, high catalytic activity for ORR, and excellent durability.

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Figure Captions

Figure 1. (a) Schematic illustration for the synthesis process of N-G@CoNi/BCNT. (b-e) FESEM images of N-G@CoNi/BCNT at different magnifications.

Figure 2. TEM images (a-e) and HRTEM image (f) of N-G@CoNi/BCNT. The inset of (b) shows the EDX spectrum from the area labeled by the circle in (b).

Figure 3. (a) XRD pattern, (b) Raman spectrum, (c) high-resolution N 1s XPS spectrum, and (d) Nitrogen adsorption-desorption isotherm curve and BJH pore-size distribution derived from the adsorption branch of the isotherm (inset) of N-G@CoNi/BCNT.

Figure 4. (a) LSV curves (scan rate 5 mV s^{-1}) in 1.0 M PBS solution, (b) H_2O_2 yield (left y-axis, large dots) and electron transfer number (right y-axis, small dots) as a function of potential obtained from RRDE measurements at a rotating rate of 1,600 rpm, and (c) CV curves in 1.0 M PBS solution for durability test (scan rate 100 mV s^{-1}) of N-G@CoNi/BCNT. Partial data for Ni-NBCNT, Co-NBCNT, CoNi-NBCNT, and Pt/C are also shown.

Figure 5. (a) Current density of the MFC equipped with different cathode electrodes, (b) the polarization curves, and (c) current density of with Pt/C and N-G@CoNi/BCNT in different catholyte.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.