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Highly efficient oxygen reduction on porous nitrogen-doped nanocarbons directly synthesized from cellulose nanocrystals and urea

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ABSTRACT

This study displays an easy preparation of high-performance electrocatalyst from cellulose nanocrystals for oxygen reduction reaction (ORR) that occurs at cathode of fuel cells. Through a direct pyrolysis of cellulose nanocrystals and urea, porous nitrogen-doped carbon nanosheets (NCN) are successfully synthesized without involving any catalysts or post treatments. As-prepared NCN displays very high specific surface area ($\sim$1362.36 $m^2\,g^{-1}$), large pore volume ($\sim$3.36 $cm^3\,g^{-1}$) and high graphitic-/pyridinic-N proportion ($\sim$80% in total N content). This metal-free material demonstrates a superior catalytic performance in terms of a comparable electrocatalytic activity, a better tolerance to the methanol crossover effect and an improved long-term durability toward ORR in the alkaline media when compared with the commercial Pt/C catalyst. Interestingly, the addition of $FeCl_3$ catalyst to the reaction system does not benefit ORR activity of the resultant material; the replacement of urea by NH_3 gas brings about much poorer material features of morphology, structure and catalytic activity. It is suggested that urea is irreplaceable during this catalyst-free synthesis of nitrogen-doped nanocarbons while cellulose nanocrystal is an unique choice for preparing high performance ORR electrocatalyst. The study herein contributes a very promising Pt-alternative cathode catalyst and also a facile and practical preparation of advanced carbon materials.

1. Introduction

As a potential alternative to the fossil-fuel technology, the fuel cell has been recognized as a very promising future energy source for portable or stationary applications such as zero-emission electric vehicles and distributed home power generators. A main limiting factor for the degradation of fuel-cell efficiency is the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode. Platinum (Pt) and its alloys are currently the most active ORR electrocatalysts. However, Pt is expensive, scarce and also suffers from poor operation durability and crossover deactivation. To propel the commercialization of fuel cells, Pt-alternative catalysts that are far cheaper, sufficiently efficient and durable are highly required [1,2]. The class of metal-free carbon cathode catalysts with unique electronic and nanostructural properties has attracted intense interest [3], especially the N-doped carbons which represent the most investigated metal-free ORR electrocatalyst because of their wide availability, environmental benignity, outstanding activity and long durability [4,5].

However, the ORR electrocatalytic performances of N-doped carbons significantly change with diverse preparation conditions such as the type of nitrogen, carbon precursors and the heat treatment temperature; because of the resultant differences of structural properties in pore structure, specific surface area, electronic conductivity, doping content and doping state [6–8], most of them are far away from satisfactory. Numerous direct-synthesis methods, such as chemical vapor deposition [9,10], solvothermal reaction [11], spray pyrolysis [12] and segregation [13], have shown to be effective in preparing N-doped carbons with various morphologies, but the stringent process and very low yield are their common drawbacks. The post-treating methods mostly by the pyrolysis of preformed carbons with nitrogen precursors, are quite suitable for the large-scale synthesis [7,14] but cannot ensure homogeneous doping thus leading to poor catalytic performance. Therefore, despite of great efforts on various synthetic methods, it is still a great challenge to produce N-doped nanocarbons via easy preparation process but with excellent catalytic performance for ORR.

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Herein, we thus try to explore further improved approaches based on the direct pyrolysis technique to extend strength and to dodge shortages of the two traditional methods mentioned above. First, a structure-defined carbon precursor with very low cost is required. Cellulose, being the most abundant organic material on the planet and also a kind of one-dimensional (1D) nanocrystals [15,16], is a prime choice as the carbon precursor; it differs from other extensively used biomass materials with amorphous form such as saccharides [17], collagen [18], and tannin [19]. Then, a foreign nitrogen source and a structure-directing agent are required to form N-doped carbons with desirable nanostructures. [20]. Urea can condense at ~500 °C to be graphitic carbon nitride (g-C_3N_4) with a C-N sp^2 graphitic sheet, and then decompose completely at 700 °C. Urea as well as g-C_3N_4 was also demonstrated as an efficient nitrogen precursor for post-doping graphene-like materials [21–24]. As such, urea is assumed to be an ideal dual-actor to dope carbons and also to assist formation of nanosheet structure [25,26]. Accordingly, through heating cellulose nanocrystals with urea at 1000 °C, we obtained porous N-doped carbon nanosheets (NCN) with significantly enhanced catalytic performance toward ORR when compared with commercial Pt/C catalyst, which suggests a cheap but very promising Pt-alternative cathode catalyst for alkaline fuel cells. In contrast, NH_3 as a nitrogen source was used to replace urea to dope carbonized cellulose, and $FeCl_3$ was used as the catalyst to promote graphitization; both products displayed unsatisfactory morphology, lower nitrogen content, and poorer catalytic activity, thus indicating the irreplaceable role of urea and the unnecessary use of metal catalyst for the synthesis of high-efficiency NCN materials.

2. Experimental

2.1. Material Preparation

Cellulose nanocrystals (CNs) were prepared as in reference [27]. The concentration of as-prepared CNs slurry was determined as ~3.75 wt.%. Then NCN was prepared typically as follows: CNs (1 g) and urea (15 g) were mixed by vigorous stirring for 30 min. The even mixture was lyophilized and then transferred into a crucible with the cover for the following pyrolysis. In Ar atmosphere, the heating started from room temperature (RT) up to the ultimate temperature of 1000 °C during 5 h, kept at 1000 °C for 5 h and natural cooled to RT at last. Without any post-treatments, NCN was kept its original form for further characterizations. The control samples were prepared as detailed description in Supplementary information.

2.2. Material Characterizations

The morphology and microstructure of as-prepared samples were investigated by JEOL6700 field-emission scanning electron microscopy (SEM), JEOL JEM-3010 transmission electron microscopy (TEM) operating at 200 kV, and an AIST-NT SmartSPM atomic force microscopy (AFM). N_2 adsorption-desorption isotherms were collected on a Micromeritics (ASAP 2010) Porosimetry analyzer. X-Ray diffraction (XRD) data were measured by a Bruker D8 Advance X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation. Raman spectra were obtained on a micro-Raman setup with LABRAM HR800 microspectrometer at wavelength of 532 nm (2.34 eV). X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific ESCALAB210-XPS photoelectron spectrometer with Mg Kα X-ray source.

The electrocatalytic characterization was performed on a μAutolab III workstation equipped with a three-electrode cell and a gas flow system. An Ag/AgCl electrode and a platinum pole were employed as the reference and counter electrodes, respectively. Working electrode (WE) was prepared as follows: First, 4 mg of catalyst was added into 1 mL of 0.02 vol.% Nafion water/ethanol solution (V_{water}:$V_{ethanol}$ = 4:1), and then the mixture kept sonication until a homogeneous ink was obtained; 5 μL of catalyst's Nafion ink was loaded onto the glass carbon electrode (3 mm in diameter), then the electrode was dried under an infrared lamp. The catalyst loading was ~0.283 mg cm^{-2} for all samples. The commercial 20%Pt/C (Alfa Aesar) was used as the reference catalyst, and Pt/C electrode was prepared as the same procedure. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) methods were applied to reveal the electrocatalytic activity toward ORR. The stabilities for methanol crossover effect and long-term duration were estimated at −0.45 V under continuous oxygen flowing.

3. Results and discussion

Cellulose is the most abundant biomass, and the ability to use it generating products with value-added properties is highly desirable for many practical applications. CNs, one-dimensional (1D) nanowhiskers with 2–3 nm in diameter (Fig. A.1a), is considered favourable to form sheet like structure [28]. During the slow pyrolysis of the mixture of cellulose and urea, 1D cellulose nanocrystals are carbonized and gradually graphitized [29], whereas g-C_3N_4 sheets are generated [20] (Fig. A.2) and then sacrificed at ~700 °C for the nitrogen doping and the preferential etching of amorphous carbons and graphitic layers [30], resulting in the final 2D nanosheets with abundant N-involved defect sites and large surface area.

3.1. Structural properties of NCN

The AFM image in Fig. A.1b displays the crumpled NCN nanosheet with plentiful edges and its thickness is ~2.5 nm, close to 3–4 layers graphene oxide. SEM images in Fig. 1a and b display the uniform structure of NCN with porous architecture which is assembled by curved thin sheets, and there is no obvious aggregation even though no post-treatments were conducted after the pyrolysis. Crumpled voile-like sheet structure can be further observed in TEM image (Fig. 1c). In comparison, carbonized cellulose (CC) shows a graphite-like structure (Fig. A.3), suggesting that urea is critical to form ultrathin sheet morphology. According to the HRTEM comparison (Fig. A.4), CC possesses a turbostratic structure, showing the presence of graphitic crystallizations with obvious defects [31]. But for NCN, the lattice fringes of multilayer graphene were only observed in the crumpled region, suggesting the decreased ordering after the nitrogen inclusion [6,30].

Specific surface area (SSA) and pore distribution of NCN were determined by N_2 adsorption-desorption experiment. Fig. 1d presents N_2-sorption isotherm curves of NCN. A type IV hysteresis loop in the high relative pressure region indicates the formation of asymmetric, slit-shaped mesopores. This is probably attributable to the rapid gas evolution from the decomposition of g-C_3N_4, which results in a high pressure thus creating open channels between 2D nanostructures. Based on the Brunauer-Emmett-Teller (BET) method, NCN possesses a high SSA value of 1362.36 $m^2\,g^{-1}$ than most of graphene-based materials (lower than 1000 $m^2\,g^{-1}$) [30,32]. NCN also displays an ultra large pore volume of 3.36 $cm^3\,g^{-1}$ as defined at a predetermined $P/P_0 = 0.989$. For many reported carbon nanotubes [33,34] and hard template-assisted nanocarbons [35,36], such high pore volume is hard to be achieved in spite of high surface area (their pore volume normally less than 2.5 $cm^3\,g^{-1}$). CC, prepared via a route similar to NCN-1000 but without g-C_3N_4 coating, exhibits a specific surface area of 612.24 $m^2\,g^{-1}$ with a pore volume of 0.35 $cm^3\,g^{-1}$ (Fig. A.5). The high SSA of CC surpasses most of directly carbonized biomass