



Original scientific paper

The performance of heteroatom-doped carbon nanotubes synthesized *via* a hydrothermal method on the oxygen reduction reaction and specific capacitance

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Abstract

Due to the increasing demand for electrochemical energy storage, various novel electrode and catalysis materials for supercapacitors and rechargeable batteries have developed over the last decade. The structure and characteristics of these catalyst materials have a major effect on the device's performance. In order to lower the costs associated with electrochemical systems, metal-free catalysis materials can be employed. In this study, metal-free catalysts composed of nitrogen (N) and sulfur (S) dual-doped multi-walled carbon nanotubes were synthesized using a straightforward and cost-effective single-step hydrothermal method. Carbon nanotubes served as the carbon source, while L-cysteine amino acid and thiourea acted as doping elements. As a result of the physicochemical characterization, many defects and a porous structure were noted, along with the successful insertion of nitrogen and sulfur into the carbon nanotube was confirmed. According to the cyclic voltammetry tests for the dual-doped samples in alkaline conditions, the D-CNT2 catalyst exhibited onset potential of -0.30 V higher than -0.37 V observed for the D-CNT3 catalyst. This indicates enhanced oxygen-reduction reaction due to the synergistic effects of the heteroatoms in the structure and the presence of chemically active sites. Moreover, the outstanding specific capacitance of the D-CNT2 catalyst (214.12 F g⁻¹ at scanning rate of 1 mV s⁻¹) reflects the effective porosity of the proposed catalyst. These findings highlight the potential of N/S dual-doped carbon nanotubes for electrocatalytic applications, contributing to efficient energy conversion.

Keywords

Metal-free catalyst; electrochemical energy storage; catalytic activity; porous structure

Introduction

In recent years, fostering a sustainable society has been a focus [1-3]. Developing renewable energy is important in achieving sustainable development and reducing pollution from fossil fuels [4-6]. The creation of clean energy storage and generation with low costs and great efficiency has garnered a lot of interest [7-9]. Traditional energy supplies, according to the Exxon Mobil paper titled 2018 Outlook for Energy: a view of 2040, will play an irreplaceable part in our future daily lives. Despite efficiency increases between 2016 and 2040, it expected worldwide energy consumption to increase by approximately 25 %, while they expected global electricity demand to climb by 60 %. Thus, building green electro-based energy systems is urgently needed to support economic progress and accomplish the Paris Agreement's climate targets, and it surely bears enormous market opportunities [10].

Presently, vital research is being focused on advanced technologies for electrochemical energy storage and conversion systems such as electrochemical capacitors, regenerative fuel cells, and rechargeable batteries (including Na-ion batteries, Li-sulfur batteries, Li-ion batteries, and K-ion batteries [11]), including electrocatalysis due to their flexible capacities [12], eco-friendly [13-15], remarkable energy conversion ability, and sustainability [16,17]. Electrochemical processes, like electrocatalysis, are crucial to electrochemical energy storage and conversion systems [18]. During discharging, such energy systems undergo an oxygen reduction reaction (ORR) on their negative electrode [19]. It is important to rationally design highly active [20], durable, and low-cost electrocatalyst for effective ORR as it represents a critical reaction in energy conversion systems [21]. Although a variety of factors influence the performance of energy-related devices, the structure and characteristics of the materials utilized heavily influence the overall performance [22].

In fact, ORR is slow in an acidic medium and requires noble catalysts such as Pt to occur; however, ORR has a lower over-potential in an alkaline medium than that in an acidic medium, allowing the use of noble-free catalysts [23]. To meet the needs of industry and advanced energy systems, the advancement of cost-effective metal-free electrocatalytic materials is of great interest [24]. In this direction, numerous non-precious ORR electrocatalysts, such as transition metal chalcogenides [25], transition metal nitrogen-containing complexes, and metal-free doped carbon materials [26], have been explored and developed [27]. It is broadly acknowledged that doping nanostructured carbons with heteroatoms such as boron, nitrogen (N), phosphorus, and sulfur (S) improves oxygen-reaction activities significantly [28]. For instance, J. H. Kim *et al.* [29] used chemical vapor deposition to create sulfur-doped carbon nanotubes (S-CNTs) using dimethyl disulfide as the sulfur source. At a high discharge current density of 100 mA cm^{-2} , the proposed material exhibited excellent specific capacitance of 120.2 F g^{-1} . The doping effect was responsible for the superior electrochemical performance of S-CNTs. As earlier reported in the literature, the doped heteroatoms can modify the spin-charge densities, causing charge redistribution in the carbon matrix [30]. The S element, in particular, increases the positive charge density and spin density of adjacent carbon atoms, promoting oxygen molecular adsorption on the carbon matrix and conferring carbon materials with effective ORR catalytic activity [31,32]. The creation of C-N structures, such as graphitic-N and pyridinic-N, can aid in electron transfer during the ORR process [31]. Previous research has shown that incorporating heteroatoms improves the distribution and preserves the electrical conductivity of nanostructured carbons and, thus, catalytic activity. The doped material also has long-term durability, good stability [33], and exceptional poison resistance during the ORR process [34,35]. Raji Atchudan and co-workers [36], for example, synthesized nitrogen-doped porous carbon, which showed a high specific capacity (160 F g^{-1}) with a good cycling stability of 95 % and a high rate performance of 52 % retention from 0.5 to 5.0 A g^{-1} in a three-electrode system in an aqueous 1 M

H₂SO₄ electrolyte. To the best of our knowledge, dual or even triple heteroatom doping treatments have been employed to improve the ORR catalytic performance of carbon-based nanostructures [37,38]. Y. Zheng and colleagues [39] used a simple and straightforward template-free technique to fabricate nitrogen/sulfur dual-doped hollow mesoporous carbon nanospheres for ORR electrocatalysis. The unique hollow spherical and mesoporous structure formed in situ from an intricately engineered covalent triazine framework *via* a thermally initiated hollowing pathway. The material that resulted exhibited high N and S contents, large specific surface areas, and excellent electrochemical performance [39].

Generally speaking, carbon materials have been designed for effective energy conversion and storage due to their unique physicochemical properties, such as high electronic conductivity, large surface area, and adjustable porous structure [22]. In this direction, CNTs have sparked considerable interest in the fields of electrocatalysis, biosensors, and energy storage due to their amazing features, which include exceptional electronic conductivity, great thermal stability, and good mechanical characteristics [40]. Herein, CNTs, L-cysteine (L-Cys), and thiourea (TU) were utilized for dual-doping with a hydrothermal treatment for electrocatalysis. Although N and S dual-doped CNTs have been extensively studied, little attention has been paid to the study of CNTs treated with amino acids-co-thiourea for electrochemical catalysis. Therefore, we investigated the structural change caused by inserting dual heteroatoms into the surface of CNTs, as well as the electrochemical performance in terms of the ORR. For comparison, investigated heteroatom doping of oxidized CNTs to test the hypothesis that heteroatom-doped CNT catalysts functionalized with selective oxygenic groups (COOH or OH) can improve intrinsic reactivity. Neat CNTs, doped CNT prepared at 4 h, and doped (CNT and oxidized CNTs (OCNTs)) prepared at 16 h are denoted as CNT0, D-CNT1, D-CNT2, and D-CNT3, respectively.

Experimental

Materials

Multiwall carbon nanotubes (MWCNTs, ≥98 % purity) were provided by Sigma Aldrich. L-Cys (≥99 % purity) was purchased from Beijing Solarbio Science & Technology. Thiourea (>98 % purity), N, N-Dimethyleformamide DMF, NaNO₃ (>98 % purity), and H₂SO₄ (98 %) were supplied by R&M Chemicals. KMNO₄ (>99 % purity) and hydrogen peroxide were provided by Chemiz Sdn. Bhd., and Bendosen Laboratory Chemicals, respectively.

Oxidation of CNTs

Typically, 0.1 g of CNTs with 0.1 g of NaNO₃ were dispersed in 60 ml H₂SO₄ (78 %) and placed in the sonicated for around 40 minutes at 11 °C in an ice bath, after which 0.2 g of KMNO₄ was added to the dispersion portion wise and sonicated for 2 h at (35 to 45 °C). Then 20 ml of 30 wt.% H₂O₂ was progressively added, followed by 300 ml of deionized water. Finally, the CNTs were filtered, washed, and dried.

Hydrothermal synthesis

Typically, 0.2 g of CNTs were dispersed in 100 ml deionized water before being placed in an ultrasonic bath for 2 h at room temperature (Solution A). Then after, 0.15 g of L-Sys and T-U (weight ratio 2:1) was added to 30 ml of solution A and then sonicated for 30 min (Solution B). Solution B was placed into a Teflon-autoclave reactor for hydrothermal reaction and in an oven for the

appropriate reaction time at 160 °C. The reactor was then allowed to cool naturally before the CNTs were filtered, washed, and freeze-dried. The same method was used to treat the oxidized CNTs.

Measurements

X-ray diffractometer (XRD) (D2 PHASER – Bruker, Germany) was used to measure phase patterns of D-CNTs. Cu K α radiation, Cu anode, and a scanning rate of 10° min⁻¹ were used for measurements. Raman spectroscopy (Renishaw inVia, Germany) was used to identify the final chemical structure of modified CNTs.

To further reveal the chemical structure, a Fourier transfer infrared (FTIR) spectrometer (Nicolet iS50 FT-IR, USA) was used to characterize the functional group attached to doped CNTs. Analyses were performed by using the ATR method over a spectral range of 4000 to 500 cm⁻¹. Differential scanning calorimetry (DSC) analysis was performed by using a high-temperature DSC (METTLER TOLEDO, Switzerland) instrument. About 0.5 mg of each sample was heated in an aluminum crucible with a heating rate of 10 °C min⁻¹ from 30 to 450 °C.

The morphology and EDS elemental analysis of doped-CNTs were studied using scanning electron microscopy (SEM, JSM-5600LV, Japan). Thermo Scientific elemental analyzer (Flash smart CHNS, Italy) was employed to measure the element content inserted in the modified CNTs. About 3 mg of dried samples were used and the atomic percentage of nitrogen, carbon, hydrogen, and sulfur were determined. ORR of modified samples was carried out on a potentiostat (Auto-Lab PGSTAT302N, Netherlands).

Results and discussion

XRD phase evaluation

XRD patterns for nitrogen-co-sulfur-doped CNTs are shown in Figure 1. The XRD patterns show major peaks at around $2\theta \approx 25$ and 42° . These peaks are assigned to the hexagonal graphite structures (0 0 2) and (1 0 0), respectively [41]. Obviously, when compared to untreated samples, the intensity of reflection of all doped CNTs decreased, which may be attributable to the insertion of doping elements such as N and S. The substitution of a heteroatom (N or S) in the CNTs generates defect sites and disrupts the carbon lattice; these findings demonstrated their less crystalline nature [42]. The Raman spectra support this result, as seen in Figure 2.

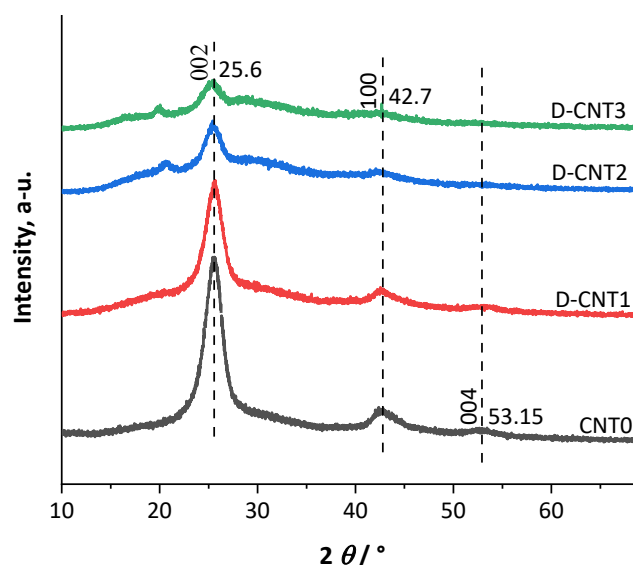


Figure 1. XRD pattern for the sample of (a) Neat CNTs, (b) D-CNT1, (c) D-CNT2, (d) D-CNT3

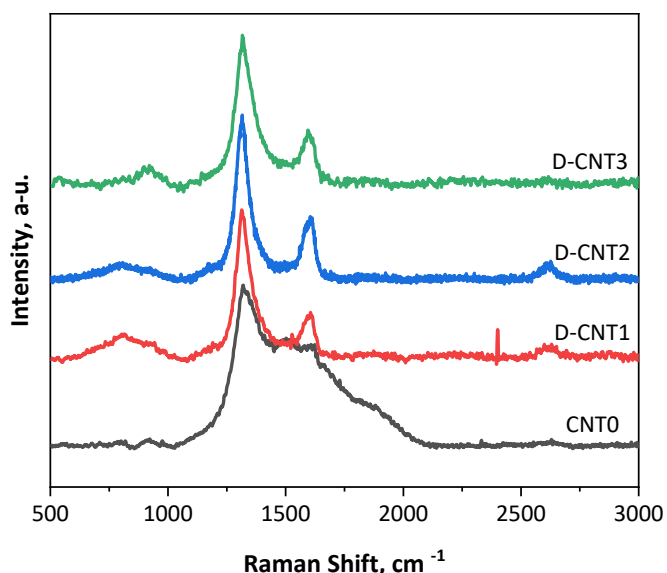


Figure 2. Raman spectra for the sample of (a) Neat CNTs, (b) D-CNT1, (c) D-CNT2, (d) D-CNT3

In particular, D-CNT2 and D-CNT3 exhibited lower intensity for both diffraction peaks than D-CNT1, which could be attributable to a longer doping time. Furthermore, the (100) graphitic plane diffraction peak appears to have vanished in sample D-CNT3, possibly because oxidizing CNTs provided more sites for chemical reactions. CNTs can, in fact, be functionalized in an oxidative environment, therefore CNTs with OH, =CO, O, COOH functionalization are more effective for subsequent reactions [43].

Raman spectroscopy analysis

Raman spectroscopy was used to explore further the sulfur-co-Nitrogen functionalization of CNTs (Figure 2). Two distinct peaks centered at 1350 and 1580 cm^{-1} are identified, corresponding to the disordered carbon (D-band) and the ordered graphitic carbon (G-band). The presence of a D-band with a high intensity indicates the existence of several defects and non-graphitic carbon in the doped CNTs sample, which may have resulted from heteroatoms doping [44]. As can be seen, sample D-CNT2 seems to have the maximum intensity when compared to the other samples. Furthermore, as shown in Figure S-1, a corresponding endothermic peak on the DSC curve was identified, which is associated with the degradation/decomposition of the carbon framework. When compared to doped CNT, neat CNT has a lower decomposition temperature. The heat of the reaction rises when doping elements are introduced. These results can be a sign of interaction between CNT and heteroatoms.

Some time ago, it was pointed out that doping with heteroatoms can create chemically active regions, which can boost electrocatalytic activity [44]. The G-band of D-CNT1, DCNT2, and D-CNT3 is obviously shifted to a lower frequency by about 10 cm^{-1} . In the literature, we observed a similar redshift behavior in sulfur-doped carbon nanotubes, indicating the electron delocalization effect caused by π - π interactions between the electron-donor doping precursors and CNT [35]. Overall, the XRD and Raman spectroscopy results suggest the nanocomposite is doped with N and S successfully by our one-step hydrothermal method and that variable doping levels are realized by varying the doping time [45]. In addition, clear evidence and additional conformation of nitrogen and sulfur incorporated into carbon nanotubes are provided in Figure S-2.

Furthermore, the D/G peak intensity ratios (I_D/I_G) of D-CNT1, D-CNT2, and D-CNT3 are 1.75, 1.43, and 1.30, respectively. Due to the fact that doping precursors wrapped around the surface of CNTs and covered the partial defect sites, the I_D/I_G ratio was slightly reduced [35].

SEM morphological observation

Figures 3 show SEM images of doped-CNTs. As can be observed, D-CNT2 and D-CNT3 samples contain more clearly irregular nanoparticles, Figure 3b and 3c. This finding indicated their porous nature and high surface area [41]. Several corners and edges are visible on the surfaces of D-CNT2 and D-CNT3, which could become active sites of oxygen adsorption in the ORR process. D-CNT2 has a significant number of pores in its morphology and appears to have a considerably looser porous structure, which helps to improve its ORR activity [46]. To the best of our knowledge, the presence of porous carbons, which give an enhanced accessible surface area for electrolyte ions, is principally responsible for the improved performance of the working electrode [44]. Furthermore, in samples D-CNT2 and D-CNT3, the particles appear densely stacked and agglomerated, implying that agglomeration occurred when amino acids were employed [22,47]. The overlapping and agglomeration behavior leads to forming complex three-dimensional stacked structures [34].

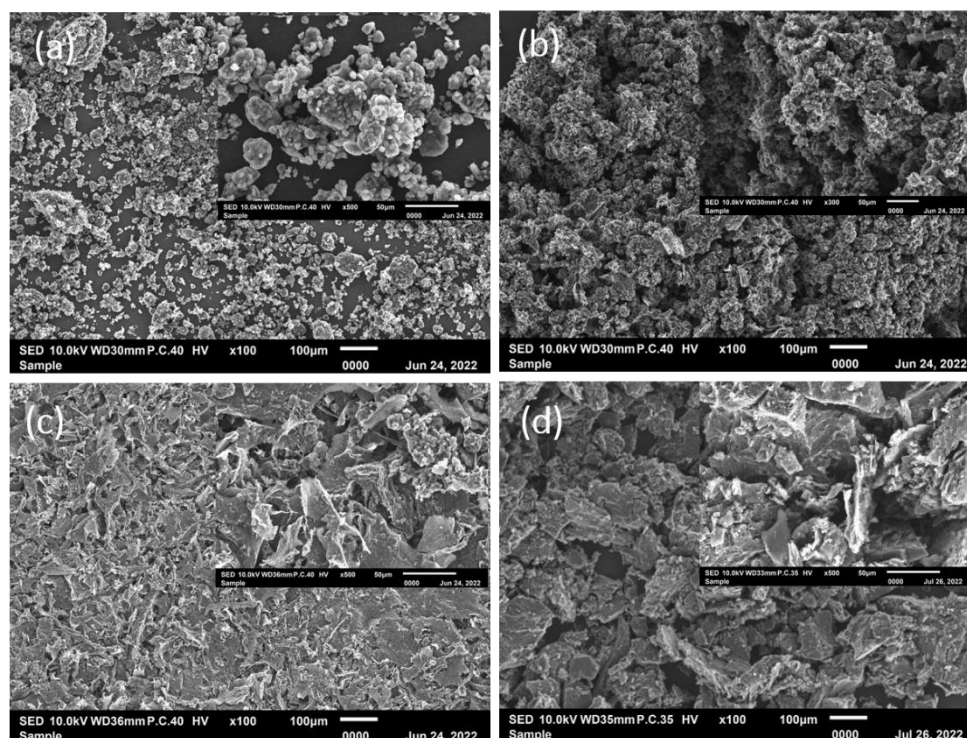


Figure 3 – SEM images with different magnifications of (a) Neat CNTs, (b) D-CNT1, (c) D-CNT2, (d) D-CNT3

Elemental analysis

The data from the (CHNS) analysis are shown in Table 1 to confirm the incorporation of doping elements into CNTs' surface. As we can see, The D-CNT3 sample has a slightly lower C content than the other samples, but it has the highest N and S content of 9.38 and 15.20 %, respectively. This is most likely because of the significant doping amount of N and S atoms caused by oxidation of the CNT prior to the doping process, which is consistent with the XRD results. The result of EDS color mapping (Figure S3) further describes the heteroatoms doping of CNTs. As seen the D-CNT3 has a higher S content than D-CNT2. Nitrogen is not detected by SEM-EDX, presumably because nitrogen has a very faint response, making detection unreliable for most materials [48]. Furthermore, EDS may detect major elements with concentrations greater than 10 wt.% [49].

Table 1. Elemental content for the doped sample

Sample	Content, wt.%			
	Nitrogen	Carbon	Hydrogen	Sulfur
CNT0	0	88.41	0.102	0.105
D-CNT1	0.572	77.11	0.893	2.744
D-CNT2	1.428	75.695	4.722	5.389
D-CNT3	9.378	41.167	1.872	15.203

Cyclic voltammetry – CV test

The catalytic activity for oxygen reduction reaction of the doped CNTs was measured using cyclic voltammetry (CV) with a three-electrode system (working electrode, counter electrode, and reference electrode) in 1.0 M KOH aqueous electrolyte with potential between -0.6 and 0.1 V at a scanning rate of 1 and 10 mV s^{-1} . The working electrode was prepared without the addition of any binding materials. The following procedure was used to prepare all working electrodes; 4 mg of D-CNTs were dispersed in $500 \mu\text{L}$ Alcohol and sonicated for 30 minutes. 1 to $2 \mu\text{L}$ of dispersion was loaded to the electrode's surface and dried.

Typical cyclic voltammogram curves of doped CNTs cathode/catalyst for the first two or three cycles are displayed in Figure 4. On the CV curves of the D-CNT2 and D-CNT3 samples, a significant ORR peak was observed. D-CNT2 and D-CNT3 have ORR onset potentials of -0.30 and -0.37 V, respectively, while the reduction (cathodic) peaks are at -0.26 and -0.35 V, respectively. The reduction peak of DCNT2 and DCNT3 marginally changed to -0.24 and -0.39 V, respectively, when the scanning rate was increased to 10 mV s^{-1} . These findings demonstrated that D-CNT2 catalysts have stronger ORR catalytic performance than D-CNT3 catalysts. Furthermore, the higher onset potential of D-CNT2 than D-CNT3 implies that the ORR occurs more easily on its surface [34].

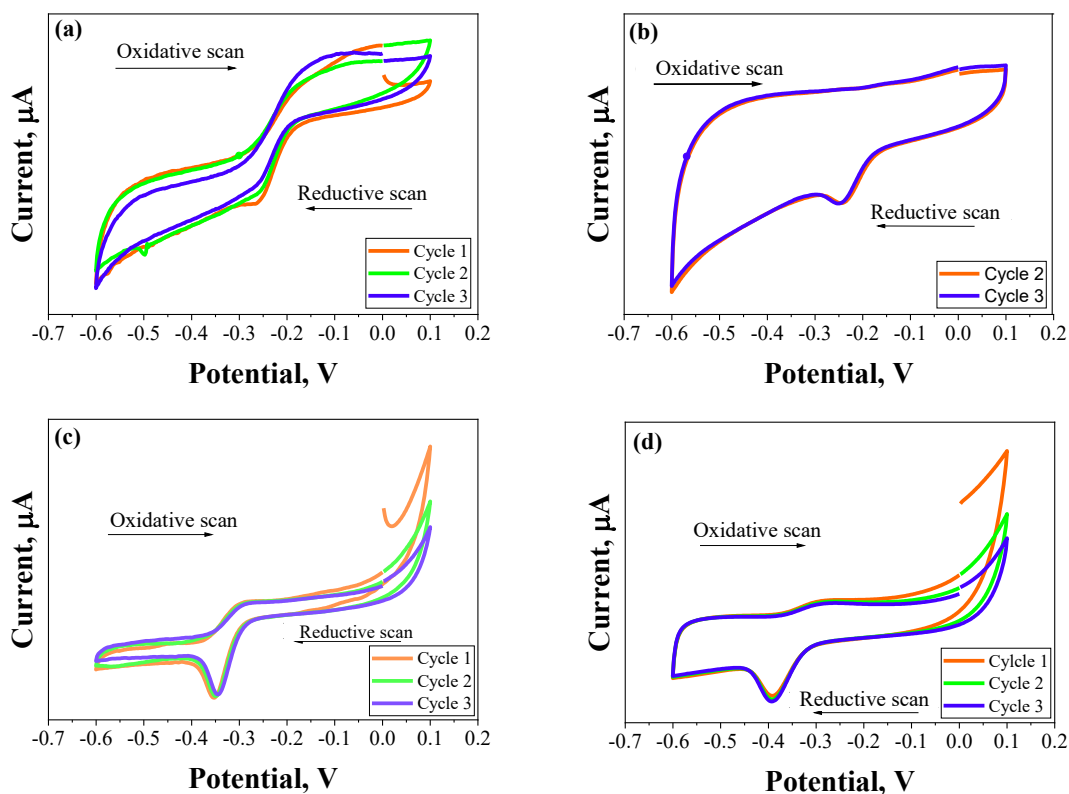


Figure 4. Cyclic voltammogram variations with altering scan rates of proposed catalysts (a) D-CNT2, scan rate 1 mV s^{-1} ; (b) D-CNT2, scan rate 10 mV s^{-1} ; (c) D-CNT3, scan rate 1 mV s^{-1} ; (d) D-CNT3, scan rate 10 mV s^{-1}

Because of the large number of holes and edges, the DCNT2 electrode has increased activity and a positively shifted onset potential compared to the DCNT3 electrode [50]. To our knowledge, doping with heteroatom can improve the electron-transfer kinetics and consequently the catalytic activity [34]. Besides, Due to a unique electron distribution, the synergistic effect of dual-doping with two dopant elements of different electro-negativities can enhance catalytic activity [51].

Although D-CNT3 contains more N and S than D-CNT2, the latter demonstrated higher ORR catalytic activity, which could be attributed to oxygen-containing functional groups being primarily eliminated below 400 °C [34]. As a result, the reduced oxygen functional group of D-CNT3 during the hydrothermal reaction slightly inhibits ORR activity. According to the Raman analysis, another impact could be the wrapping of doping precursors on the surface of OCNTs and the coverage of partial defect sites.

Additionally, because heteroatom doping can alter surface activity via conjugation between a lone pair of electrons and the π -system of the carbon lattice, it has the potential to generate further pseudo-capacitance improved electrocatalytic activity [22]. Using the CV data, the following equation was used to calculate the variation of specific capacitance with changing scan rates [52]:

$$C_p = \frac{A}{2mk(E_2 - E_1)} \quad (1)$$

where; A is the CV loop's enclosed area and m is the mass of material at the working electrode, k is the scanning rate, and $(E_2 - E_1)$ is the potential window (*i.e.*, the entire voltage range through which the electrode system was tested for electrochemical behavior). Table 2 compares the specific capacitance of each doped sample. As shown, C_p is noticeably higher when the scanning rate is low (1 mV s^{-1}) and higher in D-CNT2 samples than in D-CNT3 samples, reflecting their effective porosity. To the best of our knowledge, determining specific capacitance at differing scan rates is an essential step in understanding the inherent properties of any electrode material, particularly porosity influences ionic diffusion [52]. The analysis suggests that the dual-doped CNT can be used as an electrocatalyst, and D-CNT2 appears more capacitive than the other sample.

Table 2. Specific capacity C_p for two differing scanning rates

Dual-doped samples	Scan rate, mV s^{-1}	Specific capacity, F g^{-1}
D-CNT2	1	214.12
	10	91.14
D-CNT3	1	197.70
	10	124.18

Conclusions

The nitrogen and sulfur dual-doped carbon materials were successfully synthesized with various morphological aspects through a hydrothermal method using l-cysteine and thiourea as precursors. After freeze drying, the resulting D-CNT2 and D-CNT3 exhibited a porous structure. The examination of elemental content proved the existence of sulfur and nitrogen functional groups in CNTs after dual heteroatoms doping. The finding of the electrochemical characterization of the proposed catalysts demonstrates the great ORR activity, which can be attributed to the synergistic effect of dual-doping with dopant elements of different electro-negativities, in addition to the presence of numerous active sites and effective porosity. Besides, heteroatom doping generated the electrochemical capacitance characteristics. The proposed D-CNT2 catalyst achieved stronger ORR catalytic performance and higher specific capacitance at a lower scanning rate than D-CNT3 catalysts.

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