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Effect of Annealing Techniques in Enhancing Nitrogen Doped Graphene Synthesis by Ball Milling Method

(Kesan Teknik Penyepuhlindapan dalam Meningkatkan Sintesis Grafin Terdop Nitrogen melalui Kaedah Pengilangan Bebola)

NURUL AIN HUZAIFAH MOHD NORIZAN[1], NORDIN SABLI[1,2,*], SHAMSUL IZHAR SIAJAM[2] & ROSHASNORLYZA HAZAN[3]

[1]*Institute of Nanoscience and Nanotechnology (ION2), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
[2]*Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*
[3]*Materials Technology Group, Industrial Technology Division, Malaysian Nuclear Agency, 43000 Kajang, Selangor, Malaysia*

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ABSTRACT

Catalysts play a crucial role in addressing global challenges related to clean energy conversion and environmental sustainability. Among various catalyst materials, nitrogen-doped graphene (NDG) has emerged as a promising metal-free electrocatalyst for oxygen reduction reactions (ORR) due to its tunable electronic structure and high surface area. However, conventional synthesis of NDG via ball milling requires prolonged processing times, limiting its scalability and energy efficiency. This study focuses on optimizing NDG synthesis by employing annealing techniques to explore the potential for reducing production durations. NDG was synthesized by milling graphite and melamine, followed by annealing as a modification process to expedite synthesis. Key results show significant improvements in structural and catalytic properties. Raman Spectroscopy showed an I_D/I_G value of 1.73, indicating enhanced structural integrity. X-ray Diffraction (XRD) analysis confirmed the formation of graphene layers with a broad peak at 26°. X-ray Photoelectron Spectroscopy (XPS) identified a nitrogen content of 38%, crucial for catalytic activity. Electrochemical performance, evaluated via Open Circuit Potential (OCP) measurements, demonstrated a notable current of 19 mA, with variations attributed to annealing temperature and milling duration. The synthesis optimization through ball milling and annealing not only enhances material properties but also addresses the challenge of time-intensive production, making NDG more feasible for large-scale applications. These advancements pave the way for efficient and scalable NDG catalyst production, essential for advancing technologies in various industrial and environmental sectors.

Keywords: Annealing; ball milling; electrocatalysis; nitrogen doped graphene; synthesis optimization

ABSTRAK

Pemangkin memainkan peranan penting dalam menangani cabaran global berkaitan penukaran tenaga bersih dan kelestarian alam sekitar. Dalam kalangan pelbagai bahan pemangkin, grafin terdop nitrogen (NDG) telah muncul sebagai pemangkin elektrokimia bebas logam yang berpotensi untuk tindak balas penurunan oksigen (ORR) kerana struktur elektroniknya yang boleh diubah suai serta luas permukaan yang tinggi. Walau bagaimanapun, sintesis konvensional NDG melalui kaedah penggilingan bola memerlukan tempoh pemprosesan yang panjang, sekali gus mengehadkan kebolehskalaan dan kecekapan tenaga proses tersebut. Penyelidikan ini memfokuskan kepada pengoptimuman sintesis NDG dengan menggunakan teknik penaikan suhu (anli) untuk meneroka potensi pengurangan tempoh pengeluaran. NDG disintesis melalui proses penggilingan grafit dan melamin, diikuti dengan proses anil sebagai proses pengubahsuaian bagi mempercepatkan sintesis. Keputusan utama menunjukkan peningkatan ketara dalam sifat struktur dan keupayaan pemangkin. Spektroskopi Raman menunjukkan nilai I_D/I_G sebanyak 1.73, menandakan peningkatan keutuhan struktur. Analisis Pembelauan Sinar-X (XRD) mengesahkan pembentukan lapisan grafin dengan puncak lebar pada sudut 26°. Spektroskopi Fotoelektron Sinar-X (XPS) mengenal pasti kandungan nitrogen sebanyak 38%, penting untuk aktiviti pemangkin. Prestasi elektrokimia yang dinilai melalui pengukuran Potensi Litar Terbuka (OCP) menunjukkan arus sebanyak 19 mA dengan variasi yang dikaitkan dengan suhu penaikan (anil) dan tempoh penggilingan. Pengoptimuman sintesis melalui penggilingan bola dan penaikan suhu (anil) bukan sahaja meningkatkan sifat bahan tetapi juga menangani cabaran penghasilan yang memakan masa, menjadikan NDG lebih berdaya maju untuk aplikasi berskala besar. Kemajuan ini membuka jalan bagi penghasilan pemangkin NDG yang lebih cekap dan boleh diskalakan, penting untuk memajukan teknologi dalam pelbagai sektor industri dan alam sekitar.

Kata kunci: Elektrokatalis; grafin terdop nitrogen; penggilingan bola; pengoptimuman sintesis; penyepuhlindapan

INTRODUCTION

Graphene-based materials have attracted substantial attention in recent years due to their remarkable properties and potential applications across various fields, including catalysis. Among these materials, NDG has emerged as a promising catalyst in electrochemical systems, specifically in oxygen reduction reactions (ORR) with exceptional catalytic activity (Sheng et al. 2011; Skorupska, Ilnicka & Lukaszewicz 2021). Nitrogen doping in graphene shows changes in the diffusion of charge carriers, enhancing its potential as an alternative to platinum (Kurungot, Maraveedu & Ramadas 2016; Maddi et al. 2018; Sheng et al. 2011). Furthermore, NDG can improve the electrical conductivity and surface area of graphene and be useful in energy conservation and storage such as fuel cells and supercapacitors (Sheng et al. 2011; Xue et al. 2015; Yokwana et al. 2023).

NDG can be synthesized from mixed graphite and melamine using a ball milling method, which is eco-friendly and capable of large-scale production (Ranjan, Rai & Bajpai 2020; Xue et al. 2015). Different ball milling parameters including materials ratio, balls to powder ratio, milling speeds and milling duration can be controlled during the ball milling process (Wu et al. 2018). However, ball milling synthesis methods demand extended milling times, making the production process resource-intensive and less scalable. This prolonged milling duration increases energy consumption and restricts the feasibility of large-scale applications. To address these limitations, there is a critical need to explore innovative post-milling techniques that can significantly reduce the milling time required for NDG synthesis. These techniques should either maintain or enhance the catalytic activity of the material. This research aims to study the milling duration and the effect of the post-milling annealing technique in expediting NDG synthesis while improving its properties.

The annealing technique can be employed to modify the mechanical and physical properties, heat resistance, material stability and interlayer bonding of NDG (Alyobi, Barnett & Cobley 2017; Kaplas et al. 2019; Seok et al. 2023). This technique also helps to degrade unreacted material such as melamine (Jiang et al. 2019). The high-temperature annealing can lead to increased defects in graphene structure thus enabling the attachment or doping of nitrogen particles from melamine precursor to the edges of the graphene nanoplates but extensive increase in temperature may damage the structure of the materials. The annealing with high temperatures significantly increases the electrical conductivity and doping in graphene (Kaplas et al. 2019). This process may improve the ORR performance of synthesized NDG (Jiang et al. 2019; Lemes et al. 2019). During thermal annealing, melamine undergoes stepwise decomposition between 300-500 °C, generating reactive nitrogen-containing species such as ammonia (NH_3), cyanic acid, and intermediate C–N fragments (Jiang et al. 2019; Sheng et al. 2011). These reactive species interact with defect sites and edge planes of exfoliated graphene generated during ball milling. The high defect density introduced by mechanochemical exfoliation provides active sites for nitrogen incorporation via substitutional doping or edge functionalization. At moderate temperatures, nitrogen atoms are primarily incorporated as pyridinic and pyrrolic nitrogen at defect sites, while higher annealing temperatures promote partial graphitic nitrogen formation through substitution within the sp^2 carbon lattice (Ning et al. 2019; Xing et al. 2014). This thermally assisted incorporation mechanism enhances electronic modulation of graphene, improving charge distribution and facilitating oxygen adsorption during ORR. However, excessive annealing temperatures may lead to structural degradation or excessive defect formation, thereby necessitating optimization of the annealing conditions.

Unlike previous studies that primarily focus on demonstrating nitrogen-doped graphene synthesis via ball milling and annealing, this work integrates factorial statistical optimization to systematically define a scalable processing window that balances defect density, nitrogen configuration, and catalytic performance. This optimization-driven approach directly addresses production efficiency and practical scalability challenges in NDG synthesis.

In line with this objective, the present study proposes, a mechanochemical–thermal hybrid strategy is proposed, where ball milling is employed to generate defect-rich graphene sheets followed by controlled annealing to promote efficient nitrogen incorporation from melamine decomposition products. This approach aims to reduce milling duration while preserving or enhancing ORR catalytic activity.

MATERIALS AND METHODS

CHEMICAL AND MATERIALS

Graphite powder, melamine powder, ethanol (5% by mass) and sulphuric acid (H_2SO_4, 0.5 mol) were all sourced from R&M Chemical. The Nafion solution was purchased from Sigma Aldrich and distilled water was obtained using a FAVORIT W4L machine.

EQUIPMENT

The synthesis of NDG utilized a Planetary Ball Mill Pulverisette 6 from Fritsch Ball Mills for ball milling. Sample dispersion was facilitated using an Wisd Ultrasonic Laboratory Instrument and samples were annealed using a Carbolite Box Furnace. Characterization equipment included an RDE from HZ-5000 Hokuto Denko, Confocal Raman Spectroscopy on a REINSHAW system, FESEM imaging on a Carl Zeiss Gemini SEM500, X-ray Diffraction (XRD) on an X'Pert PRO MPD PW 3040/60 from PANalytical, and X-ray Photoelectron Spectroscopy (XPS) on an Axis Ultra DLD Kratos/Shimadzu.

PREPARATION OF NDG SYNTHESIS

NDG was synthesized using ball milling of graphite and melamine for 1.5 h and 50 h at 500 rpm and maintaining the best powder of graphite to melamine ratio of 1:10 (Huzaifah et al. 2020). This process facilitated the exfoliation of graphite into graphene while attaching nitrogen from melamine. Annealing techniques were used to remove unreacted graphite and melamine and optimize the NDG structure. Annealing temperatures from 300 °C to 500 °C were tested at consistent milling durations to determine the optimal conditions. To systematically evaluate the interaction between milling duration and annealing temperature, a two-level factorial design was employed using Minitab statistical software. The independent variables (factors) were milling duration (low level: 1.5 h; high level: 50 h) and annealing temperature (low level: 350 °C; high level: 500 °C). The primary response variables were onset potential and current density obtained from LSV and CA measurements. The factorial design enabled the assessment of both main effects and interaction effects of the processing parameters on ORR performance. Optimization criteria were defined based on achieving higher current response and more positive onset potential, indicative of improved catalytic activity. The relationship between milling duration and annealing temperature using a two-level factorial design. To investigate the impact of annealing on reducing milling duration, it was applied to the optimal temperature across various milling durations in NDG synthesis.

CHARACTERIZATION OF NDG

The synthesized samples were characterized using various analytical techniques to assess their properties and performance. RDE was employed to evaluate ORR performances through LSV and CA analysis. Additionally, the synthesized catalysts underwent characterization using Raman Spectroscopy, XRD, FESEM, and XPS. These analyses aimed to identify the structural, morphological, and chemical characteristics of the synthesized NDG.

RESULTS AND DISCUSSION

THE EVALUATION OF ANNEALING TEMPERATURE

The NDG was produced by using ball milling methods. The structural and chemical bonds of graphite begin to break down due to the impact of ball milling over time. This was supported by the position of Raman shift and intensity of D and G band mentioned in Childres et al. (2013). Raman spectroscopy is used to identify the doping effect of the carbon material. The value of I_D/I_G will give more information about the defect caused by the structural modification and doping of nitrogen atoms that occurs during ball milling and annealing.

Figure 1 shows the Raman spectra of NDG for different annealing temperatures. Four annealing temperatures were set in this study: 350 °C, 400 °C, 450 °C, and 500 °C. The sample had the same D, G and 2D peak location at 1340 cm^{-1}, 1581 cm^{-1} and 2689 cm^{-1}, respectively. All the peak locations were comparable to the standard NDG Raman spectra range (Jin et al. 2011). Based on the peak from Raman spectroscopy, the value of I_D/I_G can be obtained to provide information about the defect caused by the doping. The value of I_D/I_G for different milling durations increases as the annealing temperature rises. The increase in I_D/I_G from 1.66 at 350 °C to 1.73 at 500 °C indicates a higher level of defects in the NDG at the higher annealing temperature. The increase in the I_D/I_G value to 1.73 when annealed at 500 °C suggests that while more nitrogen is being incorporated, the process also introduces more structural defects compared to NDG when annealed at 350 °C, which shows an I_D/I_G value of 1.66. The results show that higher annealing temperatures create more defects, increasing defect intensity (Luo et al. 2018).

Higher annealing temperatures provide extra thermal energy that helps nitrogen atoms from melamine incorporate into the graphene lattice while disrupting carbon-carbon bonds, creating more defects in the structure (Luo et al. 2018). The defect of NDG can be identified by peak shifting and broadening (Seok et al. 2023). The peak in Figure 1 shows broader when annealed at 500 °C compared to other annealing temperatures. Based on the Raman Spectroscopy results, the synthesized sample was confirmed to be NDG as the peaks fell within the standard NDG Raman spectra range. The sample treated at higher temperatures exhibited more pronounced defects, indicating better nitrogen incorporation but more structural disruption. Further analyses of NDG are performed by using XRD to identify the material's crystallinity at different annealing temperatures (350 °C, 400 °C, 450 °C, and 500 °C).

In Figure 2, samples annealed at 400 °C, 450 °C, and 500 °C show similar broad peaks at $2\theta = 28°$ which correspond to the [002] diffraction planes, demonstrating that the NDG has been successfully synthesis by the ball milling process (Dan et al. 2021). The broadening peak and lower intensity are due to the disorder induced by the nitrogen atoms in the graphene lattice (Coros et al. 2020). However, the presence of a melamine peak in the sample when annealed at 350 °C suggests that the temperature was insufficient to remove excess melamine from the sample. The post-treatment of synthesized NDG, such as annealing, has successfully removed excess melamine, as shown by the reduced melamine peak after annealing at higher temperatures. The presence of residual melamine at lower annealing temperatures may negatively influence electrochemical performance by introducing insulating domains and partially blocking active graphene sites. Such residual precursor could hinder effective charge transfer at the electrode–electrolyte interface, thereby reducing ORR kinetics. This further supports the necessity of sufficient annealing temperature to ensure complete precursor decomposition and optimal catalytic behavior.

At temperatures approaching 500 °C, melamine-derived intermediates undergo further condensation and rearrangement reactions, promoting the transformation of less stable pyrrolic nitrogen species into more thermodynamically stable graphitic nitrogen configurations (Liu et al. 2010; Lv & Terrones 2012). This structural evolution enhances electronic conductivity and facilitates improved electron transfer kinetics within the graphene lattice (Qu et al. 2010). Consequently, the superior ORR performance observed near 500 °C can be attributed not only to increased nitrogen incorporation but also to improved electronic modulation of the carbon framework (Xing et al. 2014).

Next, the ORR performance of NDG was evaluated using LSV based on the onset potential observed in the curve. Onset potential is the potential that ORR begins to occur (Zhuang et al. 2016) and the more positive the onset potential, the better the ORR performance (Paton-Carrero et al. 2020). Figure 3(a) shows an increasing trend of current density and onset potential observed when the annealing temperatures increased. The most positive onset potential for sample NDG milled for 50 h is -0.202 V at the highest annealing temperature of 500 °C while annealed at 350 °C showed the most negative onset potential. This trend indicated that annealing temperature affected the catalyst's current density and onset potential. The LSV performance depends on the nitrogen doping. In addition, annealing techniques to milled NDG synthesis with the highest temperature help in nitrogen doping (Zhang et al. 2013). Annealed at 500 °C showed the best ORR performance after comparing the voltammograms shown in Figure 3(a).

In Figure 3(b), the samples showed the trend towards higher current could be observed when the ball annealing temperature increases. This can be due to the different annealing temperatures that affected the nitrogen doping efficiency thus enhancing the ORR performance. NDG annealed at 500 °C exhibited the most current produced at the time (t) = 0.01s among the samples which is 19.83 mA, while NDG annealed at 350 °C exhibited the least current production which is 1.49 mA at t = 0.01s. The current value showed that sample NDG that annealed at higher temperature (500 °C) showed the best ORR performance among other annealing temperatures. Based on the evaluation, 350 °C and 500 °C were selected as a baseline to compare lower annealing temperatures with higher annealing temperatures. Next, the annealed technique is applied to two different milling durations (1.5 and 50 h) using a Design of Experiment (two-level factorial design).

DESIGN OF THE EXPERIMENT AND CATALYTIC PERFORMANCE

The relationship between milling duration and annealing temperature are using two-level factorial design. Samples underwent RDE testing, and subsequent analysis was conducted using Minitab software. Figure 4(a) compares samples annealed at 500 °C and 350 °C, demonstrating the better performance of the sample annealed at the higher temperature. The coefficient of determination (R^2) was calculated to be 51.84%, indicating that over half of the variability observed in the results can be attributed to the relationship between milling duration, annealing temperature, and the properties of nitrogen-doped graphene (NDG). This statistical measure emphasizes the significant influence of annealing temperature on enhancing NDG properties.

The onset in the LSV curve works as indicator of ORR performance, with a more positive onset potential suggesting superior catalytic activity (Xue et al. 2015). Figure 4(a) compares the LSV curves between NDG samples synthesized with 1.5 h milling, annealed at 350 °C and 50 h milling, annealed at 500 °C. Consistent with previous analyses, the sample at longer milling duration and higher annealing temperature (50 h, 500 °C) exhibits enhanced catalytic activity. This improvement can be attributed to the increased incorporation of nitrogen atoms from melamine into the graphene lattice, leading to the formation of defects that serve as active sites for ORR (Granzier-Nakajima et al. 2019). The contours plot in Figure 4(b) (red dashed circle line) confirms that the best catalytic properties with better current response at lower potential can be achieved when milling at 10 h with an annealing temperature of 480 °C to 500 °C. More reaction sites were present for a longer ball milling duration leading to more nitrogen being doped into graphene compared to a shorter ball milling duration (Zhuang et al. 2016). These findings are consistent with previous discussions, where higher annealing temperatures promoted greater nitrogen incorporation and improved structural characteristics. The results highlight the importance of optimizing processing conditions to achieve desired material properties, striking a balance between nitrogen doping efficiency and structural integrity.

The CA were performed at a rotational speed of 1500 rpm with a constant potential of 1V for 5 s in the same oxygen-saturated 0.5M H_2SO_4 electrolyte. This analysis focuses on the current generation without compromising stability. Notably, the current response at 1V for 0.1 s is significantly higher for the 50 h, 500 °C annealed sample (2.5 mA) compared to the 1.5 h, 350 °C annealed sample (0.9 mA) as shown in Figure 5(a). This disparity underscores the superior electrocatalytic properties of the longer milling duration and higher annealing temperature sample, further validating its enhanced ORR performance. The R-squared value for this comparison was exceptionally high at 98.3%, indicating a strong correlation between annealing temperature and material performance. Figure 5(b) (red dashed circle line) shows that the best catalytic performance, with superior current response at lower potentials, can be achieved with milling durations of less than 50 h and annealing temperatures ranging from 480 °C to 500 °C. This highlight that optimal catalytic performance can be achieved depends on both annealing temperature and milling duration. To confirm this, two samples milled for 12 and 24 h were analysed using RDE as shown in Figure 6(a) for LSV and 6(b) for CA.

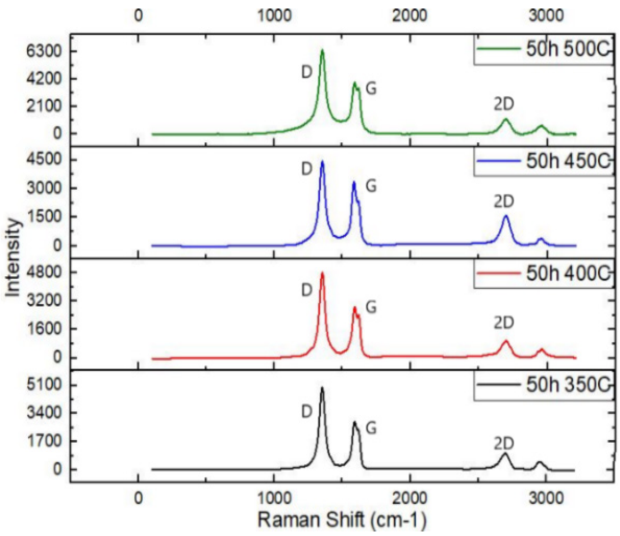

FIGURE 1. NDG for different annealing temperatures

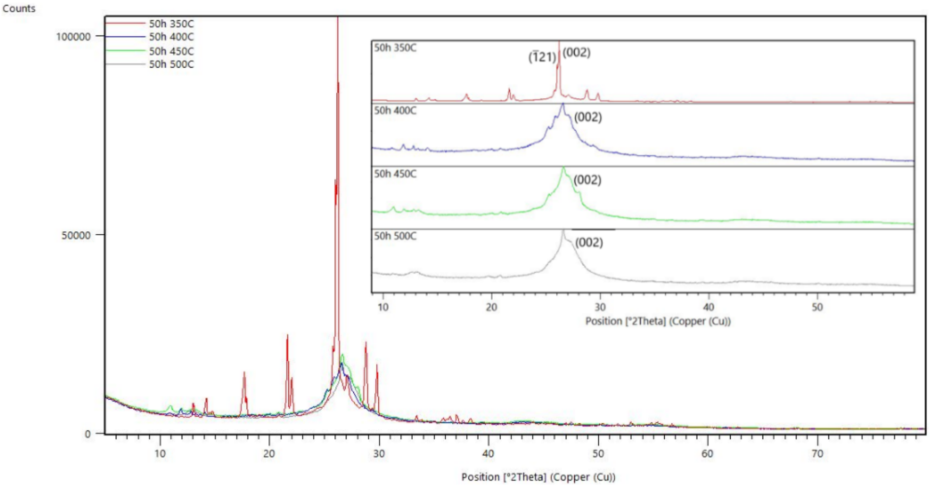

FIGURE 2. XRD of NDG for different annealing temperatures

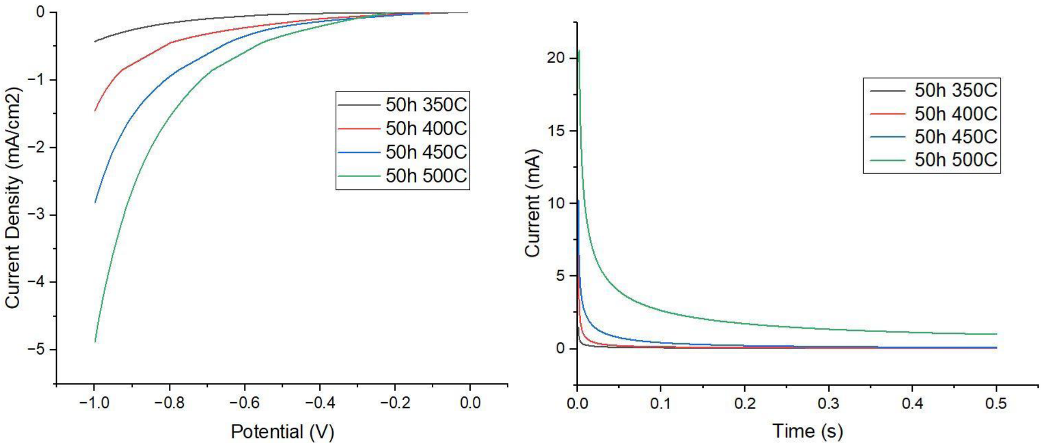

FIGURE 3. Different annealing temperatures for a) LSV and b) CA

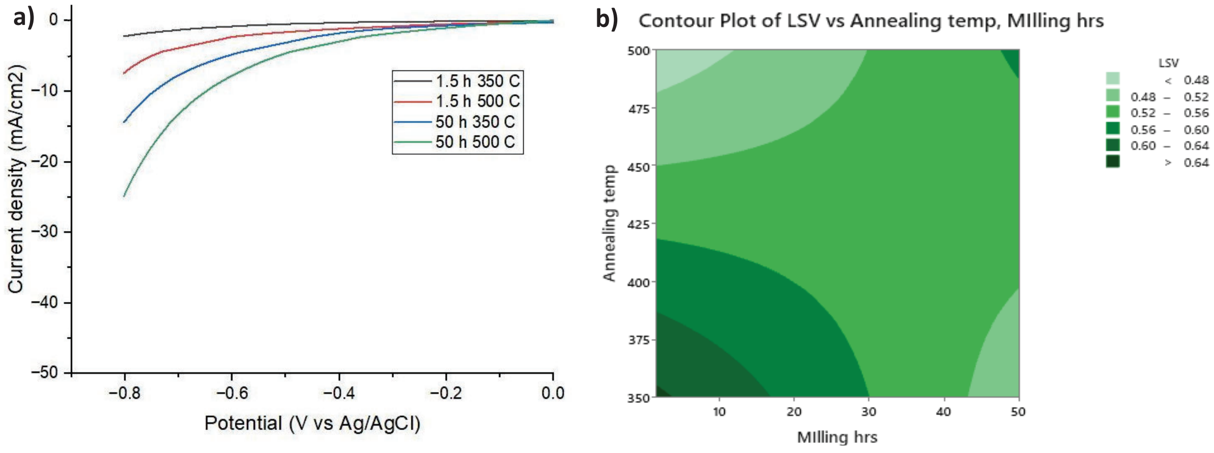

FIGURE 4. a) LSV analysis for two-level factorial design and b) Contour plot of LSV

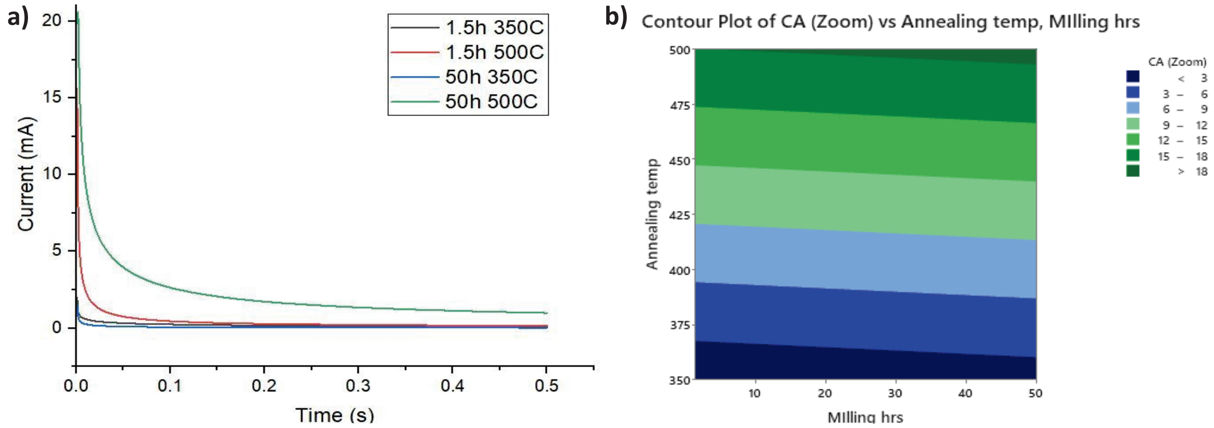

FIGURE 5. a) CA analysis for two-level factorial design and b) Contour plot of CA

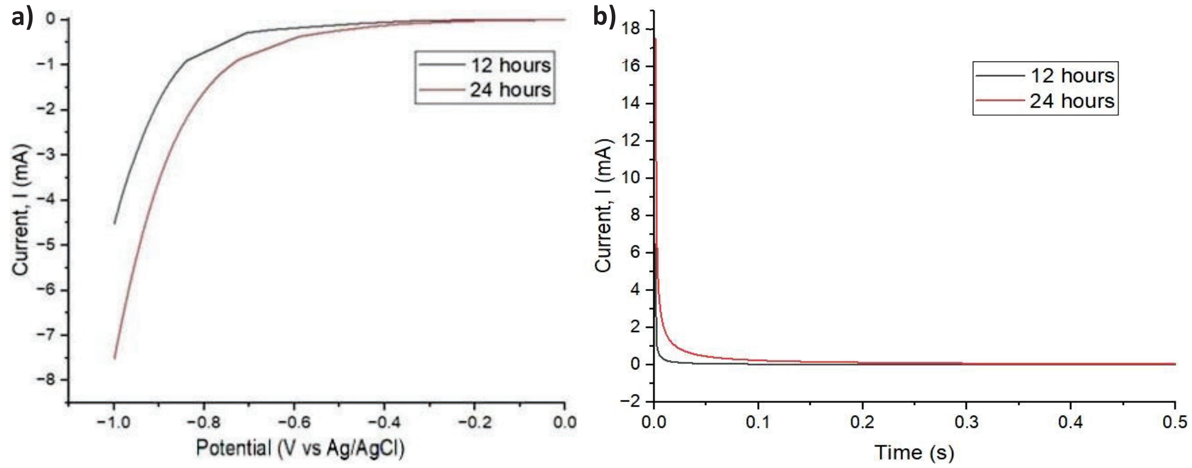

FIGURE 6. a) LSV and b) CA of the best annealing temperature at different milling hours

Based on the evaluation, two samples were chosen for comparison. The baseline sample was milled for 1.5 h and annealed at 350 °C, resulting in limited nitrogen incorporation and insufficient graphite exfoliation, leading to lower quality and more impurities. In contrast, the optimal sample was milled for 50 h and annealed at 500 °C, promoting through exfoliation and higher nitrogen doping. Although this increased structural defects, it significantly improved the catalytic properties and overall performance of NDG.

Several studies have demonstrated that nitrogen doping in graphene indeed enhances its catalytic activity for oxygen reduction reactions (ORR). The doping of nitrogen atoms into the graphene lattice creates various types of nitrogen functionalities when melamine is used as a nitrogen source. These nitrogen configurations introduce defects and active sites within the graphene structure. For example, Granzier-Nakajima et al. (2019) reported that nitrogen doping in graphene through thermal annealing processes increases the density of defects and active sites, thereby enhancing the material's performance for ORR. Additionally, another study highlighted treatment such as thermal annealing with nitrogen precursors like melamine, significantly enhance the nitrogen content in graphene, leading to improved catalytic properties (Yokwana et al. 2023).

STRUCTURAL AND MORPHOLOGY ANALYSES

Based on the DOE results, the sample milled for 1.5 h and annealed at 350 °C was classified as 'bad', while the sample milled for 50 h and annealed at 500 °C was classified as 'good'. Figure 7 presents the Raman spectra of NDG for the good and bad samples. The defect of NDG can be identified by peak shifting and broadening (Seok et al. 2023). Both samples exhibited D, G, and 2D peak locations at 1340 cm^{-1}, 1581 cm^{-1}, and 2689 cm^{-1}, respectively, although with differing intensities of these bands (Jin et al. 2011). The I_D/I_G ratio, indicative of defect density, was notably higher for the longer milling duration with a high annealing temperature (50 h, 500 °C) which is 1.73, indicating superior structural integrity and higher defects compared to the shorter milling duration with a lower annealing temperature (1.5 h, 350 °C) which is 0.40. The value of I_D/I_G increases simultaneously with the increases in milling duration. The intensity of the D band increases while the G band decreases when the milling duration increases (Xue et al. 2015). This is because the defect was created more at longer milled NDG. The value of I_D/I_G also shows the sample milled for a longer milling duration was better than the sample milled for a shorter time (Childres et al. 2013).

The morphology of NDG samples can be observed in Figure 8(a)) with the 1.5 h milled NDG annealed at 350 °C and Figure 8(b) shows the 50 h milled NDG annealed at 500 °C, respectively. Both figures show a thin layer morphology with a magnification scale of 500 nm, indicating the presence of graphene layers achieved through optimized annealing techniques. Higher annealing temperatures facilitate greater nitrogen incorporation and improve the structural characteristics of NDG. This enhancement is further supported by the morphology images, which illustrate well-defined graphene layers in the good sample compared to the less structured morphology observed in the bad sample. This structural difference correlates with the observed differences in Raman spectra and I_D/I_G values between the samples. Although transmission electron microscopy (TEM) can provide atomic-scale lattice visualization, the exfoliation degree, defect formation, and nitrogen incorporation of NDG in this study were sufficiently confirmed through complementary Raman spectroscopy, XRD peak broadening analysis, and XPS nitrogen configuration characterization.

The systematic comparison of milling duration and annealing temperature confirms that longer milling durations coupled with higher annealing temperatures lead to superior NDG properties, in terms of structural integrity and defect density. This understanding of the critical importance of optimizing processing parameters to achieve desired material characteristics for advanced applications like catalysis.

To investigate the content of nitrogen atoms in NDG synthesis, XPS was performed. XPS analysis was performed on 20 mg of NDG powder by measuring single random spots on the pressed sample with a scanning area of 300 × 700 µm. The measurement sensitivity was 0.1 atomic percent (0.1 at. %). The elemental composition at the analysed spots the sample milled for 1.5 h and annealed at 350 °C was C=66.99 %, N=28.94%, and O=4.08%, while for the sample milled for 50 h and annealed at 500 °C, the composition was C=58.51%, N=38.19%, and O=3.31%. The XPS survey confirms that the sample annealed at 500 °C exhibits a higher nitrogen content, aligning with findings from Raman spectroscopy and FESEM analysis. Further analysis of XPS spectra in Figure 9(a) and 9(c) shows the binding energies of C elements for the 1.5-h, 350 °C sample and the 50-h, 500 °C sample, both showing characteristic sp^2 bonding (C=C, 284.6 eV). Figure 9(b) and 9(d) details the binding energies for N elements, indicating the presence of various nitrogen species such as pyridinic (N6, C-N, 399 eV), pyrrolic (N5, C-N, 400 eV), and graphitic (C-N, 401 eV) (Lee et al. 2017). These nitrogen forms are recognized as catalytically active sites for ORR, with pyridinic and graphitic nitrogen suggested as primary active sites due to their low electron transfer barriers and high selectivity (Liu et al. 2012).

XPS spectra commonly differentiate pyridinic-N (binding energy ~398.1-399.3 eV) and graphitic-N (401.1-402.7 eV) in nitrogen-doped carbon materials and their ratio (NP:NG) is widely recognized as a key factor modulating electrocatalytic activity by affecting active site availability and electronic properties. Pyridinic-N often serves as active sites at edges facilitating ORR intermediates adsorption, while graphitic-N contributes to conductivity and electron transfer. Based on Figure 9, it indicates that the sample milled for 50 h and annealed at 500 °C contains elevated amounts of both pyridinic-N and graphitic-N. Consistent with Ning et al. (2019) who reported that ORR catalytic activity in nitrogen-doped carbons depends not merely on the total nitrogen content but on the pyridinic-to-graphitic ratio (NP:NG) - which affects electron transfer kinetics. The sample shows an optimized NP/NG ratio correlating with its observed high onset potential and current density (Lv et al. 2018; Ning et al. 2019). Furthermore, edge-site pyridinic-N is identified as active adsorption sites for ORR intermediates via XPS in Xing et al. (2014) study. These findings validate that both nitrogen configurations in appropriate proportions are necessary for improved ORR electrochemical performance.

The synergistic presence of pyridinic-N and graphitic-N modulates the local charge density of adjacent carbon atoms, lowering the energy barrier for oxygen adsorption and facilitating a more favorable four-electron ORR pathway (Qu et al. 2010; Xing et al. 2014). Pyridinic-N primarily enhances adsorption of oxygen intermediates at edge sites, while graphitic-N improves electron mobility within the basal plane and contributes to enhanced electrical conductivity (Ning et al. 2019). This electronic modulation provides a mechanistic explanation for the enhanced onset potential and current density observed at higher annealing temperatures.

While increased I_D/I_G values and higher nitrogen incorporation enhance the density of catalytically active sites, it is important to consider the trade-off between defect generation and structural integrity. Excessive defect formation may disrupt the sp² carbon network, potentially reducing electrical conductivity and long-term material stability. However, in electrocatalytic applications such as ORR, a moderate level of defects is desirable as defect sites serve as adsorption and reaction centers for oxygen intermediates. The results of this study suggest that annealing at 480-500 °C provides an optimal balance, where nitrogen incorporation and active site density are maximized without severely compromising structural continuity. Therefore, although defect density increases at higher annealing temperatures, the improved catalytic performance indicates that the structural disruption remains within an acceptable range for practical electrocatalytic applications. For large-scale production, this balance between defect-induced activity and structural stability is critical and has been considered in determining the optimized processing window.

In summary, comprehensive characterization techniques validate the correlation between processing parameters and NDG properties. While higher annealing temperatures generally enhance NDG performance. This understanding is pivotal for advancing NDG synthesis optimization for diverse applications, including catalysis.

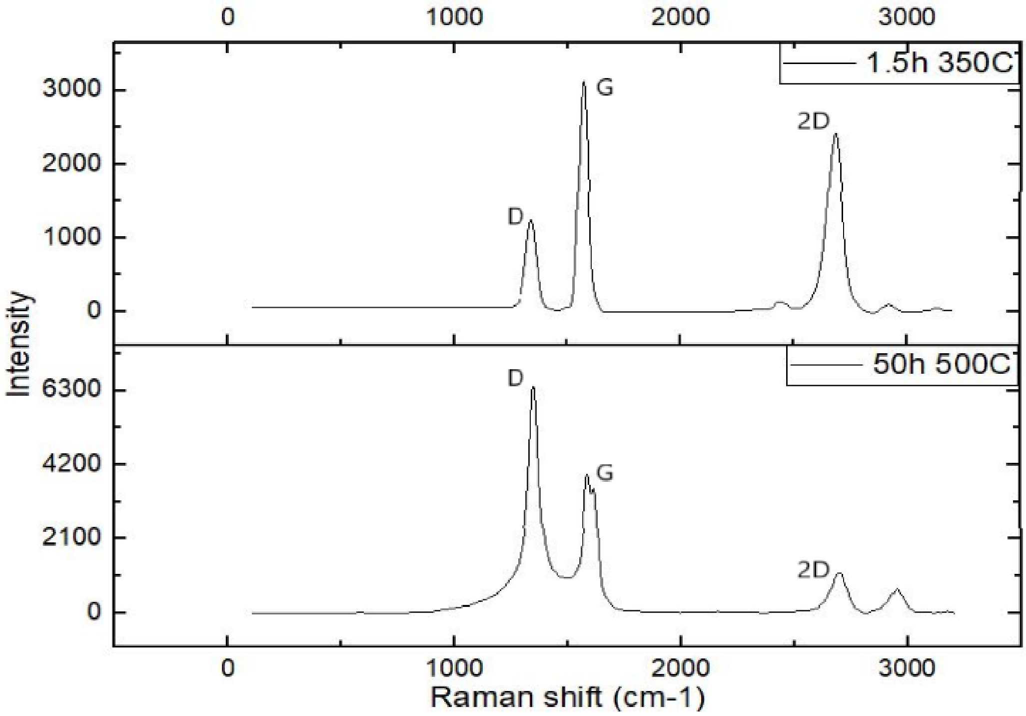

FIGURE 7. Effect of bad and good condition from the annealing temperature for Raman spectra

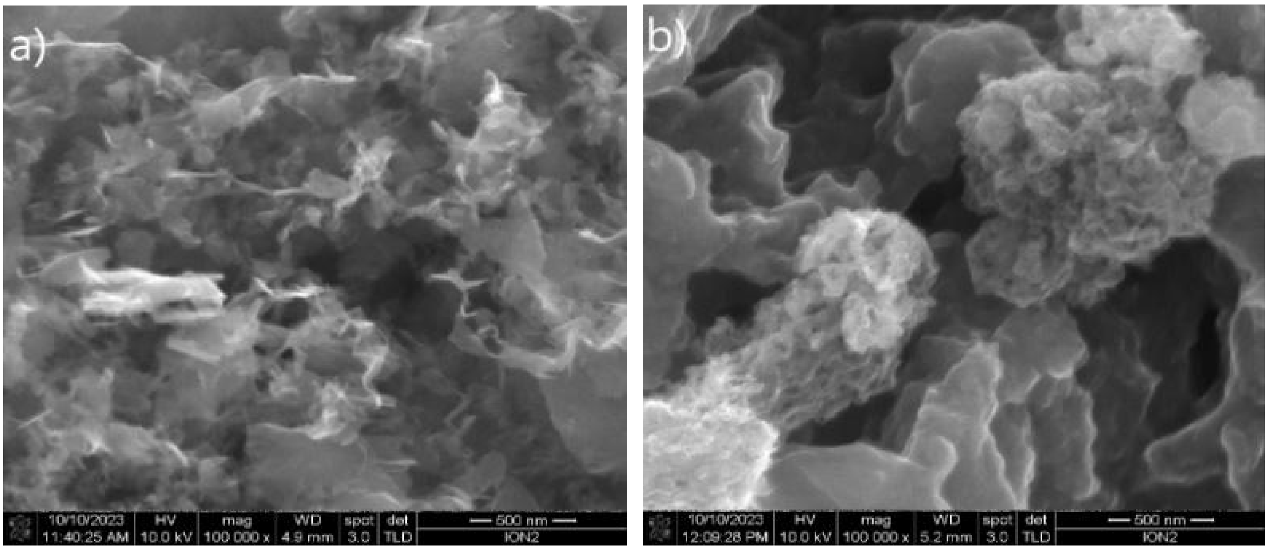

FIGURE 8. FESEM for a) 1.5 h, 350 °C and b) 50 h, 500 °C

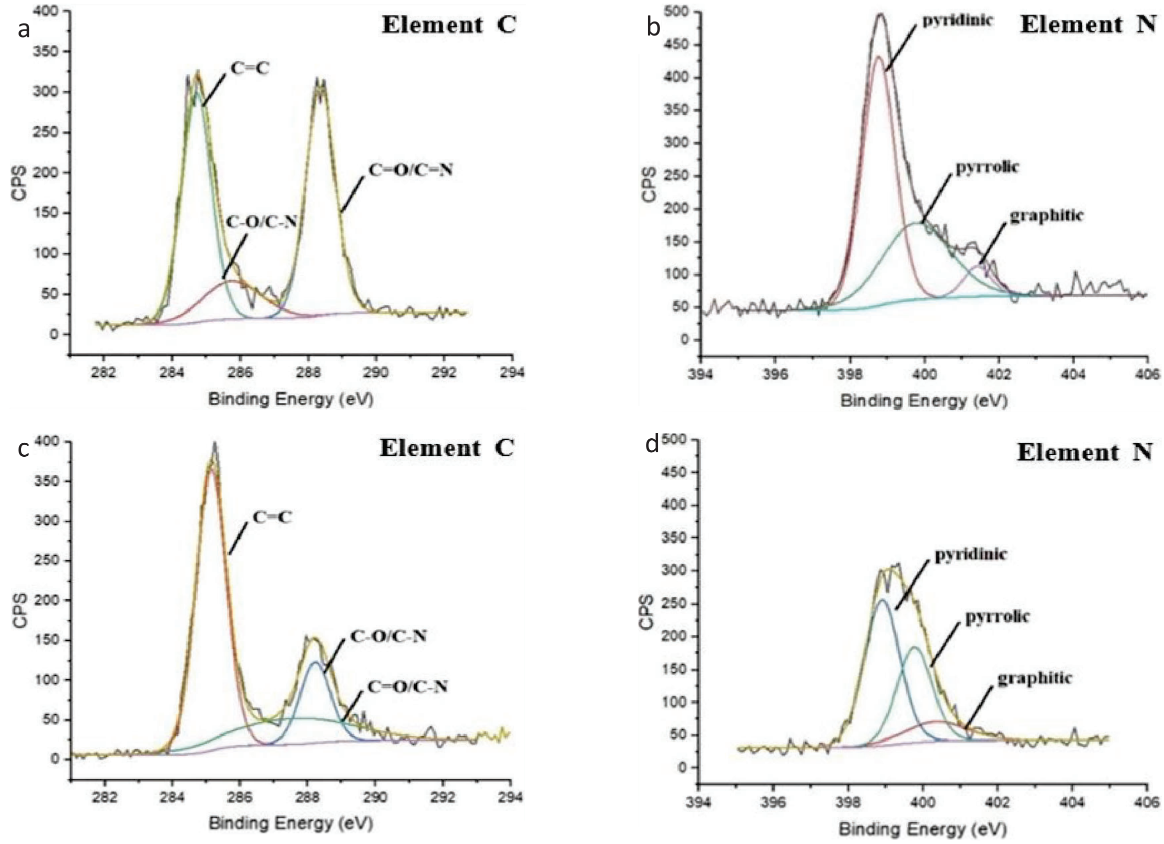

FIGURE 9. Binding energy for 1.5 h 350 °C a) C, b) N and 50 h 500 °C c) C, and d) N

CONCLUSION

The study has successfully demonstrated that annealing techniques significantly expedite the synthesis of NDG catalysts, effectively overcoming the time-intensive limitations inherent in traditional ball milling processes. Comprehensive analyses using Raman Spectroscopy, XRD, XPS, and OCP measurements showed notable enhancements in structural integrity, nitrogen incorporation, and catalytic performance. The optimized NDG samples exhibited an I_D/I_G value of 1.73, a nitrogen content of 38%, and a robust electrochemical current of 19 mA, confirming their enhanced suitability for catalytic applications. These findings suggest that annealing not only improves the efficiency of NDG production but also enhances the material's functionality, making it a promising candidate for various advanced catalytic applications.

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*Corresponding author; email: nordin_sab@upm.edu.my