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The role of biocatalysts in the synthesis of graphene nanosheets from sub-bituminous coal

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ABSTRACT

The synthesis of graphene nanosheets (GNs) from sub-bituminous coal aims to increase the added value of coal in a cheap, easy and proclaimed this method on an industrial scale. The addition of biocatalyst (BFS) in the pyrolysis process can reduce the reactive temperature of the pyrolysis process so that the combustion reaction runs better at low temperatures of 200-300℃. Followed by hydrothermal carbonization of coal at 180℃ for 6 h with the addition of pyrolysis liquid smoke. Filter the results and exfoliate using 24 kHz ultrasonication for 30 min. Then centrifuge at 10,000 rm for 10 min to separate the solids. Wash the solids with deionized water to obtain a neutral pH. Using FESEM and TEM to obtain the morphological characteristics of GNs, structural characterization was studied using XPS, FTIR, and XRD. The GNs produced using BFS yielded 7–8 layers of Graphene, and a crystal size of 2.7 nm showing promising efficiency from the methodology used.

1. Introduction

In recent decades, phenomenal developments have been in Graphene's commercially viable large-scale synthesis [1–3]. Graphene is a multi-functional nanocarbon for various applications, especially energy storage [45678], composites [7810], sensors [9111213], and membranes[141516]. Several methods in manufacturing graphene nanosheets, such as graphene oxide chemical reduction [171819], thermal exfoliation [20212220], solvent-thermal method [2324], liquid phase exfoliation [252627], and CVD[28298] still need help with problems such as small-scale preparation, complex processes, or high costs, thus limiting broad GNs applications[303132]. Therefore, developing a simple and efficient method to produce GNs for industrial use is necessary.

Coal is cheap but has a high carbon content[333435]. Currently, the role of coal as a fossil fuel is discouraged, especially after the Paris Agreement guidelines[363738], because its combustion directly releases greenhouse gases [3940] and other pollutant components if its disposal is not treated first[4142]. Thus, coal is environmentally and economically beneficial to produce new value-added materials such as Graphene[4344]. Coal can produce Graphene of good quality[24546]. Conventional graphene production methods such as Hummers[474849] require a long time, risk explosion, and are bad for the environment[5051]. Some researchers use the pyrolysis process in converting coal to Graphene[252], but other processes must be combined to minimize carbon compounds' loss and exhaust gases' loss. Pyrolysis is currently attracting the attention of researchers to obtain charcoal (biochar) based on the carbonization of dry raw materials in O_2-free conditions [5354]. This pyrolysis process is straightforward and inexpensive [55]. Vijapur et al. synthesized Graphene from sub-bituminous coal by a pyrolysis process which decomposes coal into carbon gas as graphene domains to form graphene sheets[56]. Fuertes et al. (2010) analyzed Graphene's chemical and structural carbon properties resulting from pyrolysis and hydrothermal corn cobs[57]. Hao Xu et al. (2014) prepared graphene nanosheets from coal-tar pitch by adding Al as a catalyst using the pyrolysis method[58].

Biocatalysts are a promising strategy for supporting the concept of green chemistry, which is essential for the industry[59]. As a biocatalyst, enzymes have particular characteristics and are active, readily available, and environmentally friendly[60]. Charles D. Scott (1994) modified enzyme-reducing agents to increase coal conversion to liquid[61]. Enzymes act as biocatalysts that work

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effectively at moderate temperatures and pressures close to the environment[62]. Biocatalyst is a heterogenous catalyst based on organic matter[63]. Ishenny (2018) patented a Biocatalyst Fuel Saver (BFS) product derived from used cooking oil enzymes as an environmentally friendly liquid medium, has an international patent, and has been developed commercially as a fuel-saving biocatalyst. Carbonization technology adds BFS to biomedical waste before the combustion process. BSF can inhibit activation energy so that it inhibits the reactive temperature of combustion from 2400 °Fto 800 °F at normal pressure[64].

Based on the preceding, we report a new method for producing environmentally friendly and mountable graphene nanosheets for industrial needs. Sub-bituminous coal in Selensen Village, Riau, Indonesia, is used as a raw material for graphene nanosheets. We use pyrolysis and hydrothermal techniques in the synthesis of GNs. We also compared the GNs obtained by adding BFS as a biocatalyst.

2. Experimental

2.1. Sample preparation and pyrolysis process

Sub-bituminous coal in Selensen Village -Riau, Indonesia, begins by removing the external surface impurities of coal, such as soil originating from the mining process in coal with 70 % alcohol, followed by drying in an oven at 70°Cfor 1 h. Coal that has been cleaned and dried, crushed, and sieved (size 100 mesh = 150 μm), This coal powder is called BS. Put 50 g of BS into the pyrolysis reactor. Fig. 1 shows a series of pyrolysis devices. Set the temperature at 200-300℃; the pressure is 1 atm, and the slow stirring is 300 rpm. Perform the pyrolysis process for 3 h. The pyrolysis process produces carbon residue (BS-1); Syngas condenses into 3.8 ml of liquid smoke (LS) with pH 3.5.

As much as another 50 g of BS, add 12.5 g of BFS, mix thoroughly, and put into the pyrolysis reactor. Carry out the pyrolysis process under the same conditions and time as BS-1. The carbon residue produced by adding BFS is called BS-2, and the resulting liquid smoke (LS) is 4.6 ml with a pH of 3.0.

2.2. Hydrothermal process and exfoliation

Furthermore, hydrothermal processes were carried out on BS-1 and BS-2 to increase crystallinity and obtain smaller carbon particle sizes[65]. Ten grams of BS-1 was added immediately from pyrolysis liquid and deionized water (100 g), stirred until well blended, transferred into a Teflon-coated stainless-steel autoclave, and maintained at a temperature in the range of 180 °C for 6 h under autogenous pressure. Then it is allowed to cool naturally to room temperature. To separate large solids, use a cellulose ester membrane (MCE with a pore size of 0.45 µm. Transfer the black filtrate to a beaker glass. Exfoliate with ultrasonication at a frequency of 24 kHz for 30 min. Ultrasonication weakens and breaks the Van der Waals bonds between graphene layers[66]. Use - then centrifuged at 10,000 rpm for 10 min, remove the supernatant, and bathe the solid in deionized water until the pH is neutral. Collect the black solid, and dry it in an oven at 105 °C for 6 h (Fig. 2). Do the same with BS-2, producing 4.73 g of BS-1 and 5.17 g of BS-2.

2.3. Material characterization

Analyze the characteristics of the synthesized Graphene: XPS (Kratos Axis Supra) spectroscopy, XRD (Shimadzu XRD-6000, 10-80°, step 2°/minute, step size 0.02°), FESEM (JEOL7600 F, accelerated voltage 20 kV), and TEM (JEOL 2100F, accelerated voltage 200 kV).

3. Results and discussion

Table 1 shows the results of testing Proximate and Ultimate Coal before (BS) and after processing coal into GNs without BFS (BS-1) and using BSF (BF-2).

In the pyrolysis process, coal undergoes compound cracking resulting in the water content and coal carrier gas evaporation [67]. The gas then goes through a condensation process, and the heavy fraction of the gas collects in the tar lifting cone (A). At the same time, the rest, which is in the form of fast light, will pass through the spiral cooler to be cooled with the help of flowing water from the water pump and accommodated in sample con-

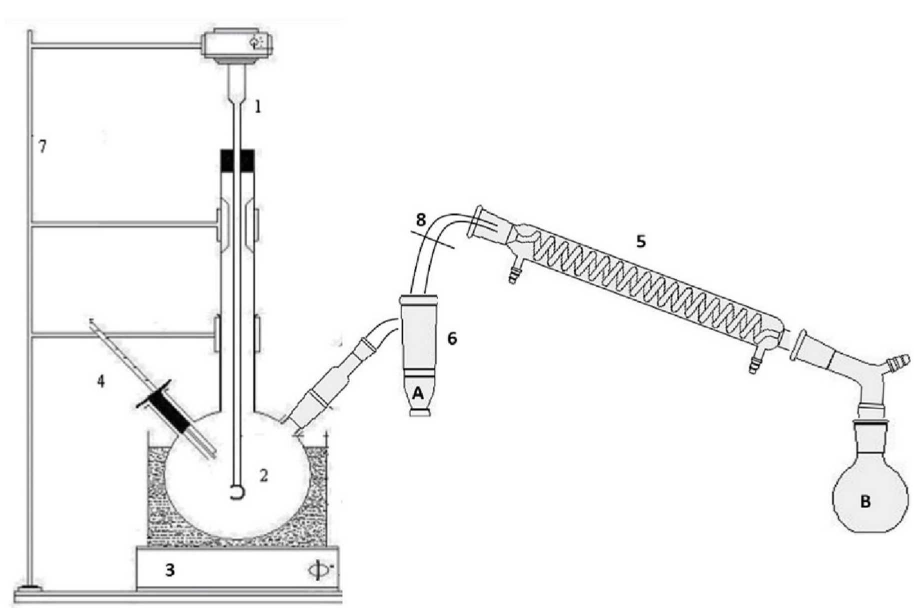

Fig. 1. Pyrolysis Process Description: 1. Stirrer; 2. The reactor, 3. Mantle Heater, 4. Thermocouple, 5. Condenser, 6. Separator (Cyclone), 7. Statives and Clamps, 8. Outlet Control Valve, A. Wax/Heavy Oil/Tar, B. Condensate (immediately liquid).

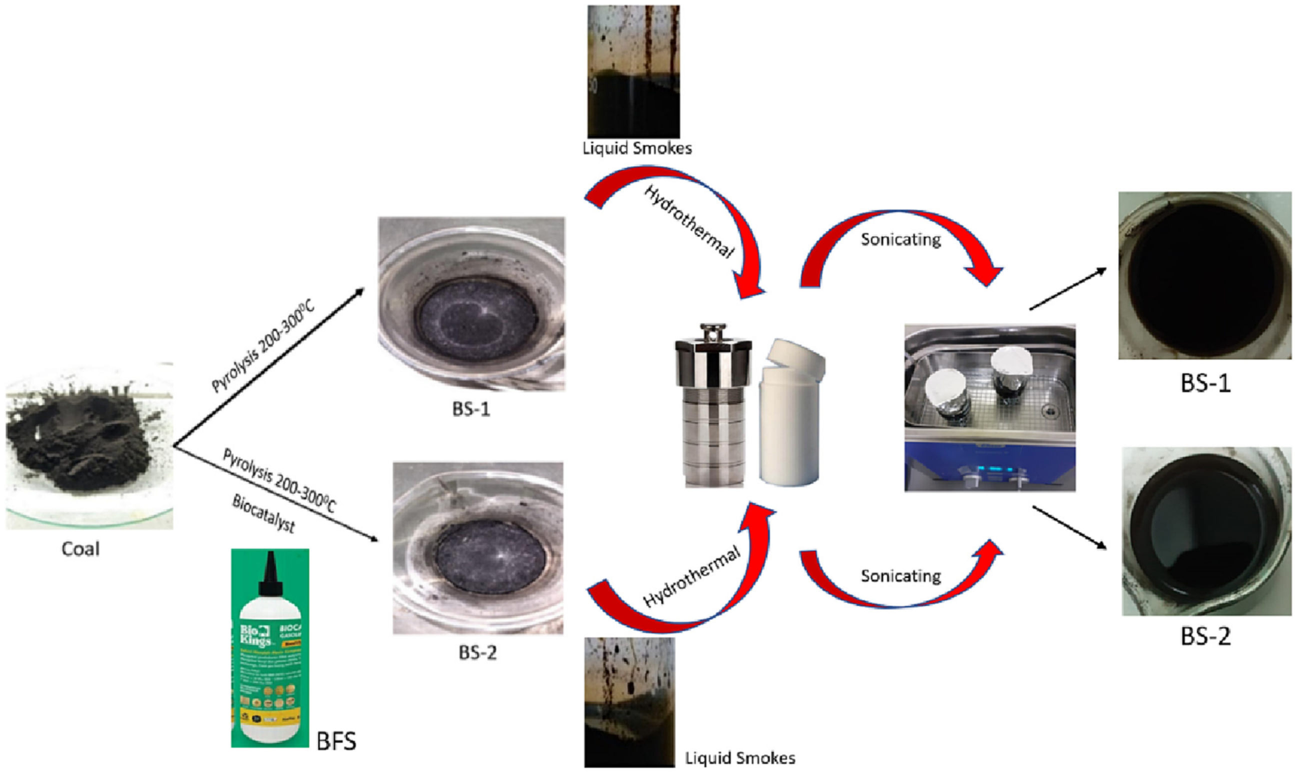

Fig. 2. Synthesis of Graphene Nanosheets from Sub-Bituminous Coal.

Table 1
Analysis Results Proximate and Ultimate.

Sample	Proximate Analysis (wt %, db)				Main Analysis (wt %, daf)			
	IM	Ash	VM	FC	C	H	N	HI
BS	11.54	9,72	45,66	33.09	66,16	5.95	1.01	26,53
BS-1	8.04	4.98	43,52	43,47	71,69	6,24	1.36	19.69
BS-2	1.40	2.49	16,68	79,44	89.48	4.84	1.70	2.84

tainer (B). The complex reactions that occur during the pyrolysis process are bond-breaking, evaporation, and condensation reactions; these reactions are due to changes in the density of aliphatic and aromatic groups[68]. Coal undergoes a reduction process in hydrogen bonds and breaks weak chemical bonds to produce light gas and low molecular weight carbon components (tar)[69]. The condensed gas forms a liquid with compounds from the functional groups that make coal[3470]. The hydrothermal process aims to increase the surface area of the pyrolysis carbon residue[71]. Adding liquid smoke to this process aims to produce porous nanocarbon. The acetic acid contained in the liquid immediately has a group (=O) as an electron donor and ($-CH_3$) as an electron acceptor, so it is advantageous in the process of exfoliation and extraction of Graphene by breaking hydrogen bonds [72](Fig. 3).

Table 1 shows significant changes in carbon bonds with the addition of BSF. The changes occur because the BFS can reduce the Activation Energy Combustion so that the Thermochemistry process runs more perfectly[64] at a temperature of 200–300 ℃. Burning without adding BSF only adds a small score of carbon bound (33.09 – 43.47 %). Reduction volatile matter values indicate change Becomes Syngas forms in the form of H_2 and CH_4 as in the following reaction:

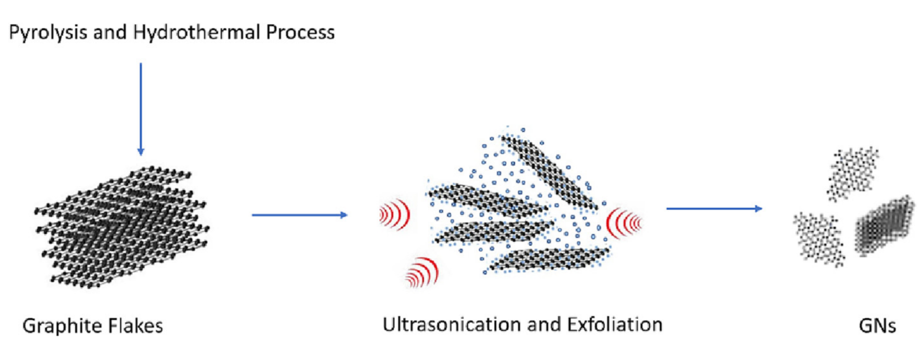

Fig. 3. GNs Preparation Process.

Tar is a particulate and organic impurity or contaminant as a condensation form of this complex mixture. The gasification process of coal and tar needs to be solved. Adding biocatalysts (BFS) can reduce tar formation in the pyrolysis process because some tar has cracked into gas and some into solid carbon[73]. (Fig. 4).

X-ray Photoelectron Spectroscopy was carried out on BS-1 and BS-2 to identify the characteristics of the constituent components of BS-1 and BS-2, shown in Fig. 5.

The spectra of each sample, C 1 s, and O 1 s, are shown in Fig. 5 (a) and (b). With the addition of biocatalyst (BS-2), Fig. 5a peak of 288.7 eV shows an increase in the area of 23.67 %, meaning that there was an increase in the number of sp2 hybridized carbon atoms (C═C), a decrease in the peak area of 26.95 % at 284.7 eV indicates a decrease in the number of sp3 hybridized carbon atoms (C—C)[74]. These C1s spectra prove that BFS plays a role in forming more aromatic rings.

On the other hand, Fig. 5b shows that the O1s BS-2 spectra have a slightly wider area of 17.69 % than the O1s BS-1 spectra[74]; this reduction clarifies the role of BFS in reducing the hydroxyl, carboxyl, epoxy, and carboxylic functional groups in coal.

Fig. 6 (a) Fourier transform infrared (FT-IR) spectroscopy performances from BS, BS-1, and BS-2. BS showed broad peaks at 3219 cm^{-1} and 1365 cm^{-1}, related to the stretching vibration of the OH groups of the adsorbed water molecule. The peaks in wavenumber 2992 cm^{-1} and 2893 cm^{-1} are symmetrical and asymmetrical strain vibrations of $-CH_3$. The peak at 1595 cm^{-1} corresponds to the C═O strain vibration pattern and the aromatic C═C bond. The peak at 1433 cm^{-1} shows the CH bending vibration of the hexane cyclone ring. The peak at 1227 cm^{-1} shows an aliphatic CH vibration. The peak at 1048 cm^{-1} indicates the presence of CO strain vibration[75].

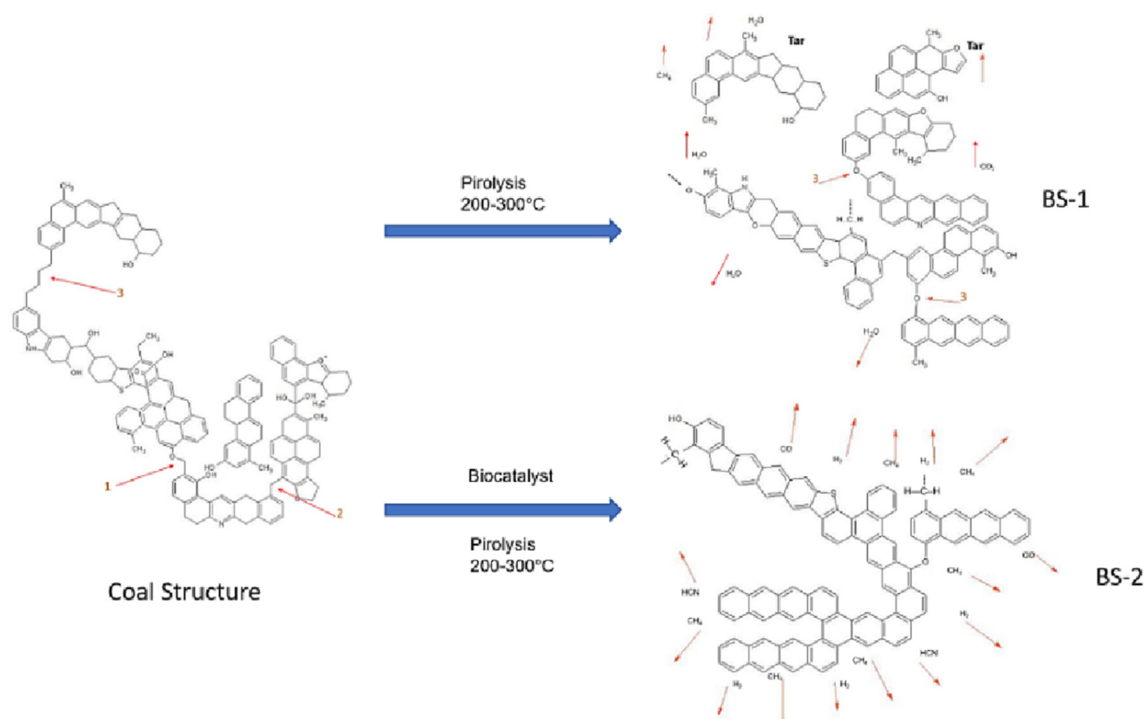

Fig. 4. Thermochemical reactions in coal (BS-1 and BS-2).

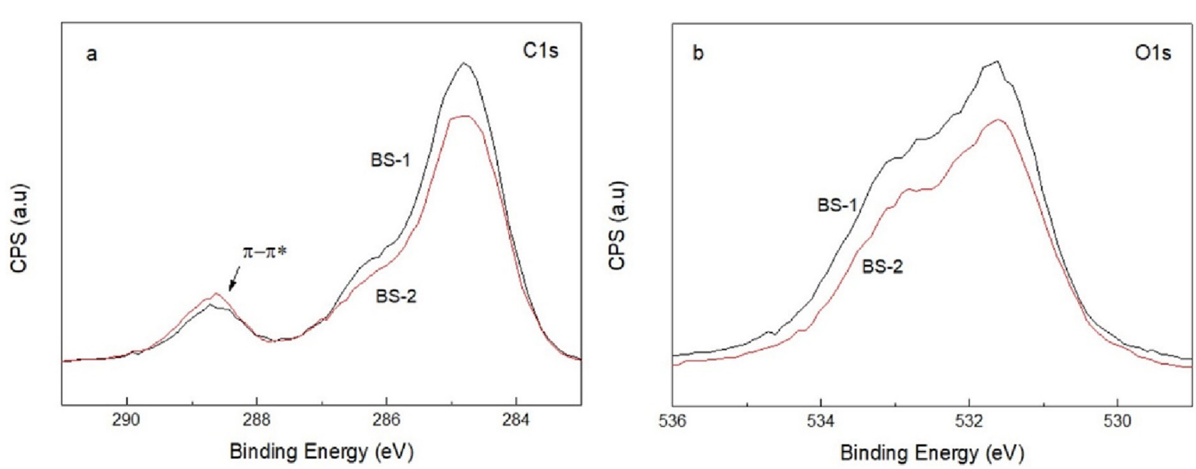

Fig. 5. XPS Spectra (a) C1s, (b) O1s from BS-1 and BS2.

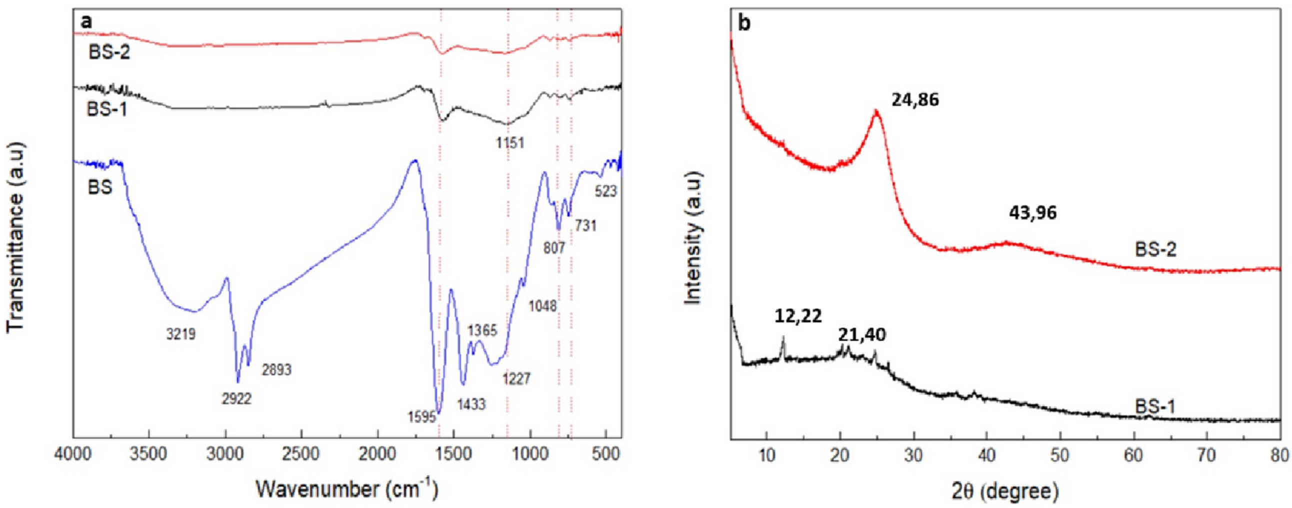

Fig. 6. (a) FT-IR Spectra of BS, BS-1, and BS-2, (b) X-ray Diffraction Spectra of BS-1 and BS-2.

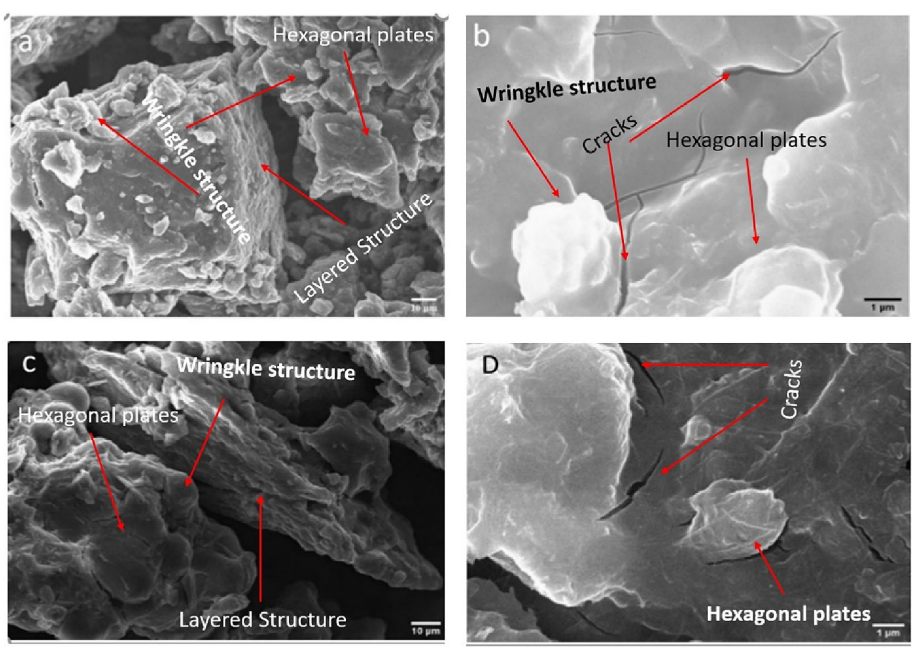

Fig. 7. FESEM morphology (a) BS-1 surface morphology (10 μm) (b) BS-1 surface morphology (1 μm) (c) BS-2 surface morphology (10 μm) (d) BS-2 surface morphology (1 μm).

Meanwhile, the peak at 900–720 cm^{-1} indicates the aromatic group's presence of C—C and C—H[76]. This information illustrates that BS, which is Sub-bituminous coal, has a structure similar to graphite oxide, making it very potential as a raw material for GNs synthesis. There was also the elimination of some of the oxygen functional groups after the synthesis process (pyrolysis and hydrothermal), showing a significant decrease in intensity from BS to BS-1, and seen in (BS-2) there was a slight decrease in relative intensity with the addition of biocatalyst.

Fig. 6b provides information on the structure of the coal during the conversion process (BS-1 and BS-2). The results of X-ray Diffraction Spectroscopy Analysis, which represents the BS-1 and BS-2 XRD patterns where the BS-1 spectral peak is 21.40°broad and low intensity, the peak of 12.22° indicates the presence of carbonyl groups with the distance between layers (d) 7.336 Å. Based on the Scherer equation, BS-1 has a crystal diameter of 21.94–23.85 nm and more than ten stacks of graphene nanosheets. BS-2 XRD data confirmed the presence of graphene nanosheets (2theta peaks 24.86° and 43.96°), the distance between layers (d) 2.583 Å. Calculations based on the Scherer equation, BS-2 has a particle size of 2.78 nm, with 7–8 graphene nanolayers[77]. The above data confirms the successful synthesis of Graphene from coal (BS) by pyrolysis and hydrothermal methods using BFS as a biocatalyst.

The morphology of BS-1 (Fig. 7 a and b) at 800x magnification shows that there is still an uneven distribution of particles on the surface and the presence of non-uniform (amorphous) particles. However, each resulting small sphere with a transparent surface at 1 μm showed the formation of graphene nanosheets which was almost similar to GO[78]. Observations at 800x magnification

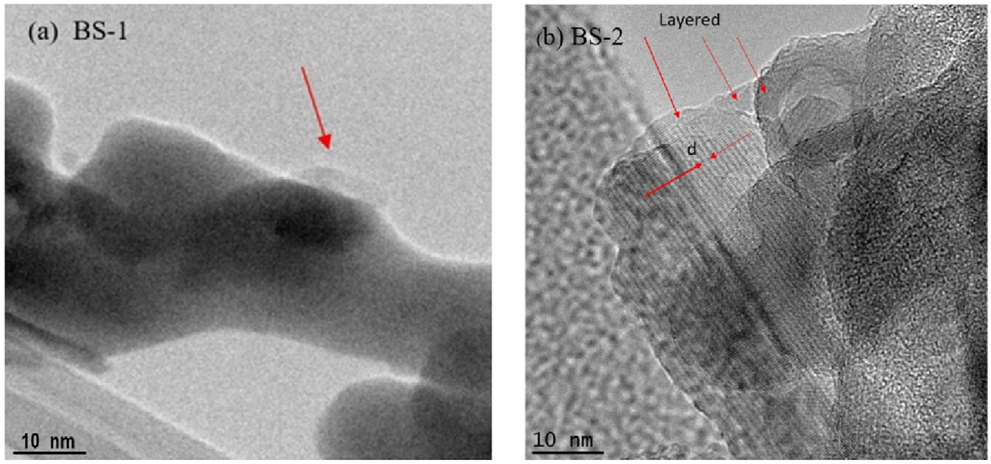

Fig. 8. TEM micrographs of (a) BS – 1 and (b) BS – 2.

on sample BS-2 (Fig. 7 c and d) show an even distribution of particles on the surface and edges that are regular and interconnected, indicating a good increase in density resulting from the pyrolysis process in the presence of a biocatalyst. In contrast, there is a transparent sheet at 2500x magnification observations (Fig. 7c). It consists of multiple sheets (layered) of Graphene with a smooth and even surface. The formation of these graphene sheets indicates that the coal between the graphene layers has been successfully exfoliated[79].

TEM micrograph (Fig. 8) shows that BS-1 and BS-2 have formed GNs. Monolayer graphene sheets are shown as the thinnest and most transparent sheets, as indicated by the red arrows in the figure. In contrast, multilayer sheets are shown in the form of dark spots and dark lines at each edge of the sheet, indicating the detected folds of the graphene sheet parallel to the electron beam[80].

4. Conclusion

We have developed a simple, environmentally friendly, and efficient way to synthesize GNs by adding a biocatalyst to coal in a pyrolysis reactor. The synthesis of GNs goes through the stages of pyrolysis, hydrothermal, and ultrasonication processes. This method does not use hazardous chemicals, produces no waste, synthesizes conditions at low temperatures, is fast, and produces GN with a particle size of 2.7 nm, 7–8 layers, and in an amount of 51 % so that this method can produce GN on an industrial scale.

CRediT authorship contribution statement

Vivi Purwandari: Conceptualization, Investigation, Project administration, Resources, Software, Validation, Visualization, Writing – original draft. **Martha Rianna:** Data curation. **Marpongahtun:** . **Isnaeni Isnaeni:** Investigation. **Yiming Zou:** . **Mahyuni Harahap:** Software, Writing – original draft. **Gratianus Halawa:** Writing – original draft. **Ronn Goei:** Data curation, Investigation, Resources, Software, Writing – review & editing. **Alfred Iing Yoong Tok:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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