N-doped Porous Carbon from Palm Male Flower via Hydrothermal Carbonization

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Abstract: N-doped porous carbon materials were produced from palm male flower using hydrothermal carbonization processes at 200 °C for 24 h followed by N-Doping and carbonization at 700°C for 2 h. N-doping was carried out by impregnation using NH₄OH at 0.5, 1.0, 1.5 M and 2 M. Products were characterized by means of chemical composition and morphology using SEM, XPS, and XRD to characterize specific properties such as physical morpholog, porosity, elemental composition on surface and crystalline structure of PMF. After applying hydrothermal carbonization processes, the results showed substantially increased porosity and surface area with suitable microstructure for N-doped electrodes applications. The highest porosity was obtained at NPC–1.5 M.

1. Introduction
Oil palm industry is one of main economic activities in Thailand. Overgrown of palm male flower become a problem which decrease productivity due to unbalanced proportion between male and female flower. Oil palm planters then require removing this male flower and become agricultural waste. Basically, planters use cut male flower as fertilizer. However, male flowers have fascinating potential to transform to carbon materials because they have organic structure as same as other biomass [1, 12]. Resulting carbon materials can be applied for various applications such as activated carbon and carbon fiber. Using wasted palm flower can help protecting the environment by reducing wasted materials and increase valve on agricultural by-products [2, 3].

Thermochemical process is the main activity in order to transform biomass such as chemical vapor deposition, hydrothermal treatment and pyrolysis or carbonization are examples of thermochemical process [4]. These process porous carbon material which shows adsorptive, mechanical and electrical properties, suitable for novelty applications. Porous carbon materials are increasing in popularity of environmental and energy utilizations [13, 14, 15]. Due to porous carbon’s high porosity, it’s perfectly used as electrodes. Unfortunately, electrochemical properties are limited by charge accumulation mechanics [5, 6]. Therefore, the study introduced N-doping with porous carbon derived from palm...
male flower. The procedures are divided to 2 steps – hydrothermal treatment and doping of nitrogen using NH\textsubscript{4}OH solution. Another step is carbonization process to generate porous structures at high temperature and inert gas flow. Furthermore, characterization by means of morphology and chemical compositions are carried out to investigate and confirm the resulting products for further applications.

2. Material and method

2.1 Material
Palm male flower was obtained from cultivator in south of Thailand.

2.2 Preparation of N-doped Porous Carbon from palm male flower
Palm male flower (PMF) that used as feedstock for synthesis of N-doped Porous Carbon (NPC). Firstly, the feedstocks were crushed and sieved into the size of 800 µm, then, dried in an electrical oven at 90 °C for overnight. 20 g of prepared PMF was mixed with 40 g of several concentrations of ammonium solution (0.5, 1, 1.5, 2 M). Subsequently, the slurry was packed into a stainless-steel autoclave, and heated to 200 °C for 24 h to serve a nitrogen doping. Afterwards, the solid product was quenched via water and dried at 100 °C until dried. Finally, PMF-NPC were obtained from the carbonization at 700°C for 2 h. Furthermore, the prepared NPC was washed several times with deionized water for cleaning up impurities and then dried and kept for further characterization.

2.3 NPC characterization
N-doped porous carbon from palm male flower via hydrothermal carbonization were characterized for physical morphology, porosity, elemental composition, and crystalline structure by scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffractometer (XRD), respectively.

3. Results and discussion

3.1 Physical Morphology of N-doped Porous Carbon (NPC)

Figure 1. SEM micrographs of NPC products under 1.5 M of ammonium solution a) side view and b) top view.

Figure 1 shows the SEM micrographs of NPC obtained from hydrothermal and carbonization approaches. The surface of NPCs at the ammonia concentration of 1.5 M was best condition, as illustrated in Figure 1a and b, respectively. This is because ammonia was served as activating agent. Moreover, results indicate that the decomposition reactions occurred during the carbonization had led to the production and release of volatiles from the raw feedstock, and the activation was occurred simultaneously remaining the NPC product with high porosity.
3.2 Elemental Composition of N-doped Porous Carbon (NPC)

**Table 1.** Elemental composition of NPC conducted by X-ray photoelectron spectroscopy, XPS.

| Conditions      | Elemental compositions (%) |
|-----------------|----------------------------|
|                 | N 1s          | O 1s          | C 1s          |
| Palm male flower, PMF | 1.072        | 23.465        | 75.462        |
| PMF-0.5 M       | 1.202        | 22.449        | 76.348        |
| PMF-1 M         | 1.650        | 20.732        | 77.616        |
| PMF-1.5 M       | 2.504        | 20.271        | 77.225        |
| PMF-2 M         | 2.845        | 18.626        | 78.529        |

XPS was conducted to confirm the elemental composition on NPCs surface. As listed in Table 1, the carbon contents are 75.462 – 78.529 at. %, the oxygen contents are 18.626 – 23.465 at. % in PMF and PMF-NPC, respectively. The existence of oxygen in the surface of the PMF-NPC is an oxygen atom in biomass structure [1, 3, 5]. The nitrogen functional groups that usually come from the doping agents and precursors tends to increase by concentration of NH₄OH.

3.3 Crystalline structure of N-doped Porous Carbon (NPC)

[XRD spectra image]

**Figure 2.** XRD spectra of palm male flower under conditions of several concentrations of ammonium solution a) 0, b) 0.5, c) 1, d) 1.5 and e) 2 M.

XRD measurement was investigated to examine the phase structure of NPC after activation with NH₄OH, as shown in Figure 2. The broad diffraction at a 2θ angle around 10 - 80° was evidently noticed for all samples, corresponding to the carbon. The broad characteristic feature indicates the major presence of amorphous phase. In addition, the peak is found the structure of carbon and nitrogen that may be left from activation of NH₄OH after washing.

4. Conclusion

NH₄OH solution decorated in hydrothermal treatment explores the efficient technique for synthesis of nitrogen-doped porous carbon as a novel carbon material. However, the combination step using carbonization could be implied that the pore formation and purification of pure carbon have been existed. The nitrogen percentage of NPCs are significantly enhanced with an increasing of concentration of NH₄OH. Besides, the nitrogen contained in carbon structure, their porosity and carbon content were also developed since ammonium molecules on carbon surfaces assisted an activation under a high temperature during carbonization, simultaneously. The highest porosity was
obtained at NPC–1.5 M. Regarding vast physicochemical characteristics (i.e. huge surface area, containing N atom, high C composition), it can be implied that produced NPC could be further applied in various areas of electronic devices.

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