



Preparation and Characterization of APTES-functionalized Graphene Oxide for CO₂ Adsorption

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ABSTRACT

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The increase of carbon dioxide (CO₂) concentrations in the atmosphere is one of alarming issues nowadays. Thus, development and optimization of new solid adsorbents is highly demanded for the establishment of energy-efficient and high-throughput CO₂ capture processes in industry. Herein, graphene oxide (GO) adsorbent was prepared and further functionalized by amine functionalization, 3-aminopropyltriethoxysilane (APTES). GO was prepared using Modified Hummer's Method followed by functionalization with APTES. GO and APTES-GO were characterized using Fourier Transmission Infrared Spectroscopy (FTIR), Raman spectroscopy, scanning electron microscope (SEM), and N₂ adsorption isotherm. The N₂ adsorption capacity for APTES-GO at 15 bar is the highest (179 mmol/g) compared to other lower pressures and pristine GO at any pressure. FTIR analysis showed significant peaks at 1474 cm⁻¹ and 1440 cm⁻¹ indicating the presence of N-H and NH₂ groups, respectively.

Keywords:

Graphene oxide; carbon dioxide; functionalization; CO₂ adsorption

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1. Introduction

Recently, issues on global warming have been widely discussed around the world. Increasing amount of carbon dioxide (CO₂) in the atmosphere, is mainly caused by fossil fuel combustion for power generation [1] has led to global warming [2] and climate change [3]. Statistic shows that CO₂ emission has elevated around 80 % between 1970 and 2004 which causes the concentration of CO₂ in the atmosphere exceeds by 25 % as compared to 1950 [4]. Alarmingly, it is reported that the global temperature of the earth is increasing about 1.5 °C since 21st century. Hence, the release of CO₂ in the atmosphere need to be minimized instantly [5]. To reduce the concentration of CO₂ in the atmosphere, carbon capture and storage (CCS) technologies have been studied to store the gas in geological formation [6]. There are a few separation techniques that can be implemented in CCS

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system which includes physical absorption [6], adsorption [7], membrane absorption [8], and cryogenic separation [8].

Previously, researchers have conducted many studies on graphene-based adsorbents for CO₂ capture. Graphene-based adsorbents including mesoporous graphene oxide/TiO₂ nanocomposite, thermally treated graphene nanosheets, holey graphene frameworks and 3-D graphene-based porous adsorbent [9] have been proven to be efficient adsorbents for the CO₂ capture. Meanwhile, the mechanisms and the kinetics of adsorption using these types of adsorbents were not sufficiently studied [10]. Researchers recently favoring CO₂ capture using solid adsorbents since it is more cost effective and energy efficient [11]. Adsorbents such as zeolite [12], metal organic frameworks (MOFs) [12-13], carbon fiber [14] and carbon materials [15] were efficient enough to capture CO₂. However, when it comes to industrial applications that use enormous amounts of adsorbents, there are some complications occurred [11]. For instance, zeolites are good adsorbents but have low adsorption capacities at high temperature while other chemical adsorbents need more complex preparation [16] causing the cost to be more expensive.

Graphene oxide (GO) is an oxygen-containing derivative of graphene [17] is one of a potential material for carbon capture [18]. Its high surface area, high porosity [11] and active surface functionalities [16] has made GO as a value added material for CO₂ adsorption. Unfortunately, the application of GO for CO₂ adsorbent is limited due to low CO₂ adsorption capacity [18]. Therefore, modification of GO is vital to overcome the aforementioned issue. Since GO consists of hydroxyl and carboxyl, on its edges and epoxy on basal plane [19] functionalization have shown a great modification method [17]. These are all oxygen-containing chemical groups that tremendously vulnerable to chemical modification especially with nitrogenous compounds such as amine [11]. Functionalization of GO with nitrogen atoms in amine groups greatly increase the interfacial binding with CO₂ [4, 16].

In this study, APTES is used to functionalize GO because of its available nitrogen sites and high affinity towards acid gases. APTES is also a promising functionalization agent because of the presence of silylating moieties favorable for the covalent attachment of the functional group [20]. The functionalization of GO with amine-functional group is expected to increase the yield of CO₂ adsorption compared to the use of conventional adsorbents such as activated carbon and graphite. This is because, functionalization of amine on GO will greatly enhance the reactivity towards CO₂ [21]. The ultimate aim of this work is to provide adsorbent with high CO₂ adsorption capacity of by functionalizing GO using APTES and study its physicochemical properties and adsorption capabilities. GO was obtained by oxidation of graphite via simple and easy to replicate modified Hummer's method followed by functionalization of GO with APTES. The GO and the synthesized APTES-GO were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy, Scanning Electron Microscopy (SEM), and nitrogen adsorption isotherm. Hence, it is expected that the findings of this study will contribute a new knowledge to the community as the synthesized material will help in reducing the CO₂ in the atmosphere and resolving the global warming issue.

2. Experimental

2.1 Materials

Graphite powder, sulphuric acid (H₂SO₄, 98 %), hydrochloric acid (HCl, 35 %) hydrogen peroxide (H₂O₂, 30 %), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), (3-aminopropyl) triethoxysilane (APTES, 99 %) ethanol (95 %), were purchased from Sigma Aldrich.

2.2 Synthesis of GO

The GO was synthesized by using Modified Hummer's method. 4 g of graphite powder was added into 100 mL of concentrated H_2SO_4 followed by slow addition of 4 g of NaNO_3 . The solution was stirred using magnetic bar while the temperature need was maintained below $10\text{ }^\circ\text{C}$ in an ice bath. 12 g of KMnO_4 was slowly added into the solution and after the addition; the temperature of the solution increased slowly. Once the temperature reached $35\text{ }^\circ\text{C}$, the brownish mixture was stirred for 30 min. 100 mL of deionized water was added to the mixture and the color of the mixture turned yellowish brown. At this step, the beaker was removed from the ice bath until the temperature increased to $95\text{ }^\circ\text{C}$. The mixture was stirred again for 30 min. After the formation of a brilliant yellow color with bubbles in the solution, 600 mL of distilled water, 20 mL of 30 % H_2O_2 aqueous solution and 100 mL of 10 wt% HCl was added to the mixture. The mixture was inserted in dialysis tubing and soaked in deionized water to expel metal ion and acid until the pH turns neutral. 15 mL of GO was transferred into a clean petri dish and dried for 12 h at $60\text{ }^\circ\text{C}$ [22].

2.3 Synthesis of APTES-GO

GO produced by the previous steps was functionalized using APTES. 5.11 g of APTES was poured into 150 mL of ethanol containing 3.01 g of GO. Next, the mixture was sonicated for 30 min before heated with reflux at $80\text{ }^\circ\text{C}$ for 6 h. The suspension was filtered over a polytetrafluoroethylene (PTFE) membrane with a 0.45 mm pore size followed by washing with 150 mL of ethanol. The solid obtained was dried under vacuum overnight at room temperature [23].

2.4 Characterizations

FTIR was used to study the functional groups that exist on the surface of GO before and after functionalization. Solid sample of GO and APTES-GO were taken in a small size ($\approx 0.3\text{ cm} \times 0.3\text{ cm}$) and were put on the surface of the FTIR scanner. The IR spectra were collected after 32 scans in the $4000 - 500\text{ cm}^{-1}$ region in ATR mode at a resolution of 4 cm^{-1} . A molecular vibrational spectroscopy technique known as Raman spectroscopy has been used for identification and quantitation of samples by providing information about their molecular vibration. This technique involved the shift in wavelength of the inelastically scattered radiation from monochromatic light source (i.e. laser) to identify the chemical and structural information of the samples. Each molecule has a different set of vibrational energy levels, and the photon emitted have unique wavelength shifts. Different peaks in the spectrum correspond to different Raman excitations. Moreover, the Raman spectrum can be interpreted similar to the infrared adsorption spectrum. In this study, Raman spectrum of the samples (RMP-510 with serial number A3S61601) was analyzed in the range of $500-4000\text{ cm}^{-1}$. Scanning electron microscopy (SEM) images were collected using a FEI Quanta 200 ESEM with XL30 microscope.

2.5 N_2 Adsorption Test

In this study, the N_2 uptake for each sample was tested with a custom-made adsorption rig with a simple static volumetric measurement method. This unit is basically equipped with an adsorption cell (AC) and loading cell (LC), a vacuum pump, a K-type thermocouple (to monitor the temperature changes inside the cells) and a digital pressure transducer (to monitor the pressure changes in both the AC and LC). Each GO and APTES-GO was loaded into the AC while N_2 was loaded into the LC until

the pressure reached the required levels. The adsorption capacity of N_2 was tested with various pressure (5, 10, and 15 bar). Because the pressure was set to the desired levels, the experiment was initiated by opening the valve between the LC and AC to introduce N_2 with the GO and APTES-GO in the AC. The pressure changes in both cells were recorded continuously at 5 min intervals until the equilibrium pressure was achieved. The equilibrium state was determined when both the temperature and pressure were constant for approximately 10 min.

3. Results and Discussion

3.1 Morphological Properties

The characterizations of GO and APTES-GO composites were performed through its surface morphology analysis by SEM. Figure 1(a) shows the structure of the pristine graphene oxide sheet. The image shows that GO sheets were well distributed without agglomeration. The surface of GO appears to be flat and smooth. The situation is absolutely different with APTES-GO, the surface appears to be rougher because of the agglomeration and many small scales can be seen.

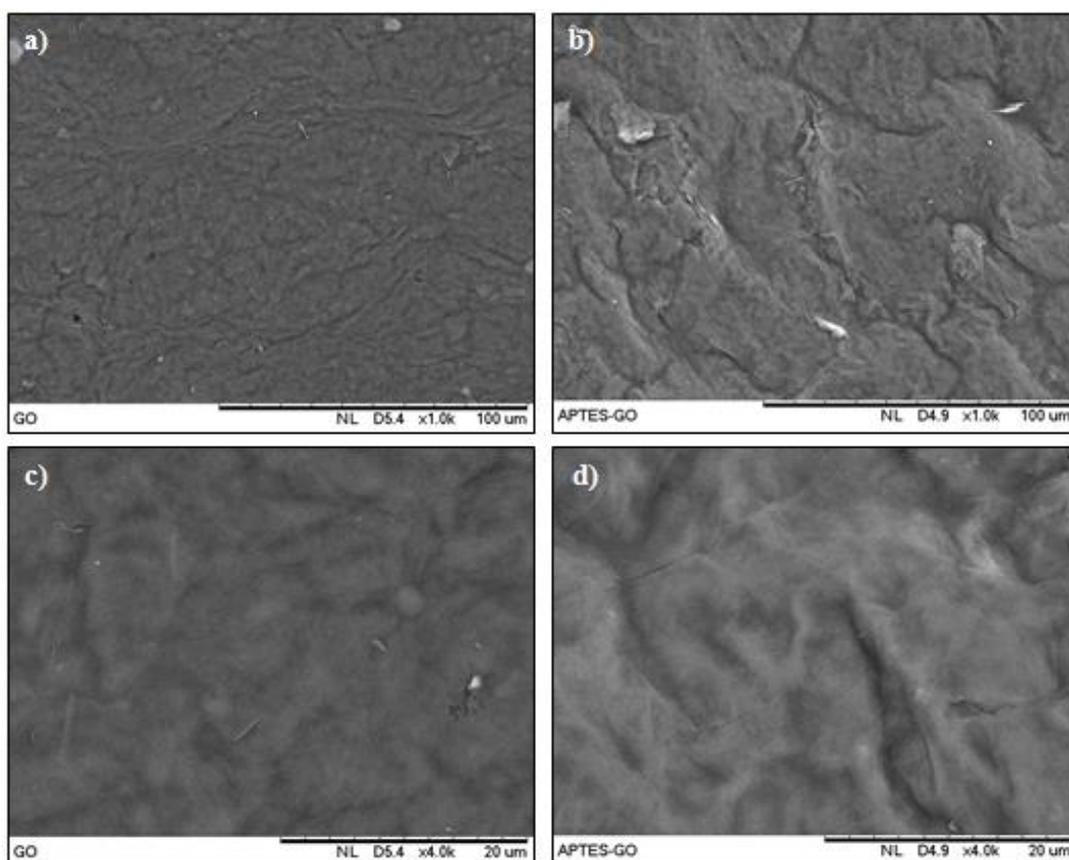


Fig. 1. Morphology of (a) GO (b) APTES-GO under 1000x magnification and (c) GO (d) APTES-GO under 4000x magnification

After APTES grafting, the GO sheets went through strong interfacial interaction with organic layers, which enhances the compatibility between GO sheets [24]. It can be seen in Figure 1(b) and (d) that the APTES-GO show comparatively less uniformity and more roughness than the pristine GO, indicating well grafting of aminosilane and also the compact surface structure.

3.2 Functional Group Study

Figure 2 shows the FTIR spectra of GO and APTES-GO. The peaks of GO attributed to -OH stretching can be seen at 3560 cm^{-1} . The sharp peak at 1715 cm^{-1} is attributed to the C=O stretching of carboxylic acid group [25], 1614 cm^{-1} to the $\text{sp}^2\text{ C=C}$ and conjugated C=O stretching, 1650 cm^{-1} and 1040 cm^{-1} to C-O stretching of phenolic and epoxy groups, respectively. In APTES-GO, the bands in the range of $2850\text{-}3000\text{ cm}^{-1}$ correspond to the bending vibration of CH_2 confirming the attachment of APTES chain molecules. Carbon and hydrogen content also increases because of the alkyl chains associated with APTES [20]. The bands at 1474 cm^{-1} and 1440 cm^{-1} correspond to NH and NH_2 due to the deformation of the hydrogen-bonded amine groups respectively. N-H stretching vibrations are present at 3430 cm^{-1} and C-H stretching bands in the region $2860\text{-}2960\text{ cm}^{-1}$. As an evidence of covalent functionalization, the appearance of absorption peaks can be seen at 1048 cm^{-1} and 1210 cm^{-1} indicating Si-O-C and Si-O-Si , respectively [26].

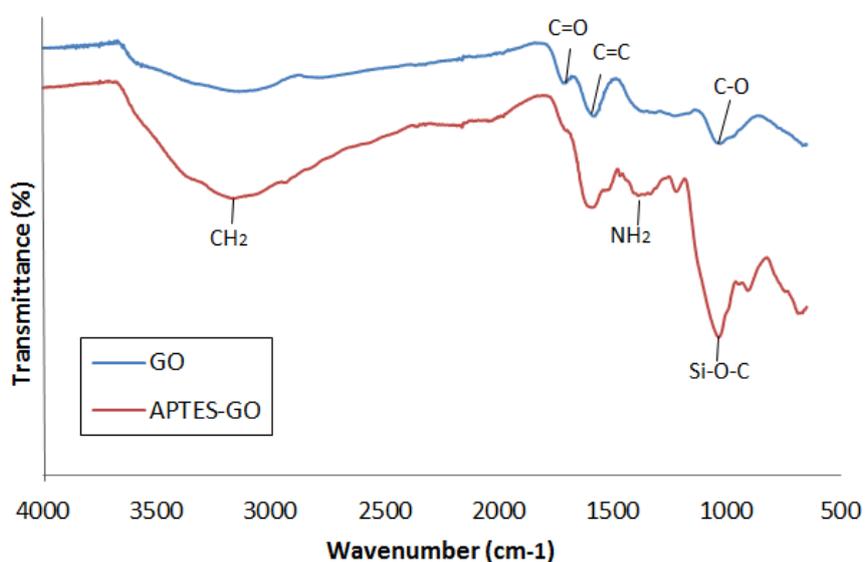


Fig. 2. FTIR spectrum of GO and APTES-GO

3.3 Raman Spectra Analysis

Raman spectroscopic measurements were carried out to support the structural changes from surface modification of GO by APTES. There are two broad overlapping peaks centered near 1250 cm^{-1} (D line) and 1550 cm^{-1} (G line) can be detected in Figure 3. Typically, the D line represents the defect and disordered of carbon structure while the G line represents the ordered graphitic crystallites of the carbons that associated with sp^2 carbons [27]. These D and G peaks in both figures were fitted using a Gaussian Lorentzian mixed. It can be seen that both D and G peaks for APTES-GO tilt to left after the functionalization with amine functional group. This is because grafting induces positive inductive effect on the amine functional groups attached to GO, which act as electron donor substituents [28]. Specifically, the D band broadens significantly and G-band grows in intensity. Both of the bands display a shift to higher frequencies. The peak intensity ratio of D to G bands (I_D/I_G) indicates the degree of disorder in the sample, originated from edges, defects or ripples. Our results showed that there is no significant variation in the samples. The I_D/I_G intensity ratio for APTES-GO and unmodified GO are 1.05 and 1.10, respectively. The value of I_D/I_G of APTES-GO that is almost similar to unmodified GO indicates that grafting of amine molecules took place on the oxygen functional

groups on the surface without disturbing the defective sp^3 -hybridized sites in the basal planes of GO [20].

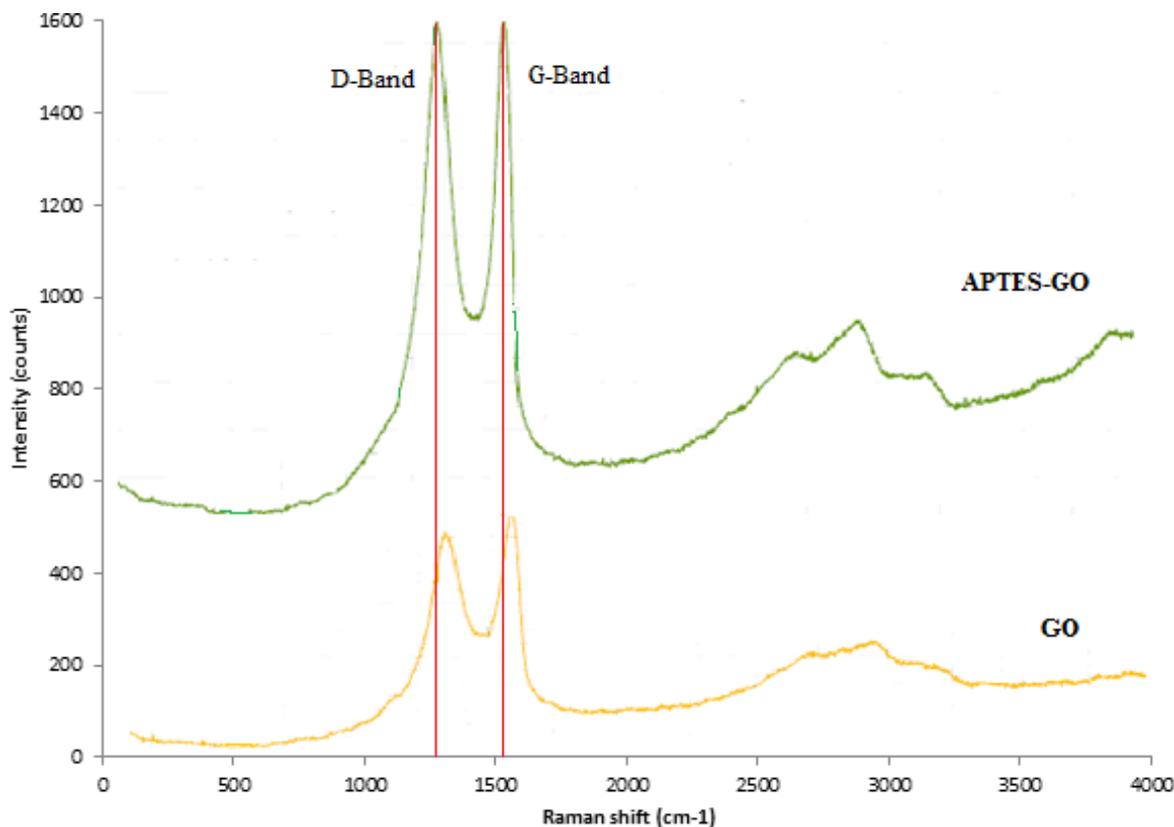


Fig. 3. Raman spectra of GO and APTES-GO

3.4 Nitrogen Adsorption Isotherms

Evaluation of N_2 adsorption capacity was carried out at fix temperature, $30^\circ C$ and varied pressure up to 15 bar. A significant improvement was detected on the quantity of nitrogen adsorbed for both GO and APTES-GO at increasing pressure of adsorption. It is worth to highlight that at highest tested pressure, APTES-GO yields higher N_2 adsorption capacity compared to GO. All of the samples adsorb nitrogen ranging between 11 to 179 mmol/g as shown in Figure 4. The nitrogen adsorption capacities APTES-GO have increased about two times higher at 15 bar as compared to pristine GO. Therefore, it can be concluded that APTES-GO with adsorption pressure of 15 bar adsorbs the most nitrogen compared to the other samples and pressures with a value of 179 mmol/g for its adsorption equilibrium. It is also noteworthy to mention that GO at 5 bar adsorbed the least amount of nitrogen due to its smaller effective surface area and the lower starting adsorption pressure [20].

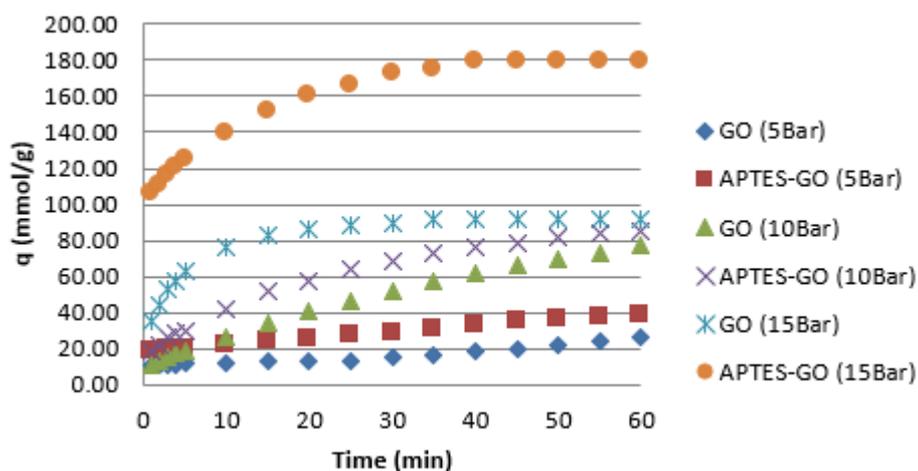


Fig. 4. The differences of nitrogen adsorption capacity between GO and APTES-GO at various pressures (5, 10, and 15 bar)

4. Conclusions

In this study, GO were successfully prepared using Modified Hummers' Method and being functionalized by amine functional group, APTES. This finding highlights the potential of APTES-GO as an efficient adsorbent for CO₂ capture for a more sustainable environment. Through our study, it can be concluded that the amine-functionalized GO, APTES-GO can adsorb higher N₂ compared to the pristine GO up to 179 mmol/g of N₂. The effect of pressure on adsorption was also studied. N₂ adsorptions with various pressures (5, 10, and 15 bar) were tested. It was found that, the greater the adsorption pressure, the higher the amount of gas adsorbed. This shows that, APTES-GO have a potential use in carbon capture and storage.

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References

- [1] Patiño, Gerardo Geovanni Esquivel, and Fabricio Nápoles Rivera. "Global warming potential and net power output analysis of natural gas combined cycle power plants coupled with CO₂ capture systems and organic Rankine cycles." *Journal of Cleaner Production* 208 (2019): 11-18.
- [2] Yee, Lai Kok, Tan Lit Ken, Yutaka Asako, Lee Kee Quen, Chuan Zun Liang, Wan Nur Syahidah, Koji Homma et al. "Cloud Optical Depth Retrieval via Sky's Infrared Image For Solar Radiation Prediction." *Journal Advanced Research Fluid Mechanics and Thermal Sciences* 58, no. 1 (2019): 1-14.
- [3] Yulia, Fayza, Agustino Zulys, and Rizky Ruliandini. "Metal-organic framework based chromium terephthalate (MIL-101 Cr) growth for carbon dioxide capture: A review." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 57, no. 2 (2019): 158-174.
- [4] Sim, Kyohyun, Nakwon Lee, Joonseok Kim, Eun-Bum Cho, Chamila Gunathilake, and Mietek Jaroniec. "CO₂ adsorption on amine-functionalized periodic mesoporous benzenesilicas." *ACS Applied Materials & Interfaces* 7, no. 12 (2015): 6792-6802.
- [5] Gómez-Pozuelo, G., E. S. Sanz-Pérez, A. Arencibia, P. Pizarro, R. Sanz, and D. P. Serrano. "CO₂ adsorption on amine-functionalized clays." *Microporous and Mesoporous Materials* 282 (2019): 38-47.

- [6] Wilberforce, Tabbi, Ahmad Baroutaji, Bassel Soudan, Abdul Hai Al-Alami, and Abdul Ghani Olabi. "Outlook of carbon capture technology and challenges." *Science of the Total Environment* 657 (2019): 56-72.
- [7] Romano, Matteo C., Paolo Chiesa, and Giovanni Lozza. "Pre-combustion CO₂ capture from natural gas power plants, with ATR and MDEA processes." *International Journal of Greenhouse Gas Control* 4, no. 5 (2010): 785-797.
- [8] Bai, Lu, Dawei Shang, Mengdie Li, Zhongde Dai, Liyuan Deng, and Xiangping Zhang. "CO₂ absorption with ionic liquids at elevated temperatures." *Journal of Energy Chemistry* 26, no. 5 (2017): 1001-1006.
- [9] Kudahi, Saeed Nazari, Ali Reza Noorpoor, and Niyaz Mohammad Mahmoodi. "Determination and analysis of CO₂ capture kinetics and mechanisms on the novel graphene-based adsorbents." *Journal of CO₂ Utilization* 21 (2017): 17-29.
- [10] Ederer, Jakub, Pavel Janoš, Petra Ecorchard, Jakub Tolasz, Václav Štengl, Hynek Beneš, Magdalena Perchacz, and Ognen Pop-Georgievski. "Determination of amino groups on functionalized graphene oxide for polyurethane nanomaterials: XPS quantitation vs. functional speciation." *RSC Advances* 7, no. 21 (2017): 12464-12473.
- [11] Chatterjee, Riya, Baharak Sajjadi, Daniell L. Mattern, Wei-Yin Chen, Tetiana Zubatiuk, Danuta Leszczynska, Jerzy Leszczynski, Nosa O. Egiebor, and Nathan Hammer. "Ultrasound cavitation intensified amine functionalization: A feasible strategy for enhancing CO₂ capture capacity of biochar." *Fuel* 225 (2018): 287-298.
- [12] Kongnoo, Aroon, Supak Tontisirin, Patcharin Worathanakul, and Chantaraporn Phalakornkule. "Surface characteristics and CO₂ adsorption capacities of acid-activated zeolite 13X prepared from palm oil mill fly ash." *Fuel* 193 (2017): 385-394.
- [13] Chen, Chao, Yu-Ri Lee, and Wha-Seung Ahn. "CO₂ adsorption over metal-organic frameworks: A mini review." *Journal of Nanoscience And Nanotechnology* 16, no. 5 (2016): 4291-4301.
- [14] Yusof, N., and A. F. Ismail. "Polyacrylonitrile/acrylamide-based carbon fibers prepared using a solvent-free coagulation process: Fiber properties and its structure evolution during stabilization and carbonization." *Polymer Engineering & Science* 52, no. 2 (2012): 360-366.
- [15] Álvarez-Gutiérrez, Noelia, M. V. Gil, F. Rubiera, and C. Pevida. "Kinetics of CO₂ adsorption on cherry stone-based carbons in CO₂/CH₄ separations." *Chemical Engineering Journal* 307 (2017): 249-257.
- [16] Creamer, Anne Elise, and Bin Gao. "Carbon-based adsorbents for postcombustion CO₂ capture: A critical review." *Environmental Science & Technology* 50, no. 14 (2016): 7276-7289.
- [17] Caliman, C. C., A. F. Mesquita, D. F. Cipriano, J. C. C. Freitas, A. A. C. Cotta, W. A. A. Macedo, and A. O. Porto. "One-pot synthesis of amine-functionalized graphene oxide by microwave-assisted reactions: An outstanding alternative for supporting materials in supercapacitors." *RSC Advances* 8, no. 11 (2018): 6136-6145.
- [18] Liu, Yamin, Baharak Sajjadi, Wei-Yin Chen, and Riya Chatterjee. "Ultrasound-assisted amine functionalized graphene oxide for enhanced CO₂ adsorption." *Fuel* 247 (2019): 10-18.
- [19] Dreyer, Daniel R., Sungjin Park, Christopher W. Bielawski, and Rodney S. Ruoff. "The chemistry of graphene oxide." *Chemical Society Reviews* 39, no. 1 (2010): 228-240.
- [20] Pokhrel, Jeewan, Nidhika Bhorla, Stavroula Anastasiou, Theodoros Tsoufis, Dimitrios Gournis, George Romanos, and Georgios N. Karanikolos. "CO₂ adsorption behavior of amine-functionalized ZIF-8, graphene oxide, and ZIF-8/graphene oxide composites under dry and wet conditions." *Microporous and Mesoporous Materials* 267 (2018): 53-67.
- [21] Shrivastava, Shashank, Shijo Thomas, C. B. Sobhan, and G. P. Peterson. "An experimental investigation of the CO₂ adsorption performance of graphene oxide forms." *International Journal of Refrigeration* 96 (2018): 179-190.
- [22] Arifin, Nur Fatimah Tajul, and Madzlan Aziz. "Effect of reduction time on optical properties of reduced graphene oxide." *Jurnal Teknologi* 79, no. 1-2 (2017): 137-143.
- [23] Saptal, Vitthal B., Takehiko Sasaki, Kei Harada, Daisuke Nishio-Hamane, and Bhalchandra M. Bhanage. "Hybrid amine - functionalized graphene oxide as a robust bifunctional catalyst for atmospheric pressure fixation of carbon dioxide using cyclic carbonates." *ChemSusChem* 9, no. 6 (2016): 644-650.
- [24] Bouazizi, Nabil, Julien Vieillard, Radhouane Bargougui, N. Couvrat, O. Thoumire, S. Morin, and G. Ladam. "Entrapment and stabilization of iron nanoparticles within APTES modified graphene oxide sheets for catalytic activity improvement." *Journal of Alloys and Compounds* 771 (2019): 1090-1102.
- [25] Zain, Norhidayu Muhamad, and Shafi, Aisyah Ahmad. "Synthesis and characterisations of polydopamine-reduced graphene oxide." *Journal of Advanced Research in Material Science* 26 (2016): 1-6
- [26] Li, Wei, Fei Xue, and Qiang Li. "Modification of bismaleimide resin by using γ -aminopropyl triethoxysilane functionalised graphene oxide." *Plastics, Rubber and Composites* 47, no. 5 (2018): 187-191.
- [27] Othman, Faten Ermala Che, Norhaniza Yusof, Hasrinah Hasbullah, Juhana Jaafar, Ahmad Fauzi Ismail, and Noor Shawal Nasri. "Physicochemical properties and methane adsorption performance of activated carbon nanofibers with different types of metal oxides." *Carbon Letters (Carbon Lett.)* 24 (2017): 82-89.

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- [28] Ryu, Sung Hun, and A. M. Shanmugharaj. "Influence of long-chain alkylamine-modified graphene oxide on the crystallization, mechanical and electrical properties of isotactic polypropylene nanocomposites." *Chemical Engineering Journal* 244 (2014): 552-560.