The differences of physicochemical characteristics of graphene-like nanomaterials directly grown on copper foil and quartz substrate in chemical vapor deposition (CVD)

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Abstract. The preparation of graphene material is possibly conducted using chemical vapor deposition (CVD) method using hydrogen, argon, and acetylene gases using a copper substrate. The use of different substrates, especially glass-based substrates, has not been widely studied. Therefore, in the present study, we analyzed the chemical and physical characteristics of the carbon materials grown in CVD on a different substrate, i.e., copper foil and quartz substrate. The XRD analysis of the carbon materials produced shows a definitive peak for carbon which is in broad feature and left-shifted to 2θ around 23°. Raman spectroscopy’s characterization shows that the material grown on copper foil revealed a 2D band, appearing around 2600 cm⁻¹, which was absent for the carbon material deposited on the quartz substrate. Physically, the carbon powder produced is hydrophobic, light, and black. The structural character of the graphene material observed by using the electron microscope consists of overlapped layers. The FTIR analysis shows that the material growth on copper foil and quartz substrate has C=C bond, concluded that the material produced as graphene-like nanomaterials.

1. Introduction
In recent years, graphene has attracted a great deal of attention. Graphene is a one-atom-thick material with a very high thermal conductivity of ~5000 Watt m⁻¹ K⁻¹ [1], ultra-high electron mobility, very high specific surface area [2], high electrical conductivity [3]. Therefore, graphene has unusual and highly promising for applications of electrical, thermal, and mechanical properties. Graphene synthesis can be done via several methods, such as mechanical peeling [4], chemical synthesis [5], epitaxial growth [6], ball milling [7], electrochemical [8], sonication [9], and chemical vapor deposition (CVD) [10]. CVD is also famous for the synthesis method of other carbon-based nanomaterials [11].

CVD is an alternative processing approach to obtain suitable materials for the heterogeneous nature of gas-liquid catalytic activities. CVD method uses a metal catalyst with polycrystalline materials, which allows the growth of graphene in the expanded area. Therefore, this method has become an attractive strategy for producing graphene industrially. The growth process in CVD consists of heating, growth, and cooling stages [12]. CVD method principle involves the thermal decomposition of a hydrocarbon vapor achieved in the presence of a catalyst [4]. CVD requires heat to break the atom bonds of the gas molecule and activated surface catalyst. The temperature used in CVD for nanomaterial synthesis is generally between 550-1000 °C depends on the desired product [13].
In CVD, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, iridium, platinum, and gold, are commonly well-known catalysts to activate graphene growth [14]. Using a copper catalyst, monolayer graphene is selectively produced. Meanwhile, a similar process using the other transition metal systems creates multilayer graphene [15]. The advantages of using a copper foil catalyst in the CVD method can recrystallize the material [10], reduce density defects in the material [16], lead to improve its mechanical properties, reduce or stabilize temperature, low-cost, and have high solubility of carbon atom [17]. Using copper as the substrates in CVD, the growth graphene characteristics such as the size, thickness, and quality of the produced graphene provide appropriate specifications in industrial application [18]. Moreover, large-area monolayer graphene growth also possible to achieve because graphene films might grow on copper by the CVD form as grains smaller than 10 µm [19].

Interestingly, the synthesis of graphene in CVD inside the quartz tube furnace allows the formation of carbon deposition not only on copper but also placed on the quartz glass. We predict that both deposited carbon might have different characteristics which have not been explored previously. Therefore, in the present study, we analyzed the chemical and physical characteristics between the carbon materials deposited on a copper foil and quartz substrate, which simultaneously produced in CVD process at the same time.

2. Experimental

2.1. Materials and equipment

The materials used in this study include copper foil 9×3 cm (technical grade), ethanol Absolute 99% (Emsure), argon, acetylene, hydrogen gas (PT. Samator Gas Industri). Some tools to support this experience are furnace OTF 1200X with quartz tube (d = 0.75 cm; t = 10 cm), beaker glass (pyrex, 50 mL), vacuum pump (Kan Den), Hotplate (Electric Warmer), and ultrasonicator.

2.2. Synthesis of graphene using chemical vapor deposition (CVD)

The CVD experimental setup with copper foil is shown in Fig. 1. The copper foil (100 µm-thick, 99.5% metal basis) was used as the growth substrate. The catalyst with various sizes ranging 9×3 cm was prepared [10]. The samples were ultrasonically cleaned in ethanol and deionized water until 10 minutes. These samples were loaded into a CVD quartz chamber with a vacuum pump. The conditions in this process are vacuum conditions. The chamber was vacuumed by a mechanical pump to remove water and oxygen molecules and impurities in the tube. The mixture of Ar : H2 : C2H2 was then added into the furnace chamber with a flow rate ratio 1 : 1 : 5. Ar gas was first flown into the chamber at a temperature of 700 °C with a pressure of 0.01 MPa. The hydrogen gas was then passed at a temperature of 790 °C with a pressure of 0.01 MPa, which has the most crucial role in activating the surface of the copper catalyst.

![Figure 1. CVD process of products at a temperature of 800 °C.](image-url)
Lastly, C₂H₂ gas was continuously flown inside the CVD chamber when the chamber temperature reached 800 °C with a pressure of 0.05 MPa for 10 min, and the valve was then closed. The growth process was kept at 800 °C for 10 minutes. After reducing the temperature, the furnace was turned off, and the quartz tube started to cool down to room temperature. The resulting material is manually separated from the copper catalyst and the well inside the quartz tube.

2.3. Characterization of product
The synthesized product was characterized using X-ray diffraction (XRD, Philips Analytical), Raman spectroscopy (Modular Raman Type iHR320), Scanning Electron Microscope (SEM, Jeol JEM), and Fourier Transformed Infrared (FTIR, Shimadzu).

3. Results and discussion
The synthesis process via the chemical vapor deposition (CVD) method was successfully carried out. During the synthesis process, the changing of the pressure from the initial pressure indicates that the deposition process occurred. The process illustration of material formed in the furnace is shown in Fig. 2. The reactions on the copper foil catalyst with C₂H₂ gas are expressed in the reactions (1-4).

![Figure 2. Illustration of making products in a furnace with copper foil.](image_url)

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\begin{align*}
\text{H}_2 + 2 \text{(s)} & \rightarrow \text{H (s) + H (s)} \quad \text{(Chemical adsorption)} \\
\text{C}_2\text{H}_2 + \text{(s)} & \rightarrow \text{C}_2\text{H}_2 \text{(s)} \quad \text{(Physical adsorption)} \\
\text{C}_2\text{H}_2 \text{(s) + (s)} & \rightarrow 2\text{C (s) + H}_2 \text{(s)} \quad \text{(Dehydrogenation)} \\
2\text{C (s) + H}_2 \text{(s)} & \rightarrow 2\text{C (s) + (s) + H}_2 \text{(g)} \quad \text{(Dehydrogenation)}
\end{align*}
\]

Dehydrogenation on copper catalysts occurred through an endothermic process [20]. The C–C sp³ bond is a temporary product before it becomes a compound aromatic on the copper surface. The physical form of deposited carbon produced is black, odorless, very lightweight, and insoluble in water (hydrophobic). The carbon powder produced revealed physical characteristics such as hydrophobic, light, and black. To confirm the exhibited physicochemical characteristics, the material results were further characterized by XRD, Raman Spectroscopy, FTIR, and SEM.

Figure 3 shows the diffraction pattern of the CVD product deposited carbon on copper foil and quartz. The spectra result had the highest peak, namely -23° (002). Meanwhile, the peak of graphite C (002) generally appears at 2θ = ~26°. Therefore, the XRD peak in Fig. 3 has a left-shifted to 29 around 23°, which probably indicates that graphene was successfully synthesized. Moreover, the diffraction spectra revealed are also similar to the research be done by previous work [21]. The resulting product has almost the same highest peak, namely at -23° (002); however, the shape of spectra is slightly different. A broader peak is observed in the diffraction spectra belong to material deposited on the quartz. The shifting 20 diffraction peak and different peak shapes represent the decreasing crystallinity of the material, which is a characteristic of the formation of graphene material having a structure.
between crystalline and amorphous materials. However, the d-spacing values of material deposited on foil and quartz are not much different as 3.58661 Å and 3.63398 Å, respectively. Therefore, the product might be graphene or deposited amorphous carbon in copper foil, further analyzed by Raman Spectroscopy as shown in Fig. 4.

Defects on graphene can be analyzed from the results of its Raman spectroscopy. The Raman spectra are shown in Fig. 4 explain the decrease of carbon graphitization after the CVD process. Raman spectroscopy on graphene has three signal peaks, namely the signal D band (~1332 cm⁻¹) to measure defect information from the material, G band (~1661 cm⁻¹) to see sp² carbon vibrations, and 2D (~2601 cm⁻¹) signal, which is a particular signal contained in graphene to provide stacking information between graphene surfaces and two phonons through resonance process representing to a number of layers in the graphene [22].

In Fig. 4, the graphene I_D/I_G ratio of carbon materials deposited on copper foil and quartz is 0.909 and 1.203, respectively. The later ratio shows significant defects in the hexagonal carbon structure of the deposited carbon. Raman profile in Fig. 4(a) shows I_D/I_G values below 1.00 or smaller than Fig. 4(b), which indicates they have lower defects and better graphitization. Meanwhile, Fig. 4(b) has a higher I_D/I_G ratio, representing a higher defect and lower graphitization. This fact concludes that the deposited carbon produced has sp³ more dominant than sp² carbon atom [23].

The smallest I_D/I_G ratio revealed in Fig. 4(a) was strengthened by the appearance of 2D band at 2610 cm⁻¹ with an I_2D/I_G ratio of 0.1028. The I_2D/I_G ratio shows the thickness information of a graphene sheet [23]. The characteristics of multilayer graphene can be estimated when the I_2D/I_G ratio is smaller. In addition, 2D band in multilayer graphene is generally in broad feature; thus, 2D band intensity becomes lower. In this study, the I_2D/I_G ratio has a minimal value; therefore, the material produced with a temperature of 800 °C on a copper catalyst is suggested as multilayer graphene material.

Fourier Transform Infrared Spectroscopy (FTIR) is used to identify functional groups. FTIR spectra of the deposited carbon are shown in Fig. 5. Generally, in the FTIR spectra of graphene, no peaks will appear below 900 cm⁻¹ [24]. As shown in Fig. 5, the differences in the appearance of bonds in FTIR analysis might represent the different structures. Fig. 5(a) shows that the deposited carbon on copper foil has a more intense C=C bending bond around ~1600 cm⁻¹, which indicates the sp² of aromatic carbon [25]. Meanwhile, for deposited carbon on the quartz (see Fig. 5(b)), the peak of the C=C bending bond is weaker but having a more intense O–H bond (3435.68 cm⁻¹) than that of deposited carbon on copper foil.

**Figure 3.** X-ray diffraction pattern of deposited carbon on (a) copper foil and (b) quartz.

**Figure 4.** Raman spectra of deposited carbon on (a) copper foil and (b) Quartz.
Figure 5. FTIR Spectra products (a) copper foil and (b) quartz.

TEM measurements were performed to analyze the characteristics of deposited carbon further, as shown in Fig. 6. The deposited carbon on quartz offers a thick layer with an amorphous-like structure, as presented in Fig. 6(a). On the other hand, the deposited carbon on the copper foil shown in Fig. 5(b) suggests forming a thin layer as suggested consisting of a few layers of graphene as indicated by the nearly transparent layer as shown in Fig. 6 (b). Therefore, the results of TEM observations are in agreement with all the data previously discussed, indicating that the carbon deposited on the copper foil is graphene multilayer different from that deposited on quartz as graphene-like nanomaterials in a more dominant amorphous structure.

Figure 6. TEM images of the deposited carbon on (a) quartz and (b) copper foil.

4. Conclusion
Based on the result's description, graphene synthesis was successfully carried out using CVD method with physical characteristics, namely hydrophobic, light, and black in color. The XRD profile of both deposited carbon on copper foil and quartz has a similar diffraction pattern with definitive peak C(002) located at ~23°. The deposited carbon's possible structure analyzed using Raman and FTIR spectroscopy, and TEM imaging shows that deposited carbon on the copper foil is suggested to have a graphene structure. Meanwhile, deposited carbon on quartz is offered as graphene-like nanomaterials in a more dominant amorphous form.
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