Increase in surface hardness of stainless steel through graphene growth on stainless steel surface by chemical vapor deposition using waste vegetable oil as a carbon source

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Abstract. Stainless steel has been widely utilized due to it high resistance of corrosion, rust, and stain more than ordinary steel. However, a hardness of stainless-steel surface is not high resulting in engineering applications of stainless steel are limited. Graphene is an extremely hard material therefore the growth of graphene on stainless steel can increase the surface hardness of stainless steel. Vegetable oil consists of triglyceride which has abundant carbon in the constituent. Vegetable oil has been widely used for cooking. After the cooking, a huge amount of the waste vegetable oil is flushed down the drain resulting in water pollution. However, the waste vegetable oil still contains abundant carbon which can be used as a carbon source for graphene growth on stainless steel by chemical vapor deposition (CVD). In this study, the surface hardening of stainless steel through graphene growth on stainless steel by CVD using waste palm oil as a carbon source is demonstrated. The results show that the fourth-used palm oil can be utilized as a carbon source for the growth of graphene on stainless steel by CVD. Moreover, the graphene growth on stainless steel by CVD using the fourth-used palm oil can increase the surface hardness of stainless steel by 175%

1. Introduction
Stainless steel is steel alloy which has been widely utilized due to it high resistance of corrosion, rust, and stain more than ordinary steel. However, a hardness of stainless-steel surface is not high resulting in engineering applications of stainless steel are limited. The surface hardening of stainless steel can improve many equipment such as cam or ring gear, bearings or shafts, turbine applications, and automotive components [1] therefore increase in surface hardness of stainless steel can broaden its application range.
Graphene is an allotrope of carbon which is arranged in a 2D honeycomb lattice [2-5]. Graphene is a superhard material [6] which has an intrinsic strength of 130 GPa, young’s modulus of 1.0 TPa, and elastic stiffness of -2.0 TPa [7]. Therefore, the growth of graphene on stainless steel can increase the surface hardness of stainless steel [8,9]. Vegetable oil consists of triglyceride which has abundant carbon in the constituent. Vegetable oil has been widely utilized for cooking. After the cooking, a huge amount of the waste vegetable oil is flushed down the drain [10]. Since the density of the waste vegetable oil is lower than that of water, the waste vegetable oil will float in water and obstruct the oxygen exchange between water and air resulting in polluted water. However, the waste vegetable oil still contains abundant carbon which can be used as a carbon source for graphene growth on stainless steel by chemical vapor deposition (CVD). In this study, the surface hardening of stainless steel through graphene growth on stainless steel by CVD using waste palm oil as a carbon source is demonstrated.

2. Experimental procedures
The growth of graphene on stainless steel was prepared by CVD using waste palm oil as a carbon source [11,12]. A 3×4×0.085 cm³ stainless-steel (S304) plate was precleaned by ultrasonic sonication in acetone for 5 minutes. After the acetone evaporated from the substrate’s surface, a tray of waste palm oil with quantity of 25 ml and the cleaned stainless-steel substrate were put into the quartz tube in the area of furnace 1 and furnace 2, respectively, as shown in figure 1 followed by evacuation until the base pressure in the quartz tube reached ~3 Pa and then the stainless-steel substrate was annealed to the graphene growth temperature of 900 °C by furnace 2. At the growth temperature, the vapor of waste palm oil was introduced to the area of furnace 2 by annealing the waste palm oil at 400 ºC using furnace 1. The substrate was annealed for 30 minutes under the vapor of the waste palm oil. After that the substrate was fast cooled down to room temperature.

The presence of graphene on stainless-steel plates was confirmed by Raman spectroscopy measured at room temperature using a 100x objective and a 532 nm laser. The laser beam size is 1 μm in diameter. Morphology and element analysis were investigated by field-emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectroscope (EDX) at incident beam of 15 keV. Surface hardness test was performed by nanoindenter using load up to 200 mN

![Figure 1. Schematic of experimental setup of graphene growth on stainless steel by CVD using waste vegetable oil as a carbon source.](image-url)
3. Results and discussion
In this study, used palm oil is utilized as a carbon source for graphene growth by CVD. The used palm oil is obtained after deep-frying sesame, pumpkin, potato, and banana, respectively. Figure 2 shows Raman spectra measured on the samples underwent the growth of graphene on stainless steel by CVD using the waste palm oil obtained by deep-frying various foodstuffs. The names of samples and types of deep-fried foodstuff are shown in figure 2 (inset). The Raman spectra of all samples show G and 2D bands which are the characteristic bands of graphene at \( \sim 1580 \text{ cm}^{-1} \) and \( \sim 2700 \text{ cm}^{-1} \), respectively [13-15]. Although Raman spectra show the graphene characteristic G and 2D bands, it cannot confirm the presence of graphene on the sample surfaces since carbon nanotube also has these G and 2D bands because both of graphene and carbon nanotube are sp\(^2\) carbon materials [16]. Figure 3 show SEM images of pristine stainless steel (figure 3 (a)) and P4 sample (figure 3 (b)). The SEM image of P4 shows there is not carbon nanotube on the surface confirming the presence of graphene on P4 sample and the fourth-used palm oil (P4) can be used as a carbon source for graphene growth by CVD. The SEM image of P4 sample also shows that the surface of P4 sample is not smooth implying that the graphene film on the sample surface is not uniform.

![Raman spectra measured on the surfaces of samples underwent graphene growth on stainless steel by CVD using various waste palm oil as a carbon source. (Inset) Table shows sample names and foodstuffs which deep-fried in the palm oil.](image-url)

**Figure 2.**
In general, the carbon source for the growth of graphene on stainless steel by CVD should be without oxygen because it obstructs graphene formation. However, the results show that palm oil which contains abundant oxygen can be utilized as the carbon source for graphene growth on stainless steel by CVD. It may be attributed to carbothermal reduction which is a process to eliminate oxide from the metal surface by annealing the metal oxide with reducing-agent carbon at high temperature [17,18]. Liu et al. show that annealing iron oxide at temperature more than 600 K with gaseous carbon can reduce the iron oxide [19]. In our case, stainless steel which is iron-rich alloy was annealed at 900 °C with the vapor of the waste palm oil which contains abundant oxygen and carbon. The reaction of reduction of iron oxide is displayed step by step as follows [11].

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\begin{align*}
3\text{Fe}_2\text{O}_3 + \text{CO} & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \\
\text{Fe}_3\text{O}_4 + \text{CO} & \rightarrow 3\text{FeO} + \text{CO}_2 \\
\text{FeO} + \text{CO} & \rightarrow \text{Fe} + \text{CO}_2
\end{align*}
\]

Figure 4 (a) shows load vs depth curves of pristine stainless steel (blue) and P4 sample (green). The average surface hardnesses of pristine stainless steel and P4 sample are 2.42 GPa and 6.66 GPa, respectively. Figure 4 (b) shows surface hardnesses of pristine stainless steel and P4 sample randomly measured 6 points on pristine stainless steel and 9 points on P4 sample. The graph shows the surface hardness of P4 sample considerably fluctuates. It may be attributed to non-uniform graphene thickness.

Figure 4. (a) Load vs depth curves of pristine stainless steel (blue) and P4 sample (green). (b) Surface hardness randomly measured 6 points on pristine stainless steel (red) and 9 points on P4 sample (blue).
4. Conclusions
In this report, we have demonstrated the growth of graphene on stainless steel by CVD using waste palm oil as a carbon source. The results show that the fourth-used palm oil can be utilized as a carbon source for graphene growth on stainless steel by CVD. Moreover, the growth of graphene on stainless steel by CVD using the fourth-used palm oil can increase the surface hardness of stainless steel by 175%.

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