Optical Absorbance Study of Carbon Nanomaterials Synthesized from Used-cooking Oil via Liquid-phase Exfoliation Using a Kitchen Blender in n-Hexane Solution

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Abstract. UV-Visual (UV-Vis) optical absorbance study in the synthesis of carbon nanomaterials produced from used-cooking oil via liquid-phase exfoliation (LE) using a kitchen blender which is dissolved in n-hexane solvent has been conducted. Here, the blending time duration and solution concentration are varied, i.e. (in hours) 1, 2, and 3, and (in milimol/mL) 0.2, 0.4, and 0.6, respectively. The solutions obtained from this study are characterized using UV-Vis spectrophotometer. The experiment is carried out by directly blending used-cooking oil and then dissolving it in n-hexane solvent. A solution of pure cooking oil in n-hexane is used as a reference solution for the UV-Vis spectrophotometer. For variation of blending time duration, the UV-Vis results show a blue shift from 269.5 nm to 235.5 nm as the blending time is increased from 1 to 3 hours and indicate the presence of graphene oxide (GO) material. A second absorbance peaks at around 349 nm to 351 nm correspond to the occurrence of carbon quantum dot (CQD) material. Moreover, for the variation of solution concentrations, a red shift from 311.5 nm to 350 nm occurs as the solution concentration is increased from 0.2 to 0.6 milimol/mL. The red shift point towards an exfoliation of used-cooking oil from GO into CQD materials.

Keywords: *graphene oxide, carbon quantum dot, UV-Vis spectroscopy, liquid-phase exfoliation, used-cooking oil, n-hexane.*

1 Introduction

In Indonesia, cooking oil is one of the basic human needs which function as a food processing media. Cooking oil provides good taste and fine texture for foods, as well as making the appeareance of food become more attractive and dry on the surface [1]. Cooking oil also gives the highest number of calories among other nutrients. It contains unsaturated fatty acids which are easily damaged when heated continuously but very beneficial for our health [2,3]. However, the problem arises when the oil is used repeatedly, or as we know as used-cooking oil. The same cooking oil should not be used for frying for more than three times as it may cause a number of diseases [4,5], reduces the nutritional values, and degrades the quality of foods itself. In addition, dumping used-cooking oil into the environment will be economically wasted and become a source of water and soil pollutions [4]. Thus, alternative efforts are needed to treat these wastes. This study shows that used-cooking oil may be recycled into carbon nanomaterials via a straightforward and inexpensive exfoliation method using a kitchen blender with n-hexane as the solvent.

Carbon nanomaterials such as graphene, grapheme oxide (GO), reduced GO (rGO), and carbon quantum dot (CQD) are products in the advancement of nanoscience by manipulating the properties and performance of a material in such a way so it becomes more effective, efficient, and useful in the nanometer scale ranging from 1 nm to 100 nm [6]. Graphene is a two dimensional (2D) form of a single layered graphite found in 2004 by A. Geim and K. Novoselov [7]. Graphene has outstanding physical properties including high electron mobility [8], high electrical conductivity, high thermal conductivity [9], good optical transparency [10], has a tensile strength harder than a diamond [11], weighing only 0.77 miligrams in 1 m^2 [12], and very thin [13]. Meanwhile, graphene oxide (GO) is an oxidized form of graphene produced by oxidizing graphite crystals [14] such as graphite oxide. In recent years, many GO derivatives, such as GO-based composites, GO-based coating and thin films, and GO-based nanoparticles emerge as functional materials for various applications [15]. Thin sheets of GO have recently arise as a new carbon-based nanoscale material [16-17]. The solubility of GO in water and other solvent are potentially useful for macroelectronics [18]. CQD is a new class of carbon nanomaterial with sizes below 10 nm. Initially, CQD are obtained by purification of single-walled carbon nanotubes (CNT) through preparative electrophoresis [19] and via laser ablation of graphite powder and cement [20]. CQD possess various atractive properties namely high stability, good conductivity, low toxicity, environmental friendly, simple synthetic routes as well as comparable optical properties to quantum dots [21]. CQD can be utilized for various applications, such as biomedicine, optoelectronics, catalysis, and chemical sensors [22]. Basically the synthesis of carbon nanomaterials can be conducted by two methods, viz.: top down and bottom up. There are several top down methods including mechanical exfoliation (ME) [23], the reduction of rGO [24], Hummers method [25,26] and liquid-phase exfoliation (LE) via ultrasound generator [27] or a kitchen blender [28]. In this study, the latter method is applied.

There are many ways in characterizing carbon nanomaterials, including transmission electron microscopy (TEM) [29], atomic force microscopy (AFM) [30], Raman spectroscopy [31,32], X-rays diffraction (XRD) [33], scanning electron microscopy (SEM) [34], and UV-Vis spectroscopy [35]. UV-Vis spectroscopy is a quantitive measurement technique in order to study the absorbance of a sample towards light, especially in the regimes of ultraviolet and visible wavelengths. GO material has peak absorbances around 223 nm [36] and 230 nm [37]. For rGO the peak is shifted to a longer wavelength of around 270 nm [36]. These peaks are related with $\pi \rightarrow \pi^*$ transition at wavelength 220 nm to 290 nm.

The objectives of this study are to synthesize carbon nanomaterials from waste-cooking oil via LE method using a kitchen blender in n-hexane solvent and characterizing the solution using UV-Vis spectrophotometer by varying the blending time duration and solution concentration. The reference solution used is pure cooking oil in n-hexane and made to suit each variation of solution concentration. n-hexane is the lightest solvent in lifting oil with a boiling point between 65 to 70 ^{0}C. Moreover, studies surrounding oil wastes have been conducted before but with different objects and methods [38,39]. This study concerns with used-cooking oil as the object and using a kitchen blender to produce nanomaterials in n-hexane, which to the knowledge of the authors has not been conducted before.

2 Experimental Method

For The materials used in this study are (i) used-cooking oil [Fig. 1(a)], (ii) n-hexane, and (iii) pure cooking oil [Fig. 1(c)]. The used-cooking oil is obtained from a restaurant in Klebengan area, Yogyakarta, Indonesia. The tools used in this study are (i) a blender [Fig. 1(b)], (ii) a measuring glass, (iii) beaker glasses, (iv) test tubes, (v) pipettes, (vi) centrifuge tubes, (vii) alumunium foil, (viii) a stopwatch, and (ix) UV-Vis spectrophotometer (Shimadzu UV-2550).

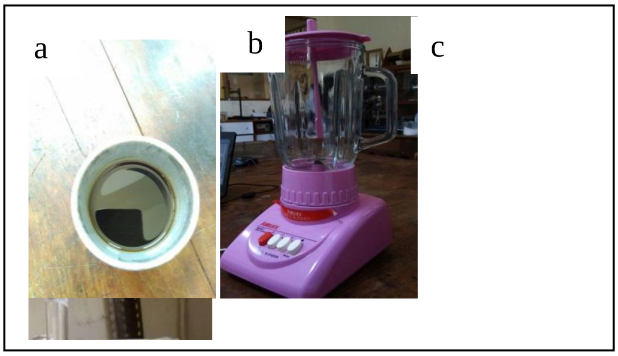

Figure 1 (a) Used-cooking oil, (b) a blender used to blend used-cooking oil, and (c) pure cooking oil.

The experimental procedure is given as follows. Used-cooking oil is directly blended using the kitchen blender. The blending process is carried out for a total of 3 hours with a pause for every 5 minutes. Sampling is conducted every 1 hour, in order to obtain the blending time variations of 1, 2, and 3 hours. Then the blended samples are left overnight in test tubes covered with alumunium foil papers (Fig. 2).

Making the solution of used-cooking oil in n-hexane solvent requires correct proportions of related materials to obtain proper concentration of the solution. Especially for blending time variation, each sample is made with the same concentration of 0.6 milimol/mL with a volume ratio of used-cooking oil and n-hexane given at 0.2 : 3. The variation of the solution concentrations of used-cooking oil in n-hexane solvent is made at (in milimol/mL) 0.2, 0.4, and 0.6. For concentrations of 0.2 and 0.4 milimol/mL, the volume ratio of used-cooking oil and n-hexane are given at 0.4 : 3 and 0.7 : 3, respectively. These samples are ready to be characterized using UV-Vis spectrophotometer [Fig. 3(a)]. For each UV-Vis measurement in this study, the reference solution used is pure cooking oil in n-hexane solvent. The concentration of the pure cooking oil solution is set to be the same as the used-cooking oil solution.

Figure 2 Samples of used-cooking oil that have been blended for an hour to 3 hours (from right to left) and left overnight.

3 Results and Discussion

This study is concerned with the synthesis of carbon nanomaterials from used-cooking oil via LE method using a kitchen blender in n-hexane solution where the quality of the synthesis results is observed optically via UV-Vis spectrophotometer. Samples of the solutions obtained in this study may be observed in Fig. 3. Fig. 3(a) depicts a comparison between used-cooking oil in n-hexane and pure cooking oil in n-hexane in terms of the solution color. Used-cooking oil in n-hexane solution is yellow colored compared to pure cooking oil in n-hexane solution which is colorless. This shows that the used-cooking oil contains certain materials formed after being treated and mixed with n-hexane. It may also relevant to be noticed that the color of used-cooking oil samples before being mixed with n-hexane (Fig. 2) are darker compared to samples of used-cooking oil in n-hexane [Fig. 3(a)]. Fig. 3(b) displays used-cooking oil in n-hexane with concentration variation of 0.2, 0.4, and 0.6 milimol/mL from left to right, respectively. It may be perceived that increasing the concentration of the solution causes the color of the solution to change from light yellow (almost colorless) to dark-yellow. This is to be expected as the concentration gets higher the solution becomes more concentrated. However, this does not happen with pure cooking oil in n-hexane, where increasing the concentration does not affect the color of the solution which remains colorless. Finally, Fig. 3(c) shows the used-cooking oil in n-hexane with blending time variation of 1, 2, and 3 hours from right to left, respectively. It may be observed that as the blending time is increased the color of the solutions change from yellow to light yellow. This indicates that increasing the blending time duration causes the exfoliation activity of the used-cooking oil to increase. The more the used-cooking oil is exfoliated the better the material is mixed within the n-hexane solvent hence the lighter the solution color.

UV-Vis results of used-cooking oil in n-hexane with varying blending time duration may be observed in Fig. 4. UV-Vis results of 1, 2, and 3 hours of blending time durations are given by the black dashed-line, red short-dashed-line, and green solid-line data, respectively. By observing the UV-Vis results in Fig. 4, we focus on wavelengths from 200 nm to 300 nm where GO or rGO exist. It can be seen that the absorbance values decline as the blending time increases. Furthermore, the wavelength at maximum absorbance (peak) gives different values as the blending time increases.

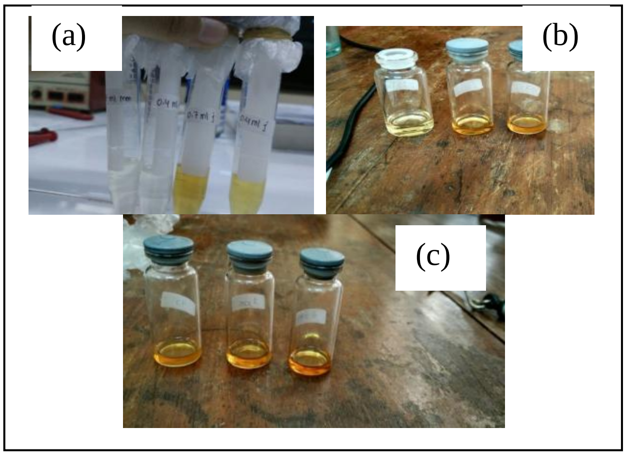

Figure 3 (a) Yellow colored solutions are used-cooking oil in n-hexane, the colorless ones are pure cooking oil in n-hexane, (b) used-cooking oil in n-hexane with concentration variation of (in milimol/mL) 0.2, 0.4, and 0.6 (from left to right), and (c) used-cooking oil in n-hexane with blending time variation of 1, 2, and 3 hours (from right to left).

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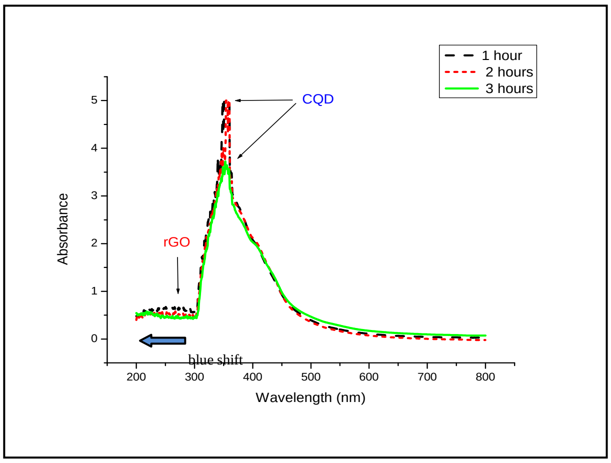

Figure 4 UV-Vis results for blending-time variation of 1 hour [black dashed-line], 2 hours [red short-dashed-line], and 3 hours [green solid-line].

There are two absorbance peaks attained for all blending time durations. For 1, 2, and 3 hours of blending time, the absorbance peaks are obtained at 269.50 nm and 351 nm; 238.5 nm and 349 nm; and 235.50 nm and 349 nm, respectively. The second peaks are quite consistent, i.e. occur around 351 nm to 349 nm and correspond to an existence of CQD nanomaterial. However, the first peaks appear to shift to shorter wavelengths as the blending time increases. This corresponds to a blue shift event as the blending time gets longer, which might be due to the increasing polarity of the solvent. The first peaks above also indicate the existence of GO material. Moreover, the absorbance values decrease as the blending time duration is increased.

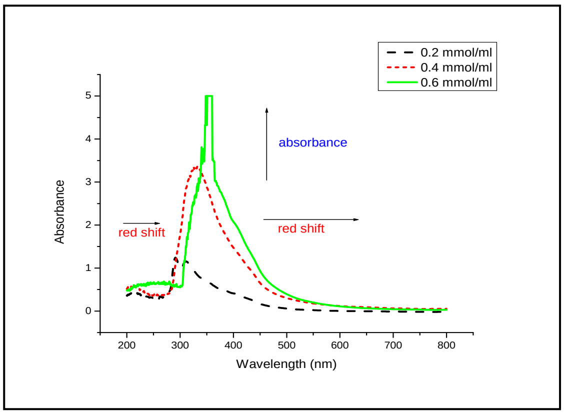

Figure 5. UV-Vis results for concentration variation of 0.2 milimol/ml [black dashed-line], 0.4 milimol/ml [red short-dashed-line], and 0.6 milimol/ml [green solid-line].

The UV-Vis results for used-cooking oil in n-hexane with solution concentration variation may be observed in Fig. 5. The UV-Vis results of black dashed-line, red short-dashed-line, and green solid-line correspond to concentrations of 0.2, 0.4, and 0.6 milimol/mL. For the concentration of 0.2 milimol/mL the absorbance peaks are obtained at 291.5 nm and 311.5 nm. For concentrations of 0.4 and 0.6milimol/mL the absorbance peaks exist at wavelengths of 332 nm and 351 nm, respectively. The results show that the greater the solution concentration, the higher the wavelength at the absorbance peak. This indicates a shift of the absorbance peaks to longer wavelengths producing a red shift. The red shift shows an exfoliation process of used-cooking oil from GO into CQD materials. Moreover, increasing the concentration of the solution increases the absorbance values of the peaks which are consistent with the Lambert-Beer law.

4 Conclusion

The results from this study show that blending time and concentration variations in the treatment of used-cooking oil in n-hexane produces absorbance peaks at wavelengths from 220 nm up to 290 nm which indicates the existence GO material. Another peak arising around 349 nm to 351 nm confirms the presence of CQD material. The results also show that the variation of blending time causes a blue shift; meanwhile the variation of concentration causes a red shift. All in all, used-cooking oil is a potential material for producing GO and CQD materials as an alternative way to utilize waste and reduce environmental pollution.

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