Evaluation of waste human hair as graphene oxide and examination of some characteristic properties

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Abstract: In this study, graphene oxide was synthesized from activated carbon obtained from waste hair for the first time using Modified Hummers method. The Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy and X-Ray Diffraction (XRD) analysis results of synthesized graphene oxide were examined. In SEM images, graphene oxide structures were observed as very thin layers. In addition, the characteristic peaks of graphene oxide were observed in FT-IR spectroscopy and Raman spectroscopy. In the XRD spectra, reflections of the graphene oxide were seen in plane (001) at 20 = 13.66°. It was determined that this structure was hexagonal crystal structure. The distance d (6.39 Å) between the planes and the weave parameters were determined to be 12.80 Å. The transformation process for activated carbon production from human hair waste was patented by Turkish Patent and Trademark Office (Turkish Patent Institute Application Number: (2017/10764)).

Keywords: Human hair; Graphene oxide; activated carbon; Modified Hummers Method.

Atık İnsan Saçının Grafenoksit Olarak Değerlendirilmesi ve Bazı Karakteristik Özelliklerinin İncelenmesi

Öz: Bu çalışmada, modifiye Hummers yöntemi kullanılarak ilk kez atık saçtan elde edilen aktif karbondan grafe noksit sentezlendi. Sentezlenen grafen oksit'in Taramalı Elektron Mikroskobu (SEM), Fourier Dönüşüm Spektroskopisi (FT-IR), Raman Spektroskopisi ve X Işını Kırınım (XRD) analiz sonuçları incelendi. SEM görüntülerinde katmanlı ve çok ince tabakalar halinde grafen oksit yapıları gözlemdi. Ayrıca, FT-IR spektroskopisi ve Raman spektroskopisinde ise grafen oksit ait karakteristik pikler görüldü. XRD spektrumunda grafen oksit ait 2θ = 13.66° (001) düzleminde yansımalara gerçekleştirdi. Oluşan bu yapının heksagonal kristal yapıya olduğunu belirtildi. İnsan saç atıklarından aktif karbon üretimi dönüşüm süreci, Türkiye Patent ve Marka Ofisi tarafından patentlendi (Türkiye Patent Enstitüsü Başvuru Numarası: (2017/10764)).

Anahtar kelimeler: İnsan saç; grafen oksit; aktif karbon; Modifiye Hummers Yöntemi.

1. Introduction

The first G20 Energy Ministers Meeting in the history of the G20 was organized in 2015 in Istanbul. Main purposes of the meeting were global warming and environmental pollution. Whole G20 countries became partners for the idea of urgent studies about these issues by scientists. Based on this, the first thing to do is the proper usage of resources and prevention of the wastage. According to the statistics covered by this study to dump more waste hair mass of 10.000 tons per annum from the Republic of Turkey it was determined to be abandoned.

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Recycling and waste management is the last important issue of G20 decisions. Waste material and environmental pollution have been rapidly increasing due to reasons as population growth, high living standard and urbanization in recent years. Thus, waste disposal become more important compared to past. Human hair waste is also a part of this pollution. Huge amounts of human hair waste which are generated by numerous barbershops in the world are disposed by incineration. Due to the high N content of human hair, this incineration process causes the emission of some gases like ammonia gas, carbonyl sulfide, hydrogen sulfide, sulfur dioxide, phenols, pyrroles and pyridines to atmosphere and triggers the global warming [1]. Otherwise, abandoning the human hair wastes in waste collection centers causes microbiological health problems due to the organic features of fatty hair roots. Because of these reasons, utilization of human hair gets important.

A single human hair acts like a nanotube which consists of 3 layers as; medulla, cortex, cuticle (Figure 1). Medulla, inner layer, contains feeding channel by its keratin, air and water blister structure. Cortex which is made of keratin fibrils, middle layer, provides flexibility and color to hair. Cuticle, outer layer, protects the cortex and contains the dead cell.

![Figure 1. Structure of human hair body](image)

Due to its high content of sulfur-containing keratin protein human hair has remarkable features such as unique chemical composition, slow degradation rate, high tensile strength, thermal insulation, elastic recovery, large and scaly surface, and unique interactions with water and oils [2, 3]. Because of these properties of hair, graphene oxide is synthesized by using activated carbon produced from human hair.

Graphene is a hexagonal, two-dimensional and monatomic, sp²-hybrid regular carbon atom layer. Graphene, which is one of the most important nanomaterials, is an interesting material with its unique properties such as thermal conductivity, high flexibility and high electrical conductivity.

Graphene can be obtained by different methods [4-6]. These methods include reduction of graphene oxide (modified hummers method), micromechanical separation of graphite layers (exfoliation) [7,8], chemical vapor deposition method [9-11], and epitaxial magnification [12].

Graphene can be produced by chemical reduction reactions of graphene oxide produced by modified Hummers method. In addition, the cost of this method is lower. Here, the first step of graphene oxide synthesis is very important for graphene to exhibit the desired properties (conductivity, mechanical, etc.) [13-15].
2. Material and Methods

2.1. Reagents and Apparatus

Crystallographic characterization of active carbon was made with Rigaku make Smart. Surface physical morphology was lightened with Jeol JSM-6610 model. ATR and Perkin Elmer Spectrum 100 were used to determine surface functional groups qualitatively, while Witec Alpha 300 R was used for Raman spectroscopy analyses. Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) were obtained from Sigma Aldrich, sodium nitrate (NaNO\textsubscript{3}) and potassium permanganate (KMnO\textsubscript{4}) were obtained from Merck.

2.2. Synthesis of Activated carbon

Human hair without hair dye and perfume was chosen for this study. The washed human hair was cut to one cm in length and placed to ceramic plates. Heat treatment was applied by 280 °C for 40 minute in air free, inert (argon) environment. During this process, human hair mass which lose the elasticity, is grinded mechanically and the magnitudes of examples downsized to 10 µM in length. At last, the degassing process was performed by waiting of the charred material for 24 hours under 2x10^{-3} Torr pressure and 110°C temperature value.

2.3. Synthesis of graphene oxide

In the literature, graphene oxide was prepared from natural graphite powder by modification of the Hummers method. In this study, instead of graphite, activated carbon produced from waste hair was used. In the first step of the synthesis process, 2 g of activated carbon from waste hair was added to 25 ml of 98% H\textsubscript{2}SO\textsubscript{4} and stirred at room temperature. After the mixture, 100 mg of NaNO\textsubscript{3} was added and stirring continued for a further 30 minutes. Then 3g of KMnO\textsubscript{4} was added to the mixture in a controlled manner. Subsequently, 60 ml of bidistilled water was added in a controlled manner for 25 minutes and finally 120 ml of distilled water and 0.4 ml of 30% H\textsubscript{2}O\textsubscript{2} were added in to the mixture. At this stage it was observed that the color of the mixture changed from black to brown. As resulted product, graphene oxide particles were removed from the solution by centrifugation and dried at 60 °C for 12 hours to yield powdered graphene oxide. [14].

3. Results and Discussion

3.1. SEM Analysis

Figure 2 shows that the graphene oxide and wast human hair structures seen in SEM photographs are observed to be several layers and sometimes scattered overlapping graphene oxide structures in accordance with the literature [16]. As a result of EDX, the presence of 48.3% carbon and 38.7% oxygen elements in the structure indicates that functional groups are formed in the graphene oxide structure.

3.2. FT-IR Analysis

In the FT-IR spectrum of graphene oxide, carboxylic acid groups, hydroxyl groups, epoxy and alkoxy groups should be observed. Figure 3 shows the FT-IR spectrum of graphene oxide. C=O stresses belonging to carboxyl groups were observed at 1708 cm\textsuperscript{-1} and O-H stresses belonging to hydroxyl groups were observed at 3144 cm\textsuperscript{-1}. C-O stress of alkoxy groups gives a wide peak at 1043 cm\textsuperscript{-1}. These results show that waste human hair will be used as nanomaterials.
Figure 2. SEM and EDX images of a) activated carbon b) graphene oxide produced from human waste hair.

Figure 3. FT-IR spectrums of sample graphene oxide
3.3. RAMAN Spectrum Analysis

Figure 4 shows the Raman spectrum of graphene oxide. Raman spectrum of graphene oxide obtained according to preliminary result were given. The bands in the spectrum in carbonized structures are defined as G and D. As known the intensity of the D band (I_D) refers to irregular crystal structures and the intensity of the G band (I_G) refers to regular crystal structures [16]. It is known from the studies that the D and G peaks observed in these structures are adjustable during the synthesis stage. In addition, by calculating the I_D / I_G ratio, information about the crystal structure of the produced sample is obtained [17-20]. As expected in the Raman spectrum, peak D is 1352 cm\(^{-1}\) and peak G is 1561 cm\(^{-1}\). Thus, Raman spectroscopy confirms the structure of the synthesized graphene oxide.

![Figure 4. Raman spectrum of samples](image)

3.4. XRD Analysis

XRD analysis is used to investigate the interlayer changes and crystal properties of the material. In the Figure 5, XRD graph of graphene oxide obtained from waste hair is given. XRD analysis yielded a peak of 2\(\theta\) = 13.659°. In general, the reflection peaks of graphene oxide are between 20(10°-20°). Therefore, XRD spectra are given between 20(10°-20°). In the XRD spectra, reflections of the graphene oxide were seen in plane (001) at 2\(\theta\) = 13.66°. It was determined that this structure was hexagonal crystal structure. The distance d (6.39 Å) between the planes and the weave parameters (c) were determined to be 12.80 Å. These results indicate that graphene oxide has been successfully synthesized from human waste hair using the modified Hummers method. However, as shown in Figure 5, severe reflections were seen at great 20. This due to the phase composition of the chemical elements used in the synthesis step. It is also known that the reflections observed between 20 = 20°-30° belong mainly to hexagonal structure.
Figure 5. XRD graph of activated carbon obtained from hair and obtained graphene oxide.

4. Conclusions

These results indicate that graphene oxide was successfully synthesized by the activated carbon modified Hummers method produced from human waste hair. This study will refer to the future graphene oxide and graphene related studies. It was understood that graphene oxide produced from waste human hair would be useful in electric-electronic, pharmaceutical, defense industry and other technological fields.

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