Superlattices and Microstructures 98 (2016) 379–384

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Large temperature-induced red shift of G-band of functionalized graphene nanosheets synthesized from humic acid

El-shazly M. Duraia [a], [b], *, Gary W. Beall [a]

[a] Texas State University-San Marcos, Department of Chemistry and Biochemistry, 601 University Dr., San Marcos, TX, 78666, USA
[b] Suez Canal University, Faculty of Science, Physics Department, Ismailia, Egypt

ARTICLE INFO

Article history:
Received 1 September 2016
Accepted 1 September 2016
Available online 2 September 2016

Keywords:
Humic acid
Graphenol
Raman analysis
Temperature dependence

ABSTRACT

For the first time, temperature dependence of the G-band frequency for the functionalized graphene nanosheets synthesized using humic acid as precursor has been investigated. The Raman measurements has been performed using the excitation wavelength 514.5 nm and in the temperature range 23–116 °C. The prepared samples showed a negative temperature coefficient as large as -0.087 ± 0.008 cm^{-1}/°C. Relatively large red shift of the G-band has been observed as the substrate temperature increases which indicates the higher sensitivity of the G-band peak position when the temperature varies. Such behavior has been attributed to the large contribution of the thermal expansion due to the lower Young's modulus of the reduced humic acid. This finding is important and opens the door for new applications of reduced humic acid as low cost, environmentally friendly and scalable material.

1. Introduction

Carbon nanomaterials such as fullerene, carbon nanotubes (CNTs) and graphene have attracted a great amount of attention in the scientific community during the past decades. Among these carbon nanomaterials, graphene has been studied intensively due to its superior physical and chemical properties [1–5]. Graphene can be synthesized by many methods such as mechanical cleavage, graphite exfoliation, annealing of silicon carbide thin film *etc.* [6]. However, for commercial production of graphene, an easy, economic and nontoxic method is required. Our group proposed a novel method for preparation of new carbon nanomaterial analogs to graphene oxide by the high pressure catalytic reduction of the humic acid. This new material is called graphenol [7,8].

The reduced humic acid (or graphenol) exhibited a planar morphology similar to graphene oxide. During the last few years our group investigated the properties of the graphenol. The new material showed good properties when it was used as filler for polymer nanocomposites [9]. Recently, the humidity sensing properties of reduced humic acid nanosheets has been investigated [10]. It has further been shown that graphenol can serve as a precursor to grow single crystals of graphene on copper [8].

---

* Corresponding author. Texas State university, Department of Chemistry and Biochemistry, 601 University Drive, San Marcos, 78666, TX, USA; Suez Canal University, Faculty of Science, Physics Department, Ismailia, Egypt.

E-mail addresses: shazly_duraia@yahoo.com, ed24@txstate.edu (E.-s.M. Duraia).

http://dx.doi.org/10.1016/j.spmi.2016.09.002

The temperature dependence Raman spectroscopy of carbon materials such as graphite, carbon fiber [11,12], amorphous carbon [13], highly oriented pyrolytic graphite (HOPG) [14], carbon nanotubes [12,14] and graphene [14] has been reported. However, there are only a few reports about the temperature dependence Raman spectroscopy of reduced graphene oxide. To the best of our knowledge, there is no report about the temperature dependence of the G band frequency for reduced humic acid in the open literature.

In present work, the results of the Raman analysis of the reduced humic acid, or graphenol have been reported. It has been found that, the G-band shifts to lower wavenumbers as the temperature increases. Additionally, relatively large red shift of the G-band position is observed. The measurements were performed at the following temperatures 23, 38, 51, 74, 89, 102 and 116 °C with uncertainty values within ±0.5 °C. The temperature coefficient "γ" was found to be as large as -0.087 ± 0.008 cm^{-1}/°C. This shift is considered to be relatively larger than the reported value for temperature coefficient of other carbonaceous materials such as graphene, graphene oxide, carbon nanotube, HOPG and graphite.

2. Experimental work

1 g of humic acid powder has been mixed by 400 ml DI-water and stirred magnetically overnight then the pH has been adjusted to be 10 using NH_4OH. Then we added acetic acid until pH drops to lower than 2. The reason for this step is to remove all fulvic acid that can dissolve at any pH but humic acid dissolve only in basic solutions, acid base treatment. So the humic acid precipitate has been collected by centrifuge and dissolve again in water by rising the pH to 10 using NH_4OH. The humic acid solution with the Ruthenium catalyst is then loaded to the Parr reactor and flushed by hydrogen gas for three times before the temperature increased to 230 °C and the pressure adjusted to 700PSI (~5.2×10^6 Pa). The humic acid solution was kept at the same pressure and temperature for 48 h under mechanical stirring. By the end of the high pressure catalytic reduction process the color of the solution changed from brownish to black which we call it reduced humic acid or graphenol [7–10,21].

Very diluted solution of the reduced humic acid has been spin coated over silicon substrate. After that the silicon substrate coated by reduced humic acid has been glued by thermal glue on the top of the controlled Peltier heater and the temperature was measured using calibrated thermometer with values reported within ±0.5 °C. The micro-Raman measurements have been performed in backscattering geometry using a lab made setup with Ar + laser of wavelength 514.5 nm as the excitation source. The laser beam size on the sample is measured to be ~3 μm. The spectral resolution and precision of the Raman system are less than 1.0 and 0.2 cm^{-1}, respectively. Local heating due to laser absorption could cause unintended red shifting in phonon energy. To estimate maximum laser power at which local heating is not happening, we carried out Raman measurement for a typical sample at two different laser powers of 5 and 4 mW. Results showed that local heating is not present at these two laser powers. For further assurance of no local heating, we repeated Raman measurement (15 times) at 4 mW for one of our samples. The results showed that, within the error bar due to fitting, there is no red shifting in G-peak position due to laser heating. This helped us to rule out completely the local heating effect at laser power of 4 mW, therefore all Raman measurements were carried out at this laser power. To reach a stable temperature value on the sample we waited 3–4 min and then Raman signals have been collected in backscattering geometry at the following temperatures, 23, 38, 51, 74, 89, 102 and 116 °C for 3–4 min at each temperature. The morphology of the reduced humic acid nanosheets has been studied using scanning electron microscope Helios 400 at accelerating voltage of 5 kV. Bruker D8 Advance Eco with a Cu Kα (1.5418 Å) has been used to study the structure of the obtained material. Transmission electron microscope JEOL JEM 1200EXII TEM has been used to investigate the morphology and structure of our samples.

3. Results and discussion

The morphology of the reduced humic acid nanosheets has been investigated using the SEM. Fig. 1a depicts the SEM image of the typical reduced humic acid nanosheets over silicon substrate. The reduced humic acid has a sheet morphology with an average size of few micrometers. Further investigations has been performed using TEM. Fig. 1b represents the TEM image confirms the sheet morphology of the obtained functionalized graphene. Additionally, the selected area electron diffraction, Fig. 1b inset, confirm crystalline structure of graphene. Furthermore the crystal structure of the as synthesized materials has been characterized by the XRD, Fig. 1c. As it is clear from the pattern there are only two peaks can be seen, the first peak at $2\theta = 24.5$ can be indexed to the (002) of the graphitic structure of carbon. The second peak at $2\theta = 43.5$ which is attributed the (001) plane reflection.

Fig. 2a demonstrates the Raman spectrum of the reduced humic acid as a function of the temperature. Peak fit software is used to obtain peak information such as peak position, linewidth and peak intensity. Raman D and G modes of the humic acid can be seen at 1350 ± 1 and 1598 ± 1 cm^{-1}, respectively. Fig. 2(b) shows a zoom in into G-band region for two temperatures, e.g 23 and 116 °C. A clear red shift of ~8 cm^{-1} can be seen from these two spectra. To establish a relationship between Raman peak position and temperature, the Raman D- and G-peak needed to be peak fitted.

Fig. 3 summarizes the D- and G-peak position as temperature varies from room temperature at 23 °C–116 °C. Although the D-peak does not red shift substantially with temperature, a slow change in energy is observed in Fig. 3a. On the other hand, G-peak red -shift significantly from 1598 cm^{-1} at room temperature to 1590 cm^{-1} at 116 °C. Linear fit to the experimental data reveals temperature coefficient to be -0.019 ± 0.008 cm^{-1}/°C, and -0.087 ± 0.008 cm^{-1}/°C for D-peak and G-peak, respectively.