

THE INFLUENCE OF TIP SONICATION ON STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF GRAPHENE

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Abstract

Although ultrasound is frequently used to disperse carbon nanomaterials in suitable solvents, the propagation of high-amplitude ultrasonic vibrations from the tip sonicator was found to be aggressive and has the potential to break down graphene sheets. Here, the effects of tip sonication time on structural and morphological properties of two types of graphene (graphene oxide and electrochemically exfoliated graphene) was investigated by UV-vis spectroscopy and Atomic Force Microscopy. It was found that the structural composition of the graphene was not affected by ultrasounds emitted from the tip sonicator even for the prolonged period of sonication (60 min). Microscopy analysis showed an increased portion of smaller graphene sheets in the sonicated samples for both types of graphene as a result of graphene sheet fragmentation caused by tip sonication.

Introduction

Graphene is a material composed of a single-atom layer of sp^2 hybridized carbon atoms arranged in a hexagonal honeycomb structure with a carbon-carbon bond length of 0.142 nm [1]. Graphene is the first true two-dimensional (2D) material to become a cornerstone in materials science research ever since its discovery in 2004 [2]. Due to its exceptional and distinctive qualities, it is frequently referred to as a wonder material for the future [3]. This unique structure endows graphene with various superior electronic, optical, mechanical, thermal, and magnetic properties, and it has fascinating applications including sensors, capacitors, photocatalysts, nanoelectronics, and nanocomposites [1].

However, graphene's limited dispersibility in water and other common solvents presents a significant processing difficulty. This issue can be solved by graphene being covalently modified by strong oxidants to introduce oxygen functional groups and obtain graphene oxide (GO). In the structure of GO, while the borders of the sheets have carboxyl and carbonyl groups coupled to sp^2 hybridized carbon atoms, the base plane of GO has hydroxyl and epoxy groups connected to sp^3 hybridized carbon atoms [4]. Although the final product, is abundant in functional groups that include oxygen, the graphene sp^2 honeycomb structure is severely disturbed, which has a negative impact on the material's performance [3]. Graphene's oxidized form contains hydrophilic functional groups that make it easier to process in solutions and enable its mass production at a minimal cost. When graphene oxide is reduced in a subsequent stage, the structure is only partially repaired and a significant number of structural flaws remain. Despite the advantages, it is important to eliminate the functional groups that include oxygen to restore graphene's original properties, particularly its electrical conductivity [2].

The electrochemical process of exfoliating graphene in liquids is another potential low-cost mass manufacturing strategy for graphene. Highly oriented pyrolytic graphite (HOPG) is synthetic graphite that is extremely pure [5].

The majority of these procedures are based on a modified Hummer's method, which includes oxidizing graphite using strong oxidants. Depending on the frequency and intensity, ultrasound

provides a strong approach to the synthesis of various nanomaterials. Understanding the effect of sonication on the surface and structure of nanosheets is important because the surface and structure of nanosheets are critical to their properties and uses [1]. If graphene can achieve uniform dispersion, its extraordinary characteristics and structural distinctiveness can increase the performance of nanocomposites. As a result, ultrasonic dispersion of graphene (tip or bath sonicator) for nanocomposite processing is commonly employed to produce uniform dispersion. The tip sonicator is found to be more aggressive, generating ten times the power of a bath sonicator while producing high-quality graphene in a fraction of the time. The solvent dispersion under tip sonication includes breaking down large agglomerates by the propagation of high amplitude ultrasonic vibrations at frequencies ranging from 20 kHz to 1 MHz. Various works have chosen various sonication settings in recent years (time, amplitude, and frequency) [6].

In this work, an investigation of tip sonication effects on two types of graphene (GO and electrochemically exfoliated graphene) was presented. Graphene was subjected to sonication for a short (10 min) and a prolonged (60 min) period of time. The objective was to compare the influence of tip sonication treatments on the GO and electrochemically exfoliated graphene characteristics by analyzing their morphology and chemical structure through complementary techniques.

Experimental

GO and electrochemically exfoliated graphene were prepared as described previously [5, 7]. Each graphene sample was dispersed in deionized MilliQ water using an ultrasound bath to obtain a graphene concentration of 1 mg/ml. After that, graphene dispersions were subjected to sonication using a tip sonicator operated at 300 W and 24 kHz working frequency (Hielscher UP400St ultrasonic processors) equipped with an S24d7 sonotrode (radiating surface of 0.38 cm²). The dispersions were sonicated at two different times (10 and 60 min) with an amplitude of 72%. To prevent sample overheating, sonication was carried out in an ice bath.

The UV-Vis absorption spectra were recorded using LLG-uniSPEC 2 spectrophotometer. Samples were recorded in quartz cuvettes at room temperature. Atomic Force Microscopy (AFM), Quesant (Agoura Hills, CA, USA), was used for the study of surface morphologies of samples. AFM was operating in the tapping mode, in the air, at room temperature. Standard silicon tip (NanoAndMore GmbH, Wetzlar, Germany) with a constant force of 40 N m⁻¹ was used. Images were obtained at a scan rate of 2 Hz, with 512 x 512 pixels scan resolution over various square areas. The average size of objects in AFM images was determined by Gwyddion software.

Results and discussion

It was speculated that the tip sonication energy and duration might induce structural changes in graphene. To test this statement, we subjected two types of graphene to tip sonication for short (10 min) and prolonged time (60 min). The temperature of the dispersions was kept constant using an ice bath to eliminate the potential effect of overheating on graphene.

GO dispersion in water has a dark brown color, while the dispersion of electrochemically exfoliated graphene is black. We did not notice any color change both for GO and electrochemically exfoliated graphene even after the prolonged sonication time. The dispersions of GO and electrochemically exfoliated graphene sonicated for 10 min possess long-term stability with no visible agglomeration or sedimentation several weeks after the treatment. However, while GO dispersion sonicated for 60 min also shows long-term stability, electrochemically exfoliated graphene sonicated for 60 min is not stable and tends to

agglomerate. To investigate the structural changes in graphene induced by tip sonication, we performed a UV-vis analysis (figure 1).

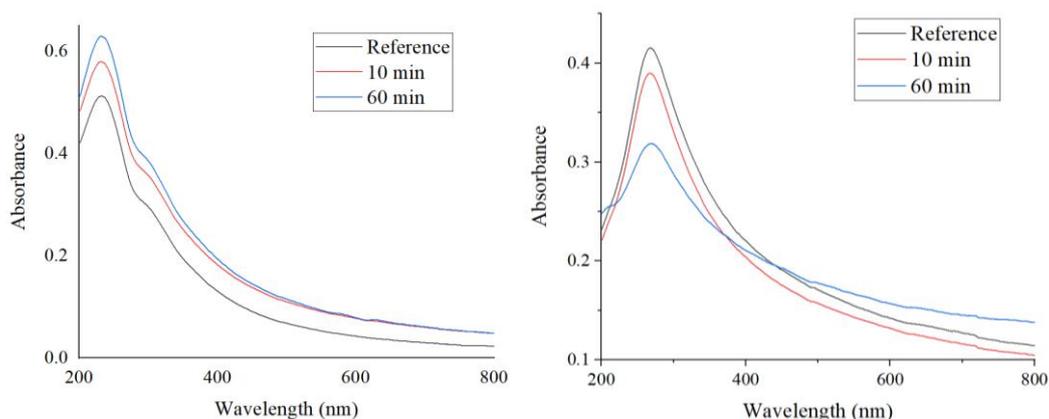


Figure 1. UV-vis spectra of GO (a) electrochemically exfoliated graphene (b) subjected to tip-sonication for 10 and 60 min.

The UV-vis spectrum of GO is characterized by the peak at 230 nm, caused by the π - π^* transition of aromatic C=C bonds, and a shoulder at \sim 300 nm attributed to n- π^* transition of C=O bonds. The peak at 230 nm remains its position after the sonication, and the shoulder at \sim 300 nm can be observed in all the spectra. Exfoliated graphene has only a single broad peak at 270 nm that originates from π - π^* transition of aromatic C=C bonds. The peak at 270 nm for electrochemically exfoliated graphene, along with the absence of a 300 nm shoulder peak, suggests that its graphene structure is largely retained [3]. As for GO, the peak at 270 nm in the spectra of electrochemically exfoliated graphene doesn't show any shift. This implies that the sonication of GO and electrochemically exfoliated graphene for selected time intervals didn't induce structural changes in these materials [3].

Morphology analyses of GO and electrochemically exfoliated graphene sonicated using the tip sonicator were conducted by AFM (figures 2-5). In the AFM images, pristine GO is dominated by large sheets with sizes of several micrometers. It was reported previously that electrochemically exfoliated graphene has a broad distribution in the sheet size (2-12 μ m) [5]. Both GO and electrochemically exfoliated graphene were present as few-layer graphene (FLG). It is undeniable that tip sonication efficiently dispersed both types of graphene in water. However, as revealed in the AFM results, high-intensity acoustic cavitation caused by tip sonication produces severe fragmentation, defect formation, and further exfoliation of graphene. The fragmentation tends to increase with sonication time which was confirmed by the larger portion of smaller sheet fragments in the images of GO and electrochemically exfoliated graphene sonicated for 60 min.

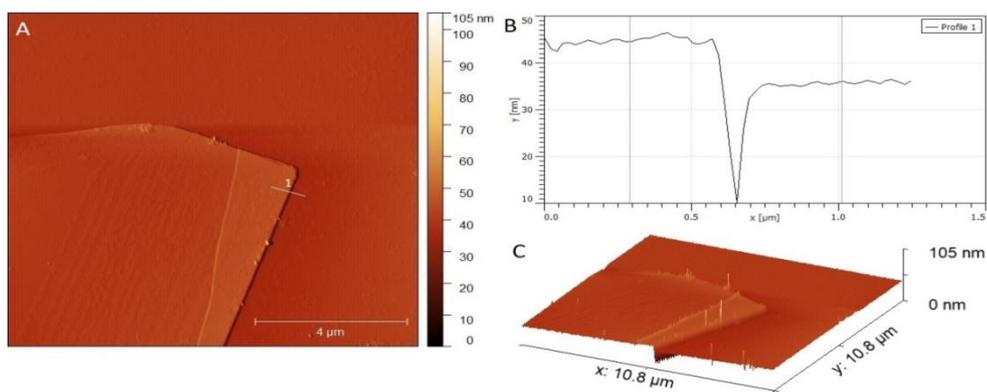


Figure 2. AFM image of GO before sonication (a) the height profile of the scanned surface (b) and 3D representation of the graphene sheet (c).

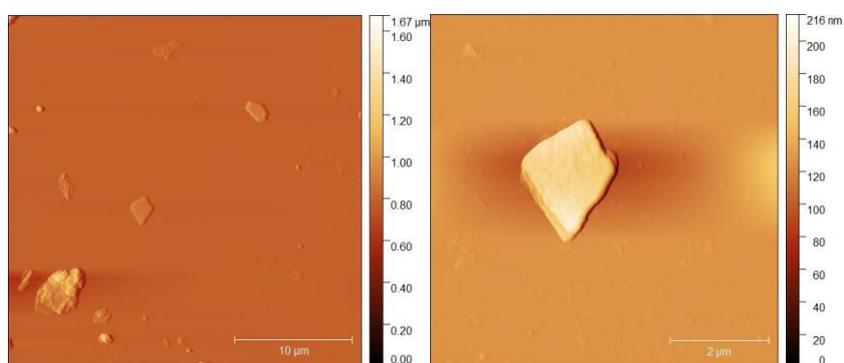


Figure 3. AFM images of GO after 10 min of sonication.

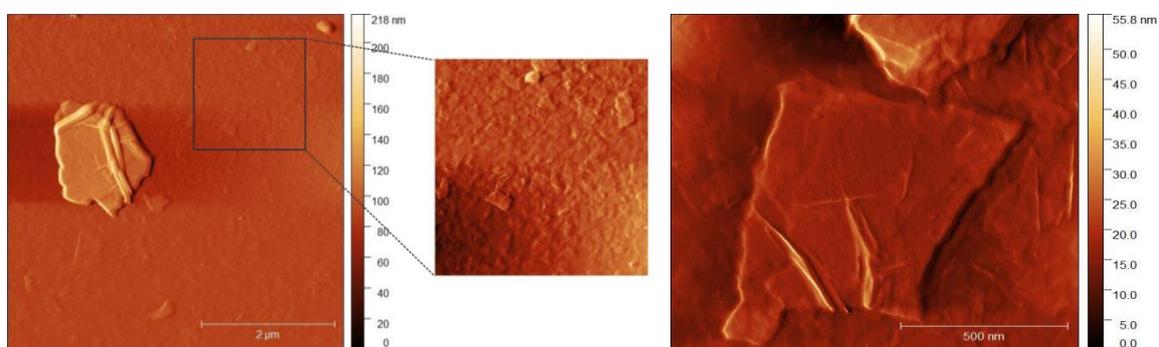


Figure 4. AFM images of GO after 60 min of sonication.

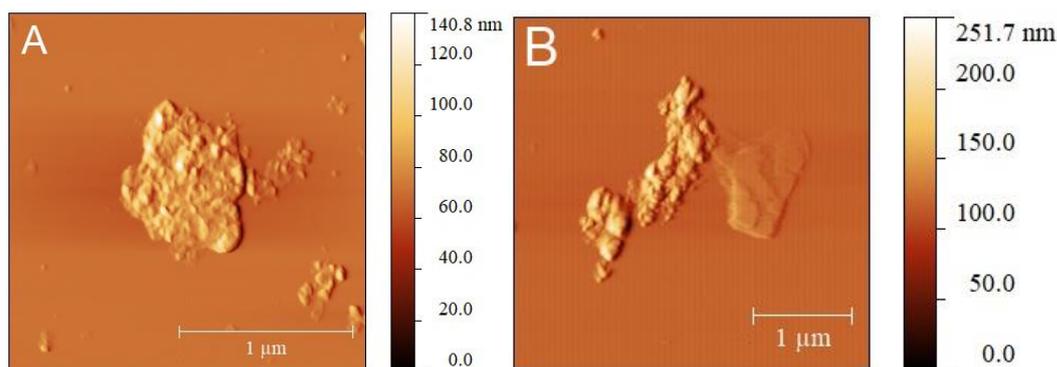


Figure 5. AFM image of electrochemically exfoliated graphene after 10 min (a) and 60 min (b) of sonication.

Conclusion

In this paper, UV-vis spectroscopy and Atomic Force Microscopy were used to explore the effects of tip sonication duration on the structural and morphological features of two forms of graphene (graphene oxide and electrochemically exfoliated graphene). The structural composition of graphene was discovered to be unaffected by ultrasounds generated by the tip sonicator, even after an extended duration of sonication (60 min). As a result of graphene sheet fragmentation produced by tip sonication, microscopy examination revealed an increased share of smaller graphene sheets in the sonicated samples for both forms of graphene.

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