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Synthesis of graphene nanofluids with controllable flake size distributions

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TITLE:

Synthesis of Graphene Nanofluids with Controllable Flake Size Distributions

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KEYWORDS:
Liquid-phase exfoliation, size selection, thermal conductivity, graphene nanofluid, particle size, centrifugation, synthesis.

SUMMARY:
A method for synthesizing graphene nanofluids with controllable flake size distributions is presented.

ABSTRACT:
A method for synthesizing graphene nanofluids with controllable flake size distributions is presented. Graphene nanoflakes can be obtained by the exfoliation of graphite in the liquid phase, and the exfoliation time is used to control the lower limits of the graphene nanoflake size distributions. Centrifugation is successfully used to control the upper limits of the nanoparticle size distributions. The objective of this work is to combine exfoliation and centrifugation to control the graphene nanoflake size distributions in the resulting suspensions.

INTRODUCTION:

Traditional methods used to synthesize graphene nanofluids often use sonication to disperse graphene powder[1] in fluids, and sonication has been proven to change the size distribution of graphene nanoparticles[2]. Since the thermal conductivity of graphene depends on the flake length[3,4], the synthesis of graphene nanofluids with controllable flake size distributions is vital to heat-transfer applications. Controlled centrifugation has been successfully applied to liquid exfoliated graphene dispersions to separate suspensions into fractions with different mean flake sizes[5,6]. Different terminal velocities used in centrifugation lead to different critical settling particle sizes[7]. The terminal velocity could be used to eliminate large graphene nanoparticles[8].

Recently, size-controllable methods used to synthesize graphene via liquid-phase exfoliation have been introduced to overcome the fundamental problems encountered by conventional methods[9-13]. Liquid phase exfoliation of graphite has been proven to be an effective way to produce graphene suspensions[14-16], and the underlying mechanism shows that the process parameters are related to the lower limits of the graphene nanoparticles size distributions. The graphene nanofluids were synthesized by the liquid exfoliation of the graphite with the help of surfactants[17].While the lower limits of the graphene nanoparticle size distribution could be controlled by adjusting the parameters during the exfoliation, less attention is paid to the upper limits of the graphene nanoparticle size distribution.

The goal of this work is to develop a protocol that can be used to synthesize graphene nanofluids with controllable flake size distributions. Because exfoliation is responsible only for the lower size limit of the resulting graphene nanoflakes, additional centrifugation is introduced to control the upper size limit of the resulting graphene nanoflakes. However, the proposed method is not specific to graphene and could be appropriate for any other layered compounds that cannot be synthesized using traditional methods.

PROTOCOL:

1. Exfoliation of graphite in a liquid phase

1.1. Preparation of reagents

1.1.1. In a dry clean flat-bottom flask, add 20 g of polyvinyl alcohol (PVA), and then add 1,000 mL of distilled water.

NOTE: If the suspension was not processed to satisfaction, the step could be repeated to obtain an additional suspension.

1.1.2. Gently swirl the flask until the PVA fully dissolves.

CAUTION: PVA is harmful to humans; thus, protective gloves and surgical masks should be used.

1.1.3. Add 50 g of graphite powder to the flat-bottom flask, and gently swirl the flask until the graphite powder fully disperses in the suspension.

1.1.4. Transfer 500 mL of the resulting suspension to a 500 mL beaker.

1.1.5. Place the beaker under a shear mixer, positioning the beaker near the center of the mixing vessel to prevent the formation of a vortex.

NOTE: All chemical reagents used are of analytical grade.

1.2. Equipment setup

1.2.1. Lower the mixing head to its lowest position (30 mm from the base plane).

1.2.2. Make a water bath by filling a 5,000 mL beaker with room temperature (25 °C) water and position the 500 mL beaker in the bath. Change the water every 30 min.

1.3. Exfoliation

1.3.1. Start the mixer and increase the speed gradually to 4,500 rpm; mix at this speed for 120 min.

1.3.2. Perform the exfoliation step five times for five predetermined times: 40 min, 60 min, 80 min, 100 min, and 120 min. The mixing time determines the lower lateral size limit of the graphene nanoflakes.

1.3.3. Collect the suspensions after each exfoliation step. Each exfoliation step will generate a 500 mL suspension. Label each suspension with the exfoliation time for further treatment.

1.3.4. Centrifuge the collected suspension at 140 x *g* for 45 min to remove the unexfoliated graphite.

1.3.5. Collect the top 80% of the supernatant from each centrifuge tube for an additional centrifugation step.

1.3.6. Collect 400 mL of each sample exposed to different exfoliation times for an additional centrifugation step.

2. Centrifugation

2.1. Centrifuge the resulting suspension at 8,951 x *g* for 45 min.

2.2. Collect the upper 50% of the supernatant in the centrifuge tube, and label the sample with a number.

2.3. Recycle the sediment on the bottom of the centrifuge tube from step 2.2. Add the PVA/water reagent prepared in step 1.1.1 to the sediments and shake the tube vigorously by hand until the sediment is well dispersed in the suspension.

2.4. Centrifuge the suspension at 8,951 x *g* for 45 min; collect the upper 80% for further measurements.

2.5. Repeat the abovementioned centrifugation step four times with four different centrifugation speeds: 5,035 x *g*, 2,238 x *g*, 560 x *g*, and 140 x *g*. The centrifugation speed determines the upper lateral size limit of the graphene nanoflakes.

2.6. Repeat the abovementioned centrifugation step five times for the five resulting suspensions prepared using step 1.3.

NOTE: The protocol can be paused here.

3. Concentration measurements of the resulting nanofluids

3.1. Obtain absorption spectra at a wavelength of 660 nm using ultraviolet–visible (UV-Vis) spectroscopy.

3.1.1. Use the PVA/water solution prepared in step 1.1.1 to calibrate a UV-Vis spectrometer; set the PVA/water concentrations to 0%.

3.1.2. Add the PVA/water suspension to a dry clean sample cell with a path length of 10 mm and obtain a readout using the manufacturer's software. Click the **obtain** button to get the measurement results graph and save the results.

3.1.3. Repeat step 3.1.2 for each of the different samples prepared in step 2.5.

NOTE: The sample cell must be cleaned carefully with distilled water and dried before use each time.

3.2. Determine the graphene weight in the resulting suspension.

3.2.1. Vacuum filter the 100 mL sample suspension using a nylon membrane with a pore size of 0.2 µm.

3.2.2. Wash the membrane film with approximately 1,000 mL of water; repeat this step three times until all the solids are washed from the membrane.

3.2.3. Determine the washed water mass with a high-precision microbalance to obtain the weight of the solids in the 100 mL suspension.

NOTE: The weights include both the weight of the graphene nanoflakes and the PVA polymers.

3.2.4. Analyze the water with thermogravimetric analysis (TGA)[18] to determine the PVA concentration.

3.2.5. Calculate the mean extinction coefficient values of the PVA-stabilized system:

$$A = \varepsilon C_G l \qquad (1)$$

where A is the absorbance measured at 660 nm using UV-Vis spectroscopy, and l is the path length travelled by the UV light during the measurement; the relationship between the absorbance A and the graphene concentration C_G is linear. The extinction coefficient ε is the slope of the curve plotted for the absorbance A as a function of the graphene concentration C_G. When the extinction coefficient ε is determined, C_G can be determined by the absorbance A.

4. Adjusting the concentration of resulting nanofluids

4.1. Vacuum-filter the suspensions using a nylon membrane with a pore size of 0.2 µm.

4.2. Dry the membrane at room temperature for over 12 h.

4.3. Subsequently, rinse the film with hot deionized water.

4.4. Dry the deionized water under a vacuum for 24 h to obtain the graphene nanosheets.

NOTE: The production rate of graphene is approximately 1 mg/mL. If the desired concentration is lower than this, then it is easy to obtain it only by adding PVA/water. If the desired concentration is higher than 1%, then the drying process is necessary. Here, we demonstrate a condition with a desired concentration of 2%.

4.5. Add the PVA/water solution or graphene nanosheets to adjust the concentration.

4.6. If the desired concentration is less than the production rate, add the PVA/water solution prepared in step 1.1.1 to obtain the desired concentration.

5. Measuring the size distributions with dynamic light scattering

5.1. Turn on the nanoparticle analyzer and adjust the detector to C label. Place the sample suspension on the test panel.

5.2. Open the correlator control window software.

5.3. Click **Non-Negative Constrained least square: Multiple Pass** in the menu.

5.4. Set the elapsed time to 2 min.

5.5. Select water as the solvent type.

5.6. Change the diameter of the detector to 100 nm.

5.7. Click the **test** button to obtain the readout and save the results.

5.8. Repeat steps 5.1–5.7 for each of the samples prepared after step 4.

REPRESENTATIVE RESULTS:

The existence of graphene nanosheets can be validated by various characteristic techniques. **Figure 1** shows the results of the UV-Vis measurement for the various flake size distributions produced by the abovementioned protocol. The spectra absorbance peak obtained at a wavelength of 270 nm is evidence of the graphene flakes. Different absorbances correspond to different concentrations. The lowest absorbance observed corresponds to the highest centrifugation speed. The spectra strongly confirm that graphene exists.

The D band and 2D band of the Raman spectroscopy could be used to determine the flake thickness of the graphene nanoflakes. **Figure 2** shows the Raman analysis for the resulting nanoflakes. The D-band of the Raman spectrum is related to graphene sp3 carbon atoms that can help to distinguish between the initial graphite and the graphene nanoflakes. Using Raman spectroscopy, it was discovered that the intensities of the D-band peaks increase with increasing centrifugation speed. At the same time, the D-band intensity is low because the graphene nanosheets that are produced could be defect-free.

Dynamic light scattering is often used to investigate the nanoparticle size distributions of the dispersion. During the experiments, more than 3,000 nanoparticles of each sample were scanned to study the size distribution. The D50 saucer diameter was used to represent the mean diameter of the resulting dispersion. **Figure 3** shows the size distribution of the resulting suspension prepared using different centrifugation speeds.

A TEM image is one of the most instinctive ways to distinguish the graphene nanosheets and graphite nanostructures. The layer number could be easily determined from the TEM image. **Figure 4** shows the transmission electron microscopy (TEM) results for the resulting nanoflakes, clearly showing that graphene is produced. **Figure 5** shows the scanning electron microscopy (SEM) results, showing that the exfoliation is successful.

As the resulting graphene dispersion has two clear size distributions, the mean diameter of each size distribution was presented in **Figure 6** to show the effect of the centrifugation step. The figure shows that the centrifugation step only worked on nanoparticles with mean diameters larger than 1,000 nm. **Figure 6** shows the mean flake sizes of the two peaks present in the size distribution, validating the assumption that centrifugation only affects large flakes.

FIGURE AND TABLE LEGENDS:

Figure 1. UV-Vis extinction spectra after centrifugation at different centrifugation speeds.

Figure 2. Raman spectra of the initial graphite powders and the centrifuged graphene nanoflakes obtained using different centrifugation speeds.

Figure 3. Size distributions of the resulting suspensions obtained using different centrifugation speeds.

Figure 4. TEM results for the resulting nanoflakes. The samples were prepared with 4500 rpm rotor speeds, and the centrifugation speed was 8,951 x *g*.

Figure 5. SEM results for the exfoliated nanoflakes. The sample was prepared using an exfoliation time of 60 min and a rotor speed of 4500 rpm.

Figure 6. Mean flake sizes of two peaks in the size distribution. The size distributions of the resulting suspension show two peaks. The graph shows that centrifugation only works on nanoparticles with mean diameters larger than 1,000 nm.

DISCUSSION:

We have proposed a methodology for synthesizing graphene nanofluids with controllable flake size distributions. The method combines two procedures: exfoliation and centrifugation. Exfoliation controls the lower size limit of the nanoparticles, and centrifugation controls the upper size limit of the nanoparticles.

Although we employed liquid-phase exfoliation of graphite to produce graphene nanoparticles, the following modifications to the protocol should be considered. Additional exfoliation parameters (e.g., rotor speed, graphite concentration, and the use of other surfactants) should be considered to obtain the lower size limit of the graphene nanosheets. During centrifugation, the terminal velocity is vital to determine the critical settling particle size, which could be used to control the upper limit of the nanoparticle size distributions. The terminal velocity, which is determined by the centrifugation speed, should be varied with different types of centrifuges. The use of a supercritical liquid, as well as other assistance methods, could be used to boost the efficiency of the proposed method.

The method presented in this work relies on several techniques (e.g., UV-Vis spectroscopy) to measure the concentration, and the flake size was not well controlled. Additionally, the method described in this work will increase the cost of production. Although this method may be sufficient to produce graphene suspensions, the graphene layer could not be controlled to obtain more efficient heat transfer.

The significance of the proposed method is that the flake lengths have a narrow size distribution. Traditional methods, such as sonication, change the size distributions of the graphene nanoflakes. This leads to unknown effects on the use of graphene nanoflakes in heat transfer applications.

As the production technology of graphene via liquid-phase exfoliation rapidly grows, supercritical liquid-phase CO_2 and ultrasound could be applied to a shear mixer to help fabricate smaller graphene nanosheets. In addition, this method could also be applied to produce other layered compounds.

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DISCLOSURES:

The authors have nothing to disclose.

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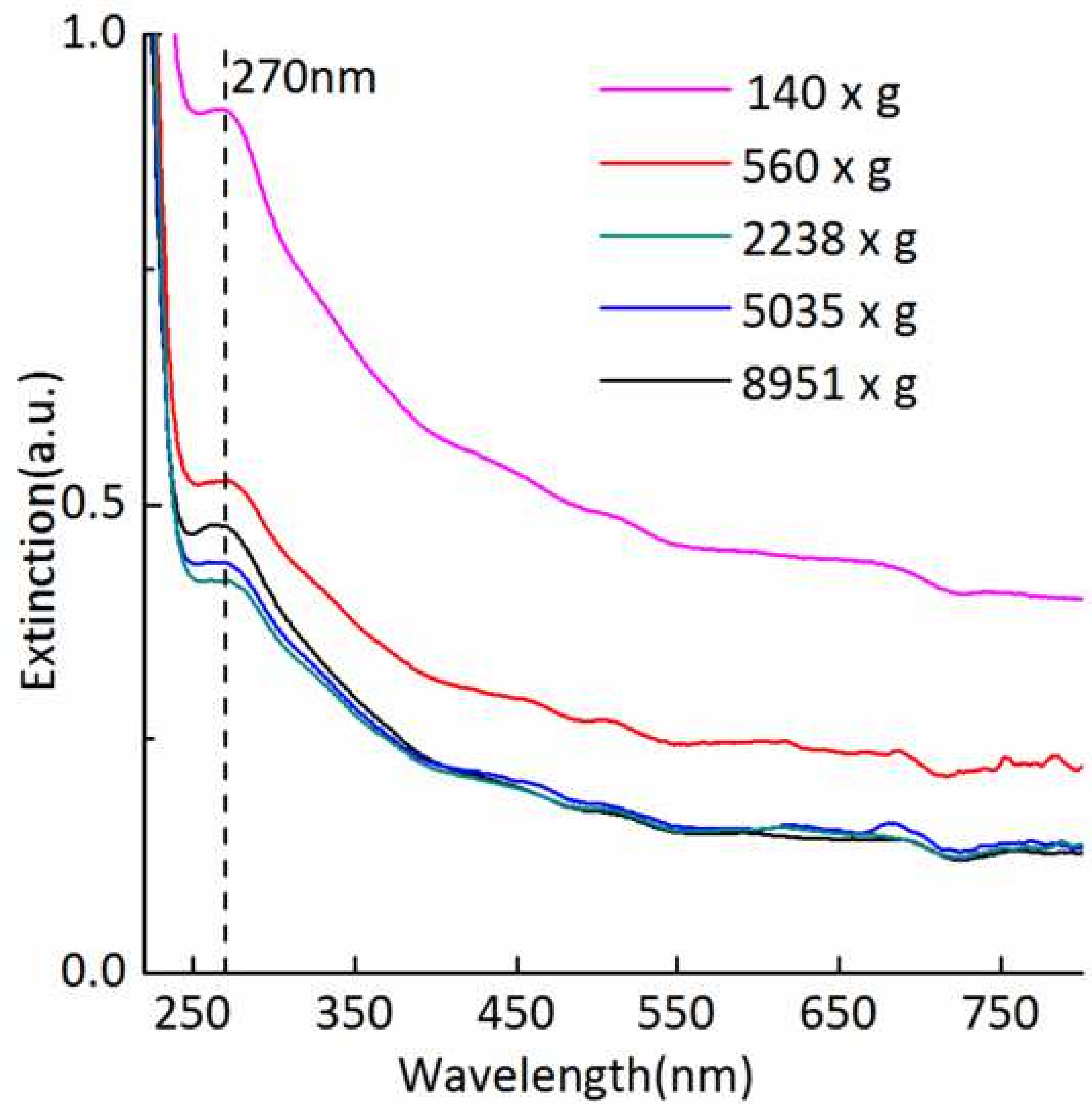
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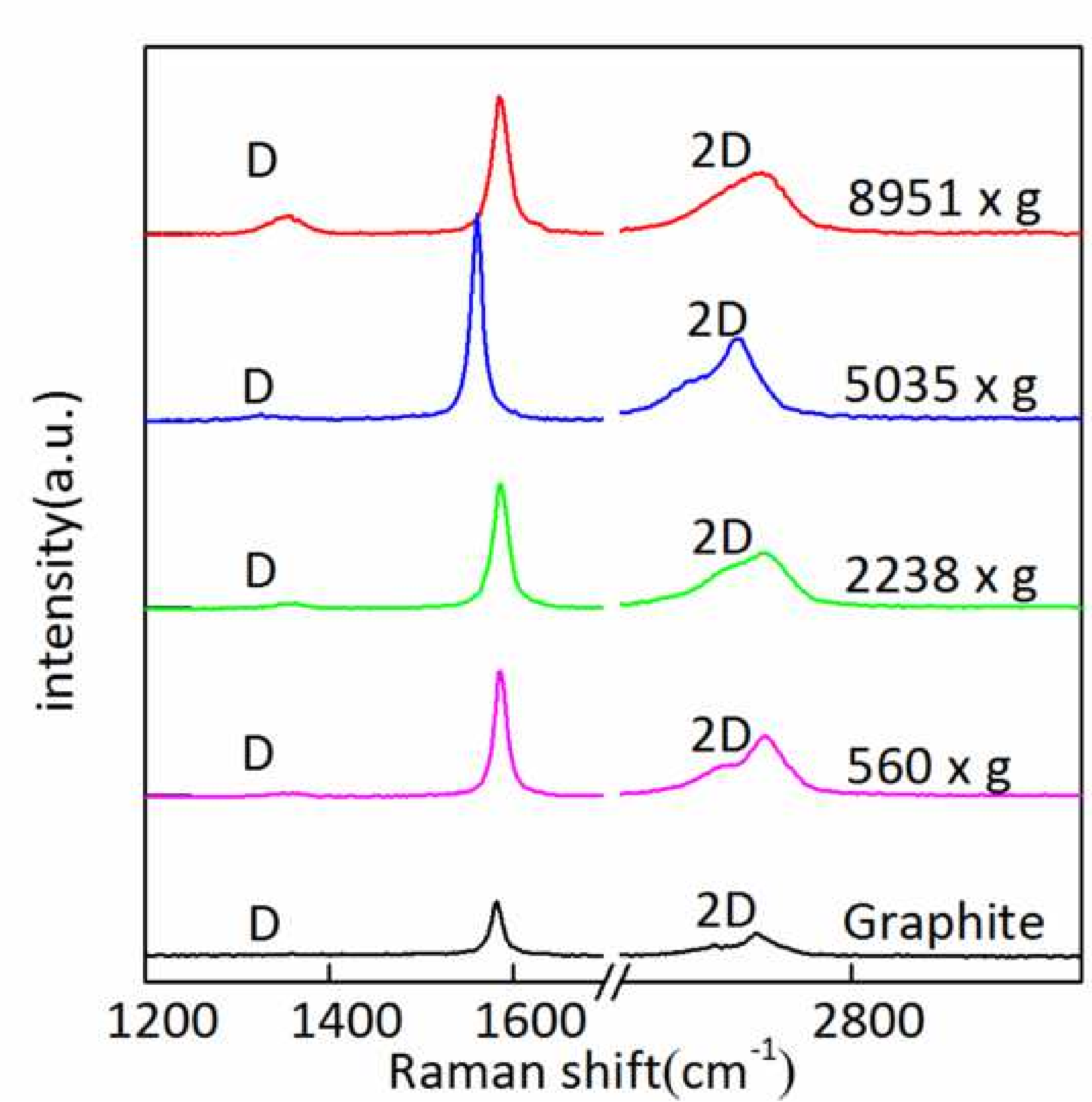

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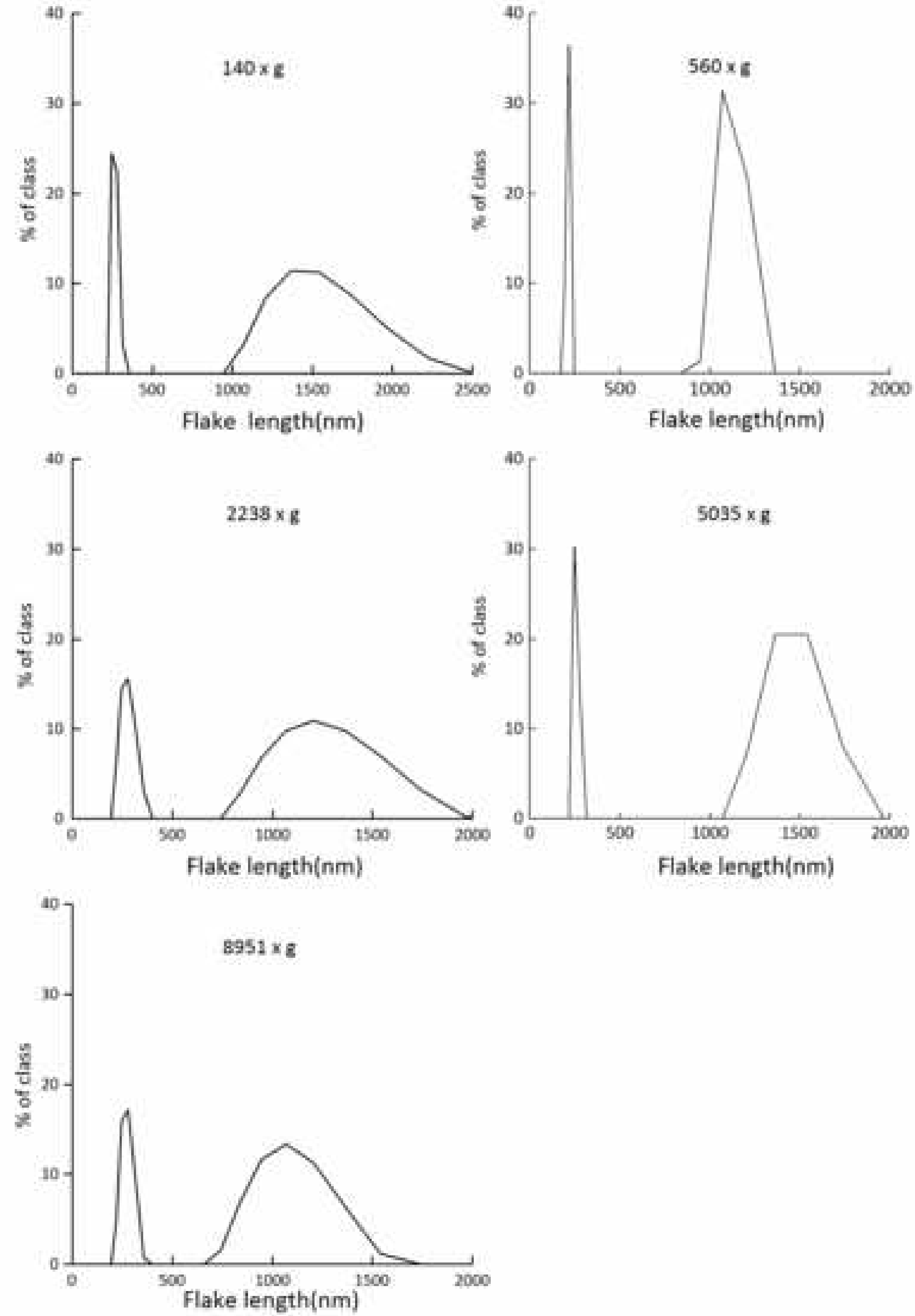
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1000
1500
2000
2500


1 µm

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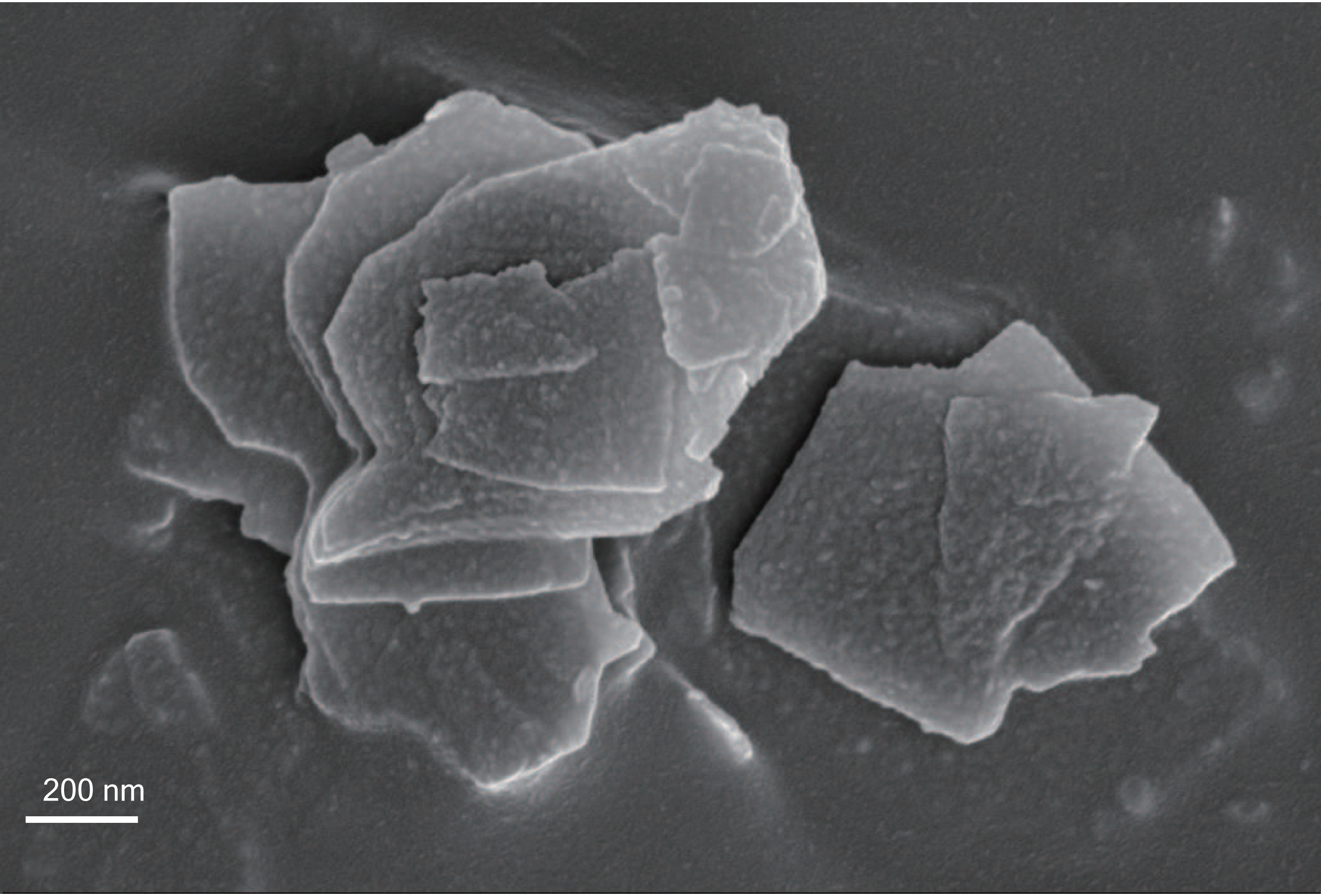

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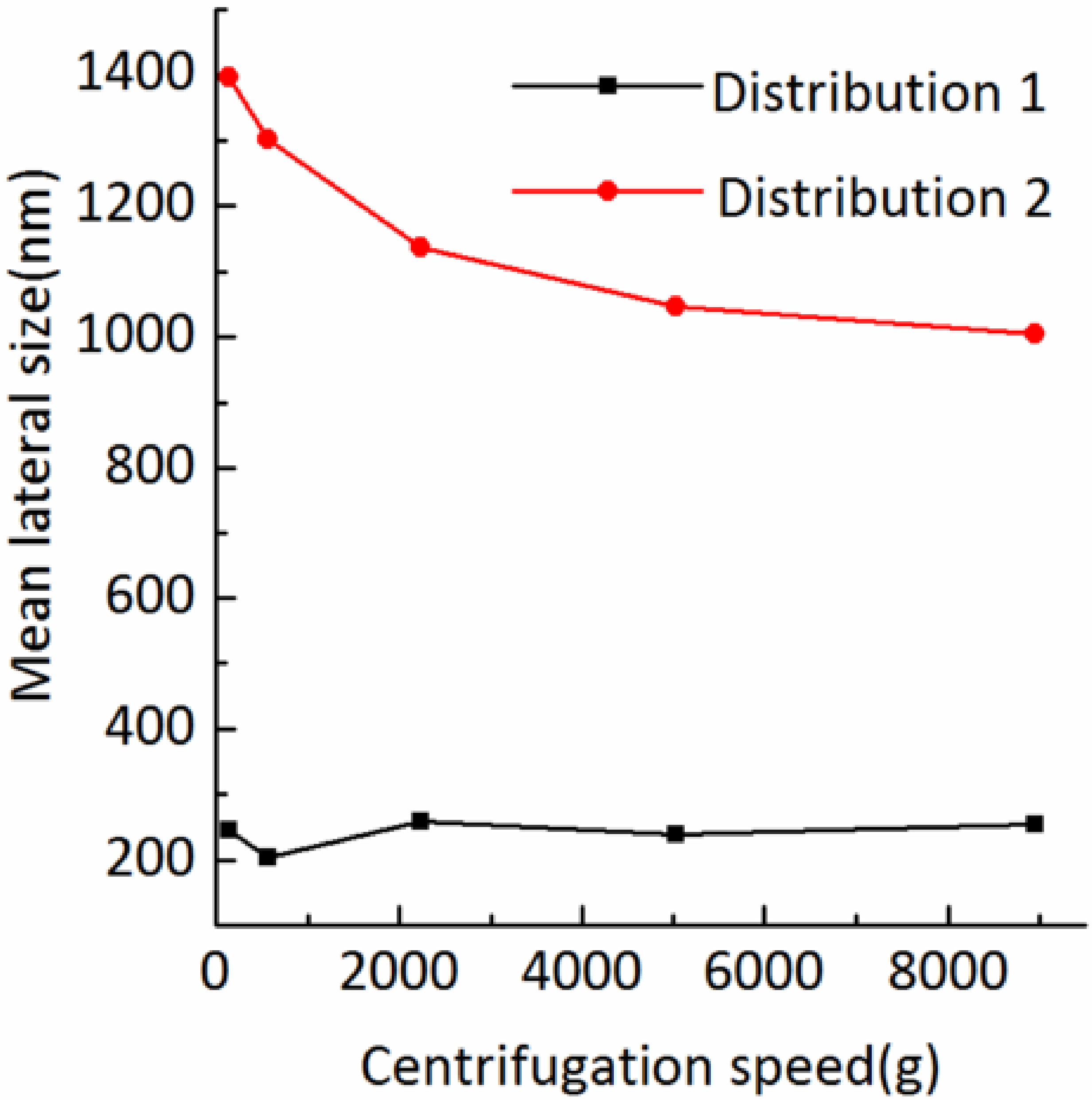

Name of Material/ Equipment	Company	Catalog Number
Beaker	China Jiangsu Mingtai Education Equipments Co., Ltd.	500 mL
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Deionized water	Guangzhou Yafei Water Treatment Equipment Co., Ltd.	
Electronic balance	Shanghai Puchun Co., Ltd.	JEa10001
Filter membrane	China Tianjin Jinteng Experiment Equipments Co., Ltd.	0.2 micron
Graphite powder	Tianjin Dengke chemical reagent Co., Ltd.	
Hand gloves	China Jiangsu Mingtai Education Equipments Co., Ltd.	
Laboratory shear mixer	Shanghai Specimen and Model Factory	jrj-300
Long neck flat bottom flask	China Jiangsu Mingtai Education Equipments Co., Ltd.	1000 ml
Nanoparticle analyzer	HORIBA, Ltd.	SZ-100Z
PVA	Shanghai Yingjia Industrial Development Co., Ltd.	1788
Raman spectrophotometer	HORIBA, Ltd.	Horiba LabRam 2
Scanning electron microscope	Zeiss Co., Ltd.	LEO1530VP
Surgical mask	China Jiangsu Mingtai Education Equipments Co., Ltd.	for one-time use
Thermal Gravimetric Analyzer	German NETZSCH Co., Ltd.	NETZSCH TG 209 F1 Libra
Transmission electron microscope	Japan Electron Optics Laboratory Co., Ltd.	JEM-1400plus
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Dear Editor and Reviewers:

Thank you for your letter and for the reviewers' comments concerning our manuscript entitled "Synthesis of graphene nanofluids with controllable flake size distributions" (ID: JoVE59740R2). Those comments are all valuable and very helpful for revising and improving our paper, as well as the important guiding significance to our researches.

We have studied comments carefully and have made correction which we hope meet with approval. The main corrections in the paper and the responds to the reviewer's comments are as flowing:

Responds to the reviewer's comments:

Editorial comments:

General:

1. 1. There are still some grammar and usage errors; please proofread, ideally by a fluent English speaker.

Response: We feel sorry that we have spelling and grammar errors. We have re-written the whole paper and tried our best to correct the errors according to the editor's suggestion. The sentences with ambiguous understanding were replaced with more clear expressions to help the understanding. And the modification does not change the frame of the paper.

2. The results and figure legends are still a bit lacking in terms of providing context for your figures; please see previous JoVE manuscripts (e.g., https://www.jove.com/video/53505/preparation-of-carbon-nanosheets-at-room-temperature) for examples of how to do this.

Response: thanks for your hint. We added some content to give an extent explanation of the representative results.

Reviewers' comments:

Reviewer #1:

(1) The author needs to further strengthen the novelty and advantages of his/her method employed in this work, and provide more mechanical understanding of the exfoliation process if possible.

Response: We feel great thanks for your professional review work on our article. As you are concerned, there are several problems that need to be addressed. In order to strengthen the novelty and advantages.

The novelty and advantages of our method is that the size distribution is narrowed by both the exfoliation and centrifugation processed. Traditional exfoliation step only account for the lower limits of the graphene nanoparticles size distribution. And our method has proved that centrifugation process only worked on the large nanoparticles bigger than 1000 nm.

Our method is a combination of exfoliation and centrifugation step. The resulting suspension size distribution could be narrowed quantitatively.

Several support materials has add to the submission to support our novelty and advantages. Figure 3 give a demonstration of the resulting size distribution .Figure 6 demonstrated that the centrifugation step only worked on the large nanoparticles.

More content were added to the submission to help understand our novelty and advantages.

(2) In the introduction part, recent development in graphene exfoliation and dispersion may be

further briefly discussed (for this, references of Carbon 2013, 64, 288 -294; Chem. Commun. 2014, 50, 10382; Phys. Chem. Chem. Phys. 2017, 19, 921 may be helpful).

Response: thanks for your suggestions. We have read the materials especially the researches recommended by the reviewers carefully to catch up the recent development of the graphene exfoliation and dispersion. We have added more details about the graphene exfoliation and graphene dispersion, and this part were reorganized to help understanding.

(3) Also, the author needs to correct some typos and refine the language asap.

Response: thanks for your careful checks. We are sorry for our carelessness. Based on your comments, we have made the corrections to make the expression harmonized within the whole manuscript.

Reviewer #3:

Manuscript Summary:

The authors have made all the necessary corrections and clarifications.

Response: thanks for the reviewer's effort.

Reviewer #4:

Accept

Response: thanks for the reviewer's effort.

In this revised version, we tried our best to improve the manuscript and made some changes in the manuscript. The typo and grammar error were corrected carefully. Thanks to the hint from the editor, the material table file format has change to xlsx. These changes will not influence the content and framework of the paper.

We appreciate for Editors/Reviewers' warm work earnestly, and hope that the correction will meet with approval.

Once again, thank you very much for your comments and suggestions.

Sincerely yours

Du Baolei

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