

A Facile and Effective Method for Size Sorting of Large Flake Graphene Oxide

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Abstract - The size of the building blocks fundamentally governs physical performances of the macro-scale graphene based structures since larger building blocks usually yields better mechanical and electrical properties. Density gradient centrifugation method has emerged as a versatile and scalable method for sorting colloidal 2D nanomaterials. This paper provides a facile and effective size sorting approach to graphene oxide (GO) flakes with large sizes up to 40 μm . The GO flakes were dispersed within distilled water. The centrifugation process parameters were calculated with respect to specific size ranges of GO flakes. Scanning electron microscopy utilized to prove the effectiveness of the separation process. Image processing analysis showed GO flakes with specific size ranges can be separate from aqueous suspension by controlling rotational speed and centrifugation time. The process was performed by using common benchtop centrifuges with low intensity centrifugal fields which requires low investment for a scalable process.

Keywords: Graphene oxide, centrifugation, size sorting, processing

1. Introduction

Graphene is a planar monolayer of carbon atoms that arranged into a two-dimensional honeycomb lattice with sp^2 hybridized bonds [1]. The unique π -conjugation in graphene endows extraordinary mechanical, thermal and electrical properties which attract great scientific attention of many theoretical and experimental studies during recent years in various fields such as energy storage [2], electronic devices [3] and nanocomposites [4]. As a consequence, various graphene based structures in nano-, micro- and macro-scale have been synthesized and characterized, including 2D graphene papers [5] and 1D graphene fibers [6, 7].

The size of the building blocks fundamentally governs physical performances of the macro-scale graphene based structures since larger building blocks usually yields better mechanical and electrical properties up to three-fold increase [8, 9]. However, the difficulty of producing high quality graphene flakes with controlled size and chemical composition still remain as a challenge especially in scalable industrial processes. Chemical exfoliation of graphite with strong acid treatment, a technique introduced by Hummers and Brodie, one of the most preferred production method to generate graphene oxide (GO) flakes [10] which afford good dispersion within water and other commonly used solvents to form liquid crystal phases due to existence of epoxy and hydroxyl groups formed in the basal plane and carbonyl and carboxylic acid groups in the edge sites [11]. However, the oxidation and exfoliation processes of the graphite results diverse sizes of GO flakes. Therefore, the separation of the graphene based flakes with well-defined size is of importance for the accurate control of the macro-scale mechanical and electrical properties of the graphene based structures.

Centrifugal separation is a simple method used for size sorting of nano-scale materials distributed in liquid medium. It has been utilized generally as a post-synthesis size selection approach including GO flakes [12, 13]. This work investigates how GO flakes distributed in aqueous medium can be sorted in definite size ranges before using to prepare macro-scale graphene based structures. First, centrifugation times for the specific size ranges are calculated based on Stokes' law to separate GO flakes from homogenously distributed aqueous medium. Next, GO/water suspensions are centrifuged by selecting appropriate angular velocity and centrifugation time. Scanning electron microscopy (SEM) is utilized to monitor centrifuged GO flakes and the size of GO flakes are calculated by image processing of SEM images and particle size analysis.

2. Theoretical Background

In general, size sorting in centrifugal fields takes place when a difference in velocity between GO flakes of different sizes is generated [14]. Neglecting interactions between particles, viscosity increment of the solvent with addition of GO flakes and diffuse effects [14], the centrifugation time (T, s) of a spherical particles in a liquid suspension is calculated by the following expression derived from Stokes's law;

$$T = \frac{9l\eta}{2r^2(\rho_p - \rho_s)g} \quad (1)$$

where T (*unit seconds*) is time taken to precipitate suspended particles, l is depth of solution (m), r is radius of suspended particles (m), η viscosity of solution ($Pa.s$), ρ_p density of suspended particles ($kg\ m^{-3}$), ρ_s density of solution ($kg\ m^{-3}$). Note that, Stokes' law is applied to spherical particles; however, GO flakes are in 2D morphology which are typically not spherical. Therefore, the particle radius in the regarding equation defines edge length of individual GO flakes assumed as squares.

As the rotor of centrifuge spins with a definite angular velocity, an apparent centrifugal force acts on the suspension and pushes radially outwards towards the side of the tube in the meantime. Schematic illustration of the centrifugation process is presented in Figure 1.

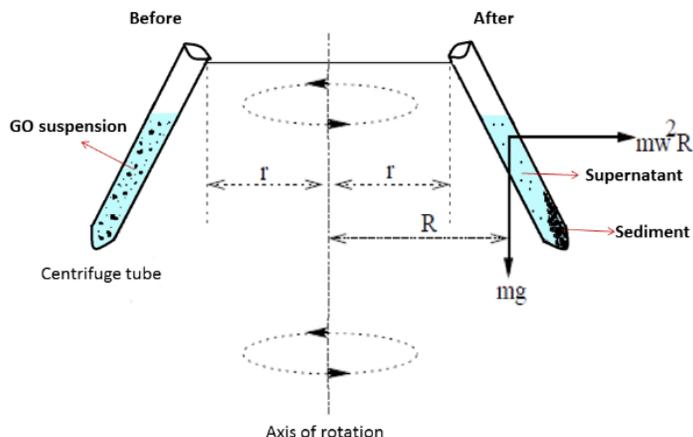


Fig. 1: Theory of centrifugation.

As seen in Figure 1, the force affected onto a particle in suspension during centrifugation depends both of the angular velocity (ω) and the radius of the centrifuge rotor (R). Since the latter varies with different models of centrifuge, this makes it difficult to compare centrifuge times and speeds across different devices. This issue is resolved by quoting centrifugation in terms of relative centrifugal force (RCF) which is defined as the ratio of the force acting on a particle by centrifugation to the force acting on the particle by gravity and expressed as follows;

$$RCF = \frac{\omega^2 R}{g} \quad (2)$$

where ω angular velocity of centrifuge ($radian\ s^{-1}$), g gravitational acceleration ($m.s^{-2}$) and R radius of the circular motion of the centrifuge (m). However, Eqs. (2) is usually rearranged as;

$$RCF = 1.118r \left(\frac{RPM}{1000} \right)^2 \quad (3)$$

where *RPM* rotational speed (*units revolutions per minute*) and *r* radius of the centrifuge rotor (*m*) which is measured as 0.03 *m* in our case.

Thus, the centrifugation time can be expressed as;

$$T = \frac{9l\eta * RCF}{2r^2(\rho_p - \rho_s)w^2R} \quad (4)$$

Based on the Eqs. (4), the centrifugation time of the GO flakes with definite sizes can be calculated. The typical values used in Eqs (4) to calculate centrifugation time of the GO flakes with definite sizes are listed in Table 1.

Table 1. Typical values used calculate centrifugation time of the GO flakes with specific sizes.

Symbol	Description	Value
<i>l</i>	Depth of solution (m)	0.08
η	Viscosity of water (at 20 °C) (Pa.s)	1.002x10 ⁻³
<i>r</i>	Radius of GO (m)	5x10 ⁻⁶ , 10x10 ⁻⁶ , 15x10 ⁻⁶ , 20x10 ⁻⁶ , 25x10 ⁻⁶ , 30x10 ⁻⁶ , 35x10 ⁻⁶
ρ_p	Bulk density of GO (g/cm ³)	1.8 (at 20°C)
ρ_s	Density of water (g/cm ³)	1.00 (at 20°C)
<i>R</i>	Radius of rotation (m)	0.086
<i>w</i>	Angular velocity (rad.s ⁻¹)	6000 RPM (628.319 rad.s ⁻¹) 5000 RPM (523.599 rad.s ⁻¹) 4000 RPM (418.879 rad.s ⁻¹) 3000 RPM (314.159 rad.s ⁻¹) 2000 RPM (209.440 rad.s ⁻¹)

3. Experimental Section

3.1. Separation of GO Flakes with Centrifugation Process

GO flakes were purchased from Graphene Supermarket, USA (single layer nanoplatelets content >97%) with flake sizes up to 40 μm. First 10 mg of GO flakes were dispersed in 10 mL distilled water effectively by aid of sonication and magnetic stirring, respectively. Following, centrifugation process was utilized to separate GO flakes with specific sizes. Hettich EBA 20 centrifuge with a rotor radius 86 mm and a maximum rotational speed of 6000 rpm was used during centrifugation process. The centrifugation times according to Eqs. (4) for fixed GO flake size ranges and rotational speeds are calculated and listed in Table 2. Since the regarding centrifuge allows to set centrifugation times as minutes, all of the calculated centrifugation times were represented in minutes. Note that, it takes thirty seconds for the centrifuge to accelerate and slow down and this time is not included into the calculated separation times.

Table 2. The calculated centrifugation times of the GO flakes with specific size ranges for the given rotational speeds.

Rotational speeds	GO flake size ranges					
	0-5μm	5-10μm	10-15μm	15-20μm	20-25μm	25-30μm
6000 rpm	6'	2'	1'			
5000 rpm	7'	2'	1'			
4000 rpm	9'	3'	1'			
3000 rpm	12'	3'	2'	1'		
2000 rpm	17'	5'	2'	2'	1'	
1000 rpm	34'	9'	4'	3'	2'	1'

The GO flakes were separated using centrifugation at different rotational speeds and centrifugation times according to Table 2 for specific flake sizes, and the supernatant solution was then decanted. The sediment was redispersed in 10 mL distilled water, and the centrifugation and decanting steps were repeated to prepare size-sorted GO flakes. The selected centrifugation process parameters for the flake size ranges as 0-5, 5-10 and 10-15 μm are 6000 rpm/6 min, 5000 rpm/2 min and 4000 rpm/1 min, respectively. The typical separation process of GO flakes with specific size ranges is schematically illustrated in Figure 2. After separation, the supernatant solution was dried in silicon mould at 60°C for 4h under vacuum conditions to obtain a powder for characterization. Since, the goal of the centrifugation process to separate at least half of the GO flakes with different flake size ranges, some process steps were repeated as shown in Figure 2.

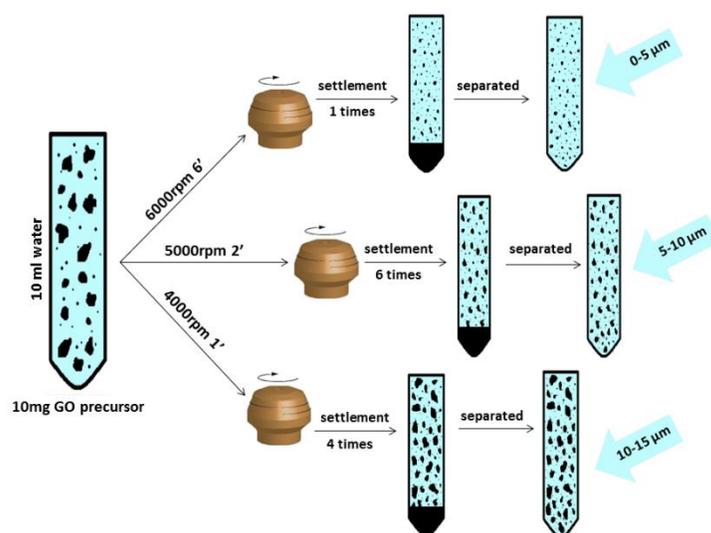


Fig. 2: Schematic representation of the centrifugation process utilized to separate GO flakes with specific sizes.

3.2. Characterization

The resulting dried GO flakes were monitored using scanning electron microscopy (JEOL SEM-7100-EDX). At least ten SEM images were recorded from different areas of the deposited samples on Si wafer, and image processing was applied to measure GO flake areas. Assuming GO flakes are square, the GO flake sizes were calculated from at least 400 GO flakes. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific K-Alpha spectrometer using a monochromic Al Ka source at 1000 eV. Perkin Elmer 1725 FT-IR spectrometer with ATR unit was used during whole experiments with scanning range 550–4000 cm^{-1} at a resolution of 4 cm^{-1} .

4. Results and Discussions

The size distribution of purchased GO flakes is represented in Figure 1a. According to the inset, the flake sizes of the GO precursor are mostly in the range of 5 to 15 μm . Therefore, we aimed to separate flakes smaller than 15 μm by choosing appropriate centrifugation process parameters to separate half of the flakes from the water suspension. The SEM image of the GO precursor is shown in Figure 1b. The size distribution graph of the GO precursor was calculated by measuring more than 800 particles from different SEM images. Fig. 2b shows the FTIR spectra of GO precursor. The peaks at 17200 cm^{-1} (C=O stretching vibrations), at 1616 cm^{-1} (skeletal vibrations C-C), at 1348 cm^{-1} (O-H stretching vibrations), at 1165 cm^{-1} (C-O-C stretching vibrations), at 1034 cm^{-1} (C-O stretching vibrations) are characteristic for the GO [15]. XPS survey spectrum (Figure 1d) shows the calculated value of C1s/O1s (atomic ratios) was 2.08. Curve fitting of the C1s was performed using a Gaussian-Lorentzian peak shape. The peaks of C1s spectra are assigned to four components that correspond to carbon atoms in different functional groups: the nonoxygenated ring C(C-C), the C in C–O bonds (C-OH), the carbonyl C (C=O), and the carboxylate carbon (O=C-OH) [16].

Figure 4a shows the GO flakes in the test tube before centrifugation process. As indicated in Figure 4b, c, after centrifugation in the 5000 and 4000 rpm the GO concentration in water suspension decreases since the light brown colour of the suspension appeared as lighter brown supernatants in colour.

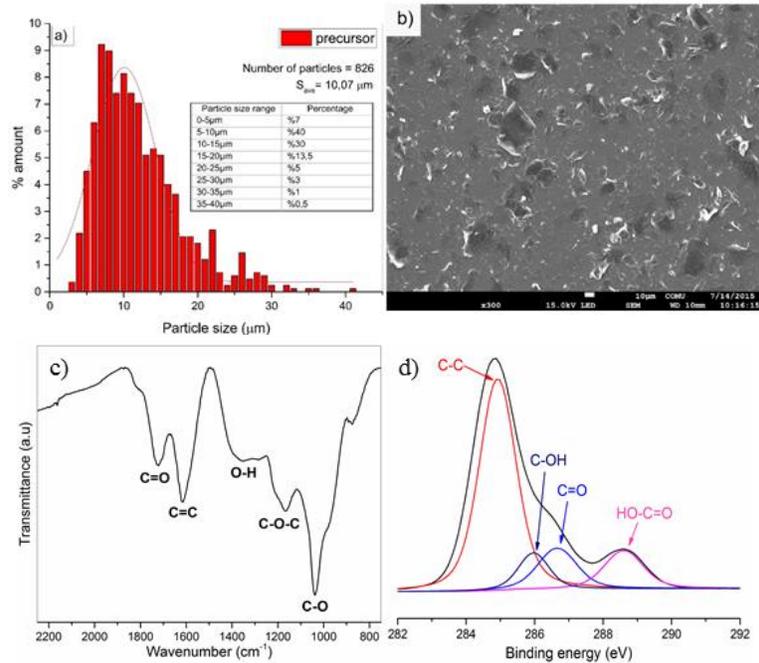


Fig. 3: The characteristic structural and morphological properties of GO precursor used in experiments, a) size distribution of GO flakes based on image processing analysis, b) A typical SEM image of GO precursor (scale bar 10 μm), c) FTIR spectrum the GO flakes, d) XPS spectrum of GO flakes.

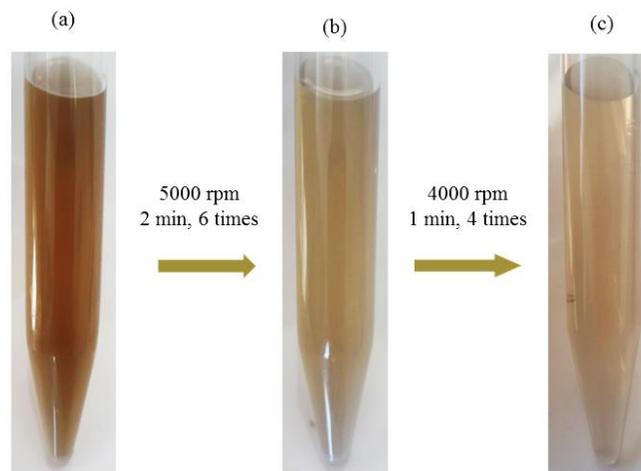


Fig. 4: Selective centrifugation of GO flakes in test tubes (a) before and (b,c) after centrifugation, in the (b) 5000 rpm (c) 4000 rpm.

The rational speed and the centrifugation time are crucial parameters for size sorting of GO flakes. In particular, by increasing the rotational speed and reducing the centrifugation time, the amount of sediment increases: by centrifugation either at 6000 rpm for 6 min, at 5000 rpm for 2 min, and at 4000 rpm for 1 min, we obtain, respectively, 6.15, 8.74 and 11.97 μm of the average GO flake sizes as shown in Figure 5. In actuality, GO flakes smaller than 5 μm were observed in all SEM images taken after second and third step of centrifugation process. This is attributed to break of large GO flakes during preparing GO sediments for next separation process. It is known that bath-sonication mixing of GO flakes results decreasing sizes and consequently decreases the average flake size of the sediment. Therefore, we applied bath-sonication to disperse GO sediment in water for 5 min to minimize damage and following mixed with vortex shaker for 2 min.

After the separation of GO flakes with sizes smaller than 15 μm, the average size of GO flake sediment at the bottom of the tube is measured as ~17 μm as shown in Figure 6. This proves the effectiveness of selective centrifugation for GO flake size sorting, while requiring low centrifugal fields, achievable with ordinary benchtop centrifuges. It must be mentioned

that particle size analysis of GO flakes was also performed for all cases to compare results obtained by image processing analysis; however, higher average flake sizes more than 20% of the regarding image processing results were obtained which was attributed to low concentration of GO flakes in water suspension.

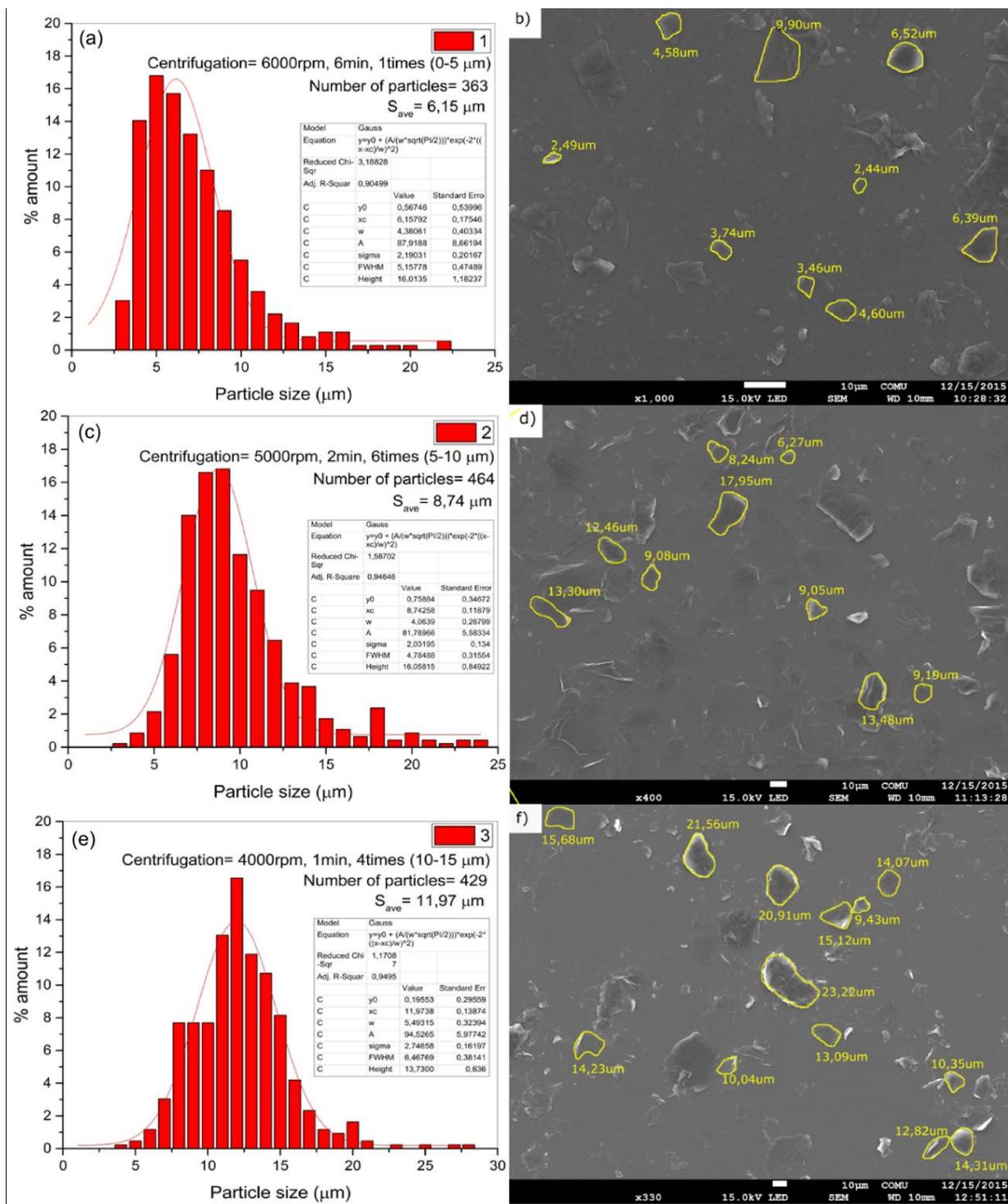


Fig. 5: The flake size distribution of separated GO supernatants a) 6000 rpm 6 min, c) 5000 rpm 2 min, e) 4000 rpm 1 min, and corresponding SEM images selected from image processing of the flakes (scale bar 10 μm), b) 6000 rpm 6 min, d) 5000 rpm 2 min, f) 4000 rpm 1 min.

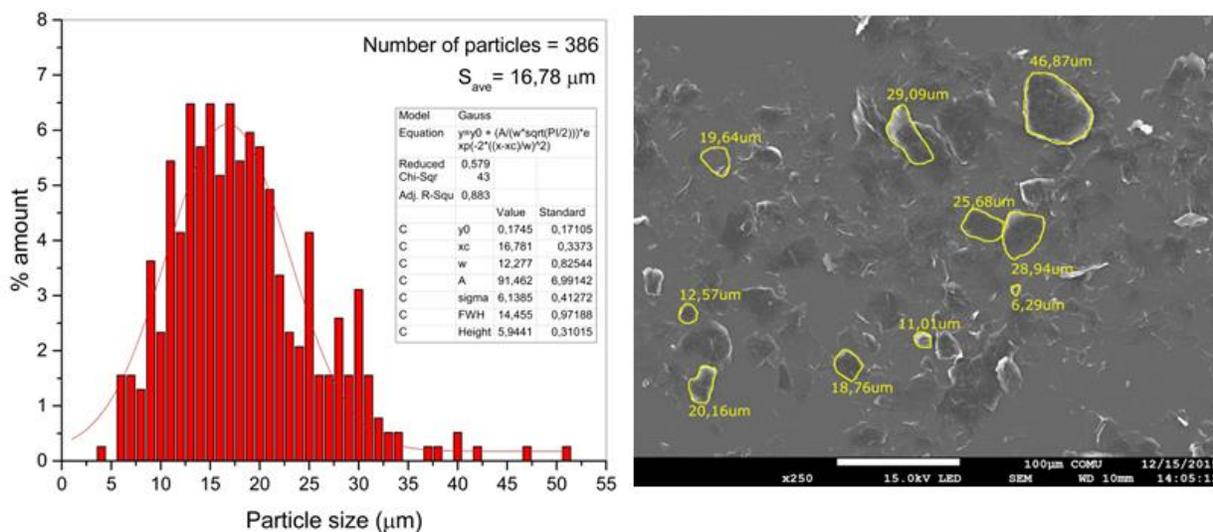


Fig. 6: The flake size distribution and corresponding SEM images selected from image processing of the flakes of GO sediment.

5. Conclusion

In this paper, it has been demonstrated the viability of centrifugation process for size selection of GO flakes with large sizes by in distilled water medium without the use of chemical additives or other solutes. The centrifugation process parameters rotational speed and centrifugation time were calculated correspond to specific GO flake sizes. The GO flakes with sizes up to 15 μm were separated into three groups with average sizes 6, 8 and 12 μm . In addition the average flake size of GO sediment was measured as 17 μm . The total calculated centrifugation time 9 min for three stepped separation process without repeat and mixing times; moreover, it takes approximately 90 min half of the matter for a single tube including 10 mg GO flakes. The proposed process to sort of GO flakes with specific size ranges effectively was implemented in common benchtop centrifuges with low intensity centrifugal fields which requires low investment for a scalable process.

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