

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry



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

Influence of the ultrasound cavitation intensity on reduced graphene oxide functionalization

Aleš Ručigaj^a, Justin G. Connell^b, Matevž Dular^c, Boštjan Genorio^{a,*}

^a University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, SI-1000 Ljubljana, Slovenia

^b Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, United States

^c University of Ljubljana, Faculty of Mechanical Engineering, Aškerčeva 6, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Keywords: Graphene oxide Poly(vinyl alcohol) Ultrasonication Surface functionalization

ABSTRACT

Graphene is a valuable and useful nanomaterial due to its exceptionally high tensile strength, electrical conductivity and transparency, as well as the ability to tune its materials properties via functionalization. One of the most important features needed to integrate functionalized graphene into products via scalable processing is the effectiveness of graphene dispersion in aqueous and organic solvents. In this study, we aimed to achieve the functionalization of reduced graphene oxide (rGO) by sonication in a one-step process using polyvinyl alcohol (PVA) as a model molecule to be bound to the rGO surface. We investigated the influence of the sonication energy on the efficacy of rGO functionalization. The correlation between the performance of the high-intensity ultrasonic horn and the synthesis of the PVA functionalized rGO was thoroughly investigated by TGA coupled with MS, and IR, Raman, XPS, Laser diffraction, and SEM analysis. The results show that the most soluble PVAfunctionalized rGO is achieved at 50% of the ultrasonic horn amplitude. Analysis of cavitation dynamics revealed that in the near vicinity of the horn it is most aggressive at the highest amplitude (60%). This causes rGO flakes to break into smaller domains, which negatively affects the functionalization process. On the other hand, the maximum of the pressure pulsations far away from the horn is reached at 40% amplitude, as the pressure oscillations are attenuated significantly in the 2-phase flow region at higher amplitudes. These observations corelate well with the measured degree of functionalization, where the optimum functionalized rGO dispersion is reached at 50% horn amplitude, and generally imply that cavitation intensity must be carefully adjusted to achieve optimal rGO functionalization.

1. Introduction

Graphene exhibits a number of unique properties, such as exceptional electrical and thermal conductivity, mechanical flexibility and optical transparency [1]. Unique structural features and outstanding performance characteristics make graphene a suitable material for the rapidly developing fields of nanoelectronics, nanocomposites, supercapacitors, and sensors. Due to its outstanding potential, the research community is exploring various aspects of graphene chemistry [2–4]. To modify and/or improve the desired properties of graphene, significant efforts have been made to modify the surface and increase the degree of graphene functionalization [5]. One of the most important features needed to integrate functionalized graphene into products via scalable processing methods is the effectiveness of graphene dispersion in aqueous and organic solvents, which can be achieved by changing the nature of the functional groups [6–8]. To achieve functionalization of graphene with good processability and high dispersity, graphene oxide (GO) or its reduced form (rGO) has been widely used as a starting material for the formation of functionalized graphene derivatives [9–11].

GO can be effectively prepared by oxidation of natural graphite using various methods such as the improved Hummers' method, the Brodie's method, and the Staudenmaier's method [12]. The relevance of GO is reflected in the oxygen-rich functional groups with a significant hydrophilic character, which yields high dispersity in aqueous media and some organic solvents, as well as affects its chemical reactivity. Postreduction of GO leads to the preparation of a reduced GO (rGO) surface also suitable for further functionalization [13]. rGO has an intrinsically hydrophobic nature and, like other carbon allotropes, it is poorly dispersible in water and most organic solvents. However, good dispersibility in various solvents is crucial for subsequent materials

* Corresponding author. *E-mail address:* bostjan.genorio@fkkt.uni-lj.si (B. Genorio).

https://doi.org/10.1016/j.ultsonch.2022.106212

Received 10 August 2022; Received in revised form 18 October 2022; Accepted 21 October 2022 Available online 26 October 2022 1350-4177/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC B

^{1350-4177/© 2022} The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

processing [14,15], making effective functionalization of rGO of paramount importance to device integration. The functionalization of rGO can be achieved by either a covalent or a non-covalent functionalization strategy [6,16]. Due to the rigorous and time-consuming organic synthesis, one of the major challenges in covalent graphene functionalization is to improve beyond milligram-scale chemical approaches in a facile and economical way [17–20].

Significant efforts have been made to utilize sonochemistry for graphene functionalization, as it has been shown to be beneficial in a wide range of other materials and chemical syntheses. Ultrasound can be used in various stages of the preparation of graphene (or its derivatives) [21], in particular for the preparation of graphene layers by exfoliation from graphite [22,23], in the preparation of various geometries of graphene [24], its dispersion, as well as in functionalization of graphene and its derivatives [25]. Sonication is particularly advantageous as it helps to avoid multi-step processing with strong oxidizing and reducing agents. Several research papers report the production of high quality graphene and its derivatives in a simple one-step process [21].

The key component of ultrasonic efficiency results from acoustic cavitation. Cavitation forms in a liquid medium when pressure locally drops below the vaporization pressure and cavitation bubbles appear. As the pressure recuperates the bubbles collapse, producing localized spots with extremely high temperatures exceeding 5000 K and pressures of hundreds of bars. This results in mechanical loads such as shock waves, liquid microjets, microstreaming and high shear forces [26]. In addition, localized hot spots generate highly reactive radicals that allow favorable reaction conditions that are not present under normal conditions [27,28]. Although ultrasound itself already has enormous potential and has therefore been used in plethora of applications, the efficiency of the process and the energy transfer still pose an inherent problem and are therefore being actively researched [29].

Surface functionalization of graphene with polymers to improve its properties has been actively explored in recent years [30-32] with most methods based on a chemical synthesis approach. In these, ultrasound has been used only in part of the segment, mainly in mechanical exfoliation [21,33]. The chemical approach of graphene functionalization by polymers includes traditional free radical polymerization [30], atom transfer radical polymerization, and reversible addition chain transfer [34,35]. On the other hand, works focusing on the direct application of ultrasound to provide functionalized graphene by macromolecules are less common. Nevertheless, some work has been done on the functionalization of graphene with polymer components using ultrasound. Yongshen Li et al. [36] took advantage of ultrasound to synthesize graphene oxide-carboxylic acid-polyvinyl alcohol polymers (GO-COOPVA) and achieved an improvement in the thermal stability. In one of their previous studies, ultrasound-assisted functionalization starting from phosphorous GO (PGO) was performed to prepare PGO/PVA polymers [37]. Functionalization of graphene sheets with polystyrene chains promoted by ultrasound was described by Xu H. et al. [38]. An interesting study was performed by Shen B. et al. where the functionalization was achieved solely by ultrasonication on the aqueous mixture of pristine graphene and PVA with the estimated content of PVA on graphene to be approximately 35 % [39]. In addition, ultrasound-assisted direct functionalization of GO with nitrogen [40], 5-aminoindazole [41], and amino-alcohol [42] were recently presented. However, most of the studies lack of systematic approach on how to control the degree of functionalization by controlling ultrasound parameters.

In this study, we aimed to achieve the functionalization of rGO by sonication in a one-step process using polyvinyl alcohol (PVA) as a model molecule to be bound to the rGO surface. We investigated the influence of the energy (power) input of the ultrasonic horn on the efficacy of rGO functionalization. The correlation between the performance of the high-intensity ultrasonic horn and the synthesis of the rGO-PVA polymer was thoroughly explained by TGA coupled with MS, and IR, Raman, XPS, Laser diffraction, and SEM analysis. The most stable dispersion of functionalized rGO was obtained at 50 % horn amplitude.



Fig. 1. Set-up of the experiment.

These results indicate that an optimal combination of both particle size distribution and relative degree of functionalization is necessary in order to realize a stable dispersion of functionalized rGO. The approach described points to a new pathway toward scalable production of functionalized graphene-based materials that can be used in several applications and new technologies.

2. Experimental

2.1. Materials

Graphene oxide (GO) precursor was prepared via Hummers' method from Graphite (Imerys, Timrex PP44). Poly(vinyl alcohol) (PVA) was purchased from Sigma-Aldrich (Mowiol 4–98, Mw ~ 27,000 g/mol, 98 % hydrolyzed), H₃PO₄ (Merck, ACS reagent, \geq 85 wt% in H₂O), H₂SO₄ (Merck, ACS reagent, 95.0–98.0 wt%), HCl (Merck, ACS reagent, 37 % wt.), KMnO4 (Merck, ACS reagent, \geq 99.0 wt%), H₂O₂ (Merck, ACS reagent, 30 wt% in H₂O), Hydrazine monohydrate (Sigma-Aldrich, reagent grade, N₂H₄ 64–65 wt%, 98 %). All aqueous solutions and suspensions were prepared with ultrapure water obtained from a Milli-Q system (Millipore) with resistivity 18.2 MΩ cm.

2.2. Synthesis of reduced graphene oxide (rGO)

rGO was synthesized by a previously published method [43]. Graphene oxide (17.0 g) was dissolved in Milli-Q water (1.5 L) and placed in a 2 L round bottom flask with a PTFE magnetic stirrer. The round bottom flask was then connected to a reflux condenser and placed on an oil bath. The reaction mixture was slowly heated to 100 °C on a magnetic stirrer with a hot plate (MSH-20D, Witeg) and stirred at 550 rpm. Then, hydrazine hydrate (170.0 mL) was slowly added via the condenser and the reaction mixture was kept at 105 °C for 24 h under reflux. During reduction, the reaction mixture changed colour from brown to black, indicating chemical reduction. After reduction, the hot reaction mixture was filtered with a 0.2 μ m PTFE membrane filter (Omnipore, Merck), the resulting rGO washed with hot Milli-Q water (1.5 L) and 96 vol% ethanol (400 mL) and air dried for 24 h. rGO (4.2 g) was further dried in vacuo at 80 °C overnight.

2.3. rGO functionalization by sonication

The PVA (0.50 g) was dissolved in Milli-Q water (100 mL) in threeneck round-bottom flask at 90 $^\circ$ C and then cooled to room temperature (Fig. 1). rGO (50 mg) was added to the PVA solution and a suspension was formed by vigorous stirring. The suspension was deoxygenated with Ar while the high-intensity ultrasonic horn was used to treat the suspension at 20 %, 30 %, 40 %, 50 %, and 60 % amplitude setting for 2 h. The suspension was immersed in an ice bath to eliminate the calorimetric effect of sonication (the temperature did not increase above 25 °C during sonication). After sonication, a stable dispersion of functionalized graphene was obtained, while the black sediment could be attributed to the non-functionalized graphene. The supernatant was resolved by centrifugation at 10000 rpm for 10 min and then filtered through a 0.2 µm polycarbonate membrane (Omnipore, Merck). The collected black precipitate was washed with boiling Milli-Q water (100 mL), then the precipitate was re-suspended on the membrane in hot Milli-Q water (90 °C) and filtered again. The process of washing, resuspending, and filtering was repeated three times. In this way, the residual non-bound PVA was removed. The removal of PVA was confirmed by adding THF to the solution until the turbidity disappeared. The collected product was dried overnight in a vacuum oven at 50 °C. Significant losses in yield were observed with this time-consuming procedure, which varied depending on the ultrasound strength. The yield of functionalized graphene was less than 5 %, based on the rGO used.

The sediment after centrifugation was repeatedly suspended in 20 mL of hot distilled water (90 °C) and centrifuged until complete removal of PVA. Removal of PVA was confirmed in the same manner as described previously. Approximately 10 wash and centrifugation cycles were required. Thereafter, the collected sediment was dried overnight in a vacuum oven at 50 °C.

Sonication, treatment by cavitation phenomena was introduced by a 12 mm titanium (Ti) tip of a 20 kHz ultrasonic horn transducer Cole-Parmer with nominal power of 750 W and with a nominal output frequency of 20 kHz. Temperature inside the flask was monitored by a Pt100 probe.

A set of measurement points were recorded at various transducer amplitudes (20 %, 30 %, 40 %, 50 and 60 % amplitude setting, 100 % corresponding to 206 μ m peak to peak amplitude). The electrical power consumption was measured by Fluke Norma 4000 power analyzer and gave at 20 % – 52 W, at 30 % – 63 W, at 40 % – 76 W, at 50 % – 89 W and at 60 % – 102 W. To further characterize cavitation, various methods were used:

- Cavitation was observed by high-speed camera Photron Fastcam SA-Z at 100,000 fps at a relatively high resolution of 256 × 256 pixels. Shutter time was set to 5 µs. Backlight illumination by high power LED was used. The setup is schematically shown in Fig. 1.
- We performed calorimetry measurements to evaluate the energy input from the horn to the sample. This was done by using a thermoinsulated vessel instead of three neck flask and tracking the temperature increase during the cavitation treatment.

- To determine the aggressiveness in the near vicinity of the horn, the probe tip was replaced by an aluminum sample and direct mass loss measurements were performed. These were performed according to the ASTM G32-16 standard [44], but on a smaller, 12 mm, sample. The mass of the specimen was measured after 1, 5, 10 and 15 min. The measurements were repeated 5 times.
- Cavitation aggressiveness further away from the horn was determined by measurements of pressure pulsations by a high frequency pressure transducer PCB 112A05 with Brüel&Kjaer 2635 charge amplifier. The sampling frequency for pressure measurement was 0.5 MHz. Pressure transducer was mounted in the same level as the horn tip and shifted from the center of the horn for 50 mm.

2.4. Characterization

Evolved gas analysis (EGA): Thermogravimetric measurements were performed on a Netzsch 449 F3 Jupiter instrument under a dynamic Ar (5.0) flow with a flow rate of 50 mL/min in a temperature range from 30 °C to 900 °C. A heating rate of 10 K/min was used. About 15 mg of sample was placed in 0.3 mL alumina (Al₂O₃) crucible. Simultaneously, mass spectrometry was performed on MS 403C Aëolos with detector SEM Chenneltron and system pressure of 2×10^{-5} mbar. Gasses evolved under TG heat treatment were transferred to mass spectrometer through transfer capillary: quartz ID 75 µm which was heated up to 220 °C. The upper limit of the mass spectrometer detector was 100 AMU.

Raman Spectroscopy: The Raman spectra were acquired using a Renishaw inVia confocal Raman microscope; 532 nm wavelength laser was used for excitation. Peak fitting of spectra was done with the Lorentzian peak shape, baseline constrain at 0 intensity and peak at center constrains as previously shown [45].

X-ray Photoelectron Spectroscopy (XPS): XPS measurements were performed using a SPECS PHOIBOS 150 Hemispherical Energy Analyzer with a monochromated Al K α X-ray source. Indium foil was used as substrate for the sample preparation, and spectra were charge referenced to the metallic In $3d_{5/2}$ peak at 444.8 eV. Spectra were acquired to maintain a similar In $3d_{5/2}$ peak intensity in order to ensure analysis of a similar amount of rGO material. Survey spectra were measured using a pass energy of 40 eV at a resolution of 0.2 eV step⁻¹ and a total integration time of 0.1 s point⁻¹. Data analysis was performed using CasaXPS software (http://www.casaxps.com/) with a Shirley-type background and 70–30 Gaussian–Lorentzian peak shapes for all peaks except sp^2 carbon, which used an asymmetric lineshape derived empirically from a highly ordered pyrolytic graphite sample in a separate experiment.

Scanning electron microscopy (SEM): Morphology characterization and visualization of graphene particles was performed by using a scanning field emission electron microscope Zeiss ULTRA plus. Samples



Scheme 1. Graphical representation of rGO functionalization by PVA using different ultrasound cavitation intensities.



Fig. 2. Solubility tests of as prepared dispersions (0 h), after 1 h storage, and after 7 days storage.

were dispersed in deionized water (resistivity 18.2 M Ω -cm) using ultrasound. Suspension was then drop cast onto Si wafer adhered on the aluminum SEM holder with the conductive carbon tape. SEM images were taken at 2 kV or 3 kV using a SE2 detector at WD 5.5 mm.

Laser Diffraction, Particle Size Analysis: Particle size distribution analysis was performed in wet conditions (aqueous dispersion) using a Microtrac S3500 Bluewave laser particle size analyzer equipped with tri–laser technology.

Fourier-transform infrared spectroscopy (FTIR): FTIR spectra were obtained on a Bruker IFS 66/S spectrometer. Samples were analyzed in KBr disks that were prepared with a 6×10^7 Pa load.

3. Results and discussion

As-prepared reduced graphene oxide (rGO) material is a highly porous, aggregated, morphologically crumpled material with relatively large area graphene domains (Figure S1). This morphology is the result of chemical reduction at high temperatures, which removes the majority of the oxygen functionalities from graphene oxide layers (GO) in aqueous solutions. When such a material is subjected to ultrasonic cavitation, several processes can occur in parallel. First, the as prepared rGO can exfoliate by breaking weak van der Waals forces, and second, strong in-plane covalent C=C bonds can be cleaved if the energy of the cavitation bubbles is high enough. Moreover, C=C bond breaking locally leads to active sites on the graphene lattice that are susceptible to functionalization. Similar results were previously shown in longitudinal splitting of multi-walled carbon nanotubes (MWCNTs), when potassium metal incorporation triggered the splitting and created carboanionic centers at the edges of graphene nanoribbons (GNRs), which are active functionalization sites [8]. In the present case, when rGO and polyvinyl alcohol (PVA) are sonicated in aqueous suspension together (Scheme 1), the possibilities of bond cleavage and consequently new bond formation (functionalization) increase even further, as PVA molecules have several single bonds that can be cleaved (C-C, C-H, C-O, and O-H), as well as all bonds in water molecules. Since multiple bonds (C=C) require the highest energies, followed by single bonds and finally the breaking of van der Waals forces, we believe that tuning the energy input from the



Fig. 3. Frequency histograms showing particle size distribution by number of PVA functionalized rGO prepared with 20% amplitude (red), 30% (green), 40% (blue), 50% (turquoise), 60% (magenta), and as prepared non-functionalized rGO (black).

ultrasonic horn into the sample could result in varying degrees of functionalization. Put simply, this means that low energies initially exfoliate graphene materials, medium energies functionalize graphene materials, and very high energies break graphene domains into smaller particles. To test this hypothesis, we designed the functionalization experiment so that all reaction parameters were held constant, and the only variable was the amplitude of the ultrasonic horn, which was set at 20 %, 30 %, 40 %, 50 %, and 60 % amplitude.

Although the solubility of non-functionalized rGO is generally known to be poor, especially in aqueous environments, a high degree of rGO functionalization with a water-soluble polymer, such as PVA, should result in stable suspensions. We compared the stability of suspensions of rGO, a physical mixture of rGO and PVA (rGO + PVA) without ultrasound, and ultrasound-treated rGO and PVA at 20 %, 30 %, 40 %, 50 %, and 60 % ultrasonic horn amplitude setting, respectively (Fig. 2), to understand whether the ultrasonic treatment leads to improved rGO solubility. From Fig. 2, it is clear that rGO and rGO + PVA are not soluble, while the solubility of ultrasonically treated rGO increases from 20 % to 50 %, where the solubility is highest, and then decreases after increasing power to 60 %. The stability during the different time intervals also shows the same trend as the originally prepared suspensions. 50 % show high stability of the suspension even after one week of storage. These results indicate the suspension stability is most likely related to the degree of functionalization and particle size distribution.

To further investigate the origin of the solubility trend, we performed a particle size distribution (PSD) analysis using laser diffraction. As mentioned at the beginning of the discussion section, ultrasound can also break strong C=C double bonds if the energy is high enough. A comparison of the PSD of materials prepared at 20 %, 30 %, 40 %, 50 %, and 60 % amplitude and non-functionalized rGO was performed. For simplicity and to make the trends clear, only the mean diameter in micrometers of the frequency distribution is given. The frequency histograms in Fig. 3 clearly show the difference between the nonultrasonicated and ultrasonicated rGO particles. The mean diameter of the as-prepared non-functionalized rGO particles is 179.5 µm, which is at least an order of magnitude higher than the value of the rGO materials functionalized with PVA. This clearly shows that ultrasonic treatment with different cavitation energies exfoliates and brakes down the rGO particles. Average particle diameters are observed to be $3.85 \ \mu m$, 5.16 $\mu m,\,4.43\,\mu m,\,2.22\,\mu m,$ and 0.28 μm for 20 %, 30 %, 40 %, 50 % and 60 % amplitude, respectively, indicating that similar results are obtained



Fig. 4. SEM images of PVA functionalized rGO using 30%, 40%, 50%, and 60% ultrasonic horn amplitude.



Fig. 5. Appearance of cavitation in water as a function of amplitude (averaged over 2000 images).

below 50 % amplitude. However, when the amplitude reaches 60 %, the mean value decreases by another order of magnitude, indicating that the ultrasonic energy is high enough to efficiently cleave C=C bonds in the graphene sheets. We hypothesize that energies equal to or lower than 50 % amplitude only exfoliate graphene, i.e., break weak van der Waals forces, while energies higher than 60 % amplitude also break the strong C=C bonds.

Interestingly, frequency histograms showing particle size distribution by volume (Figure S2) show a bimodal distribution for all 5 different amplitudes (20 %, 30 %, 40 %, 50 %, and 60 %), whereas nonfunctionalized rGO has a monomodal particle size distribution. This bimodal distribution could represent a combination of exfoliated and not fully exfoliated rGO particles. This distribution is partially confirmed with SEM images (Fig. 4), which were taken at the same magnification. Materials treated with 30 %, 40 % and 50 % ultrasonic amplitude show similar particle size distribution as well as similar exfoliation. However, materials treated at 60 % amplitude exhibit significantly smaller particles, confirming that high energies substantially break and exfoliate graphene particles.

Cavitation phenomena were thoroughly investigated to gain understanding of the influence of the sonication intensity on functionalization of graphene. Fig. 5 shows the averaged appearance of cavitation at the tip of ultrasonic horn.

As expected, the extent of the vapor cloud grows with the increase in amplitude. An important observation is that in case of lower amplitude (20 % and 30 %) the structure does not cover the whole tip of the horn – an outer perimeter of its frontal area remains completely wetted over the whole oscillation cycle. On the contrary, in cases at 40 %, 50 % and especially in the case of 60 % amplitude, the horn tip is covered by bubbles which, as it will be shown, influences the dynamics of the cavity and the progression of pressure waves through domain.

The diagrams in Fig. 6 show further measurements which characterize the flow conditions during the sonication. As a function of the horn amplitude setting in A) the energy input into the vessel, B) the size of the cavitation cloud, C) the eigen frequency of cavitation structure, D) the aggressiveness of cavitation (manifested as erosion) in close vicinity of the horn and E) the amplitude of pressure oscillations "far" from the horn tip.

Measurements of calorimetry (Fig. 6 A) show that the energy input into the sample increases linearly. This result is expected, but important, as one can observe that only part of the electrical energy that is put into the ultrasonic horn is actually delivered to the liquid (25 to 40 %). This points to the issue that calorimetric measurements should be performed every time when characterizing ultrasonic cavitation as in the opposite case, no comparison between processes by different equipment can be made.

It is obvious that the cavitation cloud size increases as the amplitude approaches 60 % (Fig. 6 B). The reason for this is likely related to self-amplification. The two-phase region near the horn tip builds up as a result of significant movement of the horn. The fluid mixture becomes



Fig. 6. Hydrodynamic analysis of cavitation. A) power input according to calorimetry, B) approximate cavitation cloud volume, C) eigen frequency of cavitation structure, D) Al sample mass loss, E) RMS of pressure.

more compressible; hence less energy can be radiated from the region in form of shock waves [46,47]. This further concentrates the energy deposited in the close vicinity of the horn and the average structure volume grows. Eventually, the horn begins to press against a highly compressible liquid–vapor mixture and the cloud seizes to grow further – a constant maximum size is reached.

Cavitation dynamics can be further discussed on the basis of the typical eigen frequency of the structure (Fig. 6 C). It was determined by the FFT analysis of the time series of cavitation size, which was obtained from the average gray level of images of cavitation (as previously in [48]). As the cavity grows its dynamics slows down (from 10 kHz to about 5 kHz). This is particularly evident for the transition from the partially to completely cavitation covered ultrasonic tip. Above 40 % amplitude, more or less constraint and well known $\sim 1/5$ driving frequency is reached [48] and one cannot claim that this parameter might influence either the functionalization efficiency or the breakup of the graphene particles.

We hypothesized above that low sonication energies initially exfoliate graphene materials, medium energies functionalize graphene materials, and very high energies break graphene domains into smaller particles. The size distribution of the particles can be correlated to the maximal cavitation aggressiveness, which lies near the tip of the horn. This can be estimated by performing direct erosion measurements. We replaced a highly resistant Ti horn tip by a soft Al one, exposed it to cavitation and measured mass loss from it – Fig. 6 D. We see that it increases exponentially with increasing amplitude of the horn. At 60 % amplitude the energy delivered to the graphene particles in close vicinity of the horn is high enough to tear them apart, resulting in their much finer size (Figs. 3 and 4). Also, the sonication time of 2 h is long enough to establish a homogeneous distribution of the particles in the reactor.

The energy level changes as we move further away from the horn. This can be determined by measurements of pressure pulsations far away (50 mm) from the horn. In Fig. 6 E we see that the maximum of the pressure pulsations is reached at 40 % amplitude – the amplitude of the pressure oscillation at the origin (at the tip) increases with increasing amplitude, yet it is attenuated as it traverses the highly compressible 2-phase flow region [46,47]. This can also be nicely related to the appearance of cavitation (Fig. 5) – the transition occurs approximately at the amplitude when the cavitation covers the entire tip of the horn (Fig. 5). This means that the energy delivered to most of the sonicated reaction volume reaches maximum at 40 % amplitude and is lower at smaller and higher amplitudes.

To find out whether the results of the solubility tests correlate with the degree of functionalization, or if it is rather simply an effect of the PSD, we performed several characterization experiments. One of the characterization techniques that indirectly provides information about the degree of functionalization is evolved gas analysis (EGA) [8]. We primarily analyzed functionalized rGO that was part of the stable suspension (i.e., separated from non-suspended particles) and compared it with non-functionalized rGO, rGO + PVA and PVA (Fig. 7a). All TGA curves clearly show that there are at least 3 distinct regions of weight



Fig. 7. Evolved gas analysis. Different colors represent rGO functionalized with different horn amplitudes; red 20 %, green 30 %, blue 40 %, turquoise 50 % and magenta 60 %. a) TGA profile of functionalized rGO (20 %, 30 %, 40 %, 50 % and 60 %), non-functionalized rGO (black), physical mixture of rGO + PVA (grey), and PVA (orange). Light blue, dark blue, and grey rectangles represent region I, region II, and region III. b) MS fragment *m*/*z* 15 correspond to $-CH_3$, c) MS fragment *m*/*z* 18 correspond to H_2O , d) MS fragment *m*/*z* 29 correspond to $-CH_2$ -CH₃, e) MS fragment *m*/*z* 44 corresponds to CO₂.

loss. Region I - light blue rectangle is between 30 °C and 200 °C and corresponds to the evaporation of water adsorbed on the surface. The region II - dark blue rectangle - is between 200 °C and 400 °C and corresponds to the depolymerization or fragmentation of the PVA chains bound to the rGO. The last region III - grey rectangle – is between 400 $^{\circ}$ C and 700 °C and corresponds to the depolymerization and defunctionalization of the rGO functionalized with PVA. These regions were defined based on the m/z fragments of the resulting evolved gases. Four different m/z fragments were observed, namely m/z 18 corresponding to the evolution of water (Fig. 7b), m/z 15 corresponding to the methyl (-CH₃) functional groups (Fig. 7c), m/z 29 corresponding to the ethyl $(-CH_2CH_3)$ functional groups (Fig. 7d), and m/z 44 corresponding to the evolution of CO₂ (Fig. 7e). Water is evolved in region I and region II (Fig. 7c) for all materials. In region I, water adsorbed on the surface of the rGO materials evaporates, and in region II, water is formed as a decomposition product mainly from the depolymerization process. The



Fig. 8. Fourier transform infrared spectroscopy (FTIR) spectra: a) PVA functionalized rGO 20 % amplitude, b) PVA functionalized rGO 30 % amplitude, c) PVA functionalized rGO 40 % amplitude, d) PVA functionalized rGO 50 % amplitude, e) PVA functionalized rGO 60 % amplitude, f) non-functionalized rGO, g) PVA, g) rGO + PVA physical mixture no ultrasound used.

second interesting decomposition gas is CO₂, which evolves mainly in region II and corresponds to depolymerization of the PVA chains. There is also a small peak in the m/z 44 signal in region III, which is attributed to thermal decomposition of the basal level oxygen functionalities of rGO. Similarly, m/z 29 appears, which is indicative of the depolymerization process in region II. The most interesting feature in the EGA analysis is the appearance of the methyl groups in regions II and III. Again, the sharp peak in the region II corresponds to the main decomposition of the polymer chain, but the broad, strong peak present throughout region III could be an indicator of covalent bonding between rGO and PVA. A similar observation was made in the case of alkyl functionalization of GNR in our previous publication [8]. To evaluate the degree of covalent functionalization, we compared the TGA weight loss in region III. At an amplitude of 20 %, 30 %, 40 %, 50 % and 60 % the weight loss was 0.65 wt%, 0.79 wt%, 0.59 wt%, 0.73 wt%, 0.64 wt %, respectively. These numbers are very close and within accuracy of the TGA. Similar results are also observed in region II, where the weight loss was 1.64 wt%, 2.51 wt%, 1.93 wt%, 2.05 wt% 2.15 wt% at 20 %, 30 %, 40 %, 50 % and 60 % amplitude, respectively. Thus, we conclude that relative concentration of the PVA on rGO does not correlate to the observed trend of the solubility test.

Residual precipitate of the functionalization process was also analyzed thermogravimetrically to show that functionalization did not occur on the precipitated material. Figure S3 clearly shows that the total weight loss for precipitated materials is lower, at least for 20 wt% compared to the functionalized materials from Fig. 7a. This indicates less PVA on the rGO. Most importantly, there are no evolved methyl groups in region III, indicating there was no covalent bonding between the rGO and PVA. The presence of m/z fragments 15, 18, 29, and 44 in



Fig. 9. C 1s XPS core level spectra with spectral deconvolution for a) PVA functionalized rGO 30 % amplitude, b) PVA functionalized rGO 40 % amplitude, c) PVA functionalized rGO 50 % amplitude, and d) PVA functionalized rGO 60 % amplitude.

region II show that region II can also represent the decomposition of adsorbed PVA molecules. From the EGA results, we conclude that region III in TGA is the indicator of covalent functionalization. The main conclusion from EGA was that PVA for functionalized samples is most likely covalently bound to the rGO scaffold.

In order to understand the chemical differences in the functionalized materials and their impact on the solubility trend, all materials were also analyzed by FTIR, XPS, and Raman spectroscopy. The FTIR results in Fig. 8 show typical adsorption values of PVA and rGO. The characteristic peaks at 3030 cm⁻¹ (O-H stretching), 2967 cm⁻¹, 2922 cm⁻¹, 2849 cm^{-1} (C–H stretching), 1778 cm^{-1} , 1725 cm^{-1} (C=O stretching), 1634 and 1558 cm⁻¹ (C=C stretching), 1080 cm⁻¹ (C–O stretching) ${\rm cm}^{-1}$ are present for functionalized materials (Fig. 8a-e). Representative peaks for PVA are 3030 cm⁻¹, 2967 cm⁻¹, 2922 cm⁻¹, 2849 cm⁻¹, 1725 cm⁻¹, and 1080 cm⁻¹ (Fig. 8g). On the other hand, rGO absorbs IR at 1558 cm^{-1} (Fig. 8f). The physical mixture rGO + PVA shows a combination of PVA and rGO adsorption peaks (Fig. 8h). However, a closer look at each functionalized material reveals some differences at the 50 % amplitude (Fig. 8d) and the 60 % amplitude (Fig. 8e). The use of the 50 % amplitude in the functionalization process results in extremely strong adsorption at 1725 cm⁻¹, which is the only difference between the other amplitudes used and corresponds to the best solubility results. 1725 cm^{-1} corresponds to C=O stretching, which could be due to carbonyl groups on the rGO or residual impurities from the precursor in PVA synthesis, poly(vinyl acetate). Another difference is also seen at the 60 % amplitude at 1778 cm⁻¹, which was not present in any of the other amplitudes used. The reason for this is not clear but could be due to the differences in particle size distribution (Fig. 3), which was discussed above.

To quantify the concentration of functional groups attached to

carbon, deconvolution of C 1s XPS was performed (Fig. 9). In addition, XPS survey spectra for 30 %, 40 %, 50 %, and 60 % amplitude were recorded (Figure S4, Table S1). Survey spectra showed the presence of the expected elements, namely C, O, N, and In (substrate). Deconvolution of the C 1s core level spectra (Fig. 9) provides information about the functional groups on the C atoms. The C 1s peak was fitted to determine the relative contributions of sp²-hyridized C (and its associated satellite feature), sp³-hyridized carbon, epoxy and hydroxy groups (C—O), carbonyl (C=O), and carboxyl (O-C=O) species. An additional peak corresponding to metal carbonates from the In foil support was also needed to fit the data, but is excluded from quantification. Quantification of the fitted peaks (Fig. 9, Table S2) reveals that rGO samples functionalized at or below 50 % amplitude achieve similar speciation, with the 50 % sample exhibiting the highest fraction of C=O functional groups, consistent with the FTIR analysis above. The presence of C-O and hydroxyl groups were also confirmed by FTIR in all functionalized materials. Furthermore, the samples functionalized at 60 % amplitude contain significantly fewer C-O species relative to the other samples, which is consistent with the fact that a lower concentration of hydroxyl groups deceases the solubility of materials in aqueous solutions. From the XPS results, it can be concluded that a decrease in functionalization in particular OH groups - contributes to the sudden drop-off in dispersion quality above 50 % amplitude.

Raman spectra were acquired to assess the degree of defects in the rGO structure and the degree of exfoliation. For this purpose, peak fitting was performed to determine the intensities of the D, G, and 2D peaks and calculate I_D/I_G and I_{2D}/I_G [45]. Fig. 10 shows that there are some notable differences between the functionalized materials. Based on the I_D/I_G ratios, all functionalized rGO derivatives are strongly structurally defective, which is characteristic of all rGO materials based on



Fig. 10. Raman spectroscopy analysis of the D*, D, D**, G, D', G*, 2D, D + D*, and 2D' bands for a) PVA functionalized rGO 30 % amplitude, b) PVA functionalized rGO 40 % amplitude, c) PVA functionalized rGO 50 % amplitude, d) PVA functionalized rGO 60 % amplitude, and e) non-functionalized rGO.

their synthesis. In addition, all I_{2D}/I_G ratios show that the materials are multilayered, which is expected since the Raman spectra were recorded in dried rGO form. During drying, the rGO materials restack due to van der Waals forces. However, comparing the I_D/I_G ratios of functionalized materials prepared at different amplitudes (Fig. 10), a trend can be seen where the 50 % amplitude has the least structural defects as the ratio is the smallest (1.25) and only slightly larger than the non-functionalized rGO material (1.22). The I_D/I_G ratios for all other amplitudes are 1.38 for 30 %, 1.4 for 40 %, and 1.37 for 60 %. The observed structural features of the functionalized materials in combination with the functional groups determined by FTIR and XPS could be jointly responsible for the better solubility of the 50 % amplitude compared to others.

4. Conclusions

The solubility test showed that 50 % of the ultrasonic horn amplitude gave the most soluble PVA-functionalized rGO. The reason for this behavior was investigated using physical measurements of the cavitation processes, PSD, SEM imaging, EGA, and spectroscopic methods (FTIR, XPS, and Raman). Physical measurements of the ultrasound, especially the pressure oscillations and erosion measurements, along with PSD and SEM images indicate that amplitudes greater than 50 % cause rGO flakes to break into smaller domains, which negatively affect the functionalization process. Functionalization occurs in a wide surrounding region of the tip (not just in its eminent vicinity), yet the pressure waves become significantly attenuated in the case of 60 % amplitude, lowering the efficiency of functionalization and resulting in particle sizes that are also too small for effective functionalization. EGA shows that methyl functional groups evolved in Region III (temperature between 400 °C and 700 °C) are related to covalent functionalization of PVA at rGO. FTIR identified functional groups on all functionalized materials and showed some specific peaks for 50 % and 60 % amplitudes in the C=O stretching region. Deconvolution of the XPS C 1s core level revealed that 50 % amplitude provided the highest concentration of C=O functional groups, consistent with the FTIR analysis, and that material functionalized at 60 % amplitude contained significantly lower C-O functionalization, consistent with a drop in dispersion quality due to a lower population of solubilizing -OH groups. Raman spectra showed that all functionalized materials are structurally highly defective, but the 50 % amplitude damages the rGO structure the least based on the I_D/I_G ratio. In summary, for optimal functionalization and consequently solubility in aqueous solvent, the amplitude of the ultrasound must be carefully controlled. By optimizing both the particle size distribution and the extent of surface functionalization, effective dispersion of functionalized rGO materials can be achieved, suggesting a new route to functionalization protocols with low- cost sonochemistry. Such protocols could be used in a variety of different applications, with a focus on those where processability is required, namely spray coating, inkjet printing, ultrasonic deposition and additive manufacturing, among many others.

5. Funding sources

This research was funded by the Slovenian Research Agency (Programs No. P2-0422, P2-0423, P2-0191, and Projects No. J2-3057, J7-1814).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors acknowledge the financial support from the Slovenian Research Agency (Programs No. P2-0422, P2-0423, P2-0191 and Projects No. J2-3057, J7-1814). XPS data were collected at the Electrochemical Discovery Laboratory, a Joint Center for Energy Storage Research facility at Argonne National Laboratory. The authors would also like to thank master students Julija Simaković, Sandra Zaplotnik, and Domen Oštir for the work in the laboratory.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2022.106212.

References

- P. Avouris, Graphene: Electronic and photonic properties and devices, Nano Lett. 10 (2010) 4285–4294, https://doi.org/10.1021/nl102824h.
- [2] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E. A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, Nature, 442 (2006) 282–286. https://doi.org/10.1038/nature04969.
- [3] L. Jiao, L. Zhang, X. Wang, G. Diankov, H. Dai, Narrow graphene nanoribbons from carbon nanotubes, Nature. 458 (2009) 877–880, https://doi.org/10.1038/ nature07919.
- [4] E.P. Randviir, D.A.C. Brownson, C.E. Banks, A decade of graphene research: production, applications and outlook, Mater. Today. 17 (2014) 426–432, https:// doi.org/10.1016/j.mattod.2014.06.001.

- [5] S.P. Lonkar, Y.S. Deshmukh, A.A. Abdala, Recent advances in chemical modifications of graphene, Nano Res. 8 (2015) 1039–1074, https://doi.org/ 10.1007/s12274-014-0622-9.
- [6] T. Kuila, S. Bose, A.K. Mishra, P. Khanra, N.H. Kim, J.H. Lee, Chemical functionalization of graphene and its applications, Prog. Mater. Sci. 57 (2012) 1061–1105, https://doi.org/10.1016/j.pmatsci.2012.03.002.
- [7] J. Liu, J. Tang, J.J. Gooding, Strategies for chemical modification of graphene and applications of chemically modified graphene, J. Mater. Chem. 22 (2012) 12435, https://doi.org/10.1039/c2jm31218b.
- [8] B. Genorio, W. Lu, A.M. Dimiev, Y. Zhu, A.-R.-O. Raji, B. Novosel, L.B. Alemany, J. M. Tour, In situ intercalation replacement and selective functionalization of graphene nanoribbon stacks, ACS Nano. 6 (2012) 4231–4240, https://doi.org/10.1021/nn300757t.
- D. Cai, M. Song, Preparation of fully exfoliated graphite oxide nanoplatelets in organic solvents, J. Mater. Chem. 17 (2007) 3678, https://doi.org/10.1039/ b705906j.
- [10] J.I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J.M.D. Tascón, Graphene oxide dispersions in organic solvents, Langmuir. 24 (2008) 10560–10564, https://doi. org/10.1021/1a801744a.
- [11] D. Chen, H. Feng, J. Li, Graphene oxide: Preparation, functionalization, and electrochemical applications, Chem. Rev. 112 (2012) 6027–6053, https://doi.org/ 10.1021/cr300115g.
- [12] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J.M. Tour, Improved synthesis of graphene oxide, ACS Nano. 4 (2010) 4806–4814, https://doi.org/10.1021/nn1006368.
- [13] O. Jankovský, P. Marvan, M. Nováček, J. Luxa, V. Mazánek, K. Klímová, D. Sedmidubský, Z. Sofer, Synthesis procedure and type of graphite oxide strongly influence resulting graphene properties, Appl. Mater. Today. 4 (2016) 45–53, https://doi.org/10.1016/j.apmt.2016.06.001.
- [14] O.C. Compton, S.T. Nguyen, Graphene oxide, highly reduced graphene oxide, and graphene: Versatile building blocks for carbon-based materials, Small. 6 (2010) 711–723, https://doi.org/10.1002/smll.200901934.
- [15] A.J. Paulista Neto, E.E. Fileti, Elucidating the amphiphilic character of graphene oxide, Phys. Chem. Chem. Phys. 20 (2018) 9507–9515, https://doi.org/10.1039/ C8CP00797G.
- [16] B. Genorio, A. Žnidaršič, Functionalization of graphene nanoribbons, J. Phys. D. Appl. Phys. 47 (2014), 094012, https://doi.org/10.1088/0022-3727/47/9/ 094012.
- [17] I.-Y. Jeon, H.-J. Choi, S.-M. Jung, J.-M. Seo, M.-J. Kim, L. Dai, J.-B. Baek, Largescale production of edge-selectively functionalized graphene nanoplatelets via ball milling and their use as metal-free electrocatalysts for oxygen reduction reaction, J. Am. Chem. Soc. 135 (2013) 1386–1393, https://doi.org/10.1021/ja3091643.
- [18] I.-Y. Jeon, S.-Y. Bae, J.-M. Seo, J.-B. Baek, Scalable production of edgefunctionalized graphene nanoplatelets via mechanochemical ball-milling, Adv. Funct. Mater. 25 (2015) 6961–6975, https://doi.org/10.1002/adfm.201502214.
- [19] M. Mao, S. Chen, P. He, H. Zhang, H. Liu, Facile and economical mass production of graphene dispersions and flakes, J. Mater. Chem. A. 2 (2014) 4132–4135, https://doi.org/10.1039/C3TA14632D.
- [20] M.T.H. Aunkor, I.M. Mahbubul, R. Saidur, H.S.C. Metselaar, The green reduction of graphene oxide, RSC Adv. 6 (2016) 27807–27828, https://doi.org/10.1039/ C6RA03189G.
- [21] K. Muthoosamy, S. Manickam, State of the art and recent advances in the ultrasound-assisted synthesis, exfoliation and functionalization of graphene derivatives, Ultrason. Sonochem. 39 (2017) 478–493, https://doi.org/10.1016/j. ultsonch.2017.05.019.
- [22] H. Gao, K. Zhu, G. Hu, C. Xue, Large-scale graphene production by ultrasoundassisted exfoliation of natural graphite in supercritical CO2/H2O medium, Chem. Eng. J. 308 (2017) 872–879, https://doi.org/10.1016/j.cej.2016.09.132.
- [23] J.A. Morton, D.G. Eskin, N. Grobert, J. Mi, K. Porfyrakis, P. Prentice, I. Tzanakis, Effect of temperature and acoustic pressure during ultrasound liquid-phase processing of graphite in water, JOM. 73 (2021) 3745–3752, https://doi.org/ 10.1007/s11837-021-04910-9.
- [24] K. Krishnamoorthy, G.-S. Kim, S.J. Kim, Graphene nanosheets: Ultrasound assisted synthesis and characterization, Ultrason. Sonochem. 20 (2013) 644–649, https:// doi.org/10.1016/j.ultsonch.2012.09.007.
- [25] S.S. Maktedar, S.S. Mehetre, M. Singh, R.K. Kale, Ultrasound irradiation: A robust approach for direct functionalization of graphene oxide with thermal and antimicrobial aspects, Ultrason. Sonochem. 21 (2014) 1407–1416, https://doi.org/ 10.1016/j.ultsonch.2014.02.022.
- [26] M. Zupanc, Ž. Pandur, T. Stepišnik Perdih, D. Stopar, M. Petkovšek, M. Dular, Effects of cavitation on different microorganisms: The current understanding of the mechanisms taking place behind the phenomenon. A review and proposals for further research, Ultrason. Sonochem. 57 (2019) 147–165, https://doi.org/ 10.1016/j.ultsonch.2019.05.009.

- [27] M. Dular, O. Coutier-Delgosha, Thermodynamic effects during growth and collapse of a single cavitation bubble, J. Fluid Mech. 736 (2013) 44–66, https://doi.org/ 10.1017/jfm.2013.525.
- [28] M. Petkovšek, M. Dular, IR measurements of the thermodynamic effects in cavitating flow, Int. J. Heat Fluid Flow. 44 (2013) 756–763, https://doi.org/ 10.1016/j.ijheatfluidflow.2013.10.005.
- [29] R.J. Wood, J. Lee, M.J. Bussemaker, A parametric review of sonochemistry: Control and augmentation of sonochemical activity in aqueous solutions, Ultrason. Sonochem. 38 (2017) 351–370, https://doi.org/10.1016/j.ultsonch.2017.03.030.
- [30] W. Lu, G. Ruan, B. Genorio, Y. Zhu, B. Novosel, Z. Peng, J.M. Tour, Functionalized graphene nanoribbons via anionic polymerization initiated by alkali metalintercalated carbon nanotubes, ACS Nano. 7 (2013) 2669–2675, https://doi.org/ 10.1021/nn400054t.
- [31] R.K. Layek, A.K. Nandi, A review on synthesis and properties of polymer functionalized graphene, Polymer (Guildf). 54 (2013) 5087–5103, https://doi.org/ 10.1016/j.polymer.2013.06.027.
- [32] B. Yuan, C. Bao, L. Song, N. Hong, K.M. Liew, Y. Hu, Preparation of functionalized graphene oxide/polypropylene nanocomposite with significantly improved thermal stability and studies on the crystallization behavior and mechanical properties, Chem. Eng. J. 237 (2014) 411–420, https://doi.org/10.1016/j. cej.2013.10.030.
- [33] S.P. Economopoulos, G. Rotas, Y. Miyata, H. Shinohara, N. Tagmatarchis, Exfoliation and chemical modification using microwave irradiation affording highly functionalized graphene, ACS Nano. 4 (2010) 7499–7507, https://doi.org/ 10.1021/nn101735e.
- [34] P. Zhang, K. Jiang, C. Ye, Y. Zhao, Facile synthesis of V-shaped copolymer brushes grafted onto the surface of graphene oxide via coupling reactions, Chem. Commun. 47 (2011) 9504–9506, https://doi.org/10.1039/c1cc12978c.
- [35] M. Fang, K. Wang, H. Lu, Y. Yang, S. Nutt, Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites, J. Mater. Chem. 19 (2009) 7098–7105, https://doi.org/10.1039/b908220d.
- [36] Y. Li, J. Li, Y. Li, Y. Li, Y. Song, S. Niu, N. Li, Ultrasonic-assisted preparation of graphene oxide carboxylic acid polyvinyl alcohol polymer film and studies of thermal stability and surface resistivity, Ultrason. Sonochem. 40 (2018) 798–807, https://doi.org/10.1016/j.ultsonch.2017.08.038.
- [37] J. Li, Y. Li, S. Niu, N. Li, Ultrasonic-assisted synthesis of phosphorus graphene oxide/poly (vinyl alcohol) polymer and surface resistivity research of phosphorus graphene oxide/poly (vinyl alcohol) film, Ultrason. Sonochem. 36 (2017) 277–285, https://doi.org/10.1016/j.ultsonch.2016.12.009.
- [38] H. Xu, K.S. Suslick, Sonochemical preparation of functionalized graphenes, J. Am. Chem. Soc. 133 (2011) 9148–9151, https://doi.org/10.1021/ja200883z.
- [39] B. Shen, W. Zhai, D. Lu, J. Wang, W. Zheng, Ultrasonication-assisted direct functionalization of graphene with macromolecules, RSC Adv. 2 (2012) 4713–4719, https://doi.org/10.1039/c2ra01098d.
- [40] G. Avashthi, S.S. Maktedar, M. Singh, Sonochemically N-functionalized graphene oxide towards optically active photoluminescent bioscaffold, Ultrason. Sonochem. 58 (2019), 104651, https://doi.org/10.1016/j.ultsonch.2019.104651.
- [41] S.S. Maktedar, P. Malik, G. Avashthi, M. Singh, Dispersion enhancing effect of sonochemically functionalized graphene oxide for catalysing antioxidant efficacy of curcumin, Ultrason. Sonochem. 39 (2017) 208–217, https://doi.org/10.1016/j. ultsonch.2017.04.006.
- [42] U. Sierra, E. Cuara, A. Mercado, E. Díaz-Barriga, A. Bahena, A. Cortés, J. P. Martínez, M. Solà, S. Fernández, Efficient synthesis of amine-functionalized graphene oxide by ultrasound-assisted reactions and density functional theory mechanistic insight, Appl. Nanosci. 11 (2021) 1637–1649, https://doi.org/ 10.1007/s13204-021-01798-4.
- [43] S. Wolf, M. Roschger, B. Genorio, M. Kolar, D. Garstenauer, B. Bitschnau, V. Hacker, Ag-MnxOy on graphene oxide derivatives as oxygen reduction reaction catalyst in alkaline direct ethanol fuel cells, Catal 12 (2022) 780, https://doi.org/ 10.3390/catal12070780.
- [44] Standard test method for cavitation erosion using vibratory apparatus, ASTM G32-16(2021)E1. (2021). doi:10.1520/G0032-16R21E01.
- [45] A. Kaniyoor, S. Ramaprabhu, A Raman spectroscopic investigation of graphite oxide derived graphene, AIP Adv. 2 (2012), 032183, https://doi.org/10.1063/ 1.4756995.
- [46] M. Petkovšek, M. Hočevar, M. Dular, Visualization and measurements of shock waves in cavitating flow, Exp. Therm. Fluid Sci. 119 (2020), 110215, https://doi. org/10.1016/j.expthermflusci.2020.110215.
- [47] M. Khavari, A. Priyadarshi, A. Hurrell, K. Pericleous, D. Eskin, I. Tzanakis, Characterization of shock waves in power ultrasound, J. Fluid Mech. 915 (2021) 3, https://doi.org/10.1017/jfm.2021.186.
- [48] A. Žnidarčič, R. Mettin, C. Cairós, M. Dular, Attached cavitation at a small diameter ultrasonic horn tip, Phys. Fluids. 26 (2014), 023304, https://doi.org/10.1063/ 1.4866270.