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Hydrogen storage in bulk graphene-related materials.

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Abstract

Hydrogen sorption properties of graphene-related materials were studied by gravimetric and volumetric methods at 293K and 77K. Rapid thermal exfoliation of different types of graphite oxide (GO) precursors yielded samples with maximal surface areas up to 850 m^2/g, whereas surface areas up to 2300 m^2/g were achieved by post-exfoliation activation treatments. Therefore, hydrogen storage parameters of graphene materials could be evaluated in a broad range of surface areas. The H_2 uptake vs surface area trend revealed in this study shows that hydrogen storage by graphene materials do not exceed 1 Wt% at 120 Bar H_2 at ambient temperatures. Linear increase of hydrogen adsorption vs surface area was observed at 77 K with maximal observed value of ~5 Wt% for 2300 m^2/g sample. It can be concluded that bulk graphene samples obtained using graphite oxide exfoliation and activation follow standard for other nanostructured carbons hydrogen uptake trends and do not demonstrate superior hydrogen storage parameters reported in several earlier studies. Nevertheless, graphene remains to be one of the best materials for physisorption of hydrogen, especially at low temperatures.

Keywords
Graphene, graphene oxide, hydrogen storage

1. Introduction

Hydrogen storage remains to be the main obstacle in development of hydrogen technology. Carbon materials have been considered as promising candidates for hydrogen storage applications due to possibility to use them both for physisorption and chemisorption. [1],[2] Chemisorption is less attractive due to relatively high temperatures required for

hydrogenation and release of hydrogen. Therefore, a lot of attention has been focused during last decades on studies of hydrogen physisorption on different new nanostructured carbon materials.

Advantage of nanostructured carbon materials is high surface area, stability and possibilities of large scale production. The main disadvantage is relatively low hydrogen storage capacity at ambient temperatures which is below 1 Wt% at reasonably high H_2 pressures.

Various carbon materials, such as activated carbons [3],[4] , carbon nanotubes [5],[6],[7] graphite nanofibers [8] and carbide derived carbons [9] have been actively studied on hydrogen adsorption during last 20 years. It is well known that hydrogen uptake by carbon materials is proportional to BET surface area and micropore volume. Typical uptake observed for these materials at ambient temperature and 100 Bar of H_2 pressure is about 0.3 Wt% per 1000 m^2/g (maximal about 1 Wt%). At liquid nitrogen temperature the maximal values reach about 4-7 Wt% [3, 10].

In recent years, the family of carbon materials studied for hydrogen storage applications was expanded to include graphene. Graphene is usually cited as promising adsorbent material [11],[12] due to its high surface area up to 2630m^2/g [13]. However, this surface area is not exceptional, since even higher values have been reported for some activated carbons [14],[15],[16] whereas the single wall carbon nanotubes are essentially graphene layers rolled into cylindrical shape.

Therefore, it is surprising that hydrogen storage values reported for graphene in several recent studies significantly exceeded those for other nanostructured carbon materials. The range of hydrogen uptakes reported for "graphene" materials at ambient conditions is also surprisingly broad. The highest reported values reach up to 3.1 Wt% at 100 Bar (room temperature) for samples with relatively small surface areas of 925 m^2/g thus exceeding standard trend by about 10 times [17]. More reasonable values have been reported in studies by Srinivas et al (0.7 Wt% for 640 m^2/g at 100 Bar) [18] and L.Wang et al, (0.9 Wt% for 2139 m^2/g and 100 Bar) [19]. However, even these hydrogen uptakes anyway exceed well known values for activated carbons or carbon nanotubes with similar surface areas [3],[14],[15]. Several other studies also reported superior hydrogen uptake values for "graphene" [20],[21].

It should be noted that the true single layered graphene is not yet available in bulk amounts and most of the previously published studies have been performed on reduced graphene oxide (r-GO) samples usually prepared by thermal exfoliation of a graphite oxide

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[17],[18],[22],[23] The surface areas reported in these studies for r-GO are far below theoretical values for pure graphene, which means that studied materials were composed mostly by multilayered flakes. Moreover, it is known that complete removal of all functional groups from r-GO is not possible and this material can be called as a "graphene" only conditionally.

Considering broad range of hydrogen storage parameters so far reported for graphene materials, there is strong need for careful verification of true hydrogen uptake values. It is especially important considering long history of initially erroneous (strongly overestimated) reports on hydrogen adsorption of e.g. carbon nanotubes [24],[25] which were later corrected to significantly lower values [3],[26],[27]. The hydrogen storage measurements on carbon materials are seemingly simple, but subject to many possible errors, especially when volumetric method is used.

Here we report hydrogen storage parameters of graphene materials obtained by exfoliation and activation of various graphite oxides. Unlike most of other studies limited to measuring hydrogen uptake on 1-2 graphene samples, we synthesized many samples with rather broad range of surface areas (100-2300 m^2/g) and performed careful study of H_2 uptakes both at ambient and liquid nitrogen temperatures. According to obtained Wt% vs surface area dependence, the graphene samples do not exhibit hydrogen storage parameters better than any other nanostructured carbons with comparable values of surface areas.

2. Experimental

Several kinds of graphite oxide were used as precursors for preparation of graphene powder using GO thermal exfoliation and activation procedures. Brodie graphite oxide (BGO) was prepared according to original method [28] using 2 oxidation cycles, resulting material exhibited C/O ratio 2.7 determined using XPS. X-ray diffraction tests confirmed that synthesized material is free from unreacted graphite with main (001) peak with d-spacings 6.3-6.6Å at ambient air-exposed state. FTIR spectra showed very good agreement with spectra of previously studied BGO samples [29]. Several samples of graphite oxide prepared by Hummers method (HGO) [30] were tested:

1) HGO purchased from ACS Materials (see detailed characterization in [31],[32]), C/O=2.47

2) HGO provided by GRAnPH® synthesized using oxidation of Grupo Antolin helical-ribbon carbon nanofibers GANF®.[33]

3) HGO synthesized using two different graphite precursors: graphite powder purchased from Alfa Aesar and graphite powder purchased from Graphitwerk Kropfmühl (Germany). The C/O ratio for these samples determined by XPS showed rather typical for H-GO value of 2.5.

The samples of graphene powders were prepared using thermal exfoliation of graphite oxides performed on-air by rapid insertion into hot furnace (250-450^{0}C). Some test exfoliation experiments were also performed at vacuum conditions and under argon. The thermally reduced graphite oxide powder was further subjected to KOH activation according to following procedures:

-grinding KOH with graphene powder followed by annealing in argon at 800°C according to procedure described in [34] .

-impregnation of graphene powder with KOH solution according to procedure described in [35].

Surface area and pore volume of graphene samples were determined by nitrogen adsorption using Quantachrome Nova 1200e surface area analyzer. Powder was also characterized using Raman spectroscopy (In via Renishaw spectrometer) and X-ray diffraction (Siemens D-5000) and FTIR spectrometer (Bruker IFS 66v/S).

Hydrogen adsorption was measured at room temperature using Rubotherm gravimetric system, see details elsewhere [36]. Precision of weight measurement using the balance is ± 0.01 mg and temperature controlled with 0.1K precision. The measurement procedure includes "zero-point correction" applied every 2 minutes which allows to exclude systematic errors due to drifts. The weight difference measurements can be performed under high vacuum conditions (turbo-pump) or inert gas, in the temperature interval 270-700K. The system also allows to perform vacuum or hydrogen annealing at pressures 50 Bar and temperatures up to 450°C. Isotherms were recorded under H$_2$ pressures up to 120 Bar with typical size of samples 100-300 mg. Degassing of samples prior to H$_2$ tests was usually performed at high vacuum conditions at 150-300^{0}C for 12-16 hours. On every step of hydrogen adsorption isotherm the temperature and pressure were stabilized for ~15 min, the temperature stabilized using circulation liquid thermostat. The precision in measured uptake values is estimated to be ± 0.02 Wt% for typical

200 mg sample based on instrumental errors of weight and temperature sensors. FLUIDCAL software was used for calculations of fluid density of hydrogen and helium. Detailed analysis of error sources and methods of their accounting for similar gravimetric system can be found elsewhere[37] Ambient temperature and liquid nitrogen temperature H_2 adsorption tests were also performed using Hiden Isochema Intelligent Manometric Instrument (IMI) [38],[39] volumetric system at ambient temperatures and at 77K (liquid nitrogen immersion cell).

3. Results

3.1 Preparation of high surface area bulk graphene samples

Thermal reduction is easiest method to produce r-GO with relatively high surface areas as it is known that rapid heating results in explosive exfoliation of graphite oxides [40],[41],[42].

Several types of graphite oxide were used as precursors for preparation of thermally reduced graphene oxide samples and several preparation parameters were optimized with the aim to increase surface area of samples to the values closer to theoretical 2630 m^2/g expected for purely single layered graphene. Best surface area was observed for samples of thermally exfoliated BGO with maximal values around 850 m^2/g. Exfoliation of HGO resulted in samples with systematically lower surface area which do not exceed ~450-500 m^2/g. Reduced HGO GRanPH samples showed smallest surface area (up to 311 m^2/g). Therefore, these were not used for further experiments aimed on optimization of exfoliation procedure.

Samples of HGO and BGO precursors were characterized by TGA/DSC in order to get better insight into thermal exfoliation process, see **Figure 1**. In agreement with earlier studies [31],[42], the BGO showed higher temperature of exfoliation compared to HGO. Distinct features of BGO TGA traces include also much sharper exfoliation step and lower weight loss at temperatures below 150°C which is typically assigned to evaporation of water. Remarkably, the weight loss observed at the main step of GO exfoliation is very similar for both samples of BGO and HGO. Therefore, higher temperature of exfoliation observed for BGO is not connected to difference in oxidation degree but should be instead assigned to difference in their structure and types of functionalization. Detailed study of differences between Brodie and Hummers GO is out of scope of this study, but it is clear that synthesis method has major influence on exfoliation temperature and surface area of final graphene powders.

The explosive exfoliation of GO occurs due to rapid buildup of pressure when oxygen and hydroxyl groups are released from graphene oxide sheets. The evidence for this mechanism was provided in our earlier study which demonstrated that increase of gas pressure (environment surrounding powder) results in decreased surface area of exfoliated samples [40]. The TGA data shown in **Figure 1** demonstrate that the main weight loss step which corresponds to exfoliation of GO occurs below 300°C. Increasing temperature of furnace over this temperature affects only the heating rate of sample but not the temperature of exfoliation. Further increase of annealing temperature results in relatively small weight loss and do not affect surface areas significantly. Our experiments with on-air exfoliation showed that highest surface area is obtained when temperature of furnace is set to ~70-90 degrees over the exfoliation point defined as inset of weight loss step determined by TGA (**Figure 1**). The surface area become smaller if exfoliation temperature was lowered (due to smaller heating rate) or if the temperature is further increased to over 400°C (possibly due to aggregation). Somewhat unexpectedly, exfoliation under argon gas, CO_2 or vacuum conditions do not show advantages compared to on–air treatment at the same conditions.

Variations of annealing temperature, gas environment and heating rate did not resulted in significant increase of surface area. This result is in agreement with other studies [17],[43] which report surface areas of r-GO samples far below the theoretical value for single layered graphene. Even the methods which include aerosol single-layered solution injected supersonically into hot furnace did not resulted in better surface areas [44]. Reduction using liquid chemistry (e.g. by hydrazine) is also known to yield samples with surface areas comparable to the ones obtained by thermal exfoliation [45]. The most likely reason for these limitations is aggregation of the graphene sheets into few layered sheets.

Large number of studies with detailed structural characterization of GO exfoliation products is available by now, see e.g. [46],[47],[40],[18]. The r-GO powders obtained by rapid thermal exfoliation are known to result in formation of few-layered defected graphene flakes with some fraction of single-layered sheets, the C/O ratio increases as a result of thermal reduction (see Supplementary information) but complete removal of all functional groups is not achieved without additional treatments.

It should be noted that procedures aimed on better reduction of GO do not result in significant increase of surface area and hydrogen adsorption. For example, annealing of

thermally exfoliated HGO under pure hydrogen at 50Bar and 400°C for 24 hours showed only rather slight increase of hydrogen adsorption by ~10%. It is clear that hydrogen annealing only removes some surface functional groups but unable to separate few layered graphene lamellae on single sheets. However, surface area of the reduced graphene oxide can be significantly increased using post-synthesis activation procedures. Only the treatments which produce significant number of defects, mainly holes, in the graphene sheets, are capable to provide interconnected system of pores with maximal surface area, for example KOH activation [35]. Depending on details of activation procedure and selected precursor powder, the samples with surface areas in the range 1000-2300 m^{2}/g were obtained.

Summarizing this section, considering both pristine r-GO and KOH r-GO, we synthesized set of samples which covers broad range of surface areas ~300-2300 m^{2}/g. Therefore, hydrogen sorption could be studied as a function of BET surface area and reliable trends established.

3.2 Hydrogen adsorption

The **Figure 2** shows hydrogen adsorption measured at 293K for several groups of graphene samples plotted versus BET surface area. Corresponding isotherms recorded using gravimetric method are shown for several samples in the **Figure 3**. The range of surface areas covered by these samples is ~200-2300 m^{2}/g and includes samples obtained by thermal exfoliation of Brodie and Hummers graphite oxides and samples of exfoliated graphite oxide activated using KOH/annealing methods. It should be noted that some samples showed change of surface area after hydrogen uptake measurements. The decrease of surface area is attributed to aggregation of some particles under hydrogen gas pressures of up to 120 Bar in our experiments. The volume of very bulky samples obtained, e.g. by BGO exfoliation was visibly decreased after H$_2$ uptake measurement and corresponding surface area become smaller by 10-15%. In this case, the final value of surface area was used for plotting Wt% vs surface area in the **Figure 2**.

Despite different nature of the studied graphene samples, carefully performed gravimetric measurements of hydrogen adsorption revealed rather precise correlation of hydrogen uptakes with BET surface area. The dependence can be considered as approximately linear below 1000 m^{2}/g but at higher surface areas goes into saturation path which limits maximal adsorption values to ~ 0.8-0.9 Wt% at ~ 3000 m^{2}/g and follows common trends in hydrogen adsorption known for

other carbon nanostructured materials [3]. The **Figure 2** shows that correlation of hydrogen uptake with surface area holds rather precisely despite the fact that composition of samples (degree of reduction), defect state and size of flakes were obviously rather different in several types of studied samples. Moreover, the same trend in H_2 uptake vs surface area extends also to other materials previously studied in our group using the same gravimetric system and nearly identical conditions. The **Figure 2** shows some points added as a reference: hydrogen uptakes by three MOF-5 samples and two carbon supported Pt nanoparticle samples characterized in our earlier study at slightly lower temperature (288K) [48]. It is obvious that the same trend is followed by all these materials.

Most of the samples shown in the **Figure 2** were degassed at moderately high temperature of $150^{o}C$. Two samples were tested also with increased degassing temperature up to $300^{0}C$ but showed negligible increase in hydrogen uptake values. It could also be argued that higher hydrogen uptake can be achieved if the r-GO samples are better reduced. Obviously, on-air exfoliation of GO does not result in complete removal of all functional groups, especially those on the edges of graphene flakes. On the other hand, presence of some residual functional groups could be one of the factors which prevent graphene flakes against aggregation and re-stacking into graphitic structure. Therefore, additional test with H_2 annealing was performed. One of the samples produced by on- air thermal exfoliation of GO and tested on H_2 uptake was *in situ* (without exposure to air) annealed in hydrogen at 50 Bar of H_2 pressure at $350^{o}C$ for 12 hours and then degassed in vacuum at the same temperature for 4 hours. Following this H_2 activation procedure the hydrogen sorption isotherm was recorded again but it showed no significant improvement of H_2 uptake: 0.20Wt% at 120 Bar prior to activation and 0.22wt% after.

Temperature dependence of H_2 uptake was also studied on selected samples: gravimetric tests were performed at temperatures slightly below ambient and several samples studied by volumetric method at 77K using immersion liquid nitrogen thermostat. **Figure 4** shows isotherms recorded for some graphene samples at 77K. **Figure 5** summarizes these results showing maximal hydrogen uptakes as a function of BET surface area.

It is obvious that the hydrogen adsorption by graphene samples correlates rather precisely with BET surface area, independently on the nature of graphite oxide precursors or activation procedures, both at ambient temperature and at 77K. Moreover, the trend obtained here can be

compared to previously published data on hydrogen storage capacity of other nanostructured carbons, e.g. carbon nanotubes [5] and activated carbons [4]. For example, surface area of carbon nanotubes vs hydrogen uptake was previously studied in the ref [3]. The **Figure 5** shows that the surface area vs Wt% trend revealed in this study for carbon nanotubes is in remarkable agreement with our data obtained on graphene samples.

The close agreement is unlikely to be co-incidence; it confirms that graphene powders do not exhibit hydrogen uptake levels exceeding other types of high surface area carbon materials. Therefore, we believe that previous reports on exceptionally high hydrogen adsorption of graphene-related materials (mostly for reduced graphite oxide) were subject to overestimation. For example, our study shows the H2 uptakes about 3-4 times lower compared to report by Srinivas et al [18] and about six times lower compared to experiments by A.Ghosh [22]. It should be noted also that all previous studies of graphene materials were performed on single samples with certain surface area while our experiments cover broad range of surface areas and several types of samples: r-GO produced by exfoliation of several GO precursors and r-GO activated using KOH.

Hydrogen adsorption measurements are seemingly simple but the history of hydrogen storage research field during last two decades showed many examples of reports with very strong overestimations of hydrogen storage capacity for various nanomaterials. For examples, hydrogen uptakes for carbon nanotubes, [24] carbon nanofibers [25] and even for MOFs [49] were initially reported to be about 5-10 times higher compared to later established hydrogen storage uptake values [3],[26],[50],[51].

Finally, it should be noted that all so far published studies of hydrogen sorption were performed with reduced graphene oxide or similar materials, which can be considered as graphene only subject to several limitations. The graphene sheets in these samples are extremely defected, perforated and possibly not flat. The true hydrogen adsorption properties of high quality single layered graphene are yet to be determined. Existing volumetric and gravimetric methods for evaluation of hydrogen physisorption require bulk amounts of materials, whereas the high quality graphene cannot be produced in bulk amounts at the moment. On the other hand, activation by KOH is rather typical method for production of high surface area activated carbons. The structural transformation of graphene in process of this heavy defect-introducing method is likely to lead to disappearance of graphene identity, basically any carbon precursor yields high

surface area materials if subjected to KOH activation at high temperatures. The structure of precursors has only limited influence on the surface area of final products.

Despite the absence of exceptionally high hydrogen uptakes in our experiments, we believe that graphene remains to be one of the best materials for physisorption of hydrogen, especially at low temperatures. MOFs possibly demonstrate better absolute values of adsorption at 77K [52],[53],[54] but their structures are typically sensitive to moisture, rather unstable and easily collapse not only due to chemical modifications but in some cases even as a result of applied pressure in tens of bars range [51]. Graphene is rather stable material which can be reproducibly synthesized using relatively simple procedures, it is air-stable and exhibits relatively large hydrogen adsorption levels at least at low temperatures. Possibly, improvement of hydrogen uptakes at ambient temperatures can be achieved by creation of graphene-related materials with ordered stacking and subnanometer slit pores [55]. Graphene oxide frameworks is one of possible examples how materials with sub-nanometer pores can be prepared [56]. However, more studies are required to further improve surface area values and hydrogen storage parameters of these materials.

In summary, bulk graphene powders with broad range of surface areas were prepared using thermal exfoliation of Brodie and Hummers graphite oxides (up to ~850 m2/g for BGO) and by KOH activation procedures of r-GO samples (up to ~2300 m^2/g). Hydrogen uptake of these samples was evaluated at ambient temperature and 77K using both gravimetric and volumetric methods. The values of hydrogen uptake plotted vs surface area showed good agreement with the dependence previously reported as typical for other carbon materials and MOFs. It can be concluded that bulk graphene-related materials do not exhibit superior hydrogen storage parameters compared to other nanostructured carbon materials like activated carbons, carbon nanotubes or nanofibers.

Acknowledgements

Appendix A. Supplementary data

Supplementary data (XPS and Raman spectra of thermally exfoliated graphite oxide samples) associated with this article can be found in the online version.

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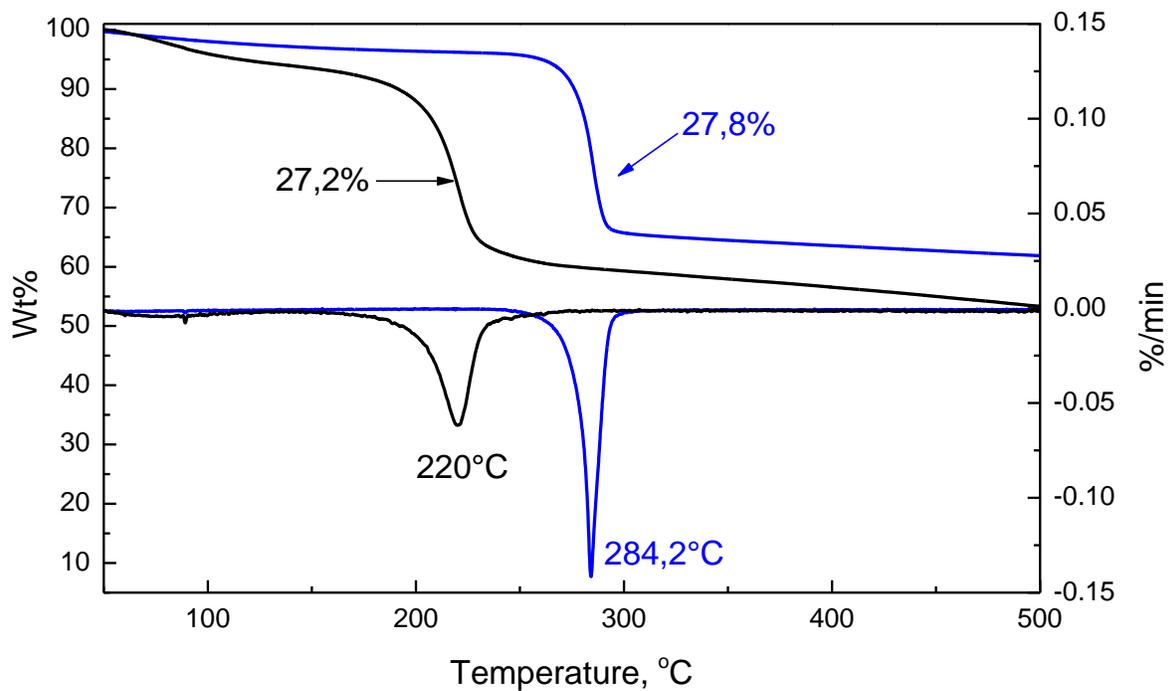
Figure 1. Thermogravimetric data for samples of Brodie (blue) and Hummers (black) graphite oxides used as a precursors for graphene powder synthesis using thermal exfoliation.
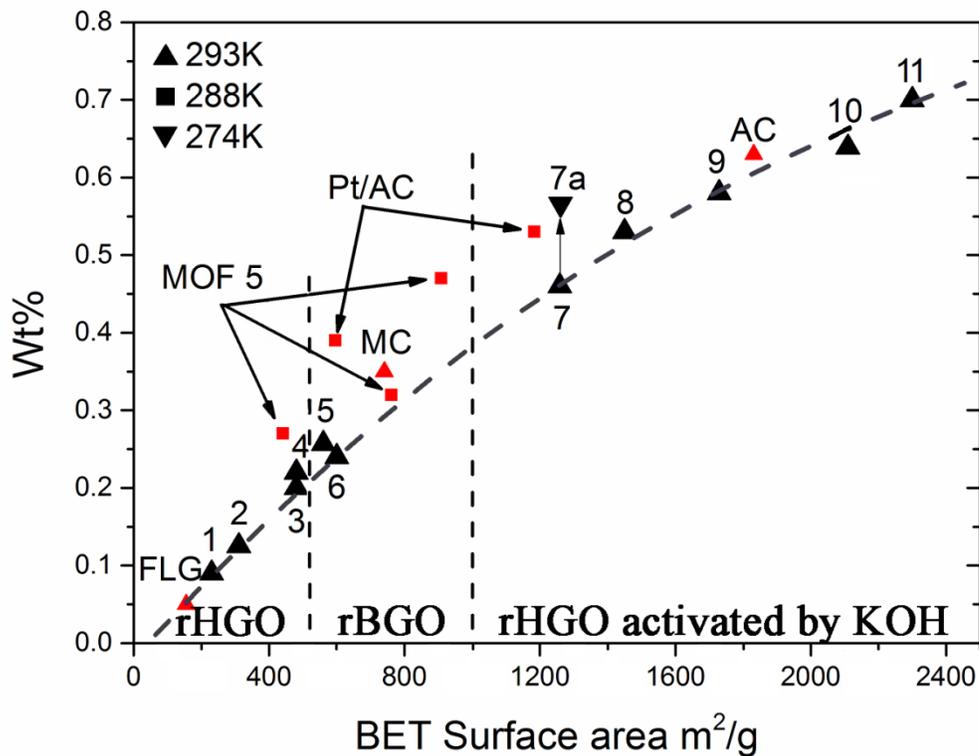
Figure 2. Hydrogen uptake (Wt%) vs BET surface area measured at ambient temperature (120 Bar) for several types of graphene samples: FLG- few layered graphene sample, 1-4- reduced Hummers graphite oxide (rHGO), 5-6- reduced Brodie graphite oxide (rBGO), 7-10- reduced Hummers GO activated by KOH(KOH-rGO) (▲). Hydrogen uptake was also measured for samples of commercial mesoporous carbon (MC) and Activated Carbon (AC) as a reference (▲). MOF's and Pt/AC samples measured in our previous studies (288K) are also shown as a reference [48].
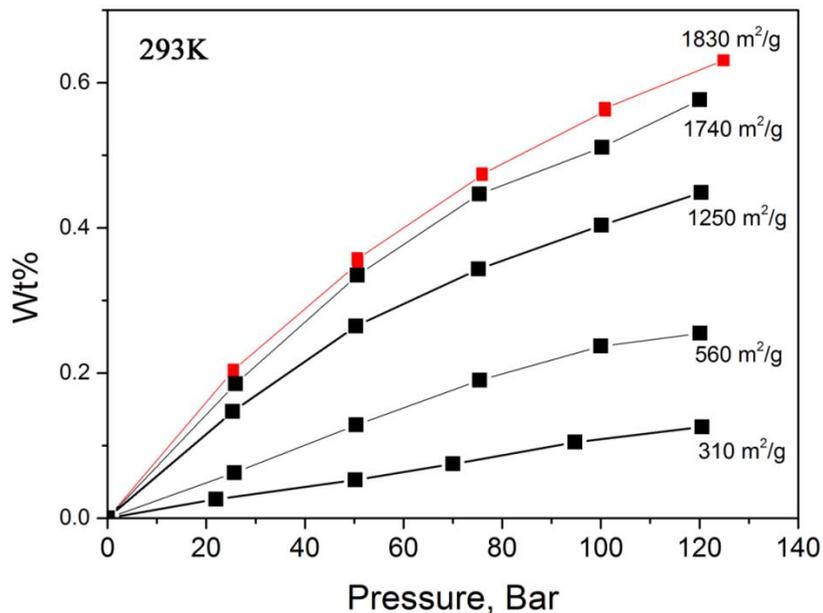
Figure 3. Hydrogen isotherms recorded for several graphene samples with different BET surface area using gravimetric method (reference sample of activated carbon highlighted by red color).
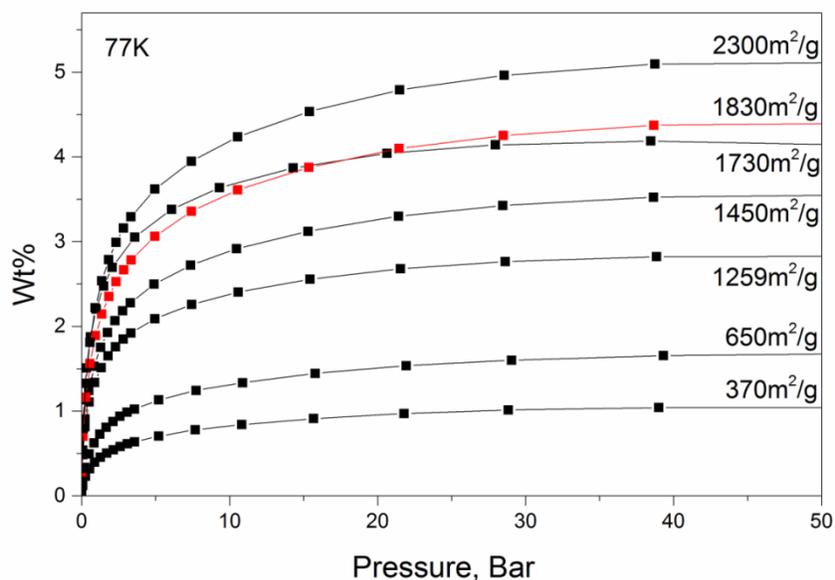

Figure 4. Hydrogen adsorption isotherms recorded for graphene samples with different surface area at 77K using immersion thermostat. Isotherm recorded from reference sample of activated carbon is shown by red symbols.
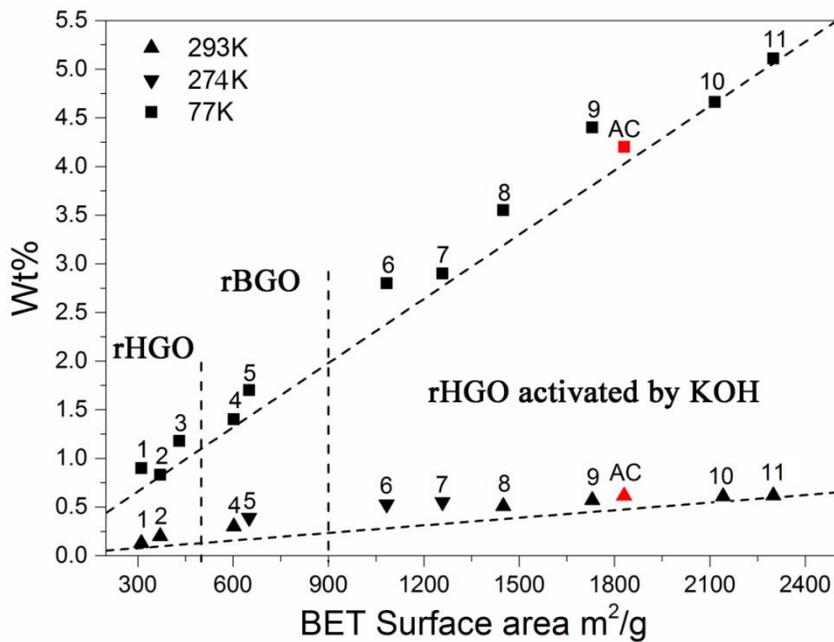
Figure 5. Hydrogen uptakes measured by volumetric method at ambient (120 Bar) and 77K (50 Bar) temperatures and plotted vs surface area for following samples: 1-3 r-HGO, 4-5 r-BGO, 6-11 KOH activated r-GO, AC − reference activated carbon. Black dashed lines show reference trend for hydrogen adsorption by carbon nanotubes according to ref [3].