HYDROGEN STORAGE PROPERTIES OF GRAPHENE OXIDE MATERIALS PREPARED BY DIFFERENT WAYS

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Abstract

Graphene-based materials show unique properties. These single layered materials consist of 2D structure of carbon atoms, belong to the strongest known materials, that are very mechanically flexible, optically transparent and that are excellent electrical and thermal conductors. Recently, several studies on these types of materials have highlighted the potential of this material for hydrogen storage (HS) and raised new hopes for the development of an effective solid-state HS media. In the present paper, the structure and HS properties of graphene oxide (GO) and chemically reduced graphene oxide (rGO) produced by different procedures were studied. Hydrogen sorption characteristics of GO and rGO were measured using the Sieverts-type gas sorption analyzer *PCT-Pro Setaram Instrumentation.* The study of HS was carried out at temperature range from 198 K to 423 K under hydrogen pressure from 1×10^{-4} to 4 MPa.

For the HS point of view, the advantage of GO or rGO compared to graphene, is the presence of multiple chemical groups that can be used for introducing modifiers and their superior spreading on the materials surface. The suitably functionalized GO or rGO materials could potentially exhibit outstanding HS properties.

Keywords: Graphene oxide, hydrogen storage, adsorption, desorption

1. INTRODUCTION

Hydrogen is a very prospective and "eco-friendly" fuel for vehicles which can bring economical and environmental benefits. It can be produced from a large number of different feedstocks such as water, coal, natural gas, biomass, and others, through thermal, electrolytic or photolytic processes. However, hydrogen poses a number of hazards to human safety, from potential detonations and fires when mixed with air to being an asphyxiant in its pure, oxygen-free form. Moreover, production of hydrogen from the sources mentioned above involves many technical and economical problems at the moment.

The storage in solid state can be one of the solutions of HS. It is the most promising and safe method to store large amounts of hydrogen in a relatively small volume. There are two basic hydrogen bonding mechanism for this solid state storage [1] - chemisorption and physisorption. Chemisorption is a way of HS, where the atoms are incorporated into the lattice of the material. However, the main shortcoming of chemisorption is the usual requirement of high temperatures to allow absorption/desorption of hydrogen due to its high binding energy. On the other side, the heat released during absorption can be recycled and affects the efficiency of the whole HS system.

A lot of attention has been focused on studies of hydrogen physisorption on different new nanostructured carbon materials during last decades. Carbon materials are considered as promising for HS applications due to possibility to use them both for physisorption and chemisorption [2,3]. The main disadvantage is relatively low hydrogen storage capacity at ambient temperatures under relatively high pressure.

In recent years, the main study of carbon materials was focused on graphene materials. It should be noted that the single-layered graphene is not available as a bulk material and the most of previously published papers

have been performed on GO or rGO usually prepared by thermal exfoliation of GO. Because the complete removal of all functional groups from rGO in not possible, this material can be labeled as graphene only conditionally. The most of previously published studies have been performed on rGO samples prepared by thermal exfoliation of graphite oxides [4]. One of other possible way is using isolation procedure of GO/rGO by lyophilisation [5]. Recently, some studies reported superior hydrogen properties for graphene. However, the study [6] outlined that the graphene materials do not exhibit hydrogen properties better than other nanostructured carbons.

This paper reports structure, temperature stability and hydrogen storage properties GO and rGO reduced by Na[BH$_4$] and hydrazine.

2. EXPERIMENTAL

All of experimental materials were made using components purchased from SIGMA-ALDRICH. The GO was prepared by chemical oxidation of 5.0 g graphite flakes in a mixture of concentrated H$_2$SO$_4$ (670 ml) and 30.0 g KMnO$_4$ according to the simplified Hummer's method [7,8]. The reaction mixture was stirred vigorously. After 4 days, the oxidation of graphite was terminated by addition of H$_2$O$_2$ solution (250 ml, 30 wt% in H$_2$O). Formed graphene oxide was washed 3 times with 1 M HCl (37 wt% in H$_2$O) and several times with Milli-Q water (total volume used 12 l) until constant pH value (3-4) was achieved. This GO was used for preparation two types of rGO.

The first material labeled as rGO-N was prepared from GO reduced by Na[BH$_4$]. 5% solution of Na$_2$CO$_3$ was added to GO to increase pH value (9-10). 800 mg of Na[BH$_4$] were added to 100 ml of GO and heated at 80 °C with constant stirring for 1 hour. The solution changed from dark brown to black. Formed reduced graphene oxide was washed with Milli-Q water until constant pH value (6-7) was achieved [7]. The second materials labeled as rGO-H was prepared from GO reduced by hydrazine monohydrate. For 3.0 mg of GO, 1.0 µl of hydrazine was used. The resulted solution was heated at 80 °C and stirred for 12 hours with constant stirring. The solution changed from dark brown to black. Formed reduced graphene oxide was washed with Milli-Q water until constant pH value (6-7) was achieved [9-11].

Bulk samples of GO, rGO-N and rGO-H were prepared by lyophilization in freeze dry system (Labconco FreeZone, Kansas City, USA). These lyophilized samples were in form of flakes. Structure and chemical composition of samples was studied at scanning electron microscope (SEM) Tescan LYRA 3 XMU FEG/SEMxFIB equipped with X-max80 EDS detector.

The thermal stability of experimental materials was tested by TGA in analyzer Q500 by TA Instruments. The samples were analyzed under nitrogen atmosphere with heating rate 10 K/min.

Hydrogen adsorption/desorption (A/D) characteristics were measured using Sieverts-type gas sorption analyzer *PCT-Pro* Setaram Instrumentation. The study was carried out at temperatures 198, 373 and 423 K under hydrogen pressure from 1x10^{-4} (desorption) to 4 MPa (adsorption). The weight of measured samples was about 50mg. The purity of both hydrogen and helium (calibration gas) was 6N. All of the samples were annealed at 473 K /1x10^{-4} MPa for 2 hours before hydrogen sorption measurement due to water adsorption.

3. RESULTS AND DISCUSSION

The morphology of all experimental materials was quite similar. The flakes consisted of thin layers occasionally in the form of thin "fibers". The structure of rGO-H contained locally also more crumpled layers or fibers than it was found in typical structure of studied samples (**Figure 1-3**). All of studied materials contained (**Figure 4**) also impurities (Cu, S, Si, Cl, K, Ca). The rGO-H contained also Ti, Fe, Mn in comparison with other experimental materials. These impurities probably caused locally anomalous morphology of rGO-H.
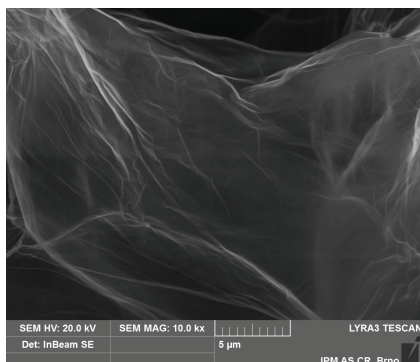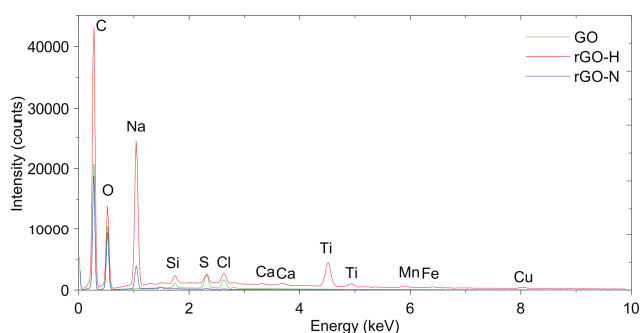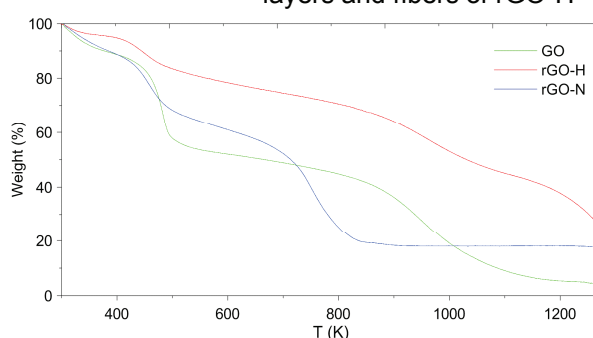
Figure 1 Morphology of GO
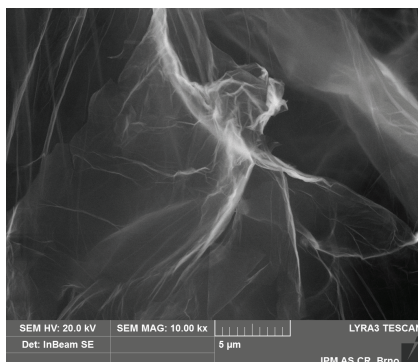
Figure 2 Morphology of rGO-N
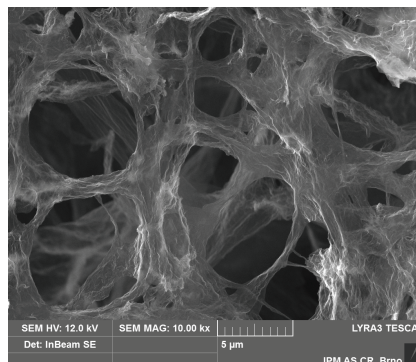
Figure 3 Locally strongly crumpled layers and fibers of rGO-H


**Figure 4** EDS spectras of GO, rGO-H and rGO-N

Figure 5 TGA lines of GO, rGO-H and rGO-N

The graphene oxide materials are generally thermally unstable materials. The thermal stability of studied materials is shown in TGA plot (**Figure 5**). The first 4, 10.3 and 10.5% weight loss for rGO-H, GO, rGO-N respectively could be attributed to the adsorbed water molecules, the second one 20.7, 37.6, 27.8% weight loss to oxide groups and the last ones to carbon groups. The higher thermal stability of rGO-H or rGO-N is probably caused by presence of higher volume of impurities than in GO. The impurities (dark particles) are shown in detailed micrograph of GO and rGO-H layer after A/D cycles in **Figures 6-7**.
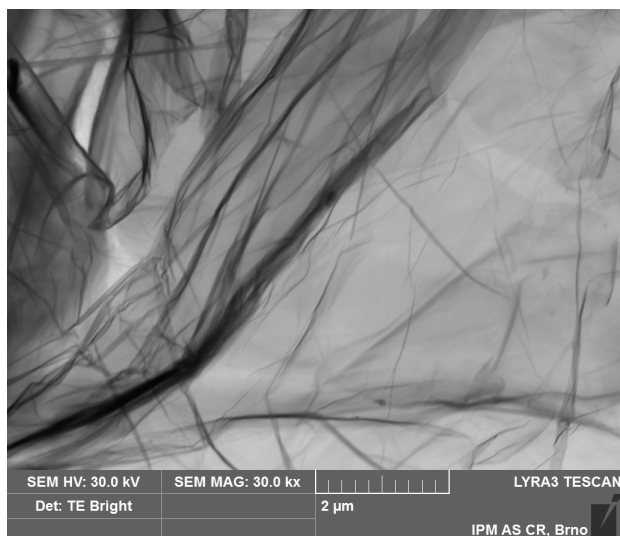
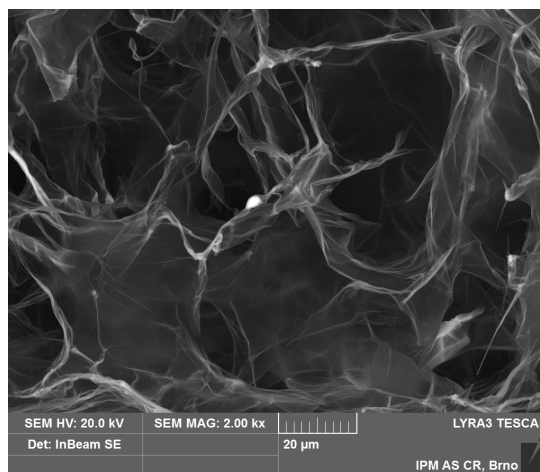**Figure 6** Detail of GO layer after A/D cycles
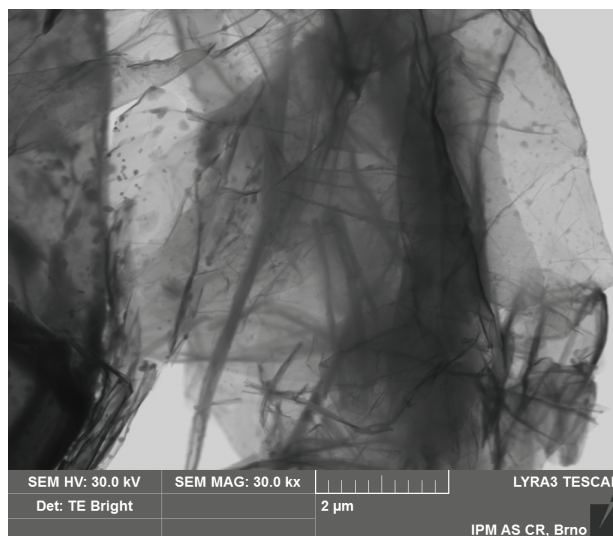
Figure 7 Detail of rGO-H layer after A/D cycles

Whereas the impurities (dark particles) can be found on layer of GO exceptionally, the layer of rGO-H contains a lot of impurities placed on the surface. All studied materials had foam-like morphology (**Figure 8**) and the layers was not influenced by A/D cycles and weight loss (water desorption).
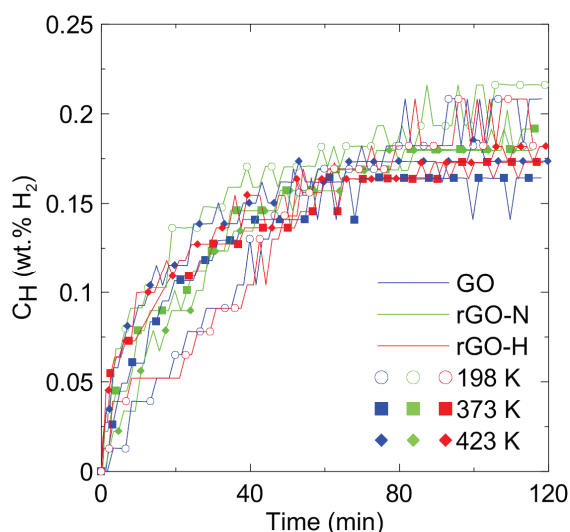
Whereas significant differences were found in morphology and composition of all studied materials, the A/D kinetic properties are very similar (**Figures 8, 9**). The maximum capacity (c_{max}) of H_2 in all materials at temperature range 198-423 K was in the range 0.22-0.17 wt.%H_2 respectively. The adsorbed c_{max} of H_2 was desorbed during several minutes. Since all desorption curves of studied materials are very similar, only desorption curves of rGO-H at 198 and 423 K are shown as examples. The c_{max} is near to value measured for rGO materials with BET surface from

Figure 8 Example of foam-like morphology of studied materials, rGO-N

1250 m^2/g [4] to 2900 m^2/g [12]. However, these materials were obtained by thermal exfoliation of Brodie and Hummers GO and activated using KOH/annealing methods. The lyophilized materials show better A/D properties than graphene prepared by chemical exfoliation method [13].

The sorption properties found in the studied materials have interesting potential for HS. They have good capacity compared to published results and the advantage of rGO compared to graphene is the presence of multiple chemical groups that can be used in the future research for introducing modifiers and its superior spreading on the materials surface. Choosing a suitable strategy or combination of various methods and elements could increase the efficiency of the material and thus ensure higher volume of trapped hydrogen. Moreover, one advantage of graphene compared to Mg-based alloys is its potential for decreasing dehydrogenation temperature. Recently, it was reported that graphene with its single atomic layer structure can also effectively inhibit agglomeration very promising HSM - MgH_2 particles and promote H atom diffusion [14].
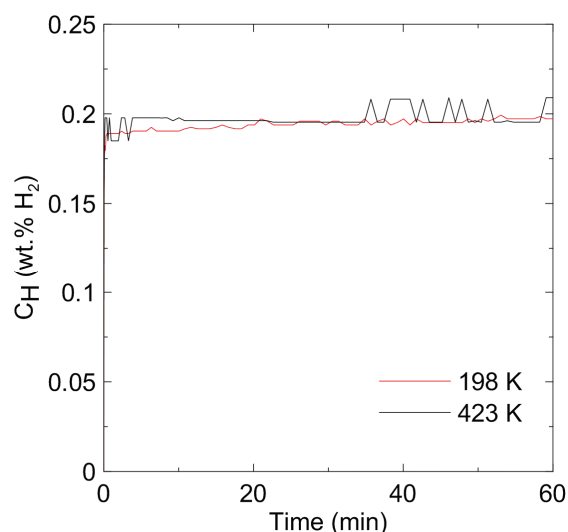
Moreover, the structure of graphene-type materials consist in "crumpled" layers of GO/rGO. These flakes have a foam-like morphology, as shown in **Figure 8**. These properties can be used for production HSM bulk graphene scaffold material, similarly as other carbon materials [15].

Figure 9 Kinetic of H_2 adsorption in studied materials

Figure 10 Example of H_2 desorption in rGO-H

5. CONCLUSION

The GO was prepared using simplified Hummer's method, the materials rGO-N or rGO-H was prepared by reduction of GO using Na[BH$_4$] and hydrazine respectively. The bulk flakes-form samples were produced by lyophilization. The final flakes have foam-like morphology composed of crumpled layers of base material. All studied materials contain also impurities originated from production processes. However, the rGO-H contained more impurities than other experimental materials. The layer of these materials was locally more crumpled.

Hydrogen A/D kinetics of these materials was evaluated at 198, 373 and 423 K using Sieverts-type gas sorption analyzer. In all cases, similar hydrogen kinetics and c_{max} of H$_2$ was shown after about two hours adsorption. The c_{max} of H$_2$ of all materials at temperature range 198-423 K is in the range 0.22-0.17 wt.% H$_2$ respectively. These lyophylised materials have interesting potential for production of bulk functionalized graphene oxide materials or bulk graphene scaffold materials for HS.

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