

Modified Graphene Sheet Stacks for Hydrogen Binding

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Graphene sheet stacks were obtained using electrochemical exfoliation method. The morphology, distribution of elements and structure of the obtained samples were investigated using scanning electron microscopy, energy dispersive spectroscopy, Raman spectroscopy and Brunauer-Emmett-Teller methods. The graphene sheet stacks mostly have been formed with open stack structures having surface area of 124 m²/g. Mg intercalation in graphene sheet structures was obtained adding MgCl₂ during exfoliation process. Hydrogen desorption were measured in the temperature range 100–473 K at the pressure 2 bar reaching maximal desorbed hydrogen amount of 0.12–0.43 wt.%.

Keywords: hydrogen storage, graphene, exfoliation, multi-sheet stacks.

1. INTRODUCTION

The interest in porous materials with high surface area for hydrogen storage having high hydrogen content, low weight, small volume and close to room temperature adsorption/desorption kinetics are still actual. Graphene having many extraordinary properties is considered as one of the most promising hydrogen storing material [1].

Usually graphene nanostructures show low H₂ adsorption capacity at ambient conditions. Although Patchkovskii et al. [2] computational data shows that H₂ adsorption capacities on graphene can approach U.S. Department of Energy goals of values of 6.5 wt.% and 62 kg/m³ volumetric density of absorbed H₂ at room temperature, experimental data up to now are substantially lower. Ghosh et al. [3] reports that H₂ adsorption on few layer graphene samples prepared by the exfoliation method reached H₂ uptake value of 1.7 wt.% at 77 K and 1 atm. It has been found [4] that adsorption of H₂ is directly proportional to the surface area of the sample, and adsorption of 3 wt.% was achieved at 298 K and 100 atm. There are no studies on hydrogen adsorption on graphene at low pressures and temperatures close to room temperature.

To achieve higher hydrogen storing capacities the chemical doping of graphitic material with catalysts are considered. A large number of scientific papers report on theoretical calculations of the modified graphene structures doped with alkali (Li, Na, K), alkaline earth (Mg, Ca), noble (Pd, Pt) and other metals [5–7]. The aim of doping graphene structures is to increase the binding energy thus increasing adsorbed amount of H₂ due to the hybridization of H₂ orbitals with transition metal orbitals and electric field caused polarisation of H₂ molecules [8].

In our research graphene sheet stacks are obtained by electrochemical exfoliation method. Hydrogen desorption in as obtained and intercalated with Mg ions graphene multi-

stack sheets is investigated with structural, morphological, spectroscopic and thermal desorption methods.

2. EXPERIMENTAL

Graphene sheet stacks (GSS) were obtained by electrochemical exfoliation method using 2 electrode electrochemical cell. Graphite industrial waste rod was used as a working electrode, Pt foil served as a reference electrode. Both electrodes were immersed in 1 mol/l H₂SO₄ electrolyte.

Electrodes were pre-treated by applying +2 V voltage for 60 seconds. Exfoliation process started by applying –10 V for 3 seconds and +10 V for 5 seconds repeating this voltage sequence for 3 hours. The gained suspension was filtered by vacuum filtration method followed by ultrasonic bath treatment procedure in deionised water at 24 kHz for 3 hours. After sedimentation the obtained sample particles were collected and dried. Part of powder was annealed in Ar/H₂ (95 : 5) gas flow at 600 °C for 4 hours.

Intercalation of Mg ions for several samples were performed during exfoliation process by adding 0.01 mol/l MgCl in electrolyte followed (identical sample preparation steps described above).

Scanning electron microscope (SEM) images of raw, reduced and intercalated samples were obtained by Hitachi S-400N with following elemental mapping by energy dispersive spectrometer (EDS) and Lyra Tescan.

Confocal inVia Raman Microscope (Renishaw) was used to get powder sample spectra in the region 200–3500 cm⁻¹ (excitation wavelength 514 nm, beam diameter 1 μm, power 35 mW and Raman spectra accumulation time 10 sec/scan, 5 scans) (Fig. 4); 50 mW 200 ns pulse laser 532 nm, 20 μm, (600 s/scan)/50 cm⁻¹, 2 scans (Fig. 5). Surface area was determined by Brunauer-Emmett-Teller (BET) method using nitrogen gas sorption measurements at 77 K with Nova 1200 E-Series,

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All samples were out gassed before hydrogen desorption measurements for 2 h at 493 K. Amount of desorbed hydrogen were measured using volumetric method in the temperature range 100–473 K at the pressure 2 bar. The composition of desorbed gases were controlled by Mass Spectrometer RGA – 100.

3. RESULTS

The morphology of all prepared samples (as prepared, reduced, and intercalated with Mg) was studied by SEM (Fig. 1–Fig. 3, respectively). The obtained SEM images show agglomerated, stacked structures reminding puff pastry with deep voids between stacked sheets (Fig. 1), where few layer sheets can be distinguished with dimensions 15–25 μm (Fig. 2) and thickness 66 to 112 nm (Fig. 3). Distinctly flaky structure promises a large specific surface area and many "pockets" where to accumulate hydrogen during adsorption process.

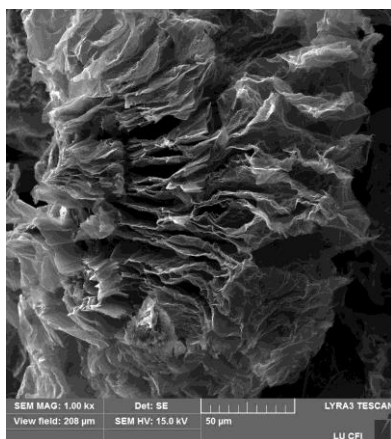


Fig. 1. SEM picture of raw GSS sample

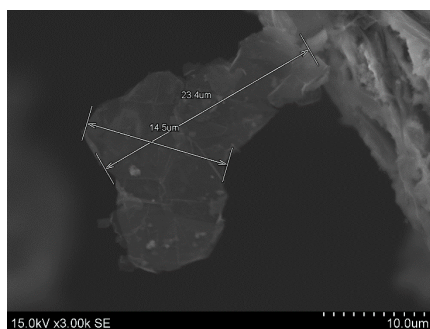


Fig. 2. SEM picture of reduced GSS sample



Fig. 3. Mg intercalated GSS

Ability to open the graphite carbon layer galleries by chemical means enables the preparation of bulk quantities of single or few-layer graphene by combining intercalation with dispersion in a polar solvent [9]. The redox-driven intercalation of ions and cations in Van der Waals layered solids involve host–guest charge transfer, which facilitates opening of the outermost galleries [10]. The process is initiated by activation of the outermost host layers mostly by acid–base reactions and the guest molecule activity must exceed a threshold value for bulk intercalation to occur.

EDS mapping of Mg-intercalated sample showed that Mg together with some impurity elements (Table 1) are mostly located on the outer surfaces of sheet stack. Occurrence of impurities is caused by use of waste graphite and cannot be avoided by heat treatment and degassing of samples.

Table 1. Element analysis (EDS) of Mg GSS

Element	norm.at.%	Error in %
Carbon	34.06	9.5
Oxygen	55.97	39.9
Sulfur	0.24	0.05
Magnesium	0.15	0.044

BET analysis confirms that the surface area of raw (non-reduced) sample and intercalated sample decreases from 124 m^2/g to 43 m^2/g , respectively. In intercalation process the interlayer spaces fills with guest ions/anions and surface area of material decrease. Variety of surface area values 270–1550 m^2/g [11] can be found in literature in close connection with experimental method used for synthesis of graphene materials.

The presence of agglomerated reduced GSS were determined by Raman spectroscopy (Fig. 4) showing G band around 1575–1581 cm^{-1} and D band around 1350–1358 cm^{-1} , and 2D at 2702–2732 that is in a good agreement with literature [12, 13]. The D band characterises disorder and number of graphene sheets. By increase of the D band intensity the number layers and disorder increases [14]. Intercalated Mg sample shows the shift by 19 cm^{-1} to lower energies of Raman 2D peak indicating more disordered state comparing with reduced GSS – in literature lower 2D values (cm^{-1}) represent fewer layers of graphene in stacks [15].

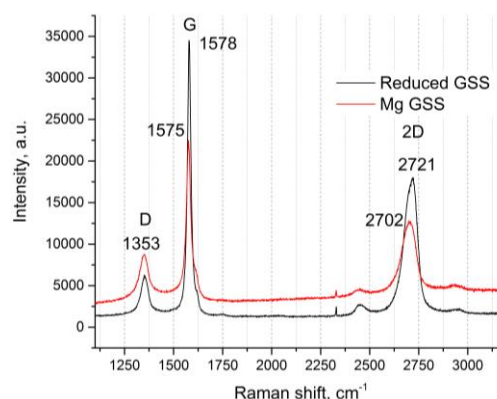


Fig. 4. Raman spectra – reduced GSS and Mg GSS

The amount of desorbed hydrogen was calculated for all samples using volumetric analysis data and shown in the Table 2. The measurements were performed in the temperature range 100–473 K applying initial hydrogen

pressure of 2 bar. Mass spectrometry analysis justified that desorbed gas is hydrogen with negligible sulphur additives.

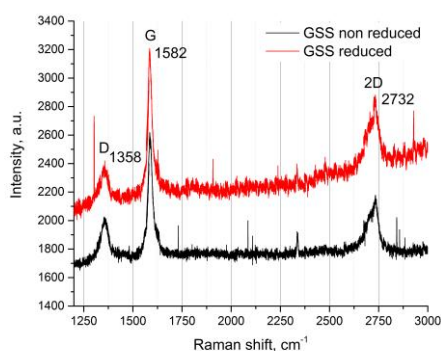


Fig. 5. Raman spectra– reduced GSS and raw-GSS

Table 2. Amount of hydrogen in different measured samples:

GSS	H ₂ des T, K	Ads H ₂ ΔP, Pa	H ₂ , wt. %
GSS reduced	–137	5000	0.12 %
Mg GSS nonreduced	–137	48000	0.14 %
GSS nonreduced	–150	33000	0.43 %

4. CONCLUSIONS

Few layer graphene multi-sheet stacks are successfully obtained from industrial waste graphite rods using exfoliation method in sulphuric acid solution. Mg intercalation is performed during exfoliation procedure. Agglomerated samples as well as single sheets of GSS are observed in SEM images. Reduction of samples ‘cracks’ the material leaving open structures with deep divided stacks. EDS mapping of Mg-intercalated few layer graphene samples shows that Mg together with other impurity elements are located on the surface of GSS. Heat treatment and degassing of samples doesn’t increase material purity. Raman spectroscopy analysis and intense D peak confirms that obtained samples are graphene sheet stacks. Amount of desorbed hydrogen is 0.43 wt.%, 0.12 wt.%, 0.14 wt.% for raw GSS, reduced GSS and Mg-intercalated samples, respectively. Mg intercalation decreased active surface of GSS that caused decrease of amount of adsorbed hydrogen.

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REFERENCES

- Klechikov, A.G., Mercier, G., Merino, P., Blanco, S., Merino, C., Talyzin, A.V. Hydrogen Storage in Bulk Graphene-Related Materials *Microporous and Mesoporous Materials* 210 2015: pp. 46–51. <http://dx.doi.org/10.1016/j.micromeso.2015.02.017>
- Patchkovskii, S., Tse, J.S., Yurchenko, S.N., Zhechkov, L., Heine, T., Seifert, G. Graphene NanoStructures as Tunable Storage Media for Molecular HydroGen *Proceedings of the National Academy of Sciences of the United States of America*

- 102 (30) 2005: pp. 10439–10444. <http://dx.doi.org/10.1073/pnas.0501030102>
3. Ghosh, A., Subrahmanyam, K.S., Krishna, K.S., Datta, S., Govindaraj, A., Pati, S.K., Rao, C.N.R. Uptake of H₂ and CO₂ by Graphene *The Journal of Physical Chemistry C* 112 (40) 2008: pp. 15704–15707. <http://dx.doi.org/10.1021/jp805802w>
4. Rao, C.N.R., Maitra, U., Ramakrishna Matte, H.S.S. Graphene: Synthesis, Characterization, and Selected Properties Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2013: pp. 1–47. <http://dx.doi.org/10.1002/9783527651122>
5. Broom, D.P. Hydrogen Storage Materials – The Characterisation of Their Storage Properties Springer-Verlag London, 2011: pp. 19–59.
6. Ding, F., Yakobson, B.I. Challenges in Hydrogen Adsorptions: from Physisorption to Chemisorption *Frontiers of Physics* 6 (2) 2011: pp. 142–150. <https://doi.org/10.1007/s11467-011-0171-6>
7. Bodrenko, I.V., Avdeenkova, A.V., Bessarabov, D.G., Bibikov, A.V., Nikolaev, A.V., Taran, M.D., Tkalya, E.V. Hydrogen Storage in Aromatic Carbon Ring Based Molecular Materials Decorated with Alkali or Alkali-Earth Metals *The Journal of Physical Chemistry C* 116 (48) 2012: pp. 25286–25292. <http://dx.doi.org/10.1021/jp305324p>
8. Srinivas, G., Guo, Z.X. Graphene-based Materials: Synthesis and Gas Sorption, Storage and Separation *Progress in Materials Science* 69 2014: pp. 1–60. <http://dx.doi.org/10.1016/j.pmatsci.2014.10.004>
9. Dresselhaus, M.S., Dresselhaus, G. Intercalation Compounds of Graphite *Advances in Physics* 51 (1) 2002: pp. 1–186. <http://dx.doi.org/10.1080/00018730110113644>
10. Kovtyukhova, N.I., Wang, Y., Berkdemir, A., Cruz Silva, R., Terrones, M., Crespi, V.H., Mallouk, T.E. Non-oxidative Intercalation and Exfoliation of Graphite by Brønsted Acids *Nature Chemistry* 6 2014: pp. 957–963. <http://dx.doi.org/10.1038/nchem.2054>
11. Sur, U.K. Graphene: A Rising Star on the Horizon of Materials Science *International Journal of Electro-chemistry* 2012: pp. 1-12 Article ID 237689. <http://dx.doi.org/10.1155/2012/237689>
12. Stankovich, S., Dikin, D.A., Piner, R.D., Kohlhaas, K.A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S., Ruoff, R. Synthesis of graphene-Based Nanosheets Via Chemical Reduction of Exfoliated Graphite Oxide *Carbon* 45 (7) 2007: pp. 1558–1565. <http://dx.doi.org/10.1016/j.carbon.2007.02.034>
13. Ferrari, A.C., Basko, D.M. Raman Spectroscopy as a Versatile Tool for Studying the Properties of Graphene *Nature Nanotechnology* 8 2013: pp 235–246. <http://dx.doi.org/10.1038/nnano.2013.46>
14. Subrahmanyam, K.S., Vivekchand, S.R.C., Govindaraj, A., Rao, C.N.R. A study of Graphenes Prepared by Different Methods: Characterization, Properties And Solubilization *Journal of Materials Chemistry* 18 2008: pp. 1517–1523. <http://dx.doi.org/10.1039/b716536f>
15. Ferrari, A.C., Meyer, J.C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K.S., Roth, S., Geim, A.K. Raman Spectrum of Graphene and Graphene Layers *Physical Review Letters* 97 (187401) 2006: pp. 1–4. <http://dx.doi.org/10.1103/PhysRevLett.97.187401>