



## Complex multilayer carbon structures for green energetics

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**Abstract.** We investigated a promising material for hydrogen storage and sensing. The material was obtained by exfoliating recycled graphite waste and simultaneously modifying the product with metal impurities (Bi, V, Cu). As a result, graphene sheet stack (GSS) powder was obtained. The material was further processed by hydrothermal annealing and reduction. Raman spectra of the GSS materials are provided to show the presence of graphene-like structures and defects in the exfoliated material. The synthesized graphene material has good semiconductor properties with a low electrical resistance for hydrogen sensing applications.

**Key words:** multilayer carbon structures, Raman spectra, resistivity, electrochemical exfoliation.

### 1. INTRODUCTION

Green energy is not imaginable without hydrogen, which is a next generation fuel for a cleaner and environmentally sustainable world. The environment, especially in larger cities, is polluted with not only exhaust gases from petrol-powered cars but also volatile organic vapours and small particles. Continuation of this thoughtless pollution marathon will further deteriorate the overall human, plant, and animal health. Already now the measurable concentration levels of small particles in our cities are usually way above the permissible particulate matter levels PM<sub>2.5</sub> or PM<sub>10</sub>. Hydrogen as fuel offers an environmentally responsible solution to such problems. Envision the future where exhaust gases of all the cars will not only be odourless but will also

consist of only water vapours without any CO<sub>2</sub>, which is a common product of combustible fuels. Already nowadays, most progressive car and solid oxide cell generator manufacturers base their newest products on the electrochemical conversion in the fuel cell of hydrogen into water and electricity. As in the case of any new and developing technology, the problem of infrastructure accessibility needs to be overcome. Serious stumbling blocks for this clean technology are issues concerning the safe usage and storage of hydrogen. Developing materials for safe room temperature (RT) storage of H<sub>2</sub> and fast leak detection is crucial.

We investigated a prospective material for H<sub>2</sub> storage and sensing with the theoretical H<sub>2</sub> storage capacity of up to 16 wt% [1]. The material was obtained by processing recycled graphite from bronze metallurgy crucibles. Such use of a recycled material means also decreasing amounts of industrial waste.

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The widespread opinion of researchers investigating graphene-like structures is that molecules adsorbed on graphene, depending on the functional groups, may work as electron donors or acceptors to the graphene plane [2], thus acting as a typical planar semiconductor sensor. The adsorbed molecules work as p- or n-type dopants, considerably changing the bulk electrical resistance of the material. For example, adsorbed NO<sub>2</sub> molecules act as electron acceptors transferring them from graphene and leaving behind electron holes because the lowest unoccupied molecular orbital of the adsorbed NO<sub>2</sub> is roughly 0.4 eV below the Dirac point of graphene [2] at around 3.3 eV for the base material [3].

The material we investigated is a recycled waste, thus providing its benefits not only by a good quality of the final material but also by diminishing the need to deposit large amounts of industrial waste. There is no good statistics about all the buried graphitic waste because people are generally lazy and do not sort waste. The only partially reliable statistics is about graphite waste from nuclear reactors, and that is a waste not admissible here yet. Still, we can say that every year hundreds of tonnes of graphite waste is generated. The yearly production of graphite reaches about a million tonnes [4].

To the best of our knowledge, V and Bi doped multisheet graphene has never before been investigated for the application in hydrogen energetics as a storage material or as a sensor material base. The modification with heavy atoms might lead to more sensitive graphene sensors as due to increased surface resistivity large current spikes might be easier to detect.

## 2. MATERIAL AND METHODS

### 2.1. Material

In our work we used industrial bronze metallurgy waste graphite crucibles and recycled this waste material into graphene sheet stack (GSS) material with consistent properties. The material was structurally characterized by scanning electron microscopy (SEM) (Phenom Pro) and transmission electron microscopy (TEM) (Tescan Lyra) techniques. This allowed us to know for sure that the produced material was defective multilayer GSS. The resistivity of the material was determined with the Linkam THMSE 600 device complex in the Institute of Technical Physics at Riga Technical University, Latvia.

### 2.2. Synthesis

If the synthesis of a material is carried out in a hydrochloric acid electrolyte against a graphite (C) or

platinum (Pt) electrode with a cycle 3 : 5 s on the graphite electrode, the final material produced will be semi-conductive GSS. If GSS production is carried out in sulphuric acid with copper (Cu) as the opposing electrode, a less conductive material will be obtained. If the stable opposing electrode method is applied, GSS will change its behaviour towards conductive after reduction, maintaining very low resistivity, but Cu synthesized GSS exhibits little change decreasing the bulk conductivity from 7.5 Ω to 2 Ω.

Synthesis of 3D GSS structures is commonly performed from any base GSS material by the hydrothermal method [5]. Its heavy influence on the first part of synthesis [6] was an indicator of the importance of adding ammonia. We used GSS powder in a solution where after washing it was vacuum-filtered. The filtered material was sonicated in 100 mL dimethylacetamide (DMA) for 24 h. The powder was vacuum-filtered again and another solution was prepared. An ammonia–water mixture (concentration 3 mg/mL) was prepared and the suspension was sonicated for an hour before putting it in a polytetrafluoroethylene (PTFE) autoclave at 150 °C for 24 h.

The reduction of our samples was carried out in a furnace with controllable atmospheric flow. It was realized with Ar/H<sub>2</sub> gas mixture of 95% argon and 5% hydrogen at 800 °C for 3 h; the gas flow was ~50 mL/min. The cooling of the samples was not forced, and the cooling till the ambient temperature was realized by leaving the samples in the furnace in a protective atmosphere. Next, samples were synthesized and tested for hydrogen storage and sensitivity applications.

### 2.3. Resistivity measurements

The temperature control system Linkam THMSE 600 coupled with an Agilent 34970A data acquisition unit was used for electrical resistivity measurements of the GSS powder samples during the heating and the cooling. The powder sample was compressed in a special home-made minichamber by screwing in a brass cylinder. To reduce the temperature gradient in the sample, the Linkam THMSE 600 heating/freezing stage chamber was modified with a 3-mm thick brass cap, which was used to cover the samples during measurements. The diameter of the chamber was 4.7 mm, and the thickness of the sample powder pressed between two electrodes (brass cylinders) was 4 mm. Information about the bulk resistivity (69.4 mm<sup>3</sup>) of the pressed powder was obtained from three temperature scan cycles (from –100 to +50 °C); the upper brass cap was tightened after every cycle. The temperature under the cap and near the sample was measured with a Pt–Rh thermocouple. Since most of the samples had a very low

electrical resistivity, the resistivity measurements were performed using the Kelvin (or 4-point probe) bulk resistivity measurement method [7].

### 3. RESULTS AND DISCUSSION

During our resistivity measurements we observed the significance of the reduction of the GSS material in its unmodified form to convert it from the semiconducting to the conductive behaviour (applicable for unmodified GSS). All Bi and V ions as well as Cu ion modified GSS samples remained good semiconductors. Although Cu GSS and 3D structured GSS exhibited conductive behaviour regardless of reduction, reduction helped to decrease the overall resistivity of the samples (Table 1). We are interested in the slope of the graph because it

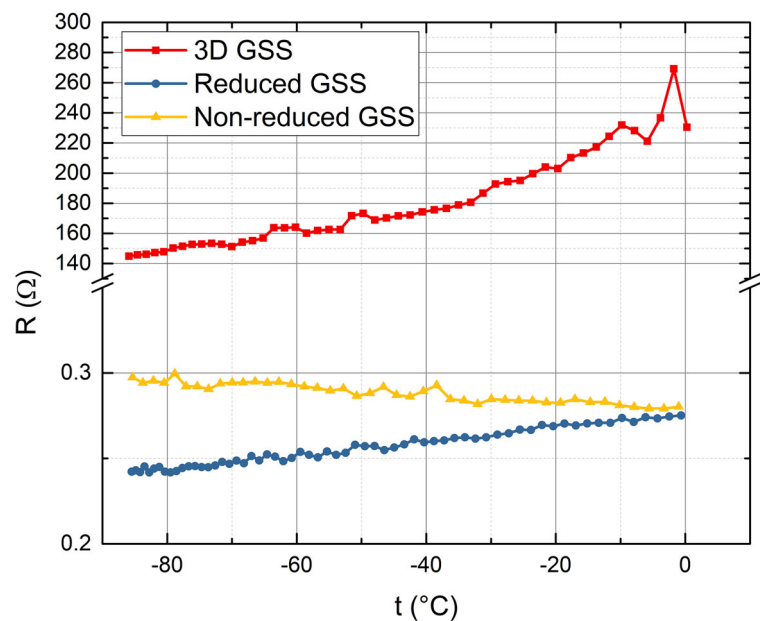
represents conductivity type (metallic or semiconductive) and its endpoints represent the overall characteristics of the samples. Although the applied temperature range was quite wide, the resulting resistivity change was small. The largest decrease of the resistivity of the GSS samples was observed in the nonreduced Bi GSS sample (Table 1). However, when hydrothermal synthesis was applied, the range approached a hundred ohms (Fig. 1).

Raman spectra (Fig. 2) indicate that the sample spectra changed upon exfoliation and reduction. The ratio of D/2D peaks in graphite (67.28 is 2D peak % of D peak etc.) and GSS spectra in Table 1 show that modifications caused the samples to become more open structures with fewer layers within single agglomerates.

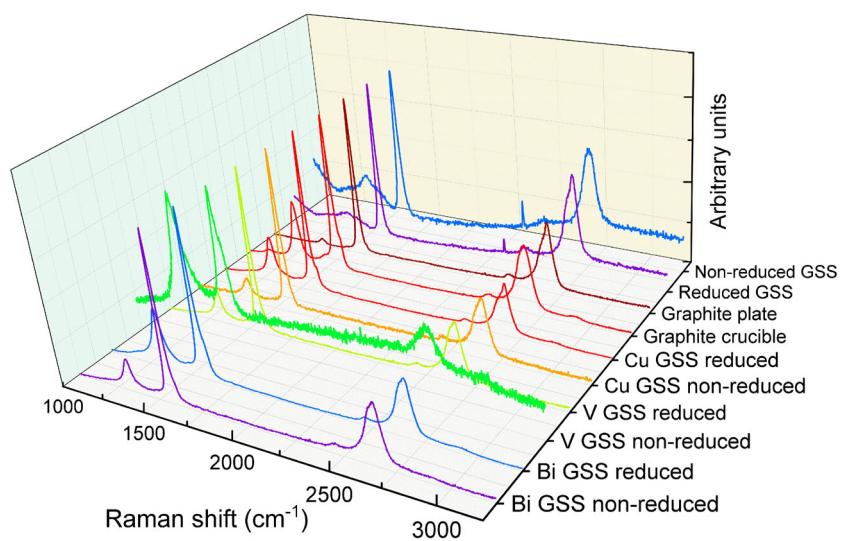
As the TEM images (Fig. 3) demonstrate, our 3D GSS material is a few-layered structure mixed with thinner sheet stacks. This intertwined structure is highly

**Table 1.** Synthesis parameters and selected physical properties of samples reported in this paper

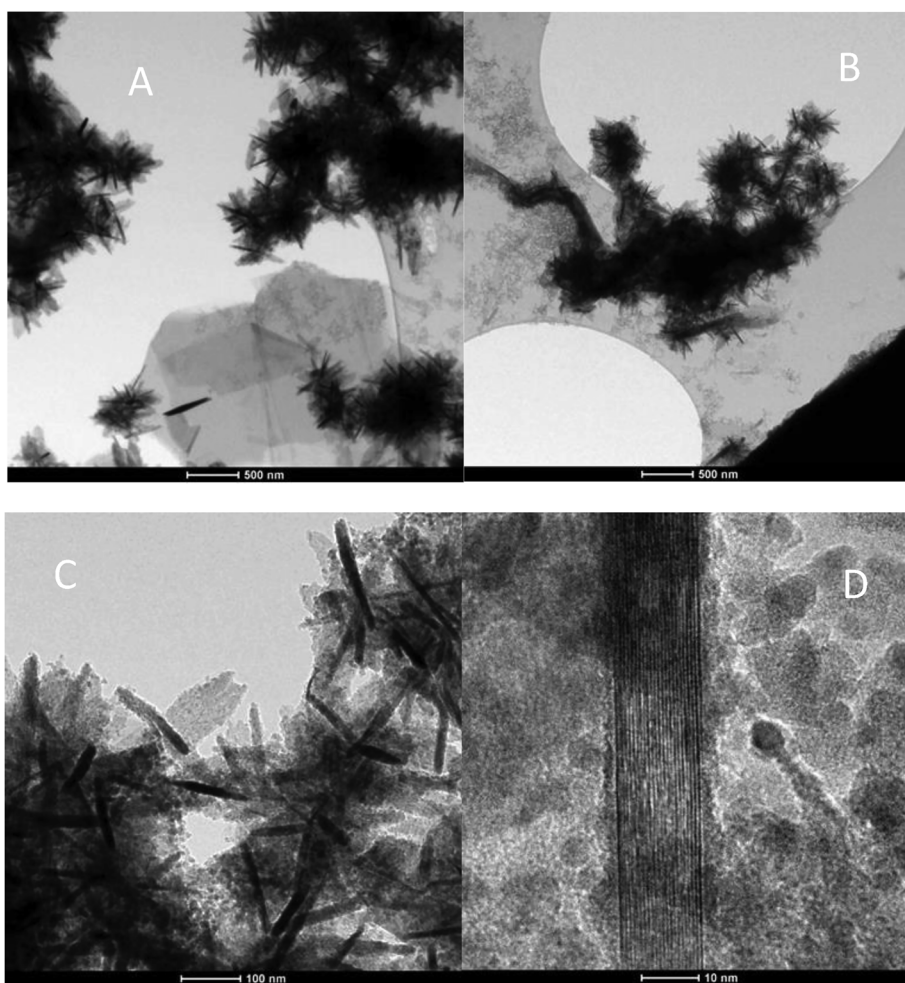
Sample	Reduction	Bulk resistivity, -100 °C, Ω	Bulk resistivity, 0 °C, Ω	$R(t\text{ °C})$ slope, $\Delta R/\Delta t$	Ratio of D/2D peaks in Raman spectra
GSS	No	0.29	0.28	-4.41	67.28 = 1.48
GSS	Yes	0.24	0.27	3.25	62.17 = 1.60
3D GSS	No	144	231	0.96	-
Bi GSS	No	2.66	2.18	-0.0031	36.22 = 2.76
Bi GSS	Yes	0.97	0.86	-4.60	33.40 = 2.99
V GSS	No	15.4	15.0	-0.044	47.77 = 2.09
V GSS	Yes	1.37	1.26	-4.50	36.22 = 2.76
Cu GSS	No	6.9	8.0	0.0024	36.44 = 2.74
Cu GSS	Yes	2.45	2.57	0.0074	31.91 = 3.13



**Fig. 1.** Resistivity ( $R$ ) of different GSS samples. Three different behaviours of  $R(t)$  dependence – quasi-linear, semiconductor, and metallic – can be observed.



**Fig. 2.** Raman shift measurements of modified GSS samples.

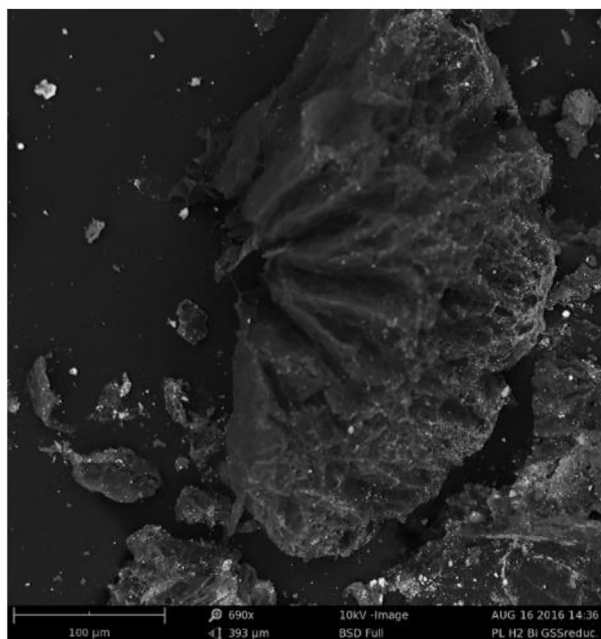


**Fig. 3.** TEM images of hydrothermally synthesized sonicated 3D GSS structures at various magnifications.

defective and has a large surface area. If a sensor were produced from this type of structures, its sensitivity would be characteristic of a material with a high resistivity. As shown by Fig. 3, hydrothermal synthesis produced sea urchin-type needle-like structures where the hydrothermal synthesis bonded them in the core and left out-facing extensions. Figure 3A shows large few-layered GSS lying on their side and remaining transparent, thus showing that this method provided also some freestanding larger GSS, but hydrothermal synthesis bonded them to the rest of the structure. The few-layered graphitic structure in 10 nm scale in Fig. 3D shows that the material is partially successfully exfoliated and nanosize. The granules in Fig. 3 testify that the experiment for synthesizing nanosized powder particles was successful. However, their usefulness still needs to be tested.

Unfortunately, as for the synthesis of this type of material a low-concentration solution has to be produced, the produced amounts are small. Although it might be possible to use this material in manufacturing gas sensors, its high resistivity is a big challenge with regard to sensitivity: smaller power consumption and higher amplitude of relative resistance variations mean that better metering conditions for lower gas concentrations are required.

The SEM image in Fig. 4 gives an insight into the type of open structures that can be produced. The microparticle consists of many nanosized layers with macropores between sheet stacks. After the sonication in dimethylformamide or dimethylacetamide, for intertwined



**Fig. 4.** SEM image of macroscopic exfoliated Bi GSS before sonication.

GSS synthesis the material is further broken into flakes, whose sizes can be seen in TEM images (Fig. 3A). Sonication in a mixtures of organic solvents of this type (planar molecule) and H<sub>2</sub>O is the most effective for further size calibration of GSS.

#### 4. CONCLUSIONS

Our graphene sheet stack (GSS) material produced from bronze metallurgy waste graphite is a material with a large surface area, which exhibits variance in its resistivity depending on whether it is in a modified or in an unmodified form. Modification with useful intercalate atoms could improve its relative resistivity towards commercially desirable levels as well as change the overall resistivity and sensitivity of the GSS. We found the 3D structures to be very promising considering the size, but the long synthesis process and high resistivity are big obstacles to be considered.

#### ACKNOWLEDGEMENTS

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### **Komplekssed mitmekihilised süsiniku struktuurid rohelise energeetika jaoks**

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Uuriti uut paljulubavat materjali vesiniku salvestamiseks ja detekteerimiseks. Materjal saadi kasutatud grafiidi jääkide pinnakihi eemaldamisel ja samaaegsel modifitseerimisel metalli- (vismut, vanaadium, vask) lisanditega. Seejärel kuumutati saadud materjali hüdrotermiliselt ja taandati. Ramani spektrid kinnitavad materjali grafeenitaolist struktuuri ja defektide olemasolu. Saadud grafeenilehtede pakkidest koosnev pulber on suure eripinnaga materjal, mille takistust saab varieerida erinevate metallide lisanditega. Materjalil on pooljuhi omadusi koos väikese elektritakistusega ja see sobib vesiniku detekteerimiseks.