Preparation and characterization of partially reduced graphene oxide aerogels doped with transition metal ions

Krzysztof Tadyszak^{1,2,*} , Łukasz Majchrzycki³, Łukasz Szyller⁴, and Błażej Scheibe¹

¹NanoBioMedical Centre, Adam Mickiewicz University, ul. Umultowska 85, 61-614 Poznań, Poland

²Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179 Poznań, Poland

³Center of Advanced Technology, Adam Mickiewicz University, ul. Umultowska 89C, 61-614 Poznań, Poland

⁴Faculty of Mathematics and Natural Sciences, University of Rzeszów, ul. Rejtana 16c, 35-959 Rzeszów, Poland

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ABSTRACT

This work presents the preparation and characterization of pristine and transition metal doped partially reduced graphene oxide aerogels. The step-by-step preparation of aerogels from graphene oxide with an assistance of VCl_3 , CrCl_3 , $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, CoCl_2 , NiCl_2 and CuCl_2 chlorides as reducing agents is shown and explained. The influence of reducing agents on the structural and magnetic properties of prepared aerogels is investigated. The use of electron paramagnetic resonance in purification during synthesis of GO and characterization afterwards is shown. It was found that VCl_3 was the strongest reducing agent leading to the formation of the most dense reduced graphene oxide aerogel, whereas vanadium is visible in EPR spectrum in form of V^{4+} complex as a VO^{2+} groups.

Introduction

Aerogels are air-filled, porous, solid-state structures, which can be prepared via lyophilization of hydrogels made of many different precursors such as amorphous carbon, carbon allotropes, carbides, silica, metals, metal oxides, polymers or composites [1]. Depending on building material, strength of the bonds between forming particles/rods/sheets and presence of the dopants in the porous matrix, aerogels can be applied as adsorbents [2], filters [3],

catalysts [4, 5] or sensors [5, 6]. Among the others, graphene oxide (GO) is one of the most interesting building materials for aerogel structures [7], which thanks to the high specific surface area and three-dimensional structure can be applied as electrodes in supercapacitors [8, 9]. The typical process of the aerogel formation from colloidal dispersion of GO sheets is based on the hydrothermal reduction in oxygen functional groups, which leads to cross-linking of individual graphene oxide sheets into partially reduced graphene oxide (prGO) hydrogel structure [10, 11]. The final step is the water removal without

Address correspondence to E-mail: krztad@amu.edu.pl

collapsing the solid structure. The formation of aerogels using this procedure is simple and efficient. However, for some specific applications like electro-catalysis [12, 13] or electrode fabrication [14, 15], there is a need of modifying the structure with transition metal ions (TMI) in order to grant electro-catalytic properties or improve the conductivity and capacity of electrodes. From the state of the art, it is known that the GO reduction and hydrogel formation can be also achieved via application of reducing agents such as NaHSO_3 , Na_2S , ascorbic acid or HI [16] and also transition metal chlorides [17]. Therefore, in this work we performed simultaneous reduction and modification of GO by TMI and investigated the influence of different type of transition metal ions onto prGO hydrogel formation process as well as structure and properties of TMI-doped prGO aerogels. Because the electrical and catalytic properties of aerogels are strongly dependent on the bonds between TMI and prGO [12, 13], we put the special attention to study the incorporation of TMI into prGO aerogel matrix and the formation of TMI complexes onto prGO surface by electron paramagnetic resonance (EPR).

Experimental

Materials

Graphite powder ($< 20\ \mu\text{m}$, synthetic), sodium nitrate ($> 99\%$), potassium permanganate ($> 97\%$), vanadium (III) chloride (97%), chromium (III) chloride (99%), copper (II) chloride (99.999%), nickel (II) chloride (98%), cobalt (II) chloride (99.999%) and iron (II) chloride tetrahydrate (99.99%) were purchased from Sigma-Aldrich. Hydrogen peroxide solution (30%) and sulphuric acid (95%) were obtained from POCH. Chloric acid (35–38%) was purchased from Chempur. All the solutions were prepared with deionized water type I ($\text{DI-H}_2\text{O}$). Tetrathiafulvalene 7,7,8,8-tetracyanoquinodimethane salt Sigma-Aldrich (CAS No. 40210-84-2, $\text{C}_6\text{H}_4\text{S}_4\cdot\text{C}_{12}\text{H}_4\text{N}_4$) was obtained from Sigma-Aldrich.

Graphene oxide preparation

Graphene oxide was prepared by the modified Hummers method [18]. Briefly, 1 g of graphite powder and 0.5 g of NaNO_3 were mixed together,

followed by an addition of 23 ml of H_2SO_4 (95%) and left for stirring (1 h). The solution was cooled down, and 3 g of KMnO_4 was gradually added to the suspension to prevent the risk of overheat and explosion. The mixture was stirred at $35\ ^\circ\text{C}$ for 12 h. Next, it was diluted with 500 ml of $\text{DI-H}_2\text{O}$ under stirring and 4.6 ml of H_2O_2 (30%) was added to complete the reaction. As-prepared mixture was washed with HCl (1%), and $\text{DI-H}_2\text{O}$ multiple times, followed by purification via multiple gentle stirring cycles in $\text{DI-H}_2\text{O}$ for a week with sequential EPR analysis until no Mn^{2+} ions were detected. Each time 0.5 ml of dried in $70\ ^\circ\text{C}$ suspension was measured by EPR first in room temperature until no contaminations were detected and then the process was repeated in 4.2 K. Further details can be found in the chapter *EPR spectroscopy of TMI-doped prGO aerogels*.

prGO hydrogels formation

Water dispersions of GO (20 ml glass vials—2 mg/ml) pristine (reference sample) or doped with transition metal chlorides (TMC): VCl_3 , CrCl_3 , $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$, CoCl_2 , NiCl_2 or CuCl_2 (6.25 mg each) were mixed together. Here, one has to notice two issues: (1) 2 mg/ml was one of the lowest GO concentrations, which led to the formation of stable hydrogels and (2) higher TMC concentration led to spontaneous reduction of GO. The concentration was dependent on specific TMC, since 6.25 mg was chosen experimentally as a safe value for all TMCs. Table 1 presents calculated concentrations of transition metal ions (TMI) applied before gelation.

Next, vials with the suspensions were mounted in 50 ml Teflon lined autoclaves. Sealed autoclaves were placed into a furnace (P300, Nabertherm) and kept at $180\ ^\circ\text{C}$ ($10\ ^\circ\text{C}/\text{min}$) for 2 h. After cooling down to room temperature, vials with TMI-doped prGO hydrogels were taken out of the autoclaves. Subsequently, the water was decanted and exchanged with fresh $\text{DI-H}_2\text{O}$ in order to remove an excess of unabsorbed TM ions. The visual step-by-step guidance for prGO hydro- and aerogel fabrication can be found in SI (Fig. S1).

prGO aerogels and xerogels formation

Prepared hydrogels were left overnight at $-80\ ^\circ\text{C}$ in the refrigerator (Binder GmbH). The frozen samples underwent freeze-drying process for 72 h at $-40\ ^\circ\text{C}$

Table 1 Transition metal chlorides with the concentration of metal ions applied before gelation

Transition metal chloride	VCl ₃	CrCl ₃	FeCl ₂ ·4H ₂ O	CoCl ₂	NiCl ₂	CuCl ₂
Molecular weight (g/mol)	157.30	158.36	198.81	129.84	129.60	134.45
Number of applied ions	2.4×10^{19}	2.4×10^{19}	1.9×10^{19}	2.9×10^{19}	2.9×10^{19}	2.8×10^{19}

and subsequent 1 h and $-65\text{ }^{\circ}\text{C}$ (Lyophilizer Alpha 2–4 LD plus, Christ). More details on preparation of aerogels can be found in chapter *Graphene oxide aerogel*.

In order to confirm a large porosity of aerogels in comparison with xerogels, we performed an experiment to determine the contraction of hydrogel volume and structural collapse during air drying. Hydrogel was cut into 2-mm-thick slices of circular shape, which were put on the laminated millimetre paper, and left until dried. The results of this experiment can be found in Supplementary Information (Fig. S2 and video SV1).

Characterization techniques

Continuous wave electron paramagnetic resonance (EPR) measurements were performed with a SE/X-2547 (9 GHz) spectrometer RADIOPAN equipped with a RCX661A TM110 resonator and CF935 Oxford cryostat at room temperature. The number of spins was estimated by direct comparison method with earlier calibrated TCNQ standard. The estimation of number of spins in TCNQ standard was performed by comparison with primary EPR standard—copper sulphate pentahydrate. In this study, only TCNQ standard was used. Due to the overlapping signals (TCNQ and aerogel), two spectra were measured one with the aerogel sample and TCNQ and second only with TCNQ. The TCNQ line was amplitude adjusted and subtracted from the sum spectrum resulting in the integral intensities of the sample and standard recorded basically in the same conditions. The comparison between samples with higher than 1/2 spins was done by applying the Curie relation $\chi = C/T \sim S(S+1)$, g factor differences between signals were not considered. Inaccuracy of spin count with this method is estimated to be about 50% [19].

Scanning electron microscope (SEM) studies were performed with 7001TTLS microscope JEOL equipped with electron dispersive X-ray spectroscopy (EDS). GO flakes on Si wafer were prepared via spin

coating (1000 rpm, 60 s) of water dispersion (0.02 mg/ml).

Atomic force microscopy (AFM) analysis was done using 5500 AFM system (Agilent) in tapping mode using All-in-One-AI cantilever C (Budget Sensors). GO flakes were deposited on freshly cleaved mica via drag and drop method and dried few hours at room temperature.

Dynamic light scattering (DLS) and zeta potential measurements were performed using LitesizerTM 500 (Anton Paar) in diluted GO water dispersion. Measurements were tripled and each time averaged $30 \times$ (DLS) and $100 \times$ (Zeta potential).

The optical absorption spectrum in UV–Vis range of GO water dispersion was recorded using Lambda 950 UV/Vis/NIR spectrometer (ParkinElmer) equipped with quartz cuvettes.

XRD measurements were performed with Empyrean diffractometer (PANalytical) equipped with Cu radiation source ($K\alpha = 1.54\text{ \AA}$) at 45 kV/40 mA in angle range 5° – 60° . Diffractogram was averaged by sample rotation—4 rpm.

The vibrational properties of prepared samples were analysed using inVia Raman microscope (Renishaw) with a $50 \times$ objective (Leica) at $\lambda = 633\text{ nm}$ ($E_L = 1.96\text{ eV}$) in $21\text{ }^{\circ}\text{C}$. All measurements were tripled. All the spectra were subtracted to straight line from 100 to 3200 cm^{-1} and normalized.

Volume measurements were performed with a caliper (accuracy 0.05 mm) only for samples, which shape could be approximated by a cylinder. (Total error is estimated as $\pm 10\%$.)

The specific surface area (SSA) of prGO and TM-doped prGO aerogels was calculated applying the Brunauer–Emmett–Teller (BET) model to the adsorption/desorption isotherms examined by ASAP 2420 analyser Micromeritics Instruments. Porosimetry measurements were conducted at 77 K using nitrogen as an adsorbate. Prior BET measurements, degas was performed at a temperature of $200\text{ }^{\circ}\text{C}$ in vacuum conditions.

Mechanical characteristics were calculated using cyclic compressive test with cylindrical shaped samples. Compressive test were conducted with a Zwick/Roell Z020 universal material testing system in the range from 0 to 60% strain in strain control mode with rate of 100% per minute.

Results and discussion

Characterization of GO

As-prepared GO material is always heterogeneous with different concentration of defects and type of oxygen-related functional groups like hydroxyl (OH), carboxylic (COOH), carbonyl (C=O), phenolic hydroxyl, lactol and lactone attached to GO surface. Introduced functional groups and defects are the source of different physical properties, which slightly differ from sample to sample. Electron dispersive spectroscopy (EDS) allowed the estimation of oxygen content at around 43% with carbon to oxygen ratio of $C/O \approx 1.35$. Figure 1 presents SEM micrographs of purified GO flakes dropped from water dispersion on Si wafer. The lateral size of GO flakes is in the range 0.7–46.4 μm (Fig. S5b), which is less than ten times the initial graphite grain size ($> 500 \mu\text{m}$, Fig. 1). In order to obtain and preserve large GO flakes ultrasonication should be avoided [20]. The analysis of the purified sample via AFM indicates that the flakes are mostly monolayer (Fig. 1). Apparent height of individual flake is 1.2 nm, which is typical for GO flakes synthesized by Hummers method. Zeta potential of diluted GO water dispersion showed the mean value of -68 mV (at $\text{pH} = 7.4$), which confirms the

formation of a stable colloidal dispersion due to hydrophilic properties granted by the presence of hydroxyl and carboxyl groups [21] (Fig. S3). Additional characterization of GO flakes via optical absorbance spectroscopy (OAS) in UV–Vis range and dynamic light scattering (DLS) can be found in Supporting Information (Figs. S4 and S5a).

Partially reduced graphene oxide aerogel

The formation of aerogels is based on 2 general steps: (1) the formation of hydrogel via gelation of GO flakes and (2) drying—critical point drying or freeze drying. Gelation is a process, in which separate GO flakes cross-link together forming larger solid structures. This process depends on several factors such as: flakes size [10], concentration, pH of solvent, temperature, presence of unsaturated hydrophobic edges [20] or impurities counteracting gelation (i.e. Na ions). The flake cross-linking can be promoted by decreased pH, elevated temperature and/or pressure [22] as well as binding agents and reducers. The freeze-drying process used here depends on freezing the gel with the remaining liquid and following this process sublimation, which is controlled by decreased pressure above the sample. The prior freezing process can determine the pore structure [23–26], which will further influence the specific surface area, adsorption [27], mechanical strength, electrical conductivity and magnetic properties [28, 29]. Figure 2a presents prGO hydrogels obtained via sol–gel technique. The reference sample was free from chlorides or reducing agents. As one can observe, reference hydrogel has the largest volume and the liquid left in the vial is darker in comparison

Figure 1 SEM micrographs (left) and AFM topography (right) of GO flakes.

with TMi-modified samples. This gel is the weakest due to low cross-linking. From all TMi-doped prGO hydrogels, the one modified with V ions was most dense and compacted in all trials. Fe-doped hydrogel has broken down during the synthesis, but the liquid remains clear, which leads to the conclusion that the FeCl_2 tetrahydrate formed complexes with GO.

As-prepared prGO aerogels are not too flexible and crumblable (Fig. 2b). Structural properties like density, volume, resistance to applied mechanical force change dependently on the reducing agent used during the process. Moreover, during multiple repetitions using the same reducing agents, spread of parameters was observed e.g. shape, volume, density. This could indicate that prGO hydrogel and further aerogel structures strongly depend on initial GO dispersions, where size, shape, and oxygenation of GO flakes are always heterogeneous.

BET surface areas of TMi-doped prGO aerogels

The nitrogen gas adsorption–desorption isotherms are shown in Fig. 3. All isotherms correspond to the Type II of isotherm according to IUPAC classification [30], which shape indicates the presence of macropores. The highest ($130 \text{ m}^2/\text{g}$) and the lowest ($7 \text{ m}^2/\text{g}$) specific surface area (SSA) was found for reference and V-doped prGO aerogels, respectively. The SSA of all the remaining TMi-doped prGO aerogels does not exceed $30 \text{ m}^2/\text{g}$. This observation is with an agreement of previous visual observations of prepared hydrogels. The strength of hydrogel cross-linking is inversely proportional to SSA of derived aerogels.

Mechanical properties of prGO

The application of aerogels, e.g. electrodes [3, 31–36] or filters [37], demands from them to be stable under mechanical stress. Large effort has been made to improve their mechanical properties and stability. To

Figure 3 Nitrogen adsorption–desorption isotherms of aerogels with BET surface areas.

determine the influence of doping on the mechanical properties of aerogels, compressive stress–strain and cyclic compressive tests (100 cycles) were performed. In the first cycles of loading during compressive stress–strain experiment, three regimes of strain were observed (Fig. 4a). First one, nearly linear elastic section, corresponds to bending of cell walls, extends up to 20% of strain. Above this value till 50% a relatively flat stress plateau, is observed which is connected with elastic buckling of cell walls. The increase in stress above 50% is connected with the increase in cells density [38]. In the first cycle (Fig. 4a), the greatest compressive stress exhibits prGO doped with vanadium 6.68 kPa, followed by copper 4.5 kPa and iron 2.3 kPa. This result in comparison with weight of the sample means also that the vanadium-doped aerogel can bear over 3680 times of its own weight at 60% strain. If normalizing by density (Table 2) the largest stress exhibits copper-doped sample 4.5 kPa and the lowest chromium doped which is also the aerogel with the lowest density. After 5 cycles of loading–unloading, significant decrease in tension was observed in samples doped with V and Cu (Fig. 4b), which was caused by

Figure 2 Optical images of **a** TMi-doped prGO hydro- and **b** prGO reference aerogel compared to 1 PLN coin ($\varnothing = 23 \text{ mm}$, 5 g).

Figure 4 **a** Compressive stress–strain curves of first cycles of loading–unloading; **b** maximum stress during 100 cycles; **c** energy loss coefficient during 100 cycles.

microcracks in cell walls [39]. Between 5 and 50 cycles, slight stress decrease is similar in all samples

and between 50 and 100 cycle it almost remains on the same level. In case of two samples: reference, and Fe doped mechanical damage occurred after only 10 cycles, and significant decrease of energy loss factor, and finally complete breakdown after 50 cycles (Fig. 4c).

Energy dispersion is one of the most important functions of cellular materials. Samples doped metals V, Cr, Co, Ni and Cu display excellent stable energy absorption properties (Fig. 4c). Hydrogel doped with vanadium in the first cycle absorbed 82% of energy, and after 100 cycles energy loss coefficient decreased to 60%, and the plastic deformation to approximately 4%. Multiple authors [36, 39] explain the energy loss values through bending of cell walls and changing their shape due to the presence of weak van der Waals forces between the flakes and the cell walls.

EDS analysis of TMi-doped prGO aerogels

SEM micrographs of the TMi-doped prGO aerogels presented in Fig. 5 show porous, rugged surface, exhibiting randomly oriented partially reduced graphene oxide sheets. Metal coating which is a typical preparative step for SEM was not necessary, due to intrinsic electrical conductivity ($\rho \approx 15 \Omega \times m$, $\sigma \approx 6.6 \times 10^{-2} S/m$). Measured here conductivity of prGO is similar to conductivity of a single-flake GO conductivity 0.05–2 S/m [40] which suggests that in case of prGO the biggest electron transport barriers are the flake connections.

The differences between reference and TMi-doped prGO aerogels can be distinguished by electron dispersive spectroscopy (EDS). The presence of all TMi in prGO aerogel samples was confirmed by the EDS analyses, and the results are presented in Table 2 along with measured masses and densities.

EDS analysis can be used for the study of the oxygen concentration in measured samples (details in SI). Measured C/O ratios were: Graphite: 32.3, GO: 1.35 (C: 57.45 wt.%, O: 42.55 wt.%), Ref: 2.35, Cu: 2.23, V: 2.45, Cr: 2.37, Ni: 2.17, Fe: 1.95, Co: 2.34. Oxygen concentration left in the sample counted for normalized carbon content (for C = 1): Graphite: 0.03, GO: 0.74, Ref: 0.43, Cu: 0.45, V: 0.41, Cr: 0.42, Ni: 0.46, Fe: 0.51, Co: 0.43 wt.%. Maximum detected oxygen decrease is 44.6% for V, but other metal ions-doped samples do not deviate strongly from this result (Reference 41.9%). One can notice that VCl_3 could be the strongest and $FeCl_3 \times 4H_2O$ the weakest

Table 2 Normalized atomic EDS composition and mass, density (inaccuracy $\pm 10\%$)

Elements	Sample						
	Ref. (%)	V (%)	Cr (%)	Fe (%)	Co (%)	Ni (%)	Cu (%)
C	70.15	70.65	70.29	65.40	69.79	68.03	68.25
O	29.85	28.84	29.60	33.54	29.84	31.42	30.58
V		0.51					
Cr			0.11				
Fe				1.06			
Co					0.37		
Ni						0.55	
Cu							1.17
Mass (mg)	31.3	32.7	29.9	–	31	31.3	30.7
Density (mg/cm ³)	7.5	21	2.5	–	6.3	10.3	4.9

Figure 5 SEM micrographs of reference prGO aerogel surface (top: scale 1 μm ; bottom: scale 10 μm).

reducing agent. The volume of the prGO aerogel samples was calculated assuming cylindrical shape of the sample. The density was counted as weighted mass divided by bulk volume. No correlation between obtained volumes and C/O ratios could be

estimated. The less dense aerogel was obtained for Cr-doped prGO aerogel (2.5 mg/cm^3), and still it is around $16 \times$ denser than the lightest reported aerogel and simultaneously, lightest solid-state material known to the mankind [41].

XRD patterns of prepared samples

The XRD measurements of GO, prGO reference and TMi-doped prGO aerogels are shown in Fig. 6. The strong reflex at 11.2° (002, FWHM 0.85°) visible for GO corresponds to interplanar distances of 0.789 nm. The crystalline size of GO in the direction perpendicular to the plane counted from Scherrer formula is 9.5 nm ($K = 0.9$). The much broader reflex for the reference aerogel, at 20.3° – 23.9° , corresponds to 0.437–0.372 nm, whereas for comparison the graphite peak at 26.5° corresponds to interplanar distance of

Figure 6 XRD patterns of dried GO powder, reference and TMi-doped prGO aerogels.

0.342 nm (Fig. S6). The reduction decreases the spacing between graphene layers by removing remaining oxygen groups. Strongly broadened reflex at around 20.3° – 23.9° corresponds to ~ 1.3 nm crystallites.

Raman spectroscopy of TMi-doped prGO aerogels

The Raman spectroscopy is a basic technique used for structural characterization of graphene-based nanostructures such as reduced graphene oxide. Figure 7 presents spectra of the reference and TMi-doped prGO aerogel samples. The typical prGO spectrum is featured by the presence of four main vibrational modes, namely D (A_{1G}) at 1320 cm^{-1} , G (E_{2G}) at 1560 cm^{-1} , 2D at 2700 cm^{-1} and S3 (D + G) at 2940 cm^{-1} [42], which are visible in all spectra. The presence of 2D mode is typical for all graphitic carbon-related materials, and S3 mode is related to lattice disorders. The intensity and shape of D mode is related to the amount of defects in hexagonal graphene sheets, the number of functional groups (or doping) and an amorphous carbon content. In comparison with G mode, which is strictly related to organized hexagonal structure, one can estimate the quality of the material via I_D/I_G ratio. No visible shifts of G or D modes which could confirm the high metal ion doping were observed (Fig. 1). Comparing

Figure 7 Raman spectra of the reference and TMi-doped prGO aerogels.

GO and prGO aerogel samples, one can notice the I_D/I_G ratio increases, which is related to removal of oxygen functional groups and the decrease in the average size of the sp^2 domains upon hydrothermal reduction process [43–46]. The highest increase of the I_D/I_G ratio was observed for vanadium modified aerogel sample ($\approx 11\%$). The detailed analysis of D mode allows to calculate mean defect distance (L_D) from an equation [47], where $E_L = 1.96\text{ eV}$:

$$L_D = \sqrt{\left(\frac{4.3 \times 10^3}{E_L}\right) \times \left(\frac{I_D}{I_G}\right)^{-1}}$$
 After transition of GO flakes to prGO aerogel, the mean defect distance was decreased from 18.51 to 16.82 nm, respectively. In the case of the TMi-doped prGO aerogel samples, the calculation of the L_D parameter allows to obtain following values: 15.99 nm, 16.66 nm, 16.98 nm, 16.90 nm, 16.98 nm, 16.74 nm, 16.82 nm, 16.66 nm, 15.85 nm for V-, Cu-, Co-, Ni-, Cr- and Fe-doped prGO aerogels samples, respectively. Taking into account highest I_D/I_G ratio and shortest defect distance, it can be deduced that VCl_3 is the strongest reducer, which influence defects concentration of aerogel forming prGO sheets. Because the L_D parameter in all cases is higher than 3 nm, the obtained prGO aerogel samples are made of stage 1 defected graphene with largely intact honeycomb lattice and carbon domains containing at least 300 atoms [47, 48].

EPR spectroscopy of TMi-doped prGO aerogels

Electron paramagnetic resonance spectroscopy is one of the most sensitive methods able to detect radicals and metal ions. Commercial EPR systems require $\sim 10^9$ – 10^{11} (pM range) spins to achieve a measurable signal [49]. The EPR signals shape, intensity, g factor, linewidth, spin concentration is source of large number of information about local site symmetry, local dynamic and electron relaxation [50]. EPR study of graphene and graphene-related materials gives an important information about interactions and magnetism sources like defects, not passivated magnetic moments on edges, surface adatoms with unpaired magnetic moments, conduction electrons, and also remaining metal ion contamination [28, 51–59]. Unpaired electrons located on edges, on/in the graphene surface, are extremely sensitive to external conditions like atmosphere (oxygen, helium and vacuum) or moisture influencing the localization of

the electron spins [60]. Electrical transport of graphene-based systems strongly depends on the large amount of adsorbed molecules and is based on the variable range hopping mechanism with energy barrier between the flakes [40]. This mechanism explains the increasing conductivity with increase in temperature [60]. Our observations confirmed the strong decrease of the resonators quality factor, due to rising electron conductivity, when increasing the temperature. The analysis of both Pauli (conduction electrons) and Curie (localized electrons) components in EPR signal in GO can be found in articles of Ćirić [61, 62].

EPR was used here as a method of confirming the purity of the GO and for the spin system characterization. The presence of impurities in the form of Mn or Na ions can influence the magnetic properties through the spin–orbit coupling [51, 55], as well as electron conductivity by influencing the density of electron states at Fermi level [63]. Such impurities can influence the EPR spectra of prGO and rGO aerogels as well. Figure 8 presents EPR spectra of the initial GO at different stages of purification. The EPR spectrum recorded at 300 K shows Mn^{2+} ions, which were later “removed” during the first purification cycle. Due to larger sensitivity at 4.2 K, remaining ions once again appear in the spectrum. Further purification cycles removed them completely. This ion removing process occurs only because of the reversibility of Mn–GO binding [29], differently than in the case of Fe–GO complexes [29]. Other reported in the literature method of obtaining GO without Mn

contamination is done by the use of different oxidizing agents, e.g. $\text{HNO}_3/\text{H}_2\text{SO}_4$ instead of KMnO_4 [64].

Reference (pristine) prGO aerogel presents a weak EPR signal which consists of two components with similar g factors ($g = 2.00$), but one has the linewidth of 0.38 mT and small intensity, and the second 9.2 mT and much stronger intensity. The narrow signal is assigned to paramagnetic defects, radicals and the broad signal to conduction electrons. In pristine graphene flakes, the contribution of conduction electrons in the total EPR signal is $\sim 1.75\%$ [53]; here, this ratio is higher. In the case of the TMi-doped prGO aerogels, we were able to record the EPR signal for V-, Fe- and Cu-doped samples (Fig. 9). Vanadium is often forming complexes with oxygen resulting in vanadyl VO^{2+} groups, observed in EPR. Vanadium $^{51}\text{V}^{4+}$ has the electron configuration $(\text{Ar})3\text{d}^1$, with electron spin $S = 1/2$, and nuclear spin $I = 7/2$. The g tensor has the main values $g_x = 2.23$, $g_y = 2.18$, $g_z = 2.05$ with total line anisotropy of 27.6 mT. The number of spins is estimated at 5×10^{21} spins/g, and it corresponds with 0.51% detected with EDS. EPR spectrum of the iron-doped prGO aerogel sample presents strong signal where the number of spins is estimated at 4.6×10^{21} spins/g (assuming Fe^{3+} and $S = 5/2$). The presence of the EPR signal of copper ions (Cu^{2+} , electron configuration $(\text{Ar})3\text{d}^9$, $S = 1/2$ and $I = 3/2$) means that copper ions formed a complex with molecular groups attached to prGO surface. The number of spins is estimated at 1.2×10^{21} spins/g, and it is in correlation of 1.15% detected with EDS. The g tensor symmetry is axial with $g_{\perp} \approx 1.94$, with total peak to peak line width of 21 mT. In case of all complexes, ions are interacting with each other through dipole–dipole interactions broadening the lines. Samples doped with Ni, Co, Cr showed no signal in room. In the case of nickel, there are two possible explanations: (1) no Ni complexes with oxygen were formed and (2) Ni ions exist in complexes in low $S = 0$ and high spin $S = 1$ states, where the detection is impossible in the first case and could be hardened in the second at least at X band depended on zero field splitting interaction. Cobalt signal due to short relaxation time broadens and vanishes in background noise in room temperatures. The lack of the chromium signal was caused by the low dissolvability of CrCl_3 in water and insufficient doping, which was previously confirmed by the

Figure 8 EPR spectra of GO at subsequent steps of purification process at 300 and 4.2 K.

Figure 9 EPR spectra of: **a** reference (inset) the same line recorded for narrower field sweep and **b** vanadium, **c** iron, **d** copper-doped aerogels.

lowest wt.% in EDS analysis. Generally, EPR signal can confirm the existence of complexes, their number and local symmetry, but the lack of the signal can be caused by multiple reasons, i.e. lack of adsorbed ions, lack of formed complexes, invisible for EPR ions oxidation states or large zero field splitting.

Conclusions

In this work, the preparation and study of TMi-doped prGO aerogels were presented. We have presented the application of the Cu, Co, Ni, V, Cr, and Fe chlorides as reducing agents during the formation of prGO hydrogels and shown their influence onto

oxygen concentration and specific surface area of derived prGO aerogels. It was found that among the other investigated transition metal chlorides, the VCl_3 possesses strongest reducing properties, which lead to the formation of the densest hydrogels and subsequently the tightest prGO aerogels, featured by the lowest oxygen content, smallest average size of the graphitic domains, shortest defect distance and the lowest specific surface area. Also the application of EPR for GO purification and analysis of pristine and TMi-doped prGO aerogels was shown. EPR was applied for quantification of Cu^{2+} , V^{4+} , Fe^{3+} ions in prGO aerogel samples.

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