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ARTICLE

Separation of thorium ions from wolframite and scandium concentrates using graphene oxide

Ondřej Jankovský[a], David Sedmidubský[a], Petr Šimek[a], Kateřina Klímová[a], Daniel Bouša[a], Chris Boothroyd[b], Anna Macková[c,d] and Zdeněk Sofer*[a]

The separation of rare metals from the ores and commercially available compounds is an important issue due to the need of their high purity in advanced materials and devices. One of the important examples where two highly important elements co-exists in the ores are scandium and thorium. Scandium containing ores and consequently also commercially available scandium compounds often contain traces of thorium which is very difficult to separate. We used graphene oxide for the selective sorption of thorium ions from scandium and thorium mixtures originating from the mined ores as well as from commercially available scandium salts. Our results showed that graphene oxide has an extreme affinity towards thorium ions. After the sorption process the graphene oxide contained over 20 wt.% of thorium while the amount of scandium sorbed on GO was very low. This phenomenon of high sorption selectivity of graphene oxide can be applied in industry for the purification of various chemicals containing scandium and for separation of thorium containing mixtures. Alternatively, this methodology can be used for preconcentration of thorium from low-grade ores and its further use in new generation of nuclear reactors.

Introduction

The depletion of highly rich ores and the necessity to explore low-quality ores, connected to reopening of old depleted mines driven by accelerating need for rare earth elements and actinides in electronic and energy devices, requires effective separation techniques of co-existing elements. Often two or more elements are present in the ore. One of the highly important examples is scandium, whose ores contain relative high amount of thorium and rare earth elements. The separation of scandium and thorium is challenging and even commercially synthesized scandium compounds contain thorium traces. Wolframite ores typically contain 500 – 800 ppm of scandium in the form of thortveitite ($(Sc,RE,Th)_2Si_2O_7$).[1] For our experiments scandium concentrates from wolframite ore were used originating from Cínovec (Zinnwald), Czech Republic.

Although scandium is not produced in large scales, it has a number of different applications. Sc-Al alloys are used for the production of aerospace industry components[2] or for sports equipment.[3] Also erbium/chromium doped yttrium-scandium-gallium garnets (Er,Cr:YSGGs) are used by dentists for cavity treatment.[4] Scandium triflates are used as catalytic Lewis acids in organic chemistry.[5] Rare earth scandates have large potential as dielectrics in MOSFET transistors.[6] Scandium oxide is used as a coating material for laser optics.[7] Metallic scandium was also used as a suitable contact material for MoS_2 based FET transistors.[8] For all these applications it is necessary to use high purity scandium and its compounds.

Due to the similar electronegativity and ionic radius it is challenging to find a simple method for purifying the mixtures containing Sc^{3+} and Th^{4+}. Currently the separation and purification procedures of scandium are complicated and take use of processes based on solvent extraction, ion exchanges and membrane separations techniques.[9] Due to the large surface area and a number of oxygen-containing functional groups graphene oxide (GO) is a promising candidate for various selective sorptions.[10] GO contains epoxides, hydroxides, ketones and carboxylic acids functional groups on its surface.[11] These groups can act as coordination ligands for various metal ions. After the sorption GO can be easily removed from solution by filtration due to the large lateral size of individual sheets. Thorium can be also simply recovered from GO in the form of thorium dioxide by combustion of GO-Th composite. Thorium sorbed on GO can be used for production of effective electrochemical catalysts based on graphene/thorium composites.[12]

We present a highly effective method for thorium separation from Sc^{3+}/Th^{4+} mixtures using GO as a sorption material. The dramatic increase of thorium uptake was observed compared to scandium. The total sorption capacity

a. Department of Inorganic Chemistry, University of Chemistry and Technology Prague, 166 28 Prague 6, Czech Republic. E-mail: zdenek.sofer@vscht.cz; Fax: +420 22431-0422
b. Ernst Ruska-Centrum und Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany
c. Institute of Nuclear Physics AS CR, v.v.i., Husinec - Řež, 130, 250 68 Řež, Czech Republic
d. Department of Physics, Faculty of Science, J.E. Purkinje University, Ceske mladeze 8, 400 96 Usti nad Labem, Czech Republic

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of GO towards scandium and thorium ions was measured together with complex characterization of such composite materials. For the practical use we successfully purified Sc_2O_3 (99.9%) from traces of thorium and demonstrated the application of GO for thorium separation from scandium concentrate obtained from wolframite ore.

Experimental

Materials

Graphite microparticles (2–15 μm, 99.9995%) were obtained from Alfa Aesar. Sulphuric acid (98%), potassium permanganate (99.5%), sodium nitrate (99.5%), and hydrogen peroxide (30%) were obtained from Penta, Czech Republic. Nitric acid (65%) was obtained from Lach-ner, Czech Republic. Deionized water was used for all syntheses. $Th(NO_3)_4.5H_2O$ (99.9%) and $Sc2O3$ (99.9%) were obtained from Merck and from Fluka AG, respectively (both Germany). The scandium oxide concentrate (95% Sc_2O_3) originates from wolframite (Cínovec mine, Cínovec, Czech Republic) and was obtained locally. The scandium was pre-concentrated in mother liquor after alkaline leaching of wolframite concentrate and crystallization of $(NH_4)_2WO_4$. This mother liquor was coagulated using hydrofluoric acid and fluorides were leached with concentrated sulphuric acid at elevated temperature. Finally Sc, Th and other RE elements were separated by precipitation with oxalic and decomposed on scandium oxide at elevated temperature.

Synthetic procedures

Graphene oxide (GO) was synthesized by a method similar to that by Hummers.[13, 14] Graphite (5 g) and sodium nitrate (2.5 g) were stirred with sulphuric acid (98 %, 115 mL). The mixture was then cooled to 0 °C. Potassium permanganate (15 g) was then added over a period of two hours. During next four hours, the reaction mixture was allowed to reach room temperature before being heated to 35 °C for 30 min. The reaction mixture was then poured into a flask containing deionized water (250 mL) and heated to 70 °C for 15 minutes. The mixture was then poured into deionized water (1 L). The unreacted potassium permanganate and manganese dioxide were removed by the addition of 3% hydrogen peroxide. The reaction mixture was then allowed to settle and decanted. The obtained graphene oxide was then purified by repeated centrifugation and re-dispersal in deionized water until a negative reaction on sulphate ions was achieved. The graphene oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

Subsequently, we analysed sorption activity and sorption selectivity of graphene oxide. In the first step, 250 mg of graphene oxide was ultrasonicated for 60 min (400 W) in distilled water in order to obtain a suspension of graphene oxide. Simultaneously, solutions of Sc^{3+} and/or Th^{4+} mixtures in weight ratios of Sc:Th = 99.98 : 0.02 (Sc_2O_3 99.9%), 95:5 (Sc_2O_3 95%) and 0:100 (pure $Th(NO_3)_2.5H_2O$) were prepared from corresponding nitrates. Mixtures containing Sc^{3+} were prepared by the dissolution of Sc_2O_3 in nitric acid. In the next

step, these solutions were poured into beakers containing graphene oxide. The volume of the resulting mixtures was fixed at 200 ml by deionized water where the concentrations of Sc and/or Th were 5 g.L^{-1} for all samples. Mixtures were stirred with a magnetic stirrer for 24 hours, filtered out, repeatedly washed with distilled water and dried in a vacuum oven at 50 °C for 48 h. The resulting Sc and/or Th doped graphene oxides were analysed in detail.

In addition we tested the sorption rate of scandium and thorium on graphite oxide from a mixture prepared from thorium-contaminated Sc_2O_3 from Cínovec mine. The powder was dissolved in nitric acid similarly as described in the previous paragraph. The solution was then poured into a beaker containing graphene oxide. We tested the chemical composition after 5 min, 15 min, 30 min, 1 hour and 4 hours.

Methods

The morphology was investigated using scanning electron microscopy (SEM) with a FEG electron source (Tescan Lyra dual beam microscope). Elemental analysis and mapping were performed using an energy dispersive spectroscopy (EDS) analyser X-Max^N with a 20 mm^2 SDD detector (Oxford instruments) and AZtecEnergy software. To conduct the measurements, the samples were placed on carbon conductive tape. SEM-EDS measurements were carried out using a 10 kV electron beam.

An Axios sequential WD-XRF spectrometer (PANalytical, Netherland) was used to perform XRF analysis. It was equipped with a Rh anode end-window X-ray tube fitted with a 50 μm Be window. The spectra were collected in vacuum using the software SuperQ and evaluated with the standardless software Omnian. The analysed powders were pressed onto H_3BO_3 pellets with a total thickness of about 5mm and a diameter of 40 mm without any binding agent and covered by a 4 μm thick supporting polypropylene (PP) film.

High resolution X-ray photoelectron spectroscopy (XPS) was performed on an *ESCAProbeP* (Omicron Nanotechnology Ltd, Germany) spectrometer equipped with a monochromatic aluminium X-ray radiation source (1486.7 eV). A wide-scan survey of all elements with subsequent high-resolution scans of the C 1s core level was performed. Relative sensitivity factors were used in the evaluation of the carbon-to-oxygen (C/O) ratios from the survey spectra. Samples were attached to a conductive carrier made from high purity indium.

Simultaneous thermal analysis (STA) was performed using *Linseis PT 1600* from 100 to 800°C in an alumina crucible. The heating rate was set to 10 °C.min^{-1} and the measurement was carried out in a dynamic air atmosphere with a flow rate 50 ml.min^{-1}.

The HRTEM images were taken using a FEI Titan "Holo" G2 60-300 field emission gun transmission microscope. The sample suspension (1 mg/mL) was dropped onto a lacy carbon grid. A Gatan UltraScan 1000 2k CCD camera was used to acquire the images. The EEL spectra were acquired using a Gatan imaging filter (Tridiem ER model 865) attached to the same microscope.

Raman spectroscopy was conducted on an inVia Raman microscope (Renishaw, England) with a CCD detector in backscattering geometry. A DPSS laser (532 nm, 50 mW) with a 100x magnification objective was used for the Raman measurements. The instrument was calibrated with a silicon reference to give a peak position at 520 cm^{-1} and a resolution of less than 1 cm^{-1}.

Fourier transform infrared spectroscopy (FT-IR) measurements were performed on a Nicolet iS50R spectrometer (Thermo Scientific, USA). A Diamond ATR crystal and DTGS detector were used for all measurements, which were carried out in the range 4000–400 cm^{-1}.

X-ray powder diffraction (XRD) was done with a Bruker D8 Discoverer diffractometer in Bragg–Brentano parafocusing geometry. A CuKα radiation was used. Diffraction pattern were collected between 5° and 70° of 2θ.

Results and discussion

First the X-ray fluorescence (XRF) was used to define the purity of starting materials. The purity of Th(NO$_3$)$_4$.5H$_2$O was declared as 99.9 %, none scandium was detected (Sc:Th=0:100), while only the traces of Cr and Fe were found as impurities. Sc$_2$O$_3$ (99.9%) contained 99.9 wt.% of Sc$_2$O$_3$, 0.02 wt.% ThO$_2$ and also traces of Al, Si and Cr were detected (Sc:Th=99.98:0.02). Th-contaminated Sc$_2$O$_3$ from Cínovec mine contained 94.525 wt.% of Sc$_2$O$_3$, 4.976 of ThO$_2$ and additional trace amounts of Al, Si, Ca, Fe, Yb and W (Sc:Th=95:5).

After the sorption of Sc^{3+}/Th^{4+} on graphene oxide (**Figure 1**, see the *Experimental section* for more details) energy dispersive spectroscopy (SEM-EDS) and XRF were used to determine the amounts of sorbed Sc^{3+} and Th^{4+} (**Table 1**). The results showed that Th^{4+} revealed much higher affinity to graphene oxide compared to Sc^{3+}. The amount of sorbed Sc in GO-Sc-99.98 was relatively low (3.4 wt.% by SEM-EDS, 1.91 wt.% by XRF) whereas the amount of sorbed Th in GO-Th-100 was extremely high (20.5 wt.% by SEM-EDS, 32.55 wt.% by XRF). We also tested the sorption activity of graphene oxide towards Pb^{2+} and Cd^{2+}. We found that 17.2 wt.% of Pb and 2.7 wt % of Cd can be sorbed on graphite oxide after 24 hours. These results make this material a promising candidate for the sorption of dangerous metals from environment.

Table 1. Results of XRF and SEM-EDS for Sc and/or Th doped graphene oxides in wt.%.

Composition	GO-Sc-99.98		GO-Sc-95		GO-Th-100	
(wt.%)	EDS	XRF	EDS	XRF	EDS	XRF
C+O	95.7	97.33	95.1	95.04	79.1	66.55
Si	0	0.02	0	0.06	0	0.07
S	0.4	0.18	0.3	0.23	0.4	0.38
Cl	0.1	0.07	0	0.06	0	0.15
Sc	**3.4**	**1.91**	**2.8**	**1.96**	**0**	**0**
Fe	0	0.03	0	0.01	0	0.24
Th	**0.4**	**0.38**	**1.8**	**2.58**	**20.5**	**32.55**
Others	0	0.08	0	0.06	0	0.06

Figure 1 The preferential sorption of Th^{4+} on graphene oxide surface.
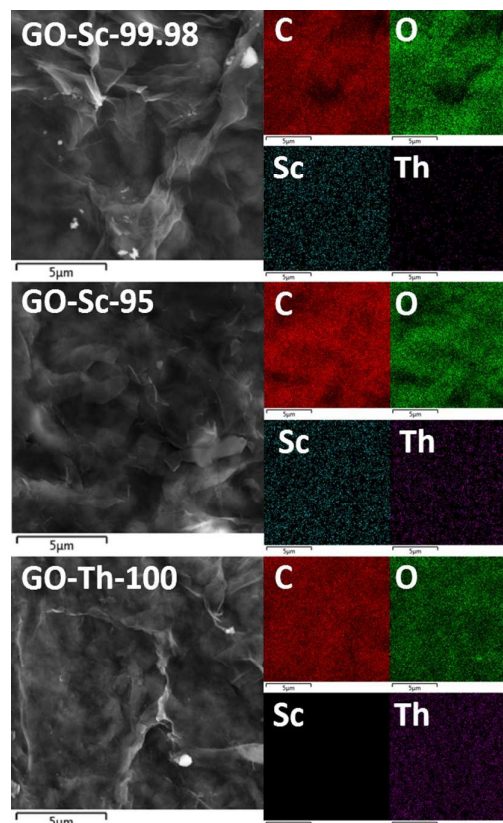
Figure 2 Elemental distribution maps of Sc and/or Th-doped graphene oxides obtained by SEM-EDS. Scale bar is 5 µm.
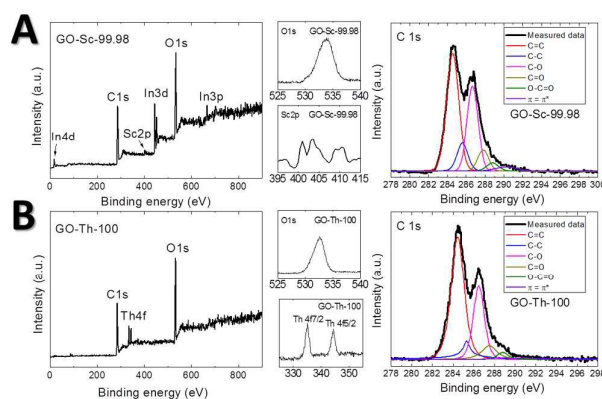
Figure 3 High resolution XPS spectra of GO-Sc-99.98 (A) and GO-Th-100 (B). Survey spectra are shown on the left; O1s, Sc2p and Th4f in the middle and C1s on the right.

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The preferential sorption led to an extreme increase of Th concentration in graphene oxide compared to the Sc/Th ratio in the solution (**Table 2**). This observation is essential for further applications in industry.

Table 2. Obtained Sc/Th ratios before and after the sorption in wt.%.

| Sample	before sorption	after sorption in GO	
	XRF	SEM-EDS	XRF
GO-Sc-99.98	99.98 : 0.02	89.5: 10.5	83.8 : 16.2
GO-Sc-95	95 : 5	60.9 : 39.1	56.8 : 43.2

SEM-EDS elements mapping showed a uniform distribution of all detected elements in all samples (**Figure 2**). The structure of the formed graphene oxide is similar to graphene foil.[15]

Consequently, we used high resolution X-ray photoelectron spectroscopy (XPS) to determine the chemical composition and structure of GO-Sc-99.98 and GO-Th-100. In contrast to XRF and SEM-EDS, XPS can provide interesting information about the surface conditions. First the XPS survey spectra of the starting graphene oxide were acquired. They are show in SI (**Figure SI1**) along with the high resolution C 1s (**Figure SI2**). The C/O ratio in the starting graphene oxide was 2.0 indicating high degree of oxidation. The results of C 1s peak deconvolution in the starting graphene oxide is shown in **Table SI1**. The survey spectra of both samples are shown in **Figure 3**. In GO-Sc-99.98 two major peaks corresponding to C1s and O1s were detected at 284.4 eV and 533.7 eV, respectively. There are also indium peaks present in the survey spectra, which originated from indium in the holder. Moreover, a very weak Sc 2p peak was detected confirming the low amount of scandium in the sample. The twinning of both Sc $2p_{1/2}$ and Sc $2p_{3/2}$ signals indicates two different binding environments of the Sc^{3+} ions. This effect might be indicative of bonding to different oxygen functional groups (hydroxyls and carboxylic acids) or of a partial hydrolysis of scandium to ScO(OH).[16] The C/O ratio was calculated to be 2.0. In the second sample, GO-Th-100, an intense Th 4f twinning peak was detected in addition to C 1s and O 1s. A detailed view of the Th 4f peak is also shown in **Figure 3**, where Th $4f_{7/2}$ is located at 335.1 eV while Th $4f_{5/2}$ occurs at 344.3 eV. A slight shift of Th $4f_{7/2}$ and Th $4f_{5/2}$ towards higher energy compared to values reported for ThO_2 may originate from Th^{4+} bonding to oxygen functional groups. The results showed that the thorium content in the sample is ~11.5 wt.%, which is the lowest measured value when compared to XRF or SEM-EDS. This difference can be attributed to surface sensitivity of XPS. The C/O ratio obtained, 1.9, was similar to that from GO-Sc-99.98.

The detailed high-resolution XPS spectra of C 1*s* showed a twinning peak with an asymmetrical tail at higher energies and a maximum at ~284.4 eV for both samples (**Figure 3**). A careful curve fitting was performed on both C 1s spectra to quantitatively differentiate the different carbon states: C=C (284.4 eV); C–C (285.2 eV); C–O of alcohol/ether groups (286.7 eV); the C=O of carbonyl groups (287.6 eV); O–C=O of carboxylic acid/ester groups (288.8 eV); and the π=π*
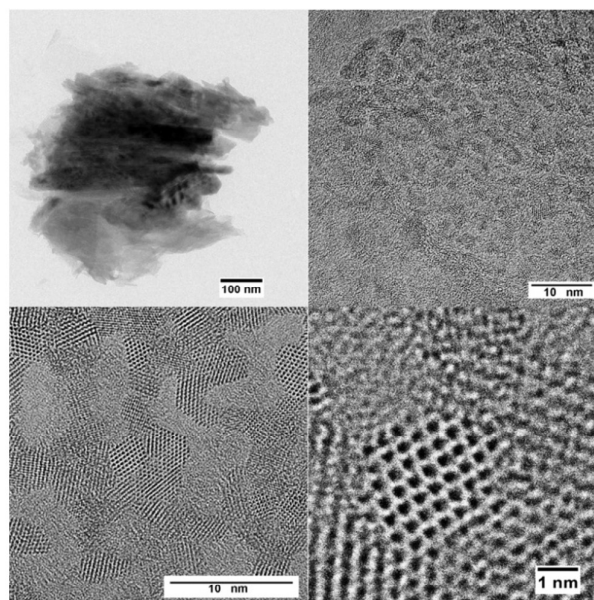
Figure 4 STEM and HT-TEM images of GO-Th-100 at various magnifications.
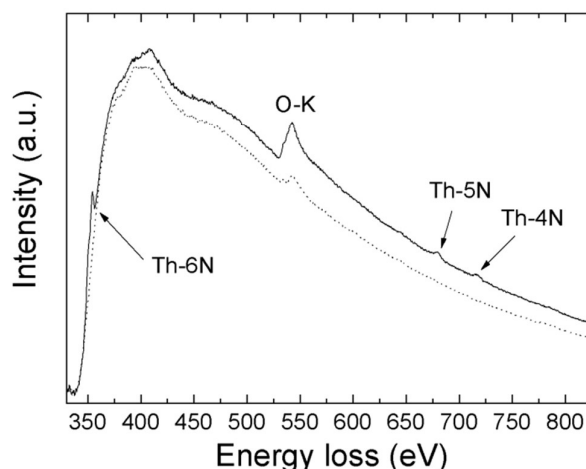
Figure 5 EELS spectrum for GO-Th-100. Solid line was measured directly on ThO_2 nanocrystal, while the dotted line was measured on pure graphene oxide.
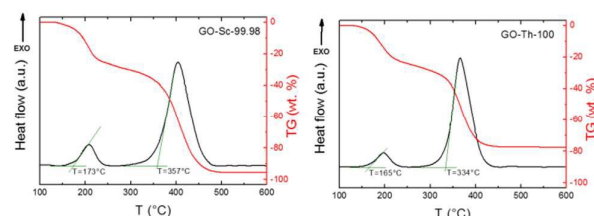
Figure 6 STA analysis GO-Sc-99.98 and GO-Th-100 in in dynamic air atmosphere.

interaction (290.8 eV).[17, 18] The relative abundance of these functional groups is shown in **Table 3**.

Table 3. Results of C1s fitting for GO-Sc-99.98 and GO-Th-100.

| Sample	−C=C	C−C	C−O	C=O	O-C=O	π=π*
GO-Sc-99.98	46.61	10.24	29.74	7.18	3.33	2.88
GO-Th-100	52.41	10.81	25.57	7.35	2.50	1.36

The Raman spectroscopy was performed to investigate the disorder and defects in graphene oxide and doped graphite oxides. In all spectra both D-band and G-band located at 1360 cm^{-1} and 1590 cm^{-1}, respectively, can be seen. The D-band is associated with defect and sp^3 hybridized carbon atoms by remaining oxygen functionalities, while the G-band is associated with sp^2 hybridized carbon atoms forming the graphene 2D skeleton. As apparent from **Figure SI3** all Raman spectra are almost identical. This suggests that the sorption of various ions on the surface does not influence the graphite oxide structure. The intensity ratio I_D/I_G (called D/G ratio) was ~0.9 in all cases. The FT-IR spectra of the starting graphene oxide as well as those of the samples GO-Th-100, GO-Sc-95 and GO-Sc-99.98 are shown in SI (**Figure SI4**). The X-ray diffractogram of GO-Th-100, GO-Sc-99.98 and the starting graphene oxide are shown in SI (**Figure SI5**). The slight shift of (002) reflection on GO-Th-100 sample compare to GO-Sc-99.98 indicate increase of interlayer distance from 0.786 nm for GO-Sc-99.98 to 0.852 nm for GO-Th-100.

High-resolution transmission electron microscopy (HR-TEM) was used to determine the exact bonding conditions between graphene oxide and thorium. Bright-field and HR-TEM images of GO-Th-100 at various magnifications are shown in **Figure 4**. A homogenous distribution of single or a few layered ThO$_2$ nanocrystals was detected with typical dimensions of approximately 3x3 nm. Electron energy loss spectroscopy (EELS) also confirmed the presence of ThO$_2$ as seen in **Figure 5**. EEL edges oxygen at 532 eV and thorium at 344 eV (N6), 676 eV (N5) and 714 eV (N4) were detected. Carbon edges were subtracted to obtain a spectrum with visible edges for thorium and oxygen. A comparison of EEL spectra for two different areas of the sample is also shown in **Figure 5**. The solid line shows a spectrum from the area where ThO$_2$ is present, while the dotted line was measured in the area where only graphene was detected. The appearance of ThO$_2$ nanocrystals indicates that Th^{4+} ions undergo hydrolysis in contact with the graphene oxide surface. It should be noted, however, that both the pH value and the Th^{4+} concentration were low enough such that a direct hydrolysis and precipitation from solution can be definitely ruled out. The primary step in thorium chemisorption process is thus clearly the attachment of Th^{4+}(aq) species on the GO surface, eventually followed by hydrolysis.

Samples GO-Sc-99.98 and GO-Th-100 were analyzed by simultaneous thermal analysis (STA) in dynamic air atmosphere to confirm the amount of sorbed ions and to test a potential method for obtaining thorium enriched oxides by graphene oxide composite combustion (**Figure 6**). The combustion process of both samples was similar. Both DTA curves showed two exothermic peaks. The first effect is connected to the exfoliation of doped graphene oxide and it was found at 173 °C for GO-Sc-99.98 and at 165 °C for GO-Th-100. During the exfoliation CO$_2$, CO, H$_2$O and other gasses are formed. This effect was thus accompanied by the weight loss ~25% for GO-Sc-99.98 and ~22% for GO-Th-100. The second thermal effect seen on DTA curves at 357 °C for GO-Sc-99.98 and 334°C for GO-Th-100 is the combustion of graphene formed by thermal decomposition of graphene oxide at lower temperatures. After the combustion the solid residue is a white powder composed of ThO$_2$ and Sc$_2$O$_3$. Calculations based on TG curves showed that there are approximately 3-3.5 wt.% of Sc and Th in GO-Sc-99.98 and 20 wt.% of Th in GO-Th-100. These results are in better agreement with the data obtained by SEM-EDS than those from XRF.

Apart from the equilibrium sorption capacity the kinetic factors are also important from the technological point of view. Hence we examined the sorption rate of both elements. Using SEM-EDS we analyzed the sample GO-Sc-95 containing high excess of scandium over thorium after 5 min, 15 min, 30 min, 60 min and 4 hours. EDS maps showed a homogenous distribution of scandium and thorium. The results are summarized in **Table 4** and visualized in **Figure 7**. The high affinity of thorium towards graphene oxide was proved by this experiment documenting much faster sorption of thorium compared to scandium. This observation is useful for the industrial applications where a relatively short time is needed for the sorption. From **Figure 7** is it obvious that the sorption of Th is nearly completed within a few first minutes and then the concentration remains almost constant. This suggests a formation of ThO$_2$ nanocrystals on the graphene oxide. By contrast the concentration of scandium increased much slowly suggesting a mechanism of physical sorption of individual scandium ions on graphene oxide sheets.
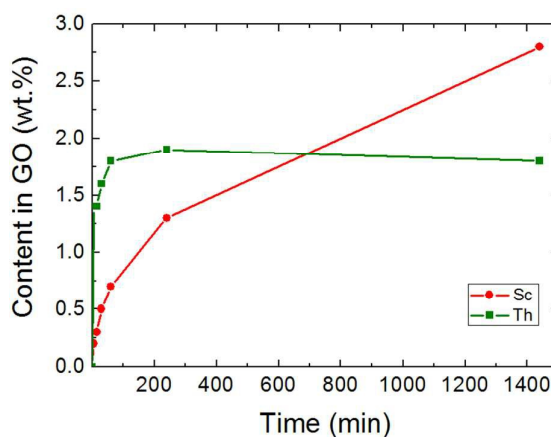
Figure 7 Time dependence of scandium and thorium content in GO-Sc-95 measured by SEM-EDS.

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Table 4. The composition of GO-Sc-95 after various sorption times obtained by SEM-EDS. Sc/Th ratio is also shown.

EDS (wt.%)	5 min	15 min	30 min	60 min	4 hours	24 hours
C+O	98.1	97.9	97.7	97.2	96.6	95.1
S	0.3	0.4	0.2	0.3	0.3	0.3
Sc	0.2	0.3	0.5	0.7	1.2	2.8
Th	1.4	1.4	1.6	1.8	1.9	1.8
Sc/Th ratio	13:87	18:82	24:76	28:72	39:61	60:40

Conclusions

We demonstrated the ability of graphene oxide for highly efficient separation of thorium- scandium compounds and concentrates obtained from mines and commercial scandium compounds. The obtained composite materials were characterized in detail by XPS, electron microscopy and X-ray fluorescence. The measured sorption capacity of graphene oxide was 34 mg Sc^{3+}/1g of GO and 205 mg Th^{4+}/1g of GO. This finding can be employed for the separation of thorium from scandium concentrates or mixtures where it occurs as a dominant impurity. Our experiments showed that the Sc/Th ratio shifted from the 95/5 in scandium concentrate to 60/40 in graphene oxide in a single step. Such a high selectivity in sorption activity towards thorium was observed even for its very low concentrations, where the thorium enrichment factor was over 500. The application of graphene oxide in purification procedures provides significant advantages compared to complicated processes based on ion exchange and membrane separation techniques. This method should find an important application potential for separation of scandium and thorium from their mixtures in the corresponding ores as well as in their commercially available compounds.

Acknowledgements

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