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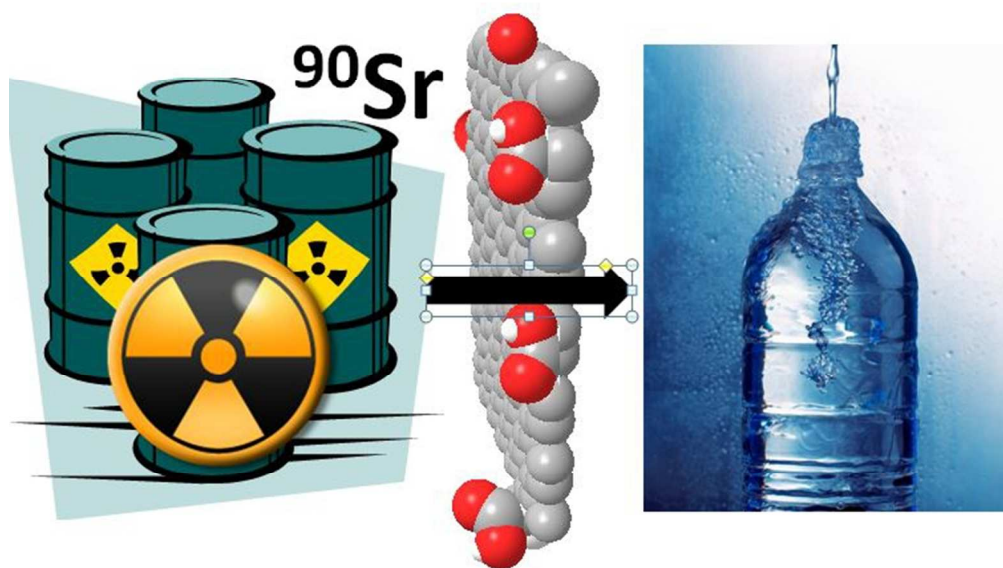


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ARTICLE TYPE

## Highly Selective Uptake of Ba<sup>2+</sup> and Sr<sup>2+</sup> Ions by Graphene Oxide from Mixtures of IIA Elements

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**We show here that graphene oxide selectively gathers heavy IIA group elements in the order of Ba<sup>2+</sup>>Sr<sup>2+</sup>>Ca<sup>2+</sup>>Mg<sup>2+</sup> with enrichment factors >100.**

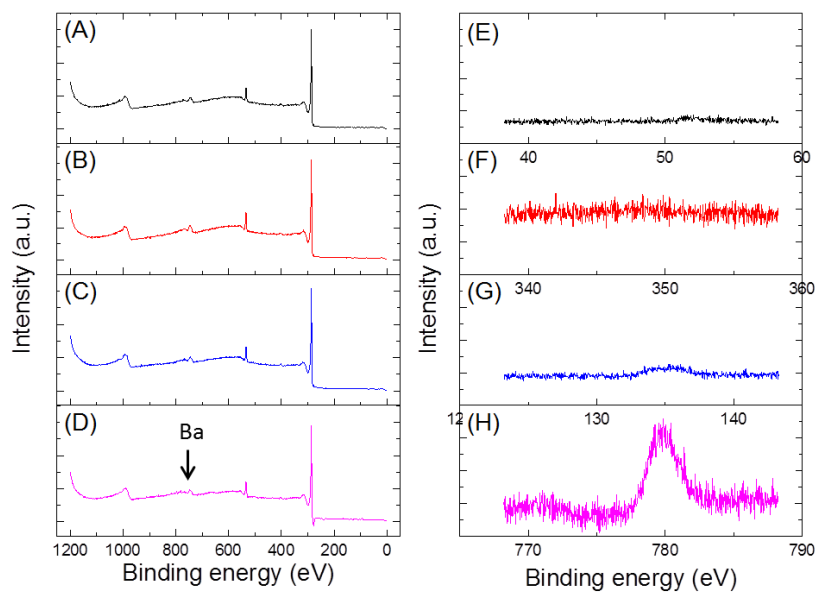
Strontium 90 (<sup>90</sup>Sr) is a radioactive isotope which the human body incorporates into its bone structure because it is not distinguished from Ca<sup>2+</sup>. Such incorporated <sup>90</sup>Sr cannot be removed from the organism and, having a half-life of 28.8 years, causes cancer. Given the large release of <sup>90</sup>Sr into the environment during the last two major nuclear power plant accidents, i.e., Chernobyl (<sup>90</sup>Sr released into the atmosphere) and Fukushima (<sup>90</sup>Sr released into seawater), there is an urgent need for efficient remediation. Barium is also presented in fission products in the form of <sup>131</sup>Ba and <sup>133</sup>Ba isotopes. Ba<sup>2+</sup> is a highly toxic element (BaSO<sub>4</sub> is non-toxic only because of its extremely low dissociation constant)<sup>1</sup> and it can affect the human nervous system by blocking potassium ion channels in ion membranes.<sup>2</sup> Removal of barium from the environment and from industrial waste are highly important applications, since this element has very broad use in paint, fireworks, and special ceramics.<sup>3</sup> However, separation of Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> pose a great challenge to ion-exchange materials.<sup>4</sup> Recently, an interesting report was made about green algae that was capable of separating Sr<sup>2+</sup> from Ca<sup>2+</sup> by coprecipitation with barite.<sup>5</sup> However, this method possesses major limitations because a particular cell culture is required.<sup>5</sup> High purity Ba and Sr compounds are important for production of ferroelectric materials and other mixed oxides compounds. In a similar line, preferential sorption of Pb(II) ions and further showed the complexability based preference among first series transition metal ions.<sup>6</sup> This interesting works shows (as we reconfirm in this report) preferential sorption selectivity increases down the Group; note that novelty of our paper is that it is focused on alkaline earth elements.

Graphene oxide has a very large surface area (up to 2630 m<sup>2</sup>/g)<sup>7</sup>, significantly larger than that of single-walled carbon nanotubes (1315 m<sup>2</sup>/g)<sup>8</sup> and graphite (10-20 m<sup>2</sup>/g).<sup>9</sup> Graphene oxide can be readily prepared from inexpensive graphite; it contains a large amount of oxygen-containing groups (C:O ratio ~2). Graphene oxide (GO) can be easily dispersed in water but it is easier to separate it from the suspension via simple filtration because the size of GO flakes is on the order of micrometers. Graphene oxide can be used as highly permeable membrane for

water filtration.<sup>10</sup>

Here, we show that graphene oxide exhibits an extremely different uptake of alkaline earth metal cations, with uptake dramatically increasing with the increasing atomic mass of the elements of IIA group, increasing in the order Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>. We also show that GO is capable of exhibiting highly preferential removal of traces of Ba<sup>2+</sup> from Sr(NO<sub>3</sub>)<sub>2</sub>, which are present as impurities in ACS purity class chemicals. Such highly preferential removal of Sr<sup>2+</sup> and Ba<sup>2+</sup> from other IIA group elements using inexpensive graphene oxide shall find application in environmental remediation.

We have prepared graphene oxide by oxidizing graphite using a mixture of sulphuric acid and nitric acid and potassium chlorate (Hofmann's method<sup>11</sup>) to yield graphite oxide, which was consequently ultrasonicated to produce graphene oxide (GO). 100 mL of 1 mol/L solution of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup> produced from their respective nitrates was then mixed with 100 mL of a suspension of 0.1 g of GO and stirred for 24 hours. The solution was filtered and the remaining material dried. Such material was labelled GO-IIA. The full characterization of the GO prepared by this method was published by our group previously. Briefly, Elemental composition of GO was 50.81% at. of C, 20.89% at. of H, 0.31% at. of S and 27.99% at. of O, based on combustible analysis.<sup>12</sup> Consequently, it was heated to 1000 °C to create a stable material not susceptible to swelling by hydration from atmospheric humidity.<sup>13</sup> The materials are indicated in the following text as G-IIA (general) or G-Me<sup>2+</sup>, where Me is substituted for the particular IIA element. The resulting G-IIA materials were analyzed for their IIA ion content using X-ray fluorescence spectroscopy and XPS and SEM/EDX. In the following text, we will first show individual IIA ion removal from the solution followed by the high selectivity of GO toward heavier IIA elements.



**Figure 1.** Left: Wide scan of (A) G-Mg, (B) G-Ca, (C) G-Sr, and (D) G-Ba. Right: High-resolution XPS of absorbed group 2 metal (same scale), (E) Mg, (F) Ca, (G) Sr, and (H) Ba.

#### Individual ion uptake

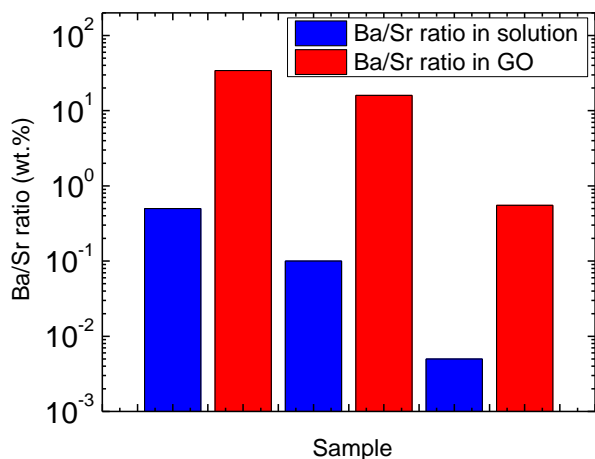
GO-IIA and G-IIA materials were analyzed by X-ray fluorescence as it is precise and the general method for determining elemental composition. GO contained 0.110% (wt.) of Mg, 0.261% of Ca, 0.541% Sr, and 2.192% of Ba. The concentration of AII ions in aqueous solution was 33 mmol.L<sup>-1</sup>. The increase of sorption capacity corresponded with the trend of ionic radius increase from 86 pm for Mg<sup>2+</sup>, 114 pm for Ca<sup>2+</sup>, 132 pm for Sr<sup>2+</sup>, and 149 pm for Ba<sup>2+</sup>.<sup>14</sup> However, other factors such as the tendency to form coordination compounds and the strength of bonds with oxygen functionalities play roles in the sorption capacity of graphite oxide. Heated samples of G-IIA contained 0.240% (wt.) of Mg, 0.277% of Ca, 0.881% of Sr, and 6.283% of Ba. One can observe a clear trend in the uptake of the heavier elements by graphene oxide, especially of Ba<sup>2+</sup>. The uptake of IIA elements is likely caused by their chelation by the oxygen-containing groups in GO. These metals are also strongly bonded and enduring in graphene after high-temperature treatment.

The elemental composition of the G-IIA samples was investigated by using X-ray photoelectron spectroscopy (XPS). According to the wide scan shown in Figure 1, among the four sample graphenes, only the Ba can be found in the wide scan (Figure 1D) as 0.087 at.%. Then, a high-resolution scan for four of the IIA group metals was performed. This is shown in Figure 1 (E-H). From the result, it is obvious that Mg and Ca cannot be detected by XPS whereas Sr and Ba can be detected; the amount of absorbed Ba is significantly higher than that of Sr. These results confirm the trend suggested by the XRF data. One should note that XPS is highly surface sensitive. This XRF provides better overall information about the elemental composition of the samples. SEM/EDX of the G-IIA samples is presented and

discussed in the supporting information (see Figures S1).

It is of high importance to assess the ability of GO to selectively gather individual elements from their mixtures. The total concentration of all AII group ions was 10 g.L<sup>-1</sup> for all binary mixtures. We have exposed graphene oxide to various mixtures containing barium and strontium nitrates. GO selectively binds (takes up) heavier elements. The selectivity towards the uptake of Ba<sup>2+</sup> was tested for a solution of nitrates with Ba<sup>2+</sup>/Sr<sup>2+</sup> ratios of 0.5, 0.1, and 4×10<sup>-3</sup>. The original mixture ratio of Ba<sup>2+</sup>/Sr<sup>2+</sup> in solution was 0.5. After the uptake of Ba<sup>2+</sup> and Sr<sup>2+</sup> by GO, their ratio increased to 34.1 in solid GO. Similarly, a solution containing a mixture of Ba<sup>2+</sup> and Sr<sup>2+</sup> in a ratio of 0.1 resulted in preferential uptake of Ba<sup>2+</sup> with a Ba<sup>2+</sup>/Sr<sup>2+</sup> ratio of 16 in solid GO (enrichment factor of 160). Finally, we demonstrated the highly preferential uptake of Ba<sup>2+</sup> over Sr<sup>2+</sup> in the

case of a trace concentration of Ba<sup>2+</sup>, which is typically presented in ACS p.a. (for analysis) purity grade strontium nitrate. These types of chemicals typically have about 0.1 – 0.3 wt.% of Ba<sup>2+</sup> (Ba<sup>2+</sup>/Sr<sup>2+</sup> ratio in ACS p.a. pure Sr(NO<sub>3</sub>)<sub>2</sub> in our case was 4×10<sup>-3</sup>). Even for such a low concentration, we observed a strong increase in the Ba<sup>2+</sup>/Sr<sup>2+</sup> ratio after the uptake by solid GO (Figure 2). This showed an enrichment factor of 139. Similar behavior was observed for mixtures containing other lighter elements from the AII group and also the AI group. We performed tests with the ratio of 0.1 in liquid phase for the Sr<sup>2+</sup>/Ca<sup>2+</sup>, Sr<sup>2+</sup>/Mg<sup>2+</sup>, and Ca<sup>2+</sup>/Mg<sup>2+</sup> mixtures. For the Sr<sup>2+</sup>/Ca<sup>2+</sup> mixtures, we observed a ratio of 0.64 in solid GO. For the Sr<sup>2+</sup>/Mg<sup>2+</sup> mixture, the ratio was 0.45 and for the Ca<sup>2+</sup>/Mg<sup>2+</sup> mixture, the ratio was 0.28. In all cases, we obtained an enrichment of the heavier ion concentration in graphene oxide compared to the ion ratio in solution. Finally, we tested a complex mixture containing Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> with equal concentrations of 2 g.L<sup>-1</sup>. In this case, we also observed enrichment of the heavier elements in GO compared to their concentrations in solution. The element ratio in GO was 0/0.28/0.39/0.60/1 for Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup>, respectively. Ions with a 1+ charge have only minimal affinity towards graphene oxide and we observed that only traces had been taken up from the solutions. The concentration of Na was below 10 ppm and the concentration of K was about 30 ppm. The higher uptake of potassium is related to the large ionic radius of K<sup>+</sup> (152 pm). The ability to form coordination compounds is also very important and a lower concentration of 1+ ions compared to 2+ ions was observed. This effect is related to the low tendency of alkali metals towards coordination with oxygen functional groups.



**Figure 2.** Sorption ratio for Ba<sup>2+</sup>/Sr<sup>2+</sup> mixtures in solution and sorption ratio on graphene oxide. Note that the Y-axis is logarithmic.

In Summary, we observed an increase in graphene oxide affinity towards alkaline earth ions with an increase in atomic number. The greatest difference was observed in the case of Ba<sup>2+</sup> ion uptake. We have shown that even traces of barium could have been selectively removed from alkaline earth elements and alkali metals. A high enrichment ratio was also observed in the case of strontium toward lighter alkali earth elements (calcium and magnesium) as well as alkali metals. The sorption capacity for monovalent ions was found to be negligible. Barium belongs to a group of highly toxic elements and graphene oxide can be used for the removal of such elements from the environment. Other applications are in the field of alkaline earth compound purification. GO can be applied for preparing high purity strontium compounds where barium is a very common impurity. The enhanced sorption capacity toward strontium in comparison with lighter elements can also be applied for the separation of strontium. This is very important for <sup>90</sup>Sr radioactive isotopes. From the increase in sorption activity for heavy elements, we can also imagine extremely high affinity toward Ra<sup>2+</sup> ions and possible applications for separating radium from mixtures. This characteristic can lead to broad applications for the separation of radium from uranium ore.

## Experimental section

### Materials

Graphite (2-15 μm, 99.99995%) and strontium nitrate (99.95%) was obtained from Alfa Aesar, Germany. Deionised water with a conductivity of 18.2 MΩ cm was used in the preparation of solutions. Sulfuric acid (98 %), nitric acid (68 %), potassium chlorate (> 99 %), hydrochloric acid (37%), silver nitrate (>

99.8%), barium nitrate (> 99%), magnesium nitrate hexahydrate (> 99%), calcium nitrate tetrahydrate (> 99%), strontium nitrate (> 99%), sodium nitrate (> 99.5%) and potassium nitrate (> 99%) were obtained from Lach-Ner, Czech Republic. Nitrogen (99.9999% purity) was obtained from SIAD, Czech Republic.

### Apparatus

The scanning electron microscopy (SEM) images were obtained by a JEOL 7600F field emission scanning electron microscopy (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) samples were prepared by compacting a uniform layer of the materials on a carbon tape. The XPS samples were measured by a monochromatic Mg X-ray radiation source (SPECS, Germany) and a Phoibos 100 spectrometer in order to obtain survey and high resolution C1s, O1s and metals spectra. Axios sequential WD-XRF spectrometer (PANalytical, the Netherlands) was used to perform XRF analysis. It is equipped with a Rh anode end-window X-ray tube fitted with 50 μm Be window. All 11 scans covering 79 measured elements were collected by software SuperQ in vacuum. The obtained data were evaluated by standardless software Omnian. The analyzed powders were pressed into H<sub>3</sub>BO<sub>3</sub> pellets without any binding agent and covered with 4 μm supporting polypropylene (PP) film. The time of measurement was 20 min.

### Synthesis

Graphite oxide prepared by the Hofmann method<sup>11</sup> was named HO-GO. 87.5 mL of concentrated sulphuric acid and 27 mL of nitric acid were added to a reaction flask containing a magnetic stir bar. The mixture was then subsequently cooled on 0 °C and 5 g of graphite was added. The mixture was vigorously stirred to avoid agglomeration and to obtain a homogeneous dispersion. While keeping the reaction flask at 0 °C, 55 g of potassium chlorate was slowly added to the mixture in order to avoid a sudden increment in temperature and the formation of explosive chlorine dioxide gas. Upon the complete dissolution of potassium chlorate, the reaction flask was then loosely capped to allow the escape of the gas evolved and the mixture was continuously stirred vigorously for 96 h at room temperature. On completion of the reaction, the mixture was then poured into 3 L of deionized water and decanted. Graphite oxide was then redispersed in HCl (5 %) solutions to remove sulphate ions and repeatedly centrifuged and redispersed in deionized water until a negative reaction on chloride and sulphate ions (with AgNO<sub>3</sub> and Ba(NO<sub>3</sub>)<sub>2</sub> respectively) was achieved. Graphite oxide slurry was then dried in a vacuum oven at 50 °C for 48 h before use.

For the measurement of sorption capacity 0.2 g of graphene oxide was dispersed in 100 ml water by ultrasonication (400 W, 60 minutes). To the suspension of formed graphene oxide was added 50 ml of 0.1M solution of alkaline earth nitrate (Mg, Ca, Sr, Ba) and stirred for 24 hours. The coagulation of graphene oxide suspension starts immodestly after addition of nitrate solution. The reaction mixture was suction filtered and repeatedly washed by deionized water. Obtained graphene oxide composite was dried for 48 hours in vacuum oven at 50 °C before characterization. For the testing of selective sorption test was used 0.2 g GO and 1 g of total amount of ions in various ratio.



The thermal exfoliation of GO composite was carried out at 1000 °C for 12 minutes, by placing the GO inside a porous quartz glass capsule connected to a magnetic manipulator in a vacuum tight quartz reactor with controlled atmosphere. This system provided a temperature gradient of over 1000 °C min<sup>-1</sup>. The sample was then flushed repeatedly with pure nitrogen and subsequently inserted into a preheated reactor in nitrogen (99.9999% purity) atmosphere (pressure: 100 kPa) to give the noble metal doped graphene hybrid material. The flow of the nitrogen was 1000 mL.min<sup>-1</sup>, resulting in the removal of the by-products of the reactions.

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