Graphene Oxide

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Synthesis of Graphene Oxide by Oxidation of Graphite with Ferrate(VI) Compounds: Myth or Reality?

Zdeněk Sofer, Jan Luxa, Ondřej Jankovský, David Sedmidubský, Tomáš Bystroň, and Martin Pumera**

Abstract: *It is well established that graphene oxide can be prepared by the oxidation of graphite using permanganate or chlorate in an acidic environment. Recently, however, the synthesis of graphene oxide using potassium ferrate(VI) ions has been reported. Herein, we critically replicate and evaluate this new ferrate(VI) oxidation method. In addition, we test the use of potassium ferrate(VI) for the synthesis of graphene oxide under various experimental routes. The synthesized materials are analyzed by a number of analytical methods in order to confirm or disprove the possibility of synthesizing graphene oxide by the ferrate(VI) oxidation route. Our results confirm the unsuitability of using ferrate(VI) for the oxidation of graphite on graphene oxide because of its high instability in an acidic environment and low oxidation power in neutral and alkaline environments.*

Graphene oxide is the most common starting material for the synthesis of graphene.[1] The synthesis of graphene oxide was first reported in the mid-nineteenth century by Brodie, who used potassium chlorate in combination with fuming nitric acid (>90 wt% HNO_3).[2] The initial methods were generally based on the oxidation of graphite using potassium chlorate in an environment of concentrated nitric and sulfuric acids. Subsequently, methods were developed that used mixtures of fuming nitric acid and concentrated sulfuric acid, as well as mixtures of concentrated nitric (68 wt% HNO_3) and sulfuric acids.[3] More recently developed methods are based on the procedure first reported by Hummers, in which concentrated sulfuric acid is mixed with in situ formed manganese(VII) oxide.[4] Hummers' procedure has been further modified in recent years to improve safety, scalability, and the degree of graphite oxidation, as well as to tune the composition of oxygen functionalities.[5] The broad application potential of graphene oxide has been widely reported.[6] Importantly, graphene oxide is a starting material for chemically modified graphenes.[7]

Very recently, a report appeared about a powerful new oxidation agent—potassium ferrate(VI)—suitable for the synthesis of graphite/graphene oxide.[8] Because there is substantial uncertainty in the literature thermodynamic data regarding ferrate(VI) stability, we herein give rather conservative estimates of its redox potentials. Ferrate(VI) redox potentials are strongly dependent on pH, giving a redox potential of at least around 1.8 V in an acidic environment (pH 0.0), at least around 0.9 V at pH 7.0, and a relatively weak redox potential in an alkaline environment (at least ca. 0.1 V at pH 14.0). Nevertheless, the oxidation ability of ferrate(VI) anion has been manifested by oxidizing water across a wide range of available pH values.[9] Thus, compared with the previously used permanganates and chlorates, the high redox potential of potassium ferrate(VI) provides an opportunity to oxidize carbon in graphite to graphene oxide. In combination with the low toxicity of iron ions, ferrate(VI) anion is a "green" oxidation agent renowned for its high oxidizing ability, especially in an acidic environment, where its redox potential is the highest.

Conversely, it must be noted that the oxidation ability of ferrate(VI) has also been linked to its instability, particularly in acidic environments. In practical terms, ferrate(VI) stability at room temperature is limited to days in a strongly alkaline environment, to hours in a neutral environment, and to seconds in strongly acidic aqueous solutions.[10] Its stability is influenced by the various metal ions, such as Ni^{2+} and Co^{2+}, that catalyze its decomposition.[11] Interestingly, the decomposition process is also catalyzed by iron oxides/hydroxides, which are the products of ferrate(VI) decomposition in an aqueous environment. Thus, ferrate(VI) decomposition is an autocatalytic process. Ferrate(VI) ions have been applied in various fields of organic synthesis,[12] including water treatment,[13] energy storage,[14] and warfare agents decomposition.[15]

In their paper, Peng et al. claimed the highly efficient and rapid oxidation of graphite by K_2FeO_4 in a sulfuric acid environment.[8] Herein, we assess the premises that underlie their use of potassium ferrate(VI) for the synthesis of graphene oxide. We investigate the degree to which the oxidation of graphite to graphite/graphene oxide by ferrate(VI) proceeds under various experimental conditions, including replicating theirs. For all conditions, we perform separate sets of experiments, using either laboratory-prepared or commercially supplied K_2FeO_4. The subsequent

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detailed characterization of the products obtained from all of these experiments enable us to determine whether or not the reported method is suitable for the oxidation of graphite to graphite/graphene oxide.

The thermodynamic instability of potassium ferrate(VI) makes its use in synthesis complicated and expensive, and has limited its application to laboratory scale.[16] Consequently, it is not widely commercially available and, thus, we first synthesized potassium ferrate(VI) according to the standard procedure.[17] Our synthesis produced K_2FeO_4 of 76 wt% purity (for its detailed characterization, see Supporting Information, Figures S1 and S2, and Table S1). Our laboratory-prepared K_2FeO_4 was used in the replication of Peng et al.'s procedure for the synthesis of graphene oxide under acidic conditions; the resulting sample was termed G-ORG. We also used our K_2FeO_4 for graphite oxidation by ferrate(VI) in environments of sulfuric acid (sample G-0), of water (sample G-7), or of 1 M potassium hydroxide (sample G-14); in other words, under acidic, neutral, or alkaline conditions as reflected by the pH value in the sample name. The main steps of graphite oxidation by sulfuric acid and the final product are shown in Figure 1. The reaction of K_2FeO_4 with sulfuric acid was extremely vigorous (to prevent an explosive reaction with sulfuric acid, K_2FeO_4 must be completely free of KOH). K_2FeO_4 underwent immediate decomposition, which was characterized by the vigorous evolution of oxygen and the disappearance of the ferrate(VI) ion's normal red color within a few minutes. The reaction mixture after the first addition of K_2FeO_4 is shown in Figure 1 A. After one hour, the slight evolution of oxygen was still evident, but no visible oxidation of graphite was observed (Figure 1 B). The reaction mixture after dilution with water and the addition of hydrogen peroxide is shown in Figure 1 C. The obtained material, shown in Figure 1 D, was highly hydrophobic, which was caused by a low degree of oxidation. There were no obvious changes with respect to the starting graphite.

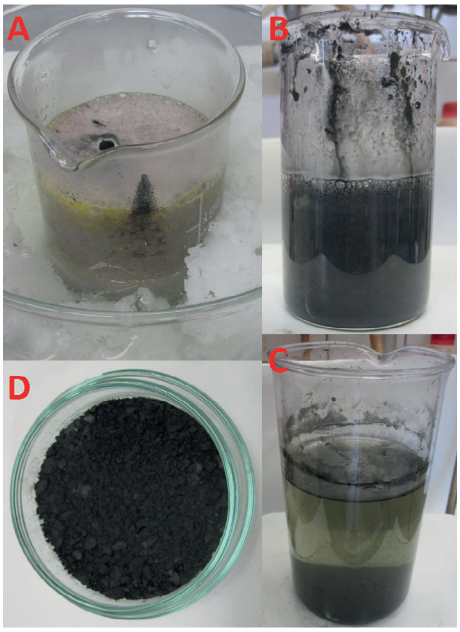

Figure 1. Image of reaction mixture after first addition of K_2FeO_4 to sulfuric acid (A). Reaction mixture after one hour (B) and after dilution with water and the addition of hydrogen peroxide (C) indicate the presence of weakly oxidized graphite with hydrophobic properties. Final oxidized graphite (D).

In addition, other experiments were performed using K_2FeO_4 commercially obtained from BOC Sciences and Chemical Point UG. Although both commercial samples were declared to have a purity of over 90 wt%, detailed analysis revealed that the concentration of K_2FeO_4 in these products was only about 20 wt%. They were also shown to contain significant amounts of impurities, including KNO_3 and $KClO_3$, both of which are strong oxidants commonly used in permanganate- and chlorate-based methods for the synthesis of graphene oxide.[3,4] For a detailed chemical analysis of the commercially-obtained K_2FeO_4, see Supporting Information and Figure S2 and Table S1. Using the commercially supplied K_2FeO_4 of low purity, we performed four further experiments similar to Peng et al.'s method (full details of the syntheses and all characterizations can be found in the Experimental Section in the Supporting Information). The presence of $KClO_3$ and KNO_3 led to the formation of a large amount of nitrous oxide during the oxidation procedure and to a slightly higher degree of graphite oxidation. However, the formation of graphene oxide was not observed in any of these experiments, not even when three-times the standard amount of K_2FeO_4 was used for graphite oxidation.[8] A control experiment performed with a purified commercial K_2FeO_4 (free of $KClO_3$, KNO_3, KCl, and K_2CO_3; 91 wt% K_2FeO_4) led only to minimal oxidation of graphite and was comparable to the results obtained with K_2FeO_4 synthesized in laboratory. Images of the oxidation reaction mixtures are shown in the Supporting Information (Figure S3).

SEM was used to compare the morphology of the samples prepared from our laboratory K_2FeO_4. It revealed no significant differences to the graphite (Figure S4), thereby indicating a negligible effect of graphite oxidation by ferrate(VI) ions.

To obtain more information about the chemistry of the obtained materials, X-ray photoelectron spectroscopy (XPS) analysis was performed. The spectra for the samples prepared from our laboratory K_2FeO_4 showed a low concentration of oxygen in the range of 1–5 at% (Figure 2). The lowest concentration of oxygen was observed in G-ORG, the sample prepared according to the Peng et al.'s procedure,[8] in which ferrate(VI) was added to sulfuric acid before the addition of graphite. Our measured C/O ratio was 56.1 compared to their reported C/O ratio of 2.2; the C/O ratio measured of the starting graphite was 89.9. The decomposition of ferrate(VI) was so fast that it did not allow for the further oxidation of subsequently added graphite. In the case of the three other samples, the concentration of oxygen was only slightly higher, yielding a C/O ratio of about 22 for the samples oxidized in sulfuric acid and neutral environments and of about 28 for the graphite oxidized in an alkaline environment. Collectively, these results show that graphite cannot be oxidized by ferrate(VI) ions because of their insufficient stability in an acidic environment and relatively

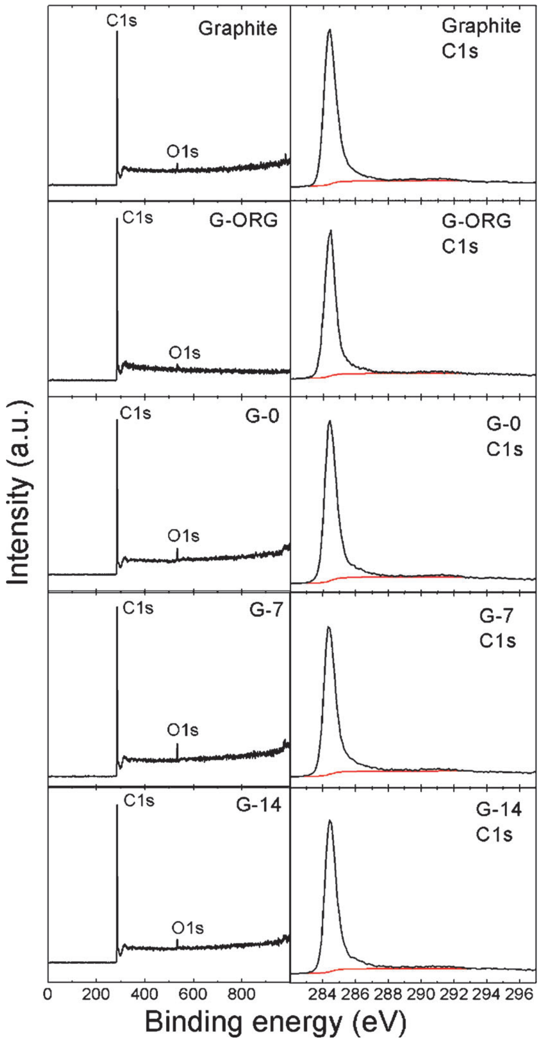

Figure 2. XPS survey spectra and C 1s detail of graphite and oxidized graphite.

weak oxidation power in neutral or alkaline reaction mixtures. These results are also supported by the high-resolution XPS spectra of the C 1s peak, in which carbon predominated in the form of $C{=}C$ bonds and only a negligible amount of oxygen functionalities was observed (Figure 2). In fact, all C 1s spectra were almost identical. Such results are incongruous with those obtained for graphene oxide prepared by the classical permanganate- and chlorate-based methods, in which the C/O ratio typically reaches values in the range of 2–4.[18]

For the samples prepared from commercially supplied K_2FeO_4, which contained high concentrations of KNO_3 and $KClO_3$ XPS analysis showed a significant increase in the C/O ratio, which reached 10–12. An even lower C/O ratio was obtained when we carried out a larger scale experiment with 60 g of commercial K_2FeO_4. These results show that the slight oxidation of graphite using commercial potassium ferrate(VI) is caused by the oxidation ability of the impurities present within K_2FeO_4 and not by its own oxidation ability. This was also proved by performing experiments with purified K_2FeO_4 free of KNO_3 and $KClO_3$ impurities. XPS spectra of the graphite oxidized by the commercially supplied K_2FeO_4 are shown in the Supporting Information (Figure S5), together with the chemical analysis results obtained from these spectra (Table S2). No higher degree of oxidation was observed in the high-resolution XPS spectra, in which the absence of ketone and/or carboxylic acid functionalities was clearly seen (Figure S5).

Our XPS analysis results are also supported by elemental combustion analysis (see Table 1 for the samples prepared from our laboratory K_2FeO_4 and Table S3 for the samples prepared from commercially supplied K_2FeO_4). Only a minute amount of oxygen and hydrogen was detected, suggesting only slight surface oxidation. Slightly lower C/O ratios were observed for the samples prepared using the commercially obtained K_2FeO_4 because of the impurities present. In particular, both KNO_3 and $KClO_3$ have the ability to oxidize graphite under strongly acidic conditions, such as those used in the chlorate method of graphene oxide synthesis. However, the C/O ratio was still about one order of magnitude higher than for the typical composition of graphene oxide. In addition, about 1 at% of sulfur was observed in the samples oxidized by the commercially available K_2FeO_4. For all samples, the obtained values were close to the C/O ratios measured by XPS.

Table 1: Content of C and O together with C/O ratios obtained from elemental combustion analysis.

Sample	C [at%]	O [at%]	S [at%]	C/O
Graphite	98.9	1.1	0.0	89.9
G-ORG	98.1	1.9	0.0	51.6
G-0	95.7	4.3	0.2	22.3
G-7	95.6	4.4	0.1	21.7
G-14	96.6	3.4	0.1	28.4

Raman spectroscopy is a very useful method for the investigation of graphene oxide-based materials. Typically, such spectra are dominated by two bands: 1) a D-band at 1360 cm^{-1} associated with the sp^3 hybridized carbon atoms and defects in the graphene structure, and 2) a G-band at 1560 cm^{-1} related to the vibrations of sp^2 hybridized carbon atoms that form the graphene skeleton.[19] In addition, a 2D-band can also be often observed around 2700 cm^{-1}.[19] However, this is not what we found. The Raman spectra were almost identical for all samples. The D-band for the samples prepared from our laboratory K_2FeO_4 (Figure 3) revealed extremely low intensities, confirming both the low number of defects and insufficient oxidation of the starting material. Only in the G-ORG sample, the D-band was slightly visible owing to the surface oxidation of the graphite. The Raman spectra for the samples prepared from commercially supplied and also purified K_2FeO_4 (Figure S6) showed a stronger, but still weak D-band that resulted from the surface oxidation of the graphite; this again was due to the oxidation ability of the impurities present in the commercial products. However, even in this case, the D/G ratio remained extremely low, indicating minimal oxidation of the graphite). Collectively, these results are in good agreement with the low

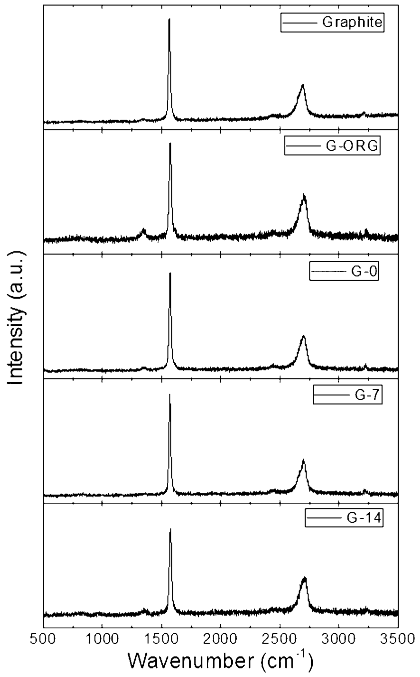

Figure 3. Raman spectra of starting graphite and prepared materials.

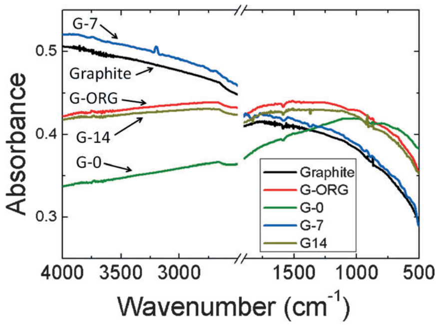

Figure 4. FTIR spectra of starting graphite and prepared samples.

degree of oxidation revealed by XPS and elemental combustion analysis.

FTIR spectroscopy was also used to characterize the prepared materials (see Figure 4 for the spectra of the samples prepared from our laboratory K_2FeO_4). In agreement with the results obtained from all other analytical methods, FTIR did not detect any functional groups on the surface of the obtained materials. For all samples, only a weak absorption band of the C=C bond can be seen at 1590 cm^{-1}. Again, no absorption bands of oxygen-containing functional groups were observed on the FTIR spectra of the graphites oxidized using the commercially-obtained samples as well as purified commercial K_2FeO_4 (Figure S7). Usually, -C=O, -OH, and -COOH groups are present even on chemically reduced graphenes.[20]

XRD was used to evaluate the structure of the oxidized graphite (see Figure 5 for the spectra of the samples prepared from our laboratory K_2FeO_4). The formation of graphite/graphene oxide typically leads to an increase in interlayer spacing from 0.34 nm to around 0.6–0.8 nm.[21] However, in this case, none of the samples showed an increase in interlayer distance compared with the starting graphite. Again, as with the chemical analyses, this indicates a negligible degree of oxidation. XRD was also performed for the graphite oxidized by commercially supplied potassium ferrate(VI) including purified K_2FeO_4 from BOC Sciences, but no significant changes were visible on the X-ray diffractograms (Figure S8).

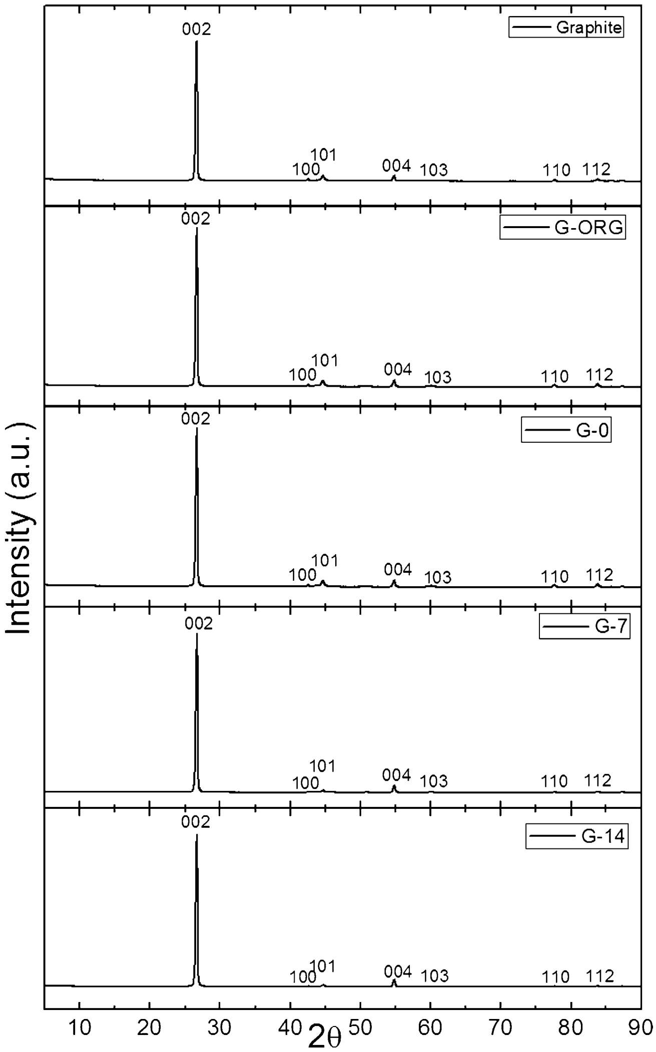

Figure 5. XRD diffraction patterns of starting graphite and prepared materials.

Thermal analysis was also performed in air atmosphere (Figure S9). Typically, the exfoliation temperature of graphene oxide is around 200 °C and accompanied by a significant reduction of mass and exothermic effects.[6a] However, none of these effects was observed on our samples below 600 °C. This shows the absence of any thermally labile oxygen functional groups in the oxidized graphite.

Generally, our careful analysis suggests that none of the above-mentioned experimental conditions led to the formation of graphene oxide. In fact, using Peng et al.'s procedure only resulted in the formation of poorly oxidized graphite with a very small amount of oxygen that resulted from the surface oxidation of the graphite. The higher oxidation of graphite observed for the samples prepared using commercially obtained K_2FeO_4 originates from oxidizing impurities like KNO_3 and $KClO_3$. It should be noted that graphene oxides prepared by either chlorate or permanganate routes typically exhibit C/O ratios in the range of 2–4.[3,4]

Our findings on the oxidation of graphite using ferrate(VI) ions show that Peng et al.'s reported method[8] is not suitable for the synthesis of graphene oxide. While ferrate(VI) ions are very powerful oxidation agents, their extreme instability, especially in acidic environments, leads to fast decomposition accompanied by water oxidation. The vigorous decomposition of water does not give ferrate(VI) ions the opportunity to oxidize graphite into graphene oxide. We have also shown that even at neutral pH or at the alkaline pH of the aqueous solution, ferrate(VI) ions are unable to oxidize graphite to graphene oxide. Only the impurities present in some commercial ferrates(VI) (such as KNO_3 and $KClO_3$) can slightly oxidize graphite surface. Thus, it is clear that chlorate- and permanganate-based methods remain the only reliable methods of choice for the synthesis of graphene oxide.

Experimental Section

WARNING: The synthesis of potassium ferrate(VI) requires the handling of gaseous chlorine, which is highly toxic. Concentrated hydroxide solution is highly corrosive and protective equipment must be used. The reaction of potassium ferrate(VI) with acid can be extremely violent. Potassium ferrate(VI) is a strong oxidation agent and mixing it with an organic compound should be avoided. High purity potassium ferrate(VI) may spontaneously decompose with a large evolution of heat and to ignite organic solvents used for purification. For full experimental details, see the Supporting Information.

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Keywords: ferrate(VI) · graphene · graphene oxide · oxidation

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Communications

Graphene Oxide

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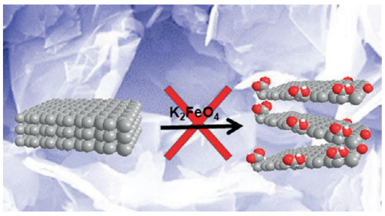
Synthesis of Graphene Oxide by Oxidation of Graphite with Ferrate(VI) Compounds: Myth or Reality?



Ferrate-ing around: The oxidation of graphite by ferrate(VI) is impossible owing to its fast decomposition in an acidic environment. Any oxidation occurring when using commercial potassium ferrate(VI) is caused by impurities.