



Review

Structure and synthesis of graphene oxide☆

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ABSTRACT

Graphene oxide (GO) is one typical two-dimension structured and oxygenated planar molecular material. Researchers across multiple disciplines have paid enormous attention to it due to the unique physiochemical properties. However, models used to describe the structure of GO are still in dispute and ongoing to update. And currently, synthesis methods for mass production are seemingly abundant but in fact, dominated by a few core methodologies. To update with the state-of-art opinions and progresses, herein we present a mini critical review regarding the synthesis of GO as well as its models and simulations of structure. Also, we discuss the perspectives.

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1. Introduction

Graphene oxide (GO) is the oxidized analogy of graphene, recognized as the only intermediate or precursor for obtaining the latter in large scale, [1] since the English chemist, sir Brodie first reported about the oxidation of graphite centuries ago [2]. About thirty years ago, the term *graphene* was officially claimed to define the single atom-thin carbon layer of graphite [3], which structurally comprises sp^2 hybridized carbon atoms arranged in a honeycomb lattice, rendering itself large surface area and some promising properties in terms of mechanical, electrical, and others [4,5]. Despite these excellent properties, purely single-layer graphene achieves limited success in practical applications due to the difficulties in the large-scale formation of specifically organized structures [6]. But the precursor GO has advanced much in both academics and industries in the last decades because of its readiness by exfoliating bulk graphite oxide facilely prepared from the oxidation of graphite [7,8]. This bottom-down chemical strategy features the utmost flexibility and effectiveness thereby arousing the significant interest in practical applications.

GO is known as a non-stoichiometric chemical compound of carbon, oxygen, and hydrogen in variable ratios which heavily relates to the processing methodologies [2,9–11]. GO possesses abundant oxygen functional groups that are introduced to the flat carbon grid during chemical exfoliation, evidenced as oxygen epoxide groups (bridging oxygen atoms), carbonyl ($C=O$), hydroxyl ($-OH$), phenol, and even organosulfate groups (impurity of Sulfur) [12,13]. In other words,

these defects of various kinds are brought into the naturally inert graphene structure, further categorized into on-plane functionalization defects and in-plane lattice defects (vacancy defects and hole defects) which semi-randomly distribute in GO's α -framework of the hexagonal lattice [1,7]. Such a defect-rich structure gives birth to unique properties of GO and renders its availability and scalability for further applications in various forms, e.g., chemically-derived graphene-like materials, functionalized graphene-based polymer composites, sensors, photovoltaics, membranes [14] and purification materials. On the structure of GO, however, it remains ambiguous, and literature reports are still in argument (Fig. 1) [11,13,15–23]. Also, methods about the synthesis of GO have been massively studied in the past few years. The effectiveness and environmental benignity were core driven forces for the continuous evolvement. Herein, we update the progress and make a short yet critical review on model structures of GO as well as the synthesis.

2. Graphene Oxide Structure and Theoretical Simulation

2.1. Models

In 1939, Hofmann and Rudolf [22] demonstrated a structural model of GO (Fig. 1, the top-leftmost schematic) in which a lot of epoxy groups randomly distribute on the graphite layer, and then in 1946, Ruess [21] updated this model by incorporation with hydroxyl entities and alteration of the basal plane structure (sp^2 hybridized model) with an sp^3 hybridized carbon system. By contrast, in 1969, Scholz and Boehm [19] proposed a less ordered structure with $C=C$ double bonds and periodically cleaved $C-C$ bonds within the corrugated carbon layers and hydroxyl, carbonyl groups in different surroundings, free from ether oxygen. Further, in 1994, Nakajima and Matsuo [18] proposed a stage 2 graphite intercalation compound (GIC)-resembled lattice framework

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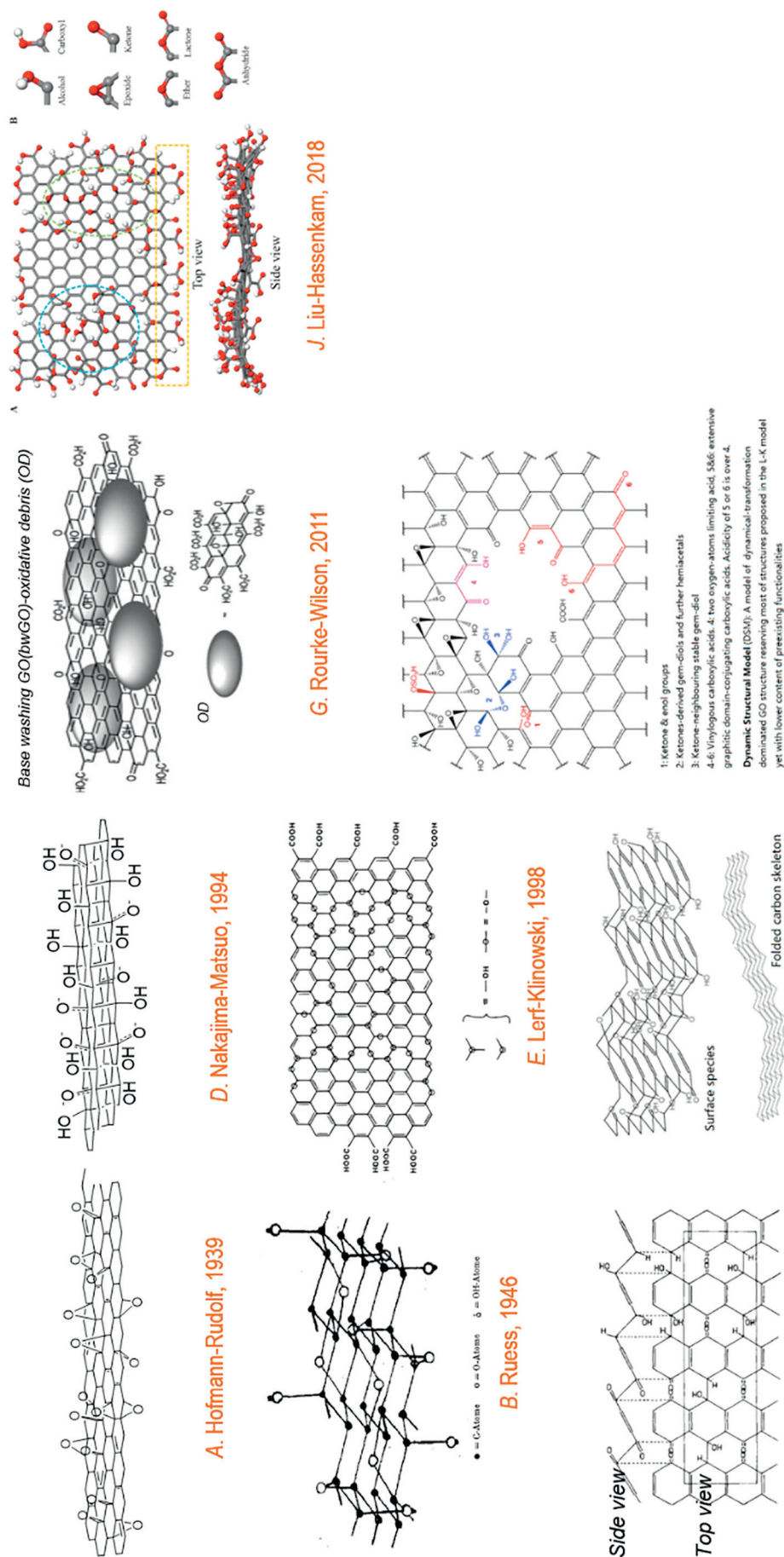


Fig. 1. Theoretical models for structures of graphite or graphene oxide.

based on the fact that fluorination of graphite oxide gives the same X-ray diffraction pattern as that of stage 2-type graphite fluoride, (C₂F). In 1998, Lerf *et al.* [17] characterized their GO by the ¹³C and ¹H nuclear magnetic resonance (NMR), and subsequently found the 60 ppm line better related to epoxide groups (1,2-ethers) other than 1,3 ethers, and the 130 ppm line to aromatic entities and conjugated double bonds. The carbon atoms attached to OH groups slightly distorted their tetrahedral structure, resulting in partial wrinkling of the layers. Accordingly, they proposed a model featuring a nearly-flat carbon grid structure with randomly distributed aromatic regions with unoxidized benzene rings and regions with aliphatic six-membered rings. This Lerf and Klinowski model (L–K model) has become one of the most acceptable for moderately oxidized samples [15]. However, all these earlier models could not well explain the origin of the planar acidity of GO, which is now a well-understood chemical property for GO. After that, Szabó and coworkers in 2006 [16] revived but a little modified the Scholz–Boehm model, *etc.* by again examining the results from elemental analysis, transmission electron microscopy, X-ray diffraction, diffuse reflectance infrared Fourier transform spectroscopy, X-ray photoelectron spectroscopy, and electron spin resonance besides NMR. They then proposed a carboxylic acid-free model comprising two distinct domains: trans-linked cyclohexyl species interspersed with tertiary alcohols and 1,3-ethers, and a keto/quinoidal species corrugated network.

Interestingly, as to the phenomenon of GO in basic solution Roukre *et al.* [23] found that GO decomposed into slightly oxygenated graphene part and strongly graphene-bound oxidative debris (OD) upon suffering a base washing, and then suggested a simple OD-base washed GO two-component model, which was much different from those previously proposed, upgrading the way we used to understand about GO. Besides, they also mentioned about the metastability of unwashed GO, which reminded us of the previous room-temperature metastable film [24], while the internal mechanism of external stimuli-responses structural instability was lack of sufficient investigation. In 2013, Dimiev *et al.* [11] revisited the structure *via* acid titration and ion exchange experiment in terms of acidity of GO and proposed a novel dynamical structural mode (DSM), which describes the evolution of several carbon structures with attached water beyond the static L–K model. More recently, Liu *et al.* [25] experimentally observed oxygen bonding and evidenced the C=O bonds on the edge and plane of GO, confirming parts of earlier proposed models, especially the L–K model.

Amongst these models from 1939 through 2018, the L–K model has been the most widely used due to the excellent interpretability over the majority of experimental observation, and easiness of further adaption/modification, for example, with which as the starting basis the Rourke–Wilson model [23], Dimie–Alemany–Tour model [11], *etc.* were successively publicized and continually paved the way forwards. Nonetheless, the unique two-dimensional geometry of GO has been widely accepted as the primary character, and this laid an essential foundation for GO subsequently blooming in enormous researches, especially after the Nobel Award honored the discovery of graphene in 2010.

2.2. Simulations

GO is considered with great versatility, as its properties are tunable by changing the type and concentration of oxygen-containing functional groups attached to its surface. In contrast to the tedious experimental observations, the Density functional theory (DFT) has been intensively used for the prediction and investigation of the atomic structure and corresponding properties based on a determination of molecule electron density [26,27]. It features a relatively low cost as a unique experiment-simulating computing tool. GO and its nearest relative graphite oxide are often targeted.

2.3. Functioning sites

The structure of GO is often simplified to be a graphene sheet bonded to oxygen in the form of carboxyl, hydroxyl or epoxy groups [28]. To understand the configuration and arrangement of hydroxyls and oxygens on the GO layers, Lahaye *et al.* [29] studied graphite oxide of different oxidation levels by DFT calculation. They found that during the oxidation plenty of carbon atoms were available to support the formation of 1,2-ether oxygens which stably attached on the adjacent carbon atoms of the carbon grid, other than 1,3-ethers because of energetical instability, but at the opposite side of the carbon plane was the hydroxyl molecules. The deformation of carbon grid around the hydroxyl bonds allows for the transverse wrinkling about 0.05 nm, yet the in-plane lattice axes retain the hexagonal features of graphene. Thus, it suggested that a stable structure requires hydroxyl groups to balance the tension on the carbon grid from the 1,2-ether oxygens. Tang and Zhang [30] investigated the evolution of epoxy and hydroxyl groups adsorbed in locations of various kinds on zigzag graphene nanoribbons and found that the adsorbed epoxy groups and both the epoxy and hydroxyl groups can be transformed to a carbonyl pair and a carbonyl–hydroxyl pair, respectively. Besides, the vacancy defects can enhance such adsorption and formation of oxygen-containing groups on graphene from the point of the energy barrier change, that manifests the extreme difficulty in ultimately reducing oxygen moieties from the planar structure. Savazzi *et al.* [15] investigated the GO at low degrees of oxidation by combining classical molecular dynamics and all-electron DFT simulations. With finding the 1,2-ether groups in the basal plane of GO from identifying XPS C-1s photoelectron peaks, a modification of the L–K model was then inclusive of ether groups. Recently, Moreira *et al.* hypothesized the hydroxyl chains were targeted sites of attack by hydroxide ions in the base medium and ultimately led to the cracking of GO sheets. As manifested by the theoretical calculation, they learned the bond breaking of the ketones at both sides of the basal plane initiated this change at the very beginning.

Oxygen functional groups are known uniformly but randomly attached on the graphene plane. But the oxygen atoms were ever in observation arranged in a rectangular lattice, displaying a series of epoxy groups present in strips previously. It suggests that such an arrangement of epoxy groups is energetically favorable according to DFT calculations [31,32]. However, this observation is inconsistent with another research, in which GO was found on average to maintain the hexagonal symmetry in order and have carbon–carbon bond length of an unmodified graphene sheet, indicating the oxygen atoms did not form periodic structures [33].

Moreover, Mkhoyan *et al.* [28] performed an *ab initio* DFT using a plane wave pseudo-potential approach and confirmed that the partial amorphization of GO occurs as a result of the sp² bonds of carbon atoms of the graphene converted into the sp³ bonds during oxidation, and corresponding carbon atoms moved from original sites to form the off-plane sp³ bonds.

2.4. Oxygen coverage

Intensive studies proposed the band gap opening of GO. *Via* a proposed model of graphite, Boukhvalov and Katsnelson [34] investigated the evolution of the electronic structure of graphite oxide with the coverage change of oxygen-containing moieties, found graphite oxide becomes conducting at 25% coverage, being an insulator at more essential coverage. And they also resolved the puzzle of the extreme value of the C:O ratio hardly above 16:1 after having optimized a variety of structures of graphite oxide. Lundie *et al.* adopted the extensive *ab initio* and hybrid DFT calculations to derive GO with optically active gap and identified fully oxidized graphene (O:C = 1:1) to be an insulator with a band gap of 6.50 eV [27,35]. However, Mattson *et al.* [36] experimentally prepared highly ordered graphene monoxide (GMO) by annealing multilayered G–O in vacuum and reported that such structure with a

stoichiometric ratio of C:O = 1:1 has semi-conductance with a band gap ~0.9 eV, which is somewhat different from that by Lundie *et al.*

Rosas *et al.* [37] reported the effect of the incorporation of hydroxyl and carboxyl groups on the electronic properties of the GO ($C_{55}H_{17} + O + (OH)_3 + COOH$, band gap 0.42 eV) structure via the DFT calculation and to control the electronic properties of GO through a careful selection of the chemical radicals adsorbed on its surface. Once upon removing hydroxyl groups the gap energy decreases (0.404 eV), the release of the carboxyl group results in a semimetal–semiconductor transition (1.14 eV). Huang *et al.* [38] hypothesized the oxidation of graphene in O_2 atmosphere or oxygen plasma, then further studied the stability of reduced GO for oxygen density ranging from 6.25% to 50% and found a series of stable oxygen configurations. The relaxation of lattice on the electronic properties was found to be negligible for low O coverage and yet crucial for higher O coverage, respectively. Corresponding bandgaps are found to be a non-monotonic function of oxygen density, with minima at O/C = 11.1% (0.78 eV) and 25% (0.354 eV), and a peak at 25% (1.135 eV). Lahaye *et al.* [29] and Chen *et al.* [39] both theoretically discovered that a higher oxygen content induces a red-shift to obtain a relatively larger band gap, while the latter explained this by that more sp^3 bonds between O and C atoms exist in a graphene sheet with more relatively small sp^2 carbon clusters. Similarly, Savazzi *et al.* [15] also found high-concentration of epoxy groups can buckle the layers and increase the band gap. Jiang *et al.* investigated the electronic structure, work function of catalyst-targeted GO, *etc.* by tuning compositions of epoxy ($-O-$) and hydroxyl ($-OH$) groups. About 40%–50% (33%–67%) coverage and the $-OH:-O-$ ratio of 2:1 (1:1) in the structures lead to both reduction and oxidation reactions for water splitting. More specifically, the GO with a composition with 50% coverage and OH:O (1:1) ratio can work even better as a visible-light-driven photocatalyst [40].

Besides, abundant DFT based research is underway in continuation to clarify characteristics of GO in different structural configurations. For instance, after Mattson's work [36], researchers such as Zhang [41] and Dabhi [42] delivered more and more theoretical insights through theoretically studying GO models with various configurations, such as ether-type GMO, epoxy GMO, zigzag GMO, armchair GMO, and graphene dioxide. More recently, Guilhon *et al.* [43] developed a combined DFT calculation to discuss the GO in terms of those aspects above, consequently derived the favorability for the formation of hydroxyl groups and epoxy groups concerning oxidation and accounted for the antiparallel orientation of hydroxyl groups. Advances of exploration towards physio-chemical properties of GO by DFT means may also refer to other review papers [26,30].

2.5. Interactions

2.5.1. Inter-layers

Duong *et al.* [44] investigated a model of graphite oxide consisting of a hexagonal in-plane structure of graphene with hydroxyl and epoxide groups, different oxidation levels and water content. Through DFT study, they found the graphitic AB stacking order of anhydrous graphite oxide has nothing to do with the oxidation levels, while the AB stacking order gets lost if water molecules enter the highly oxidized graphite oxide interspacing. The hydrogen bonding interaction of layers positively relates to the oxidation level. The calculated interlayer distance of hydrated graphite oxide was 0.73 nm, coinciding with the experimental observations. And Skákalová *et al.* [45] showed that the inclusion of oxygen functional groups on equivalent facing GO layers turned out to dramatically increase the interlayer distances, which was slightly smaller than the observed spacing in the fully oxidized sample if it did not count the steric hindrance.

2.5.2. Inter-objectives

Kovtyukhova *et al.* [46] reported that polarized graphene layers could appear in a dipolar interaction with guest molecules or ions and

thus, found that non-oxidizing Brønsted acids can reversibly intercalate graphite, such as phosphoric (85%), sulfuric ($H_2SO_4-SO_3$ (20%)), dichloroacetic ($Cl_2CHCOOH \geq 99\%$) and alkyl sulfonic acids (*e.g.*, $C_2H_5SO_3H \sim 95\%$, $C_3H_7SO_3H \geq 99\%$, $CH_3SO_3H \sim 99.5\%$). This work further expanded the knowledge about the graphite intercalation compound. Moreover, Cortés Arriagada [47] found that the global and intramolecular local reactivity of the basal plane is improved mainly by hydroxyl groups, with the investigation of changes in the local and global electronic reactivity of oxidized graphene system. For charge-controlled intermolecular interactions, hydroxyl groups allow the physisorption of small molecules, while, active carbon atoms around the functional groups would allow enhancement of the consecutive chemisorption. On the other hand, negatively-charged epoxide, carbonyl, and carboxyl groups allow an increase of intermolecular non-bonded and hydrogen bond interactions with positive centers.

3. Synthesis and Progress

3.1. Methods of solution-processed GO

Brodie reported about the changes of graphite which blended with strong oxidants, and this work can be regarded as the earliest preparation of GO, although he termed the final material as “graphic acid”, which we know now as graphite oxide. So far, the chemistry of graphite oxide has advanced much with efforts of scientists worldwide, especially from the time graphite oxide is known capable of transformation into graphene oxide/graphene as the easily-obtainable precursor. Graphite oxide-derived GO becomes one of the most tangible outcomes of the graphene research in terms of scalable production and commercialization. Such top-down strategy endows the preparation with visible flexibility and relatively low cost of input. Various methods (Table 1) adopting graphite including its expanded form as starting materials become prevailing in laboratories and industries.

Now the Hummers method of 1958 has been widely employed to delaminate and oxidize graphite because of the improved convenience as compared to those methods by Brodie and earlier followers. This way relies on a mixture of sulfuric acid and potassium permanganate (Fig. 2, the first two steps), and the whole procedure comprises three stages: a period for the intercalation of graphite and a simultaneous/subsequent oxidization of the above-mentioned graphite intercalation compounds (GICs); next, to obtain homogeneous GO solution (Fig. 2, the third step), graphite oxide then hydrolyzes and straightforward exfoliates into single sheets via mechanical peeling, like sonication [62], swirling (by shearing stress) [63], or others. Noticeably, many groups prefer using a some-time certain-strength ultra-sonication to completely break up the stacked structure of graphite oxide into GO sheets.

As shown in Table 1, Brodie [2] provided an oxidization mixture recipe of fuming HNO_3 and $KClO_3$ in 1859 before the Hummers', but the method was tedious and not benign. Then Staudenmaier [48] further adjusted the acid component via the addition of H_2SO_4 , rendering the process with fast completion in one single-vessel reaction and thereby improved the processing yield. However, it remained ample space for further cutting off the processing time and reducing the outcome of hazards, such as toxic gases. Years later, did Hummers, and Offeman [10] express the attitude to the previous methods “described in the literature is time-consuming and hazardous”, so they altered the oxidants to a water-free mixture via replacing the HNO_3 , $KClO_3$ with $KMnO_4$. The new process taking less than 2 h with a lower working temperature turned out to be more productive and less hazardous than before. Towards large-scale and safe production of GO, there remained to some extent unsatisfactory problems. Thus, variations were proposed in succession and seem to reach a research summit appearing in these years (2013–2018).

Again, the Hummers method stresses on the three-stage reaction [49]: low-temperature (below 5 °C) intercalation, mid-temperature

Table 1
Method for preparation of GO

Methods	Carbon source	Oxidants	Reaction time for graphite oxide	Temperature/°C	Features
Brodie, 1859 [2]	Graphite	KClO ₃ , HNO ₃	3–4 days	60	Earliest method
Staudenmaier, 1898 [48]	Graphite	KClO ₃ , HNO ₃ , H ₂ SO ₄	96 h	RT	Improved efficiency
Hummers, 1958 [10]	Graphite, ~44 μm	KMnO ₄ , NaNO ₃ , H ₂ SO ₄	<2 h	<20–35–98	Water-free, less than 2 h processing
Fu, 2005 [49]	Graphite	KMnO ₄ , NaNO ₃ , H ₂ SO ₄	<2 h	35	Validated NaNO ₃ unnecessary
Shen, 2009 [50]	Graphite colloidal, ~10 μm	Benzoyl peroxide(BPO)	10 min	110	Fast and non-acid
Su, 2009 [51]	Sonicated graphite, <3000 μm	KMnO ₄ , H ₂ SO ₄	4 h	RT	Large-size GO
Marcano, 2010&2018 [9]	Graphite, ~150 μm	H ₂ SO ₄ , H ₃ PO ₄ , KMnO ₄	12 h	50	Bi-component acids, high yield
Sun, 2013 [52]	Expanded graphite	KMnO ₄ , H ₂ SO ₄	1.5 h	RT–90	Size-confined high yield, safe
Eigler, 2013 [53]	Graphite, ~300 μm	KMnO ₄ , NaNO ₃ , H ₂ SO ₄	16 h	10	High-quality GO
Chen, 2015 [54]	Graphite, 3–20 μm	KMnO ₄ , H ₂ SO ₄	<1 h	<20–40–95	High-yield
Panwar, 2015 [55]	Graphite	H ₂ SO ₄ , H ₃ PO ₄ , KMnO ₄ , HNO ₃	3 h	50	Tri-component acids, high yield
Peng, 2015 [56]	Graphite, >10 μm	K ₂ FeO ₄ , H ₂ SO ₄	1 h	RT	High-yield, less pollution
Rosillo-Lopez, 2016 [57]	Defective arc-discharge carbon	HNO ₃	20 h	RT	Nano-sized GO
Yu, 2016 [58]	Graphite, ~44 μm	K ₂ FeO ₄ , KMnO ₄ , H ₂ SO ₄ , H ₃ BO ₃	5 h	<5–35–95	Less manganite impurity, less acid, high yield
Dimiev, 2016 [59]	Graphite	(NH ₄) ₂ S ₂ O ₈ , 98% H ₂ SO ₄ , fuming H ₂ SO ₄	3–4 h	RT	Lightly oxidized, 25 nm thick, ~100% conversion
Pei, 2018 [60]	Graphite foil	H ₂ SO ₄	<5 min	RT	Electrochemistry support; high efficiency and high yield
Ranjan, 2018 [61]	Graphite	H ₂ SO ₄ , H ₃ PO ₄ , KMnO ₄	>24 h	<RT–35–95	Cool the exothermal reaction to keep safe

RT: abbreviation of room temperature.

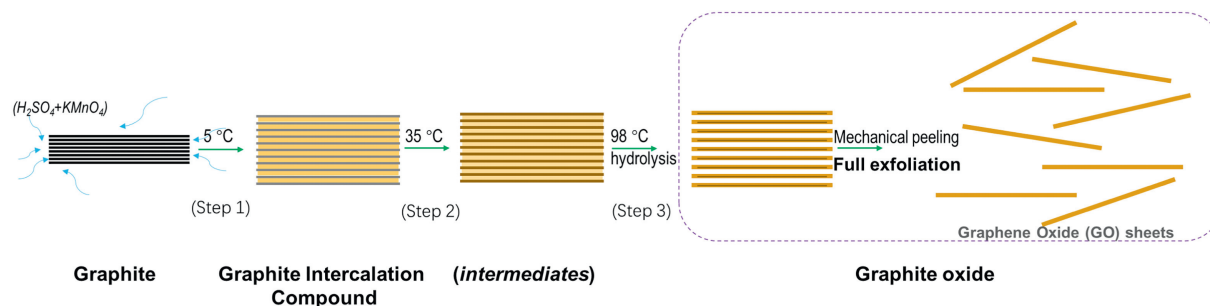


Fig. 2. Schematic diagram of GO preparation via the Hummers–Offeman method [10].

(~35 °C) oxidizing of the GIC and high-temperature (98 °C) hydrolysis of consequences. Fu *et al.* [49] investigated the details of each stage and compared the results of changes of the parameters concerning, e.g., the mass ratios amongst graphite, H₂SO₄ and KMnO₄, and the ways to add water. They concluded the NaNO₃ did not play an important role in adequate oxidization of graphite and suggested the cancellation of the use of NaNO₃. To the best of our knowledge, this probably is the earliest research to clarify the redundancy of NaNO₃ in the Hummers method. These changes not only simplify the process and the composition of discharged water but also alleviate the evolution of toxic gasses, e.g., NO₂/N₂O₄. Notably, these findings were also re-declared or replicated in other respective researches by the Tour group (2010) [9], Fugetsu group (2013) [52], Shi group (2013) [64] and others [51,55,58,59,61].

One other point we highlight is the widely accepted ingredient, the concentric H₂SO₄. It features readiness due to the relatively high boiling point, non-volatility, and low cost. Therefore, it was retained in a majority of modified Hummers method [9,51,53,55,56,58,61], except those changed either the oxidization phase [50] or the raw material [57]. The amount of acid per gram graphite consumed is so largely (>10 ml 95–98% purity H₂SO₄ per gram of graphite) that we have to take seriously the recycling of acid and the avoidance of accidental leakage into the environment. In other words, the post-treatment for the GO purification should have deserved more attention.

Considering the disposing, the overall cost per gram GO obtained remains as high as that of the skyscraper. It undoubtedly hinders the

prosperity of GO applications. However, novel methods with less acid are even scarcely reported.

Sun and Fugetsu [52] conceived a simple principle as shown in Fig. 3. They hypothesized that graphite in varying sizes and textures carried out the oxidations consuming different times: under an identical condition, the intercalation of large graphite is longer than that of the small one, the tightly-structured graphite is likewise beyond the loosely-structured graphite (Fig. 3A). With the implication, they selected commodity expanded graphite of different sizes. They observed the mixture underwent a fast and distinctly volumetric expansion along with continuous magnetic stirring and formed a pale-gray foam-like slurry in the end (Fig. 3B) [52]. The addition of water, therefore, became secure and straightforward without fearing the splashing of acid. Regarding the volumetric expansion as the visible indicator that can reflect the end of a reaction and an improved security measure, they proposed one modified Hummers method with expanded graphite. Not only did the demand for acid (10 ml vs. 13 ml per gram of graphite before) reduce but also a yield of nearly 100% with the graphite of a suitable size (D₅₀ ~ 15 μm) became available in contrast to that with a larger one (D₅₀ ~ 50 μm). Coincidentally, Chen *et al.* [54] found that the flake graphite with sizes in the range of 3–20 μm is converted entirely into GO without additional centrifugation, yet with a routine mass configuration.

The size confinement will differentiate current strategies, in which the total acid might decrease even more than one fifth or one fourth for smaller graphite (<20 μm); for the large-sized graphite, a trade-off between the acid and oxidants needs more investigations.

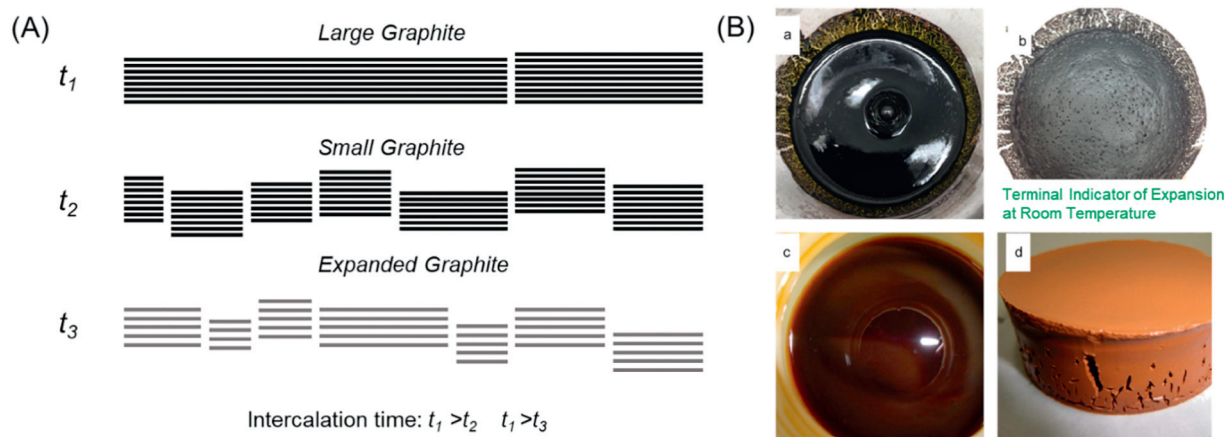


Fig. 3. (A) Difference in intercalation time for graphite with different lateral sizes or vertical textures, adapted from the Sun paper [52]; (B) photos related to the preparation procedure of GO from expanded graphite $\sim 15\ \mu\text{m}$ following the Sun–Fugetsu modified Hummers method: (a) mixing, (b) the form-like slurry after a full expansion ends, (c) a light-brown GO “cake” after high-temperature hydrolysis, (d) a stock solution of GO after purification.

For the latter, there have been a few advances. The mechanisms were evolved by either extending the time of intercalation/oxidation reaction or changing the oxidants. Huang *et al.* [65] introduced one-pot chemical oxidation method by only stirring large graphite ($\sim 500\ \mu\text{m}$) in a mixture of acids and potassium permanganate at room temperature for 72 h, achieving large-area GO sheets with nearly 100% conversion. Similarly, Eigler *et al.* [53] prolonged the low-temperature oxidation of graphite ($\sim 300\ \mu\text{m}$) over 16 h and then stepwise fed diluted sulfuric acid and water for further hydrolysis. Noticeably, the entire process was at a temperature below $10\ ^\circ\text{C}$. A new form of GO as prepared consisted of a hexagonal intact σ -framework of C-atoms, which easily reduced to graphene that is no longer dominated by defects.

In contrast to the variation on time, Peng *et al.* reported a K_2FeO_4 -based modified Hummers method (Fig. 4A), replacing KMnO_4 with K_2FeO_4 due to the higher oxidation potential [56]. Such iron-based oxidation realized a green production of GO in 1 h and enabled the recycling of sulfuric acid and elimination of the emission of heavy metals and toxic gas, as forwarded from the paper. This work ignited the ferric acid-based applications in modifying methods targeting high greenness and conversion efficiency. However, due to the instability of iron when dissolving in acidic aqueous the process as mentioned above did not go well with the repeatability [66]. Even though the difficulty exists, the improvement of iron-based methods did not hang up. Yu *et al.* [58] used K_2FeO_4 to replace KMnO_4 (Fig. 4B) partly and at the same time reduced the acid amount to the same extent as previously

reported in a modified NaNO_3 -free method by Sun and Fugetsu [52], demonstrating great effectiveness except for a longer time *versus* the original Hummers method.

Ultrasound is also capable of reducing both the vertical and lateral size of graphite, so several modifications included the pre-sonication or synchronous sonication over the graphite [57,67]. Rosillo-Lopez and Salzmann [57] pre-sonicated arc-discharge carbon source and then oxidized them in half-concentrated nitric acid to successfully obtain the nano GO. Yang *et al.* [67] proposed their method by taking advantage of the synergistic effect between intercalation and sonication, resulting in a substantial decrease in demand for time and acid as compared to that of the Hummers method. Likewise, pre-oxidization of graphite is also beneficial for synthesis. It enlarges the interlayer spacing, in other words, decrease the vertical size of graphite. It then alleviates the resistance for molecule/ion intercalation into interlayers. Having this strategy, Kovtyukhova *et al.* [68] found incompletely oxidized graphite-core/graphite oxide-shell particles always existed. In 1999, they tried a pre-oxidation with a tri-component mixture H_2SO_4 – $\text{K}_2\text{S}_2\text{O}_8$ – P_2O_5 over graphite followed by the Hummers method, which succeeded in complete oxidation of graphite. So far, this methodology remains inspiring for subsequent research. All the above techniques fell into such a liquid-phase chemical method. And some of them have been used for moderate-scale production of commercial GO despite high time cost and potential environmental risk.

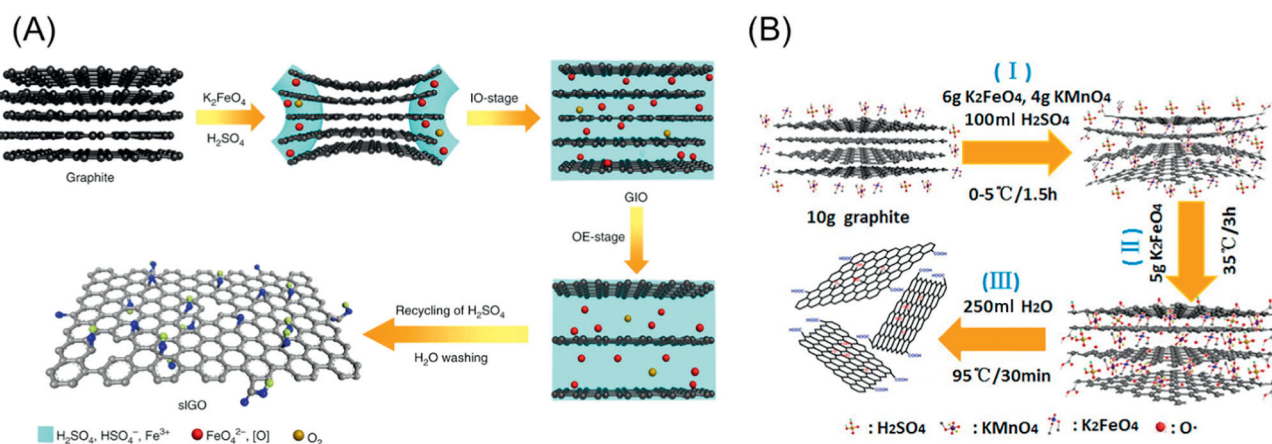


Fig. 4. Iron-based modified methods for the preparation of GO. (A). Synthesis of GO with introducing the oxidant of K_2FeO_4 following the Peng–Gao method [56]; (B). synthesis with involving the K_2FeO_4 – KMnO_4 bi-component oxidant following the Yu–Zhang modified method [58].

We also noticed some other remarkable progress had been made: (1) By electrochemical solution exfoliation. In detail, Pei *et al.* [60] employed a lower-voltage (1.6 V) power to drive sulfate radical into graphite foil to generate intercalated GICs in 98% sulfuric acid and a higher voltage (DC 5 V) to oxidize the obtained GICs into graphite oxide. This method was found based on a mechanism of water electrolytic oxidation towards graphite. Although featuring fast and high yield, somewhat greener than sole liquid-phase chemical oxidation, this method still suffers from the critical use of strong high and concentrated acids. And for industrial scale, a set of specific apparatus is necessary since it cannot work without electric power. (2) By one single-step exfoliation. Shen *et al.* [50] discovered at high-temperature (~110 °C) molten organic oxidant benzoyl peroxide can quickly intercalate and oxidize graphite to form GICs and then through sonication and wash, GICs exfoliate into GO sheets; Dimiev *et al.* [59] developed a water-free tri-component acidic system to fast splitting graphite. The expansion of graphite took place, and the mixture turned out to become a greenish-yellow foam. What they reported was graphene, however, on which were still oxygen-containing functionalities. The devotion of these methods aspires the community of continuous innovation [69, 70], but the security risk remains to hinder the way to production on a large scale.

We find the modern synthesis much depends on the intercalation chemistry of graphite in terms of the size, the time, and the kinds of oxidants. Even though less suffering from explosion risk, and environmental pollution along with the efforts from chemists, all these methods remain inherent limitations associated with acid recycle and post water treatment. However, we keep ourselves with high confidence that these issues can be step-by-step addressed by, for example, using relatively safe yet highly efficient oxidizing intercalation agents, applying electrochemical oxidation or other smarter ways. Besides, the expanded graphite as starting materials could be another way for the turning-around, due to commercial availability, pre-oxidized feature and its potential to further decrease the dose of oxidants,

3.2. Intercalation of graphite precursors

Synthesis of GO mainly follows two preparative routes: treating graphite in a mixture of acid with an oxidizing agent or electrochemically treating graphite in contact with an acid solution. Both these processes comprise three common steps [71–73]. First, the fast formation of stage-1 graphite intercalation compound (GIC) from graphite once attached in acidic oxidizing medium, namely, graphite bisulfate (Scheme 1); next, the conversion of low-stage GIC into oxidized graphite within a relatively long period; and the last step is that the above graphite converts into single/fewer-layered GO after exposure to water.

Intercalation and oxidization with the oxidant KMnO_4 [74] are accessible to implementation, and the reaction occurs by Scheme 1:

Undoubtedly, full intercalation is a prerequisite and plays a crucial role in exfoliating the stacked structure of graphite into single layers. Strong Brønsted acids, such as H_2SO_4 , HNO_3 , and HClO_3 , have manifested to form staged graphite intercalation compounds [73,75,76]. Notably, due to effectiveness and high availability, sulfuric acid has become for long one of the most-frequently used intercalants for the graphite lattice expansion and has gained much attention from thousands of literatures [2,9,10,48,49,51–53,55,56,59–61,77].

On the one hand, the concentration of acid matters. An anodic electro-oxidation report suggested the level of acid inversely affects consequent stage index of GIC [78], that means to achieve GO/GIC at lower stage indexes requires a higher level of acid. It is consistent with the current situation in which various syntheses still have high desire for extremely concentrated acids. On the other, at least one additive

oxidant is of great importance, e.g., KMnO_4 [74] or HNO_3 . The intercalation of H_2SO_4 into graphite can be accomplished by chemical oxidation in the presence of an oxidant in addition to electrochemical oxidation, but both of them occur with the same reaction mechanism, confirmed by measuring the potential of the carbon electrode by Inagaki, Iwashita, and Kouno [72]. They further demonstrated, the relation between the onset potential for stage transformation of GIC and the upper limit of saturated potential governs the intercalation reaction; the oxidation of graphite by acids leads to the accumulation of surface potential, that is oxidant molecules get reduced by the electron extracted from the carbon host (e.g., $\text{Mn}^{7+} \rightarrow \text{Mn}^{3+}$, $\text{NO}_3^- \rightarrow \text{NO}_2^-$), and if the potential goes beyond a threshold then the intercalation starts [72,79–81].

Besides, the structural properties of graphite strongly influence the intercalation reaction [79]. The degree of graphitization and the crystal-lite size along *c*-axis can affect the formation of stage-1 GIC structure and, thus, was experimentally found to be 0.2 and 20–30 nm as the criteria values, respectively [79,82]. Meanwhile, nanotexture affects the oxidation rate during the intercalation, too; as a consequence, it necessitates the high-percentage exposure of the edge surface of graphite in a reaction medium [82,83].

Accompanied by oxidizing the side-edge exposed carbon, some oxidants are capable of directly etching outer-layer surface carbon and thus form micro-passages/structural defects parallel to *c*-axis. Shin *et al.* [84] examined highly ordered pyrolytic graphite treated in a 100 °C $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture for different times and found that acid directly penetrated from the outer to inner graphitic layers, resulting in nitration and sulfonation. Such kind of structural variation conversely promotes the reactions. To some extent, this opinion agrees to that of a previous work by Rodríguez *et al.* [73], who illustrated that the oxidation rate of graphite negatively correlates with the size of graphite layers and the structural perfectness of carbon arrangement. For more intercalation-mechanistic research about graphite by other acids or chemicals, a recent review delivered by Xu *et al.* [85] is suggested although the main focus is on the rechargeable metal-ion batteries application with GIC.

3.3. Exfoliation of graphite to GO

The way to GO production remains the graphite oxide route [86] as it was a hundred years ago. Flaky graphite is the typical raw material and turns into semi-tightly stacked graphite oxide *via* intercalation along with oxidation. Subsequently comes the mono-sheet exfoliation, which is often a special process, such as sonication, stirring/shaking, homogenization, *etc.*

3.3.1. In-lab prerequisite: sonication

If the sonication (directionless force) were absent, abundant research relative to GO would have gone nowhere. As discussed above it has become one of the most straightforward measures for graphite exfoliation [7,64,86–88]. Sonication featuring magnetoelectrically-induced high-frequency soundwaves (>20 kHz) in the liquid medium, produces the cavitation to quickly split apart graphite oxide into single yet small sheets and shorten the time usage significantly. Applying a mild sonication (low power input, short time) can avoid over-cracking of graphite during the processing [86,89]. Zhao *et al.* succeeded in preparing GO sheets with the area up to 40000 m^2 with such sonication as well as mild oxidation and additional centrifugation [89].

3.3.2. Towards scalability: shaking/stirring/homogenization/vortex turbulence/micro-fluidization

In comparison to the sonication, shaking, stirring, or others likewise can deliver less destructive energy. Especially for the shaking and stirring, they have become textbook-fashioned measures in conducting



Scheme 1. Intercalation and oxidization with the oxidant KMnO_4 .

the preparation towards large sheets of GO because of the great potential in a wide span of applications [86]. In this aspect, a review published recently has demonstrated a detailed discussion, specific to the production of large-sized GO [87]. Some reports mentioned mono-layer dispersed moderately-sized GO could be obtained straightforwardly with only stirring, although subject to that dimension of raw graphite [52, 90]. In the meantime, it has stepped much farther for the production of GO beyond the lab, since such engineered exfoliation has already been practically available to satisfy the long-lasting mass-loading operation condition. For example, homogenization can well slip graphite oxide in the in-plane direction, forming the GO layers with relatively large sizes [91]. Besides, graphite precursors can also be sheared into single-layer GO by concentric cylinders-based Taylor vortex flow [63] or micro-fluidized turbulence flow [92], and the former declared to exfoliate large-area single- or few-layer GO with high yields (>90%).

3.3.3. One more: ball milling

Differently, the ball milling depends on the impact and frictional forces resulting from the relative motion between the ball and the graphite precursors. It is a reproducible and green approach to large-scale and low-cost of GO. However, a large proportion of ball-milling based research is graphene-making related. Only a few works are concerning about GO.

Fu *et al.* [93] showed the ball milling of graphite oxide prepared by the modified Hummers method using water as the medium. Along with the graphite oxide being thoroughly exfoliated to GO sheets after being ball-milled, the resultant GO sheets were found with less oxygen-containing functional groups such as carbonyl and epoxy groups on the surface which got effectively removed through the mechanochemical process. It is definitely not desirable for specifically GO-oriented preparation. Remarkably, Dash *et al.* [94] adopted an in-house designed horizontal dual-drive planetary ball milling system to directly delaminate graded graphite into GO with eliminating any addition of solvents, catalysts and harsh chemicals. As compared, the 16-hour milling was selected as the optimized condition for GO preparation concerning per the degree of oxidation, time and energy consumption. Since this work did not mention much about the yield of single layers GO, there might exist a further space to modification.

3.4. Key factors influencing the mass synthesis of GO

To date, the high price of commercially highly-pure, fully-exfoliated, single-layered GO hints the cost of production is still the tiger in the road, not to mention to incorporate with downstream industries and serve the daily human life. Excepting from the essential factor of undeveloped marketing demand, we'd better frankly face the underlying difficulties of GO production, that hinders the in-depth development.

3.5. Ambiguity in fundamental theories and methods

Not only there is no consensus on its structure now [95], but also the synthesis is still incompletely understood [45]. As introduced above, it is true that the structure model of GO is still in dispute, although some of these models have gained wide acceptance. However, it is optimistic about the precise unraveling of its structure in a short time as long as the innovation in instrumentation and characterization goes on, for instance, the cryo-electron microscopy. Clarification of the structure will help build up the concept of GO, and also perfect the synthesis procedure for multiple purposes.

As known, GO can be made from graphite following any conventional method at any configuration of the experimental parameters, with ignoring the yield. Stemming from the environmental and cost controlling requirements, innovative scientists visit the ancient preparation time after time. We continuously achieved new inspirations in terms of reaction time, temperature, additives, *etc.* On one side, these works optimize the parameters of synthesis and further advance the

research of this field. On the other, such learning certainly extends the course to precisely transferable operation conditions. Take the supplementary use of sonication as an example. Yuan *et al.* [96] re-examine the synthesis progress, particularly identifying the oxidation as a three-step reaction, and consequently introduced ultrasonic treatment over such the rate-limiting procedure, gaining higher efficiency, while it was three years before Yang *et al.* [67] had already reported a similar methodology yet with expanded graphite as the resource. Such a time gap reflects from the side that accelerating the recognition towards basis knowledge of GO is still an essential direction for mass production.

3.6. Technical factors

Selecting and controlling of size dimensions inclusive of lateral size and vertical thickness of raw graphite are still the most influential technical factors. GO is the derivative of graphite suffering from intercalation and oxidation. And the size differences of natural graphite have demonstrated in no small extent to influence the final GO products in terms of sizes, structures, yields, or even relative applications [52,97]; even further for one-pot synthesis of GO, the resulted sheets may appear with a multimodal distribution of size, and a subsequent size fractionation turns out as a consequence [39,98–103]. Thus, the variation of procedure-dependent sizes from batch to batch is still a strongly suppressive factor for mass scalability, not to mention the lengthy but tedious post-treatments [64] and the room-temperature structural metastability [24] of GO.

4. Prospective

From the static to a dynamic model, with theoretical speculation to experimental observation, the time dependence has been taken into account for intrinsic property investigation of GO. Fascinating measures and characterization are in continuity on the way to development. Therefore, it is expected that complete characters of the GO shall become fully unraveled and universally acceptable, consequently beneficial for understanding and guiding in-depth applications.

Research about the synthesis of GO now is at such a turning plateau where the Hummers method (concentrated sulfuric acid) dominates as the mainstream strategy. Greener and more effective breakthroughs are much desirable, calling more contributions from more intelligence with multi-discipline field background. Moreover, real synthesis of GO has to tackle the problems to the uniformity of sizes and properties. It is unrealistic for downstream industries to embrace GO products from upstream entities having varying performances.

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