Supplementary Information

Role of Peroxide Ions in Formation of Graphene Nanosheets by Electrochemical Exfoliation of Graphite

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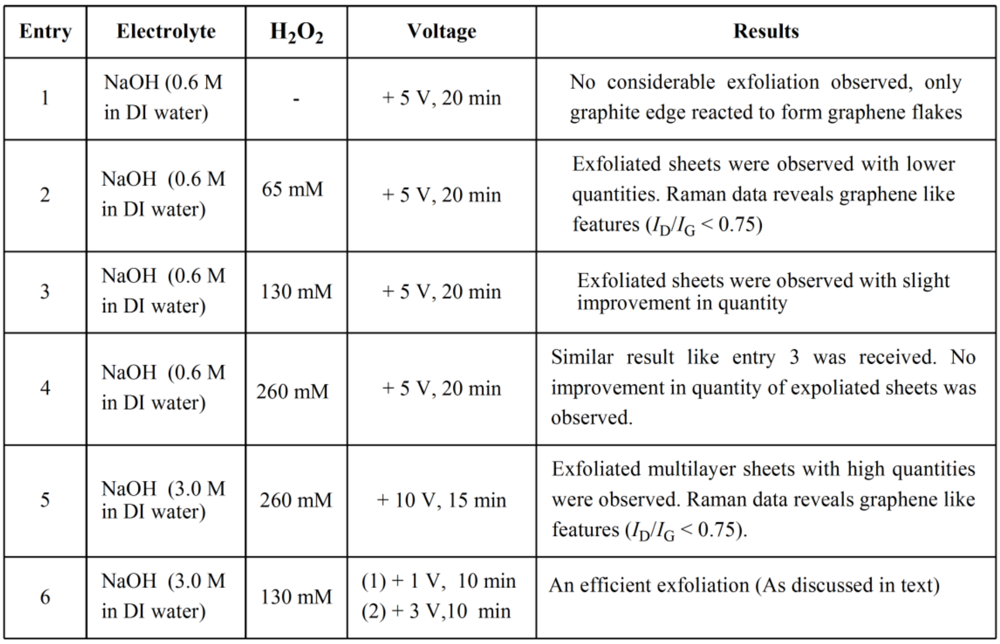
Contents

Screening studies of exfoliation



Entry	Electrolyte	H_2O_2	Voltage	Results
1	NaOH (0.6 M in DI water)	-	+ 5 V, 20 min	No considerable exfoliation observed, only graphite edge reacted to form graphene flakes
2	NaOH (0.6 M in DI water)	65 mM	+ 5 V, 20 min	Exfoliated sheets were observed with lower quantities. Raman data reveals graphene like features ($I_D/I_G < 0.75$)
3	NaOH (0.6 M in DI water)	130 mM	+ 5 V, 20 min	Exfoliated sheets were observed with slight improvement in quantity
4	NaOH (0.6 M in DI water)	260 mM	+ 5 V, 20 min	Similar result like entry 3 was received. No improvement in quantity of expoliated sheets was observed.
5	NaOH (3.0 M in DI water)	260 mM	+ 10 V, 15 min	Exfoliated multilayer sheets with high quantities were observed. Raman data reveals graphene like features ($I_D/I_G < 0.75$).
6	NaOH (3.0 M in DI water)	130 mM	(1) + 1 V, 10 min (2) + 3 V,10 min	An efficient exfoliation (As discussed in text)

Table S1. Screening studies of electrochemical exfoliation of graphite

Our initial electrochemical exfoliation experiments began by the examination of an aqueous 0.6 M NaOH electrolyte at a working bias voltage of +5 V (Table S1, entry 1). Only graphite edge reacted to form very poor yield of graphene flakes. To develop a promising system for optimal exfoliation efficiency, we adopt an idea of activating H_2O_2 by reacting with aqueous NaOH electrolyte. Therefore in the next attempt, we have manipulated our initial experimental conditions by adding 65 mM of H_2O_2 and found that this system is superior over our initial NaOH/H_2O system (Table S1, entry 2). We have achieved a remarkable improvement in the yield of graphene sheets formation however still prominent yield was not obtained. To further improve the exfoliation efficiency, a systematic study was conducted by either manipulating the molarity of H_2O_2 (Table S1, entries 3, 4) or the concentration of NaOH solution/working bias voltage towards higher magnitudes (Table S1, entry 5). However only the studies devoted to the manipulation of NaOH concentration/working bias voltage could yields higher quantities of multi-layer graphene sheets. Finally, we have successfully optimized the exfoliation conditions as described in the text (Table S1, entry 6).

Conclusions: We observed that only NaOH electrolyte is inefficient for exfoliation of graphite (Table S1, Entry 1). However, this electrolyte in presence of H_2O_2 exhibits ideal exfoliation efficiency and produces high quality graphene nanosheets by applying optimized reaction conditions (Table S1, Entry 6). Therefore, H_2O_2 is crucial for ideal exfoliation efficiency. There is no much difference in the quality of produced graphene by either changing working bias voltage and concentration of NaOH electrolyte. However layer number of produced graphene is variable.

Optimized working bias voltage: When the working bias voltage is 10 V, the exfoliation process is fast and multilayer graphene nanosheets were observed (Table S1, Entry 5). At the working bias voltage around 3 V, an efficient exfoliation was observed may be due to the presence of higher electrolyte quantity (3.0 M aqueous solution) and AFLG nanosheets obtained in higher quantities (Table S1, Entry 6). Therefore the optimized working bias voltage is at around 3V.

Optimized electrolyte concentration: Studies on the quantity of H_2O_2 reveals that 130 mM is enough for ideal exfoliation efficiency. A poor yield was observed at electrolyte concentration of aqueous 0.60 M NaOH, 130 mM of H_2O_2 and working bias voltage of +5 V (Table S1, Entry 2). Manipulation of the electrolyte concentration and bias voltage towards higher magnitudes (3.0 M NaOH, +10 V respectively) leads to the formation of higher quantities of multilayer graphene sheets (Table S1, Entry 5). Higher electrolyte concentration (aqueous 3.0 M NaOH) with 130 mM H_2O_2 and low working bias voltage (+ 1 V for 10 min, + 3 V for 10 min) was found to be an optimized condition for ideal exfoliation efficiency (Table S1, Entry

6).

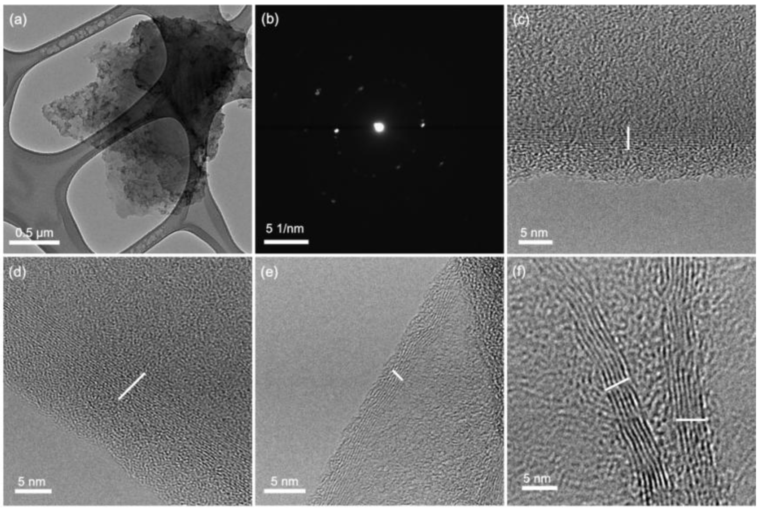


Figure S1. TEM characterizations of multilayer graphene: (a) low-magnification TEM image on lacy-carbon; (b) electron diffraction patterns of carbon lattice; (c)-(f) are HR TEM images of multilayer graphene. Conditions: Aqueous 1.2 M NaOH (75 ml), 1.0 ml H_2O_2 at a working bias voltage 10 V for 15 min.

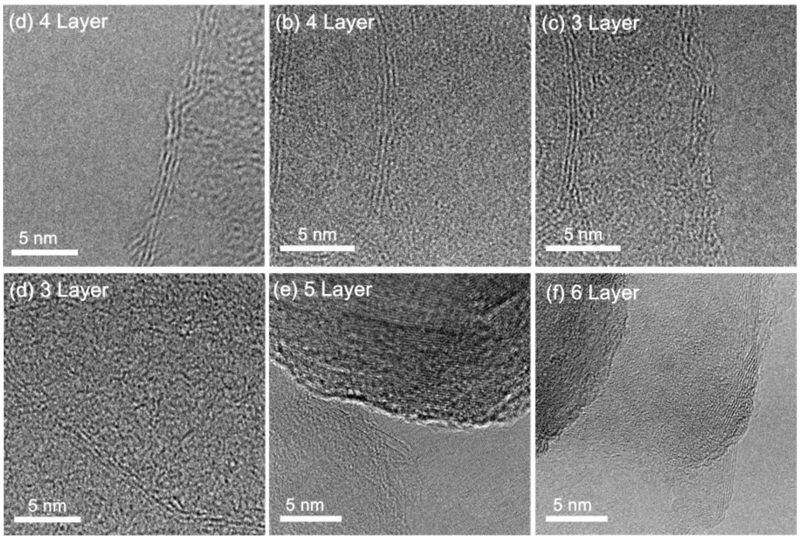


Figure S2. HR-TEM images of AFLG nanosheets showing layer numbers 3-6. AFLG prepared from electrochemical exfoliation of graphite by employing aqueous 3.0 M NaOH, 1.0 ml H_2O_2 at a working bias voltage of 1 V for 10 min, 3 V for 10 min.

Cyclic voltammetry studies: The cyclic voltammetry (CV) studies of AFLG were conducted using three-electrode system (glassy carbon electrode (GCE), platinum electrode and Ag/AgCl as reference electrode) in aqueous 6.0 M KOH at a scan rate of 50 mV/s. The CV results of bare GCE and AFLG-loaded GCE presented in Figure

S3. The bare GCE shows no electrochemical reaction. The both oxidation and reduction peaks observed in CV studies of AFLG was caused by electrochemical reactions of oxygen functional groups present in AFLG. The total charge transfer of the AFLG-loaded GCE array is considerably greater than GCE evidenced by CV curves area comparison. The CV results of AFLG are similar to few-layer graphene reported in the literature.[1] The CV studies prove that exfoliated material is graphene.

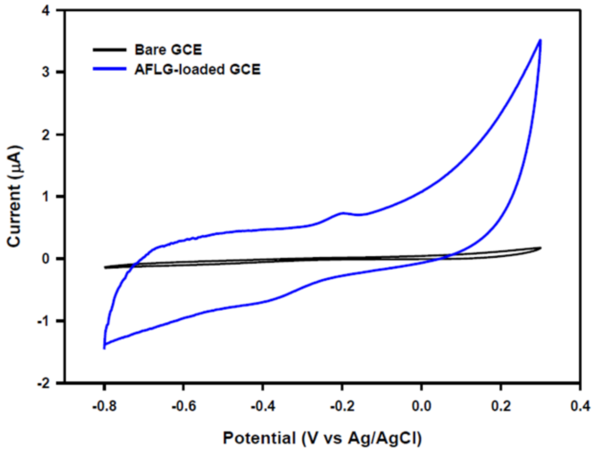


Figure S3. Cyclic voltammograms of bare GCE and AFLG-loaded GCE in aqueous 6.0 M KOH solutions at a scan rate of 50 mV/s.

Thermo gravimetric analysis (TGA): The TGA of graphite and exfoliated AFLG was performed under nitrogen atmosphere with temperature increasing rate 10 ^{o}C/min (Figure S4). The TGA curve of graphite shows almost no mass loss from room temperature to 500 ^{o}C, suggests that almost negligible amounts of functional groups present in graphite. Whereas TGA curve of AFLG shows almost 5.5% mass loss until the temperature reached 500 ^{o}C, presumably due to the decomposition of oxygen functional groups present in AFLG. The AFLG displays good thermal stability and the slight mass loss below 500 ^{o}C suggesting few oxygen functional groups introduced during electrochemical exfoliation. The TGA results are good agreement with XPS results and literature.[2] The TGA results prove that graphene is producing by proposed electrochemical exfoliation strategy.

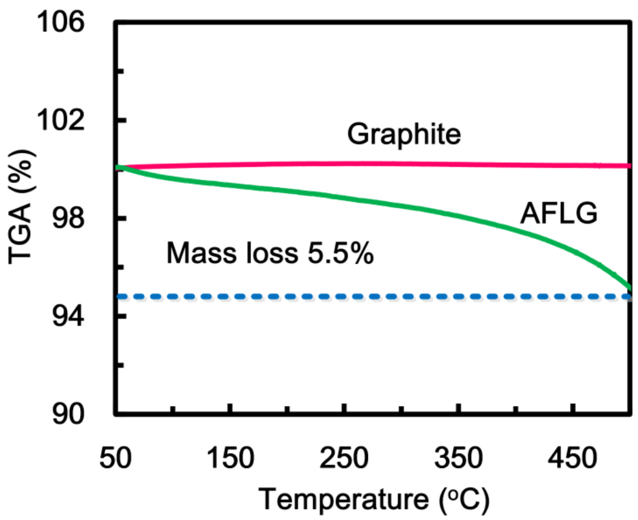


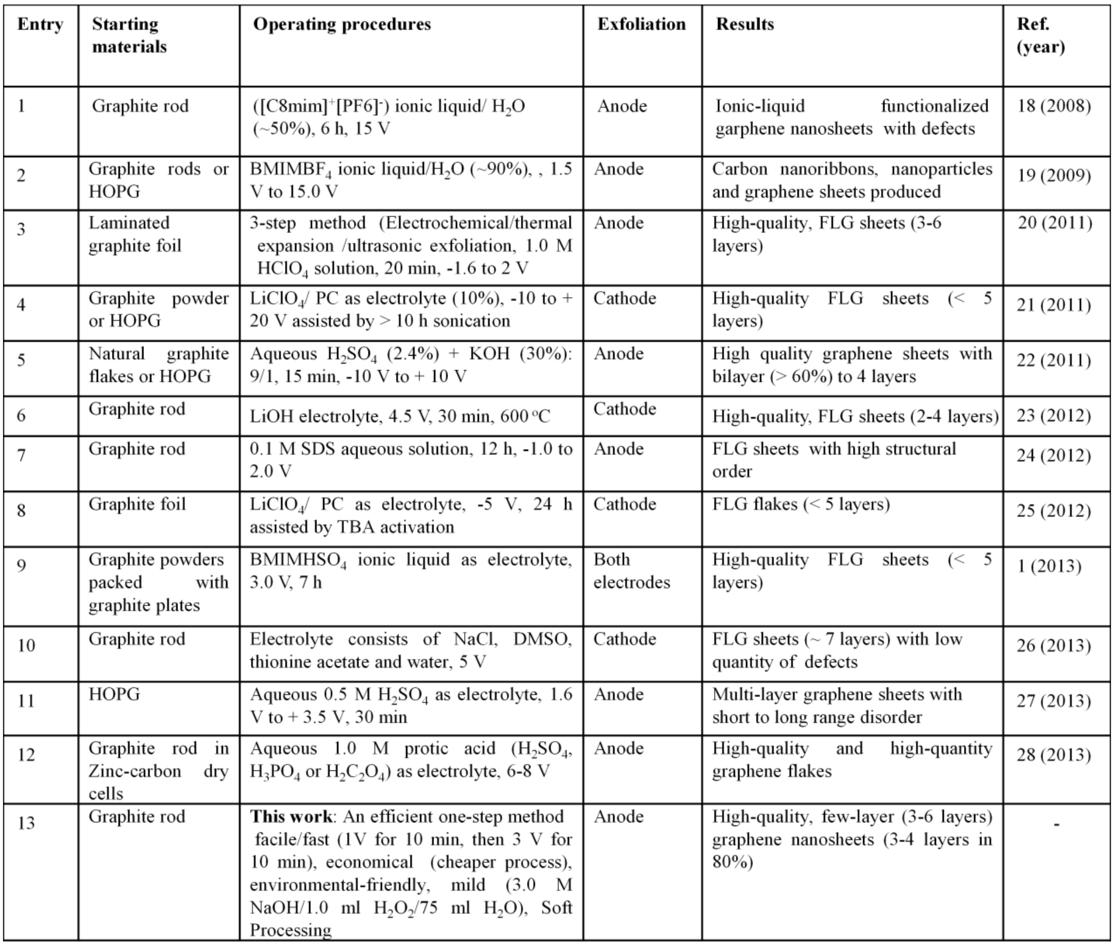
Figure S4. TGA curves of graphite and AFLG obtained from raising the temperature at a rate of 10 °C/min.

Comparative study: Since the first successful micromechanical exfoliation of graphite, several approaches such as CVD, solution-process, sonochemical liquid-phase exfoliation, volatile agents promoted intercalation-expansion are reported. Micromechanical method produces very small quantities of graphene. Despite the advantages of CVD methods, ultrahigh vacuum and/or high temperature (1000 °C), expensive substrates are main obstacles. Solution-process based exfoliation methods proceeds through either chemical route and/or thermal annealing. Time-consuming, defected graphene formation is main drawbacks of this process. Further, starting material GO synthesis needed additional Hummers oxidation step. Sonochemical liquid-phase exfoliation, volatile agents promoted intercalation-expansion methods produce highly defected graphene. Usage of high temperature, additional solvents and/or reagents/intercalants is further make the process complicated. Most of the chemical methods are suffering from environmental concerns with irrespective of the method. Thus, recently direct electrochemical exfoliation methods are proposed as cheaper and greener strategies for the synthesis of high-quality graphene (Table S2).

Entry	Exfoliation Method	Operating procedures	Results	Ref.
1	Mechanical	Etching of HOPG in oxygen plasma, then peeling with scotch tape	High-quality, monolayer to few layer graphene in very small quantities	3
2	CVD	Graphene growth on copper substrates at 1000 °C using methane at 500 mTorr and then hydrogen at 400 mTorr pressure	Large area graphene films grow on copper substrates with > 95% monolayers	4
3	CVD	Graphene growth on copper substrates at 1000 °C using hydrogen at 90 mTorr and then a mixture of hydrogen, methane at 460 mTorr pressure, 30 min	Roll-to-roll formation of monolayer 30-inch graphene films on copper substrates	5
4	CVD	Graphene growth on copper substrates at 1000 °C using methane at 500 mTorr and then hydrogen at 400 mTorr pressure	Large area graphene (monolayer to multiple layers) films grown on copper substrates	6
5	Solution-process	Hydrazine hydrate assisted reduction of GO in water at 100 °C , 24 h	Thin graphene sheets with most of the oxygen removed	7
6	Solution-process	Filtration of GO through a mixed cellulose ester membrane (25 nm pore size) under vacuum	Monolayer to few layer graphene sheets	8
7	Solution-process	Treatment of GO by $NaBH_4$ (80 °C, 1 h) and H_2SO_4 (180 °C, 12 h) followed by thermal annealing at 1100 °C in argon/hydrogen, 15 min	Pure graphene sheets with effective restoration of π-network	9
8	Solution-process	GO deposited on APTES treated substrates dried at 80 °C in vacuum oven followed by chemical (hydrazine hydrate) 40 °C, 18 h or thermal annealing (400 °C, 3 h, 100 °C, 3 h)	Highly reduced thin graphene sheets	10
9	Solution-process	GO reduction by ethanol vapors at 600-1000 °C under a mixture of argon, hydrogen	Highly integrated graphene sheets	11
10	Sonochemical liquid-phase	A dispersion of sieved graphite powder in NMP was subjected to sonication, 30 min	High-quality, monolayer graphene sheets with 12 wt% yield	12
11	Sonochemical liquid-phase	A dispersion of graphite in aqueous sodium cholate solution sonicated, 140 min	Monolayer to few layer graphene sheets stabilized by sodium cholate	13
12	Sonochemical liquid-phase	Graphene sheets sonicated in chloroform, then added water and repeated sonication	Monolayer, ultrathin and highly hydrophobic graphene sheets	14
13	Volatile agents intercalation	To the heated (1000 °C) and grinded expandable graphite, added oleum/TBA, sonicated in DMF	High-quality, monolayer graphene sheets suspended in organic solvents	15
14	Volatile agents intercalation	GIC obtained from mechanical stirring of graphite powder and potassium-napthalene solution was further stirred in NMP, 24 h	Stable dispersions of negatively charged graphene sheets and ribbons	16
15	Volatile agents intercalation	One-step exfoliation by comprising intercalation/thermal expansion process using fluorinated GIC, 5-6 h	Sonication of ESEG dispersions in organic solvents or water with SDBS surfactants	17
16	Electrochemical	Ionic liquids, acids, Li ions, Na^+/DMSO, SDS intercalation methods	Recently developed cheaper and greener strategies	*

Table S2. The summary of previously published methods on graphene exfoliation HOPG: Highly oriented pyrolytic graphite; CVD: Chemical vapor deposition; GO: Graphene oxide; APTES: (3-Aminopropyl)triethoxysilane; TBA: Tetra-*n*-butylammonium; GIC: Graphite intercalation compound; ESEG: Easily soluble expanded graphite; SDBS: Sodium dodecyl benzene sulfate; SDS: Sodium dodecyl sulfate; DMSO: dimethyl sulfoxide; DMF: Dimethyl formamide; NMP: N-methyl pyrrolidone; *: See table 2

The electrochemical exfoliation, itself has been well established. However, the reported exfoliation methods utilize either strong oxidants such as $LiClO_4$ (Table S3, SI, entries 4, 8), H_2SO_4 (Table S3, SI, entries 5, 11-12) as electrolytes and high working bias voltages (Table S3, SI, entries 1-2, 4-5) which may disrupt the exfoliated graphene π-network by damaging the honeycomb lattices of graphene. Additionally, impurities may form by side reactions. The usage of high reaction temperature such as 600 ^{o}C (Table S3, SI, entry 6), over reaction time such as 6 h -24 h (Table S3, SI, entries 1, 7-9), additional steps either by prolonged sonication (Table S3, SI, entry 4) or TBA-assisted electrochemical activations (Table S3, SI, entry 8) or thermal expansion/ultrasonic exfoliation (Table S3, SI, entry 3), expensive/large quantities of reagents (Table S3, SI, entries 1-2, 9) and additional reagents (Table S3, SI, entry 10) are further diminish the process liability by increasing process cost and low-quality graphene production. The hazardous/toxic reagents used in these methods further pollute the environment. Taking these shortcomings into an account, we have proposed soft processing approach for the synthesis of high-quality, AFLG nanosheets by electrochemical exfoliation of graphite anode. A systematic analysis and comparison of our proposed soft processing approach with reported electrochemical methods reveals the efficiency of our methodology. The major advantages of present soft processing approach are demonstrated in the conclusion part of text. Therefore, the proposed soft processing approach is superior over reported methods.



Entry	Starting materials	Operating procedures	Exfoliation	Results	Ref. (year)
1	Graphite rod	([C8mim]$^+$[PF6]$^-$) ionic liquid/ H_2O (~50%), 6 h, 15 V	Anode	Ionic-liquid functionalized garphene nanosheets with defects	18 (2008)
2	Graphite rods or HOPG	$BMIMBF_4$ ionic liquid/H_2O (~90%), , 1.5 V to 15.0 V	Anode	Carbon nanoribbons, nanoparticles and graphene sheets produced	19 (2009)
3	Laminated graphite foil	3-step method (Electrochemical/thermal expansion /ultrasonic exfoliation, 1.0 M $HClO_4$ solution, 20 min, -1.6 to 2 V	Anode	High-quality, FLG sheets (3-6 layers)	20 (2011)
4	Graphite powder or HOPG	$LiClO_4$/ PC as electrolyte (10%), -10 to + 20 V assisted by > 10 h sonication	Cathode	High-quality FLG sheets (< 5 layers)	21 (2011)
5	Natural graphite flakes or HOPG	Aqueous H_2SO_4 (2.4%) + KOH (30%): 9/1, 15 min, -10 V to + 10 V	Anode	High quality graphene sheets with bilayer (> 60%) to 4 layers	22 (2011)
6	Graphite rod	LiOH electrolyte, 4.5 V, 30 min, 600 °C	Cathode	High-quality, FLG sheets (2-4 layers)	23 (2012)
7	Graphite rod	0.1 M SDS aqueous solution, 12 h, -1.0 to 2.0 V	Anode	FLG sheets with high structural order	24 (2012)
8	Graphite foil	$LiClO_4$/ PC as electrolyte, -5 V, 24 h assisted by TBA activation	Cathode	FLG flakes (< 5 layers)	25 (2012)
9	Graphite powders packed with graphite plates	$BMIMHSO_4$ ionic liquid as electrolyte, 3.0 V, 7 h	Both electrodes	High-quality FLG sheets (< 5 layers)	1 (2013)
10	Graphite rod	Electrolyte consists of NaCl, DMSO, thionine acetate and water, 5 V	Cathode	FLG sheets (~ 7 layers) with low quantity of defects	26 (2013)
11	HOPG	Aqueous 0.5 M H_2SO_4 as electrolyte, 1.6 V to + 3.5 V, 30 min	Anode	Multi-layer graphene sheets with short to long range disorder	27 (2013)
12	Graphite rod in Zinc-carbon dry cells	Aqueous 1.0 M protic acid (H_2SO_4, H_3PO_4 or $H_2C_2O_4$) as electrolyte, 6-8 V	Anode	High-quality and high-quantity graphene flakes	28 (2013)
13	Graphite rod	**This work**: An efficient one-step method facile/fast (1V for 10 min, then 3 V for 10 min), economical (cheaper process), environmental-friendly, mild (3.0 M NaOH/1.0 ml H_2O_2/75 ml H_2O), Soft Processing	Anode	High-quality, few-layer (3-6 layers) graphene nanosheets (3-4 layers in 80%)	-

Table S3. The summary of previously published works on electrochemical exfoliation of graphite and comparison with our methodology; FLG: Few-layer graphene; PC: Propylene carbonate; $BMIMHSO_4$: 1-butyl-3-methyl imidazolium bisulfate; $BMIMBF_4$: 1-butyl-3-methyl imidazolium tetrafluoroborate ($[C_8mim]^+[PF_6]^-$): 1-octyl-3-methyl imidazolium hexafluorophosphate

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