

Tutorial review

Exfoliation of layered materials using electrochemistry

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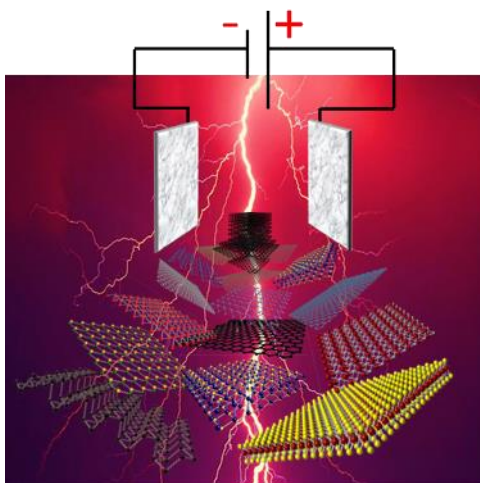
Abstract

After the isolation and discovery of the extraordinary properties of graphene, a tremendous interest has been directed towards other layered materials. Known also as van der Waals solids, these materials can offer a much wider range of properties than graphene when exfoliated to single or few-layer sheets with benefits for several different applications. Similarly to graphene, a key aspect for the actual application of these materials is certainly represented by the development of efficient fabrication methods able to produce large quantity of individual sheets of good quality. The electrochemically-assisted exfoliation of bulk crystals represents one of the most promising methods for mass-production of graphene and also other 2D materials sheets due to the mild operational conditions, short time, simple

instrumentations and high yield of individual layer obtained. We review here the latest and most representative electrochemically-assisted methods of exfoliation of layered materials categorized by the intercalation ion employed. A separate section is also included and dedicated to the recent bipolar electrochemical procedures which through different mechanistic avenues demonstrated recently efficient reduction of both lateral size and thickness of bulk particles of layered materials dispersed in solution. A summary discussion along with future perspective will be also provided in the last section.

Keywords: 2D materials, electrochemical preparation, exfoliation, bipolar electrochemistry

TOC



Key learning points

- Basic principles of electrochemical exfoliation
- Experimental conditions for exfoliation of 2D materials
- Basic principles of bipolar electrochemistry
- Use of bipolar electrochemistry for exfoliation and size reduction of layered bulk materials

1. Introduction

van der Waals solids have a crystal structure in which a multitude of one-atom-thick or polyhedral-thick neutral layers are stacked one on top of the others and held together by weak van der Waals forces.¹ Interactions within each layer are strong ionic or covalent bonding. Graphite represents a perfect example of van der Waals solid being formed by the stacking of one-atom thick graphene layers of sp^2 hybridized carbon atoms covalently arranged in a honeycomb lattice structure.² Several other 2D layered materials exist in nature or that can be easily synthesized, such as transition metal dichalcogenides (TMDs) with general formula MX_2 , MX or M_2X_3 ,^{3,4} black phosphorous,⁵ boron nitride,⁶ transition metal oxides⁷ and hydroxides,⁸ mono-atomic silicon,⁹ germanium,¹⁰ arsenic,^{11,12} antimony^{11,12} and bismuth,^{12,13} metal carbides and nitrides.¹⁴ (Figure 1).

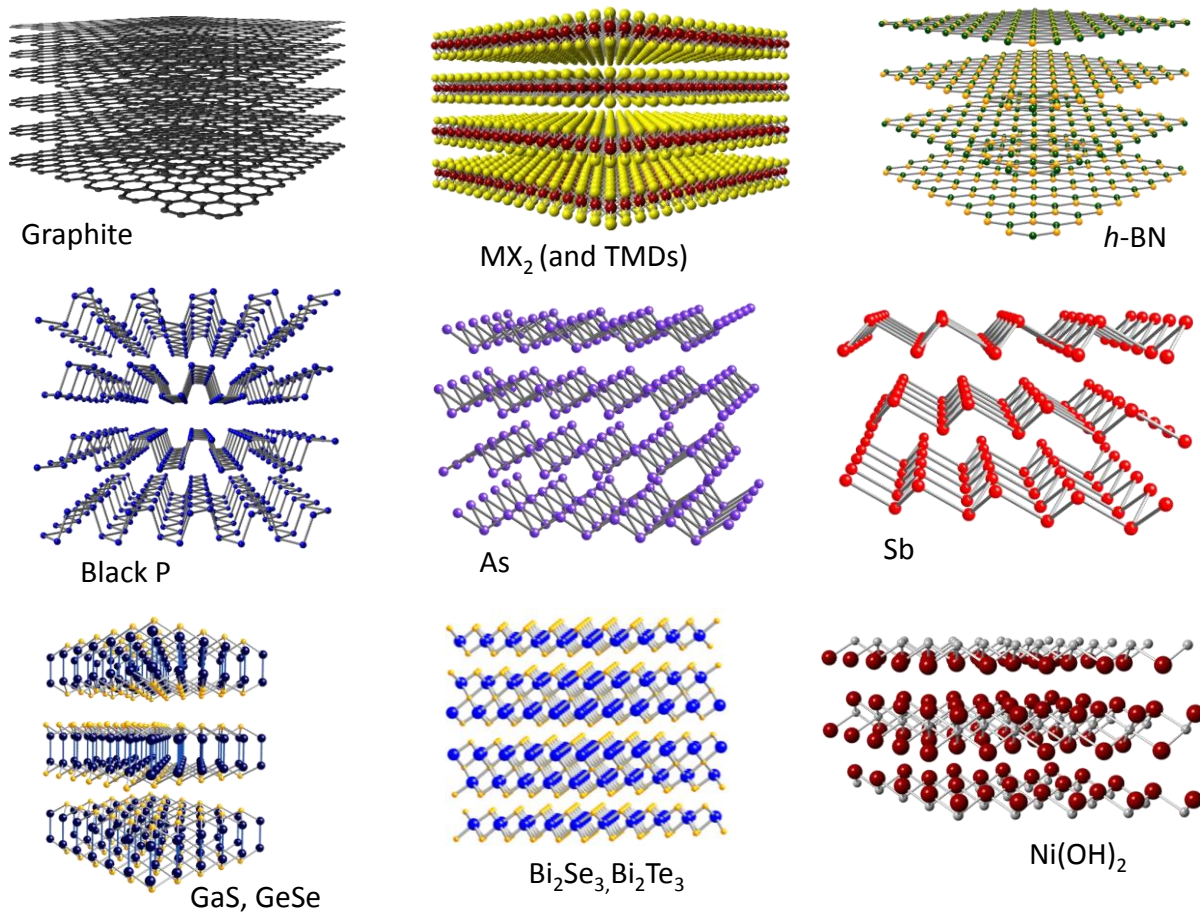


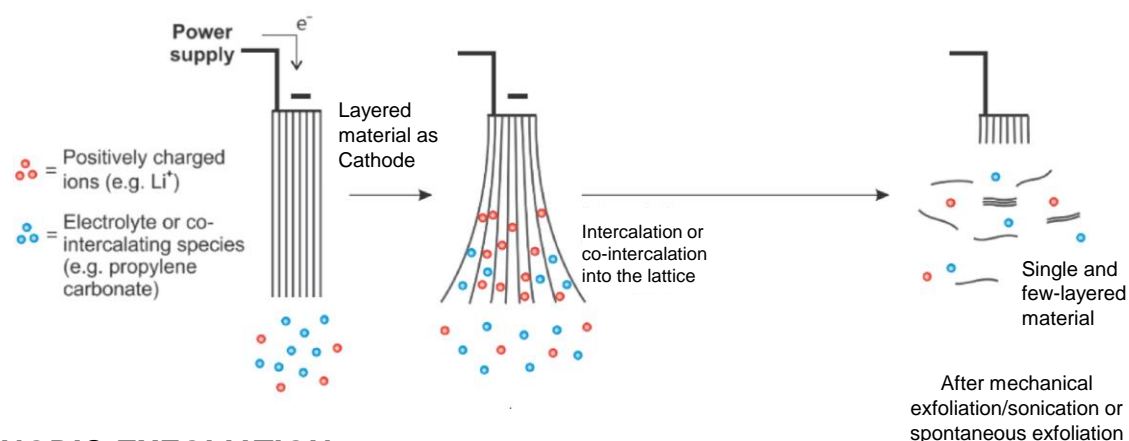
Figure 1. Examples of layered materials.

In most cases, extraordinary and useful properties appear when the thickness of the bulk multilayer solid is reduced to one or few-layer structure and which can be exploited in a myriad of optical, catalytic or electronic applications.¹⁵ For this reason a massive research interest has been focused to the development of methods of preparation of single-, few-layer of these layered materials and similarly to graphene both bottom-up and top-down approaches have been proposed. In particular, the top-down approach to exfoliate the bulk solid crystal represents the most viable to obtain good quality isolated layers in large quantities by exploiting the common characteristic of all these materials: weak van der Waals forces in the range of 40-70 meV held together adjacent layers and therefore methods able to disrupt these forces while preserving the strong covalent intra-layer interactions are

available.¹⁶ The exfoliation process of solid crystals can be accomplished in liquid-phase where solvents and/or electrolytes intercalate between the layers with the aid of three possible driving systems that can also be used in combination for enhanced efficiencies: i) ultrasonication, ii) mechanical shearing and iii) electrochemistry.¹⁷ Electrochemically-assisted exfoliation holds great potential for mass-production of 2D-layer sheets due to the mild operational conditions, simple instrumentation, fast process and high yield of exfoliated sheets of good quality.

The process consists in the application of a fixed potential or electrical current that can drive the ionic species in solution to intercalate between the layers, weakening the interlayer forces and consequently facilitate their separation and release in solution.¹⁸ This process can be carried out in aqueous and organic solvents and using anodic oxidation or cathodic reduction to intercalate negative or positive ionic species, respectively (Figure 2). Type of solvent and electrolyte play a crucial role not only on the efficiency of the exfoliation but also on the quality and properties of the exfoliated materials.¹⁹ Here we wish to present a collection of the state-of-the art electrochemically-assisted methods to exfoliate layered 2D materials categorized according to the intercalating ionic specie employed. A separate section is dedicated to the so-called bipolar exfoliation which consists of the application of a bias voltage between two inert metallic electrodes immersed into a liquid dispersion of the layered material in particulate form with the aid of vigorous stirring.

CATHODIC EXFOLIATION



ANODIC EXFOLIATION

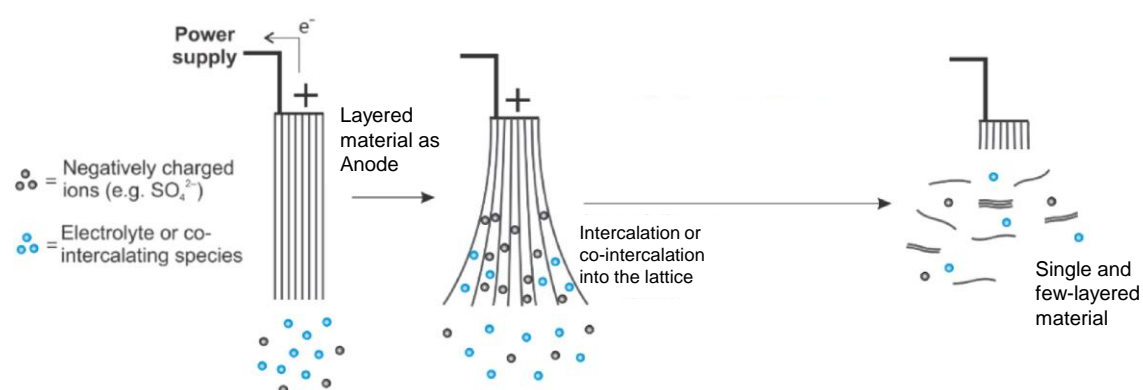


Figure 2. Schematic overview of cathodic and anodic exfoliation mechanisms. A positive or negative charge is created at the working electrode, attracting oppositely charged intercalating ions. Co-intercalating molecules may optionally be present. Reproduced from ref. 18 with permission from the Elsevier, copyright 2015.

2. Cathodic intercalation of positive ions

The application of a negative potential to the layered material can drive the intercalation of positive ions present in solution often accompanied by co-intercalation of solvent molecules which further facilitate materials expansion, followed by exfoliation. Lithium ions represent the most obvious choice of intercalant due to the well-known Li-intercalated compounds used

in batteries since the 1970s.^{20, 21} Inspired by the process occurring in batteries²² Wang and collaborators proposed the use of LiClO₄ in propylene carbonate (Li⁺/PC) to exfoliate graphite into graphene sheets by applying a negative voltage of -15 ± 5 V.²³ A post-exfoliation reaction in water with the assistance of ultrasonication was required to complete the exfoliation process. A more efficient and controlled intercalation of Li ions was accomplished by Zhang's group proposing a battery-type setup to exfoliate different layered compounds including graphite, transition metal dichalcogenides, h-BN, and other inorganic compounds (Figure 3A-D). Li intercalation process was monitored during the galvanostatic discharge enabling full control until complete insertion is achieved. Li metal is used as anode and source of Li ions while the layered materials are incorporated in the cathode of the battery test cell. Once the Li insertion is complete, the cell is disassembled and the material is sonicated in water during which the formation of Li(OH) and hydrogen gas facilitates the separation and isolation of the 2D nanosheets.^{24, 25}

Other cationic species have been proposed successfully for the exfoliation of graphite such as tetra-alkyl ammonium ions, Na⁺ and N-butyl, methyl-pyrrolidinium bis(trifluoromethylsulfonyl)-imide (BMPTF₂N) in organic, aqueous and ionic liquid solution, respectively.²⁶⁻²⁹ Swager and collaborators firstly proposed a sequential use of different intercalants in a two-step cathodic process. The smaller size Li⁺ ion is employed during the first step to intercalate and expand graphite. A second cathodic step produces hyperexpanded graphite by means of a larger ion such as tetra-*n*-butylammonium (TBA). After the expansion, an *in situ* electrochemical method is used to functionalize the graphene sheets with aryl diazonium salts producing highly functionalized graphene. This method allows control over the exfoliation as well as the functionalization.²⁶ The same group recently improved the process by employing a ramping multi step cathodic potential to intercalate TBA⁺ in anhydrous solvent, producing a graphite intercalated compound (GIC) with very

large interlayer space. A subsequent electrochemical functionalization with diazonium compounds resulted largely more efficient than the previous method.³⁰

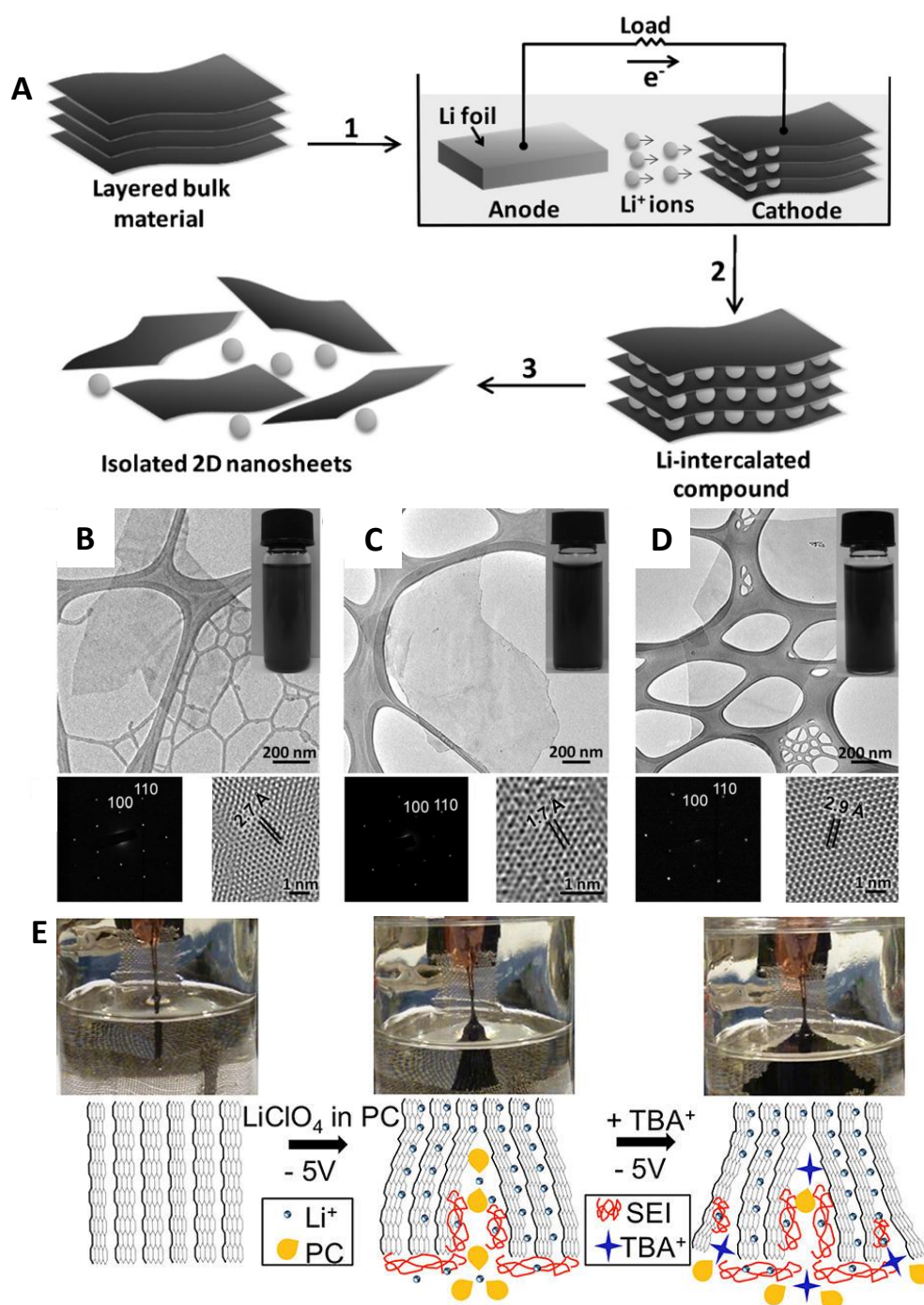


Figure 3. A) Electrochemical lithiation process for the fabrication of 2D nanosheets from the layered bulk material. B) TEM image, SAED pattern and HRTEM image of a single-layer WS_2 nanosheet. Inset: Photograph of the WS_2 solution. C) TEM image, SAED pattern and HRTEM image of a single-layer TiS_2 nanosheet. Inset: Photograph of a TiS_2 solution. D) TEM image, SAED pattern and

HRTEM image of a single-layer TaS₂ nanosheet. Inset: Photograph of the TaS₂ solution. Reproduced from ref. 24 with permission from Wiley-VCH, copyright 2011. E) Schematic and images of electrochemical expansion of graphite in organic solvents using Li⁺ first and then tetra-*n*-butylammonium (TBA). Reproduced from ref. 26 with permission from American Chemical Society, copyright 2011.

Black phosphorous (BP) is another layered material that has attracted a tremendous attention in recent years particularly for its semiconducting properties with a layer-dependent direct band-gap between 0.3 eV when present as bulk to 2.0 eV as single layer.⁵ Several photonic and electronic applications could benefit from the use of exfoliated sheets of BP. Among exfoliation methods, electrochemically assisted exfoliation of bulk crystals of BP showed several advantages compared to other processes, particularly the ease of control, short time, efficiency and sheet quality. Similarly to the graphene exfoliation, both anodic and cathodic procedures have been proposed. With regard to the cathodic ion intercalation and exfoliation, Huang and co-workers demonstrated that by tuning the applied potential in the presence of TBA⁺ intercalant ions, exfoliated BP sheets of different layers between 2 to 11, could be obtained.³¹ Following this work, Li *et al.* developed an impressive fast process employing TBA⁺ as cationic intercalant but in the presence of a polar aprotic solvent such as DMSO.³² By applying a voltage of -5 V to the cathode (BP), a fast expansion and exfoliation (below 1 min) resulted for the BP material as monitored with a custom-made cell integrated with an optical microscope (Figure 4A). SEM was employed to optimize the voltage applied (Figure 4C-E) while Raman spectroscopy and AFM provided information on the size and thickness of the BP sheets (Figure 4G-J).³²

An average thickness of 5 layers was measured for the exfoliated material and obtained with a very high yield above 80%. In this work authors tested different alkyl-ammonium ions for the intercalation, tetrabutylammonium (TBA), tetramethylammonium (TMA) and

tetraoctylammonium (TOA), as well as different electrolyte solvents (polar protic, non-polar and polar aprotic), uncovering the important role of the solvated cations rather than the size of the cations alone. Interestingly the electrochemical intercalation and expansion of BP could not proceed with polar protic solvents (eg. isopropyl alcohol, water, acetic acid) or nonpolar solvents (eg. toluene, dichloromethane) even when low charging voltage of -10 V was applied. Instead, efficient electrochemical expansion occurs only when polar aprotic solvents are used to dissolve the ammonium cations such as pyrrolidine dithiocarbamate, DMSO, propylene carbonate, N-Methyl pyrrolidone, acetonitrile, and N,N-Dimethylformamide. This is because polar aprotic solvents have similar surface tension than BP ($\sim 40 \text{ dyne cm}^{-1}$), and because alkylammonium salts can be better dissolved in polar solvents facilitating the formation of solvated alkyl ammonium cations in the electrolyte, which can be driven and inserted between BP layers at low cathodic potential ($\sim -3.5 \text{ V vs Pt}$). DMSO with TBA resulted the most efficient combination for intercalation and expansion due to the appropriate solvated cation size. When the potential is lowered to -4 V the intercalated molecules of DMSO and TBA undergo electrochemical decomposition producing gaseous species such as dimethyl sulfite and alkane which are responsible for the rapid dramatic volume expansion of BP.³²

It is important to mention that the use of cationic intercalants in cathodic conditions is ideal for the preservation of the original characteristic of the layered material since no significant structural damage or chemical modification is produced. This at the cost of much lower efficiencies compared to anodic procedures with negative ions as intercalants as it will be discussed more in detail in the next section.

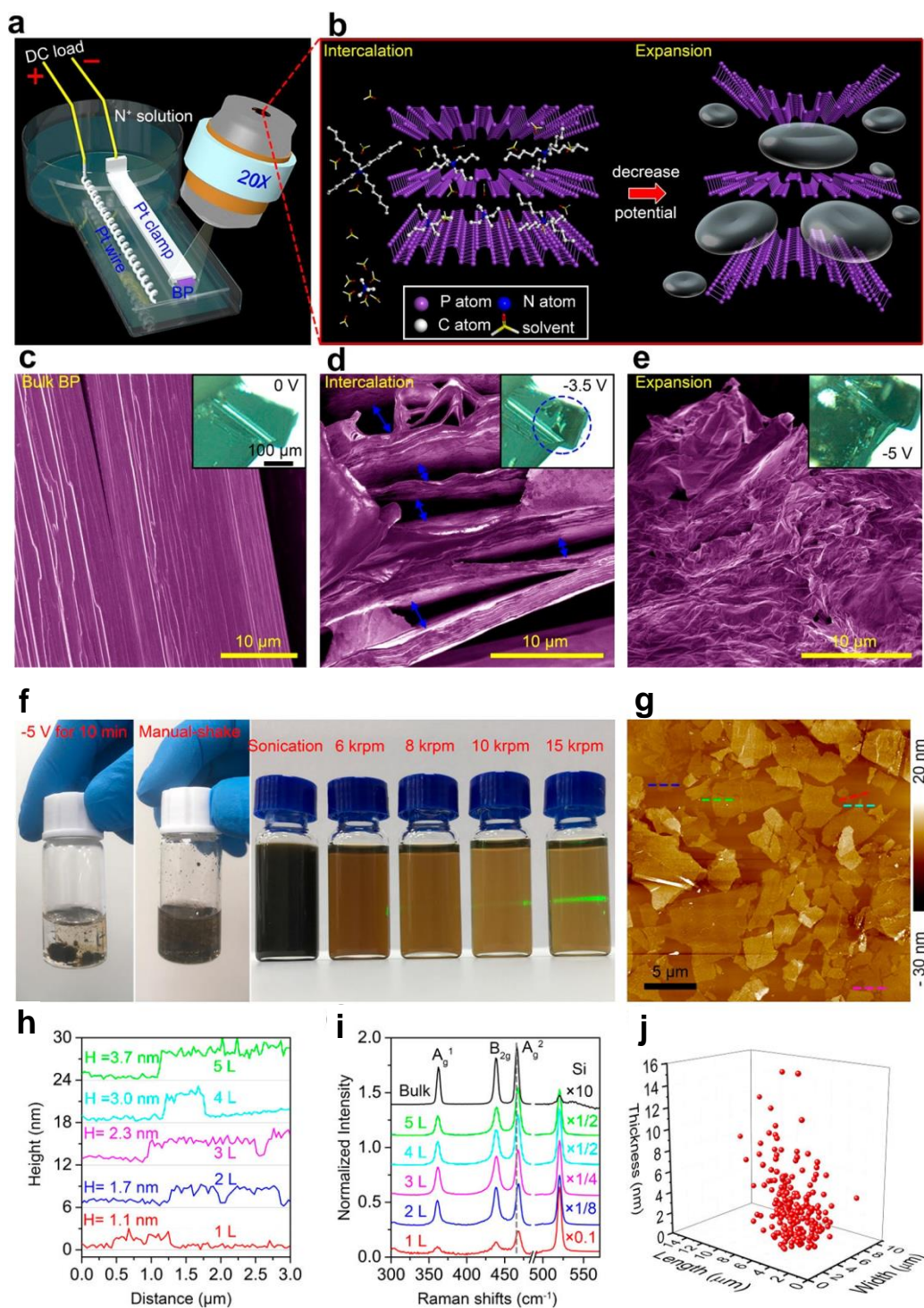


Figure 4. a) Schematic illustration of a microelectrochemical cell mounted beneath an optical microscope. b) Illustration of the intercalation and expansion of a BP cathode in organic DMSO electrolyte with TAA salts. False color SEM imaging of the edge of bulk BP before and after applying c) 0 V, d) -3.5 V and e) -5 V. Double-arrows in d highlight the expansion gap between layered BP structures. Inset: the corresponding in situ optical microscopy imaging of bulk BP before and after applying different charging voltages. f) Photographs of (left) bulk BP in DMSO after electrochemical charging at -5 V for 10 min; (center) dispersion of expanded BP via manual-shaking; (right) FLBP

dispersions centrifuged at different speeds exhibiting the Tyndall effect. **g**) Representative AFM image of FLBP flakes deposited onto a SiO₂/Si substrate via drop-casting and annealed at 250 ° C for 2 h in forming gas (H₂/Ar = 5/95). **h**) AFM height profile and **i**) Raman spectra of the exfoliated BP flakes with different thicknesses ranging from one to five layers. **j**) Size (length and width) and thickness distribution of exfoliated FLBP flakes. Reproduced from ref. 32 with permission from American Chemical Society, copyright 2018.

Table 1. Most significant cathodic exfoliation procedures.

Intercalant ion	Solvent	Bulk 2D material	Electrochemical input	Thickness (layers)	Yield	Sonication	Refs
Li ⁺	LiClO ₄ in PC	Graphite	-15±5V	1-5 L	>70%	Yes in LiCl/DMF/PC	23
Li ⁺	LiPF ₆ in EC/DMC	Graphite, MoS ₂ , WS ₂ , TiS ₂ , TaS ₂ , ZrS ₂	0.05 mA	1 L	~92%	Yes in H ₂ O or ethanol	24
Li ⁺	LiPF ₆ in EC/DMC	BN, NbSe ₂ , WSe ₂ , Sb ₂ Se ₃ , Bi ₂ Te ₃	0.025 mA	3-10 L	-	Yes in H ₂ O	25
Step1: Li ⁺	LiClO ₄ in PC	Graphite	-5 V, 15min	<5 L	100%	-	26
Step 2: TBA ⁺	TBA ClO ₄ in PC		-5 V, 24h				
TMA ⁺ , TEA ⁺ , TBA ⁺	TMA ClO ₄ , or TEA BF ₄ , or TBA BF ₄ in NMP	HOPG, Graphite rod	-5 V (vs Ag/AgClO ₄) for 12h	2-5 L	-	-	27
Na ⁺	NaCl, DMSO, thionin acetate in H ₂ O	Graphite rod (anode and cathode)	DC 5 V	~7 L	-	Yes in H ₂ O	28
BMP ⁺	BMPTF ₂ N	HOPG, Graphite rod	15-30 V	2-5 L	-	-	29

TBA ⁺	TBAP in DMF/ACN	HOPG	-2.2 to -2.8 V (vs Ag/Ag ⁺)	1-2 L	-	Mild	30
TBA ⁺	TBA PF ₆ in DMF	BP crystal	-5 V	1-5 L	-	Mild sonication	31
TBA ⁺	TBA BF ₄ in DMSO	BP crystal	-5 V for 1-3 min	5 L	80%	Mild sonication	32

PC: Polycarbonate; **EC:** Ethyl carbonate; **DMF:** N,N dimethyl formamide; **ACN:** Acetonitrile; **DMC:** dimethyl carbonate; **NMP:** N-Methyl-2-pyrrolidone; **TMA:** Tetramethylammonium; **TBA:** Tetrabutylammonium; **TEA:** Tetraethylammonium; **DMSO:** Dimethyl sulfoxide; **BMPTF₂N:** N-butyl, methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; **BP:** Black phosphorous; **HOPG:** Highly oriented pyrolytic graphite; **TBAPF₆:** Tetrabutylammonium hexafluoro phosphate; **TBABF₄:** Tetrabutylammonium tetrafluoro borate; **TBAP:** Tetrabutylammonium perchlorate.

3. Anodic intercalation of negative ions

Anodic exfoliation can be obtained by applying a positive voltage to the layered material driving intercalation of negative ions present in solution. Again the process can be carried out in aqueous and organic solvents with different anionic species involved.

Countless electrochemical exfoliation processes in anodic conditions has been proposed for the preparation of graphene sheets from bulk graphite starting material. Electrolytes in aqueous solutions represent the preferred choice as more viable for industrial production. One of the first attempts was demonstrated by Wang and coworkers who employed graphite rods as both anode and cathode, applying a bias voltage of 5 V for 4 h in the presence of poly(sodium-4-styrenesulfonate (PSS) acting as both surfactant sheet stabilizer and intercalant. Graphene sheets were released at the anode with low density of defects but with adsorbed PSS molecules.³³ Other surfactants such as sodium dodecyl benzene sulfonate (SDBS) were used by other groups for graphite exfoliation.³⁴ Without any doubts, sulfate represents the most efficient negative ion intercalant. From the experience of the formation of

graphite intercalation compounds (GIC) since the nineteenth century with sulfuric acid, early attempts of graphite electrochemical exfoliation were carried out in the presence of diluted H_2SO_4 resulting extremely efficient and enabling a fast anodic exfoliation although the resulting graphene sheets were rich in structural defects and oxygen functionalities.³⁵ Later, it was realized that sulfate ions in neutral pH³⁶ and also the addition of reducing agents³⁷ can produce higher yields of single- few-layer graphene sheets, with larger lateral sizes and lower density of defects and oxygen functionalities. In our group we tested and compare three different electrolytes: H_2SO_4 , Na_2SO_4 and LiClO_4 . Importantly, we discovered that different electrolytes used during exfoliation can produce graphene with different structural, chemical and electrochemical properties.³⁸ In particular, the use of LiClO_4 could generate highly oxidized graphene (graphene oxide, GO) which is thus obtained in a much faster fashion than the standard chemical process with concentrated strong acids and oxidants.

These works inspired other groups to explore possible exfoliation in aqueous solution of other 2D layered materials. In 2014 You *et al.* utilized diluted H_2SO_4 to exfoliate MoS_2 crystals assembled as anode in a two-electrode set-up with Pt wire as cathode. Applying firstly a voltage of +1 V to the anode to wet the crystal followed by a bias voltage of 10 V, resulted in a significant release of MoS_2 nanosheets.³⁹ The same group later improved the procedure employing sulfate ions in neutral pH obtaining MoS_2 nanosheets with larger lateral size and low degree of oxidation (Figure 5).⁴⁰ Using a similar setup but with a modified procedure we successfully exfoliate crystals of topological insulators (TIs) Bi_2Se_3 and Bi_2Te_3 .⁴¹ Neutral solutions of Na_2SO_4 were used as electrolyte during exfoliation with the TI crystals and Pt foil assembled as working and counter electrode, respectively. Pt foil was separated from the solution using a dialysis membrane which ensured ionic current to flow while avoiding physical contact with the exfoliated materials released from the crystal. The procedure involved the application of 10 V bias in alternating fashion to the working

electrode. Exfoliation and material release was observed when a combination of preliminary anodic voltage of +10 V was followed by a cathodic voltage of -10 V during 2 min.

Repeating multiple times this combination, a significant amount of material was released from the crystal (Figure 5H-J). Micrometer size sheets of Bi_2Se_3 and Bi_2Te_3 were obtained demonstrating interesting electrochemical properties.⁴¹

The anodic exfoliation in aqueous solution is generally explained by a common mechanism regardless the layered material involved. Firstly, the application of a positive bias generates $\bullet\text{OH}$ and $\bullet\text{O}$ radicals from the oxidation of water. These radicals preferentially attack edge sites and grain boundaries producing, particularly with graphene, oxygen functional groups which increase the interlayer distance. Then, more radicals, together with the anions penetrate within the layers further expanding the material. Finally, the anodic oxidation of the radicals and the anions inside the material produces gaseous species (O_2 , SO_2 , CO_2 , etc.) that completely separate the layers.

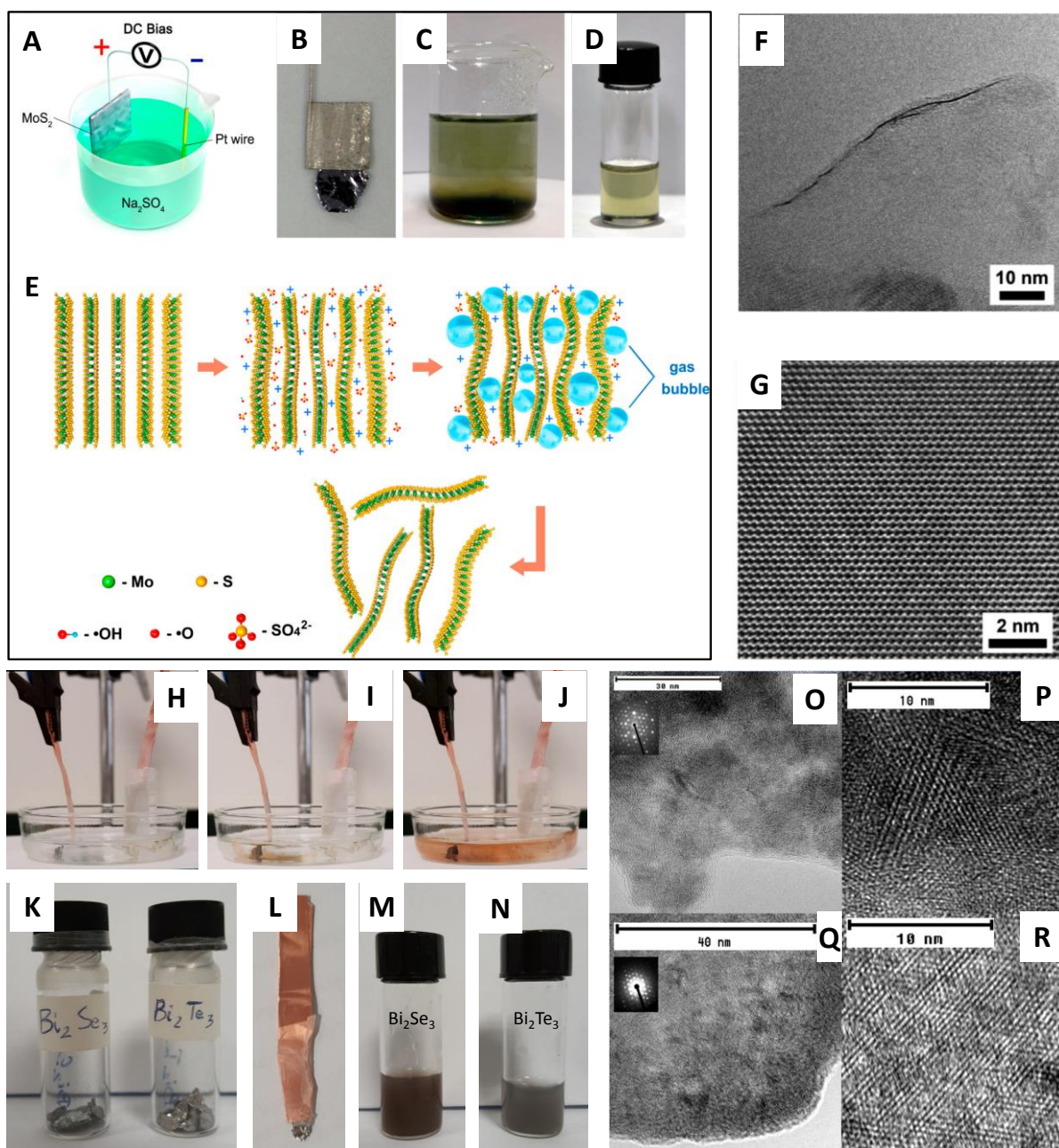


Figure 5. A) Schematic illustration of experimental setup for electrochemical exfoliation of bulk MoS_2 crystal. B) Photograph of a bulk MoS_2 crystal held by a Pt clamp before exfoliation. C) Exfoliated MoS_2 flakes suspended in Na_2SO_4 solution. D) MoS_2 nanosheets dispersed in NMP solution. E) Schematic illustration for mechanism of electrochemical exfoliation of bulk MoS_2 . F) HRTEM image of a monolayer MoS_2 nanosheet showing layer edge. G) HRTEM image of hexagonal lattice structure of a MoS_2 nanosheet. Reproduced from ref. 40 with permission from American Chemical Society, copyright 2014. H-J) Process of electrochemical exfoliation of Bi_2Se_3 . K) Bi_2Se_3 and Bi_2Te_3 crystals used for exfoliation. L) Electrical connection of the crystal using copper tape. Colloidal suspension of M) Bi_2Se_3 and N) Bi_2Te_3 obtained after the electrochemical exfoliation. O) Low-resolution TEM and P) HR-TEM images of Bi_2Se_3 . Q) Low-resolution TEM and R) HR-TEM

images of Bi_2Te_3 . Reproduced from ref. 41 with permission from American Chemical Society, copyright 2016.

As layered material, black phosphorous has recently regained enormous attention due to the interesting electronic properties of its single- (or few-layer) 2D component called phosphorene, in analogy with graphene.⁵ It is a semiconducting material with tunable direct band gap that can be used for electronic and opto-electronic applications as well as for energy storage devices and sensing. Top-down preparation procedures are the most widely adopted including liquid phase exfoliation by ultrasonication in organic solvents⁴² and micromechanical exfoliation.⁵ These methods can obtain good quality single sheets of BP but only with low yields and therefore not applicable for industrial production. We recently obtained good quality BP nanosheets within only few hours by means of electrochemical exfoliation in aqueous solution starting by a synthetic BP crystal (Figure 6A). Anodic exfoliation in the presence of dilute sulfuric acid was accomplished applying a low voltage bias of 3 V against a Pt foil used as cathode (Figure 6B-D). Characterization showed micrometer-size nanosheets, with composition relatively pure and low level of impurities (Figure 6E-G).⁴³

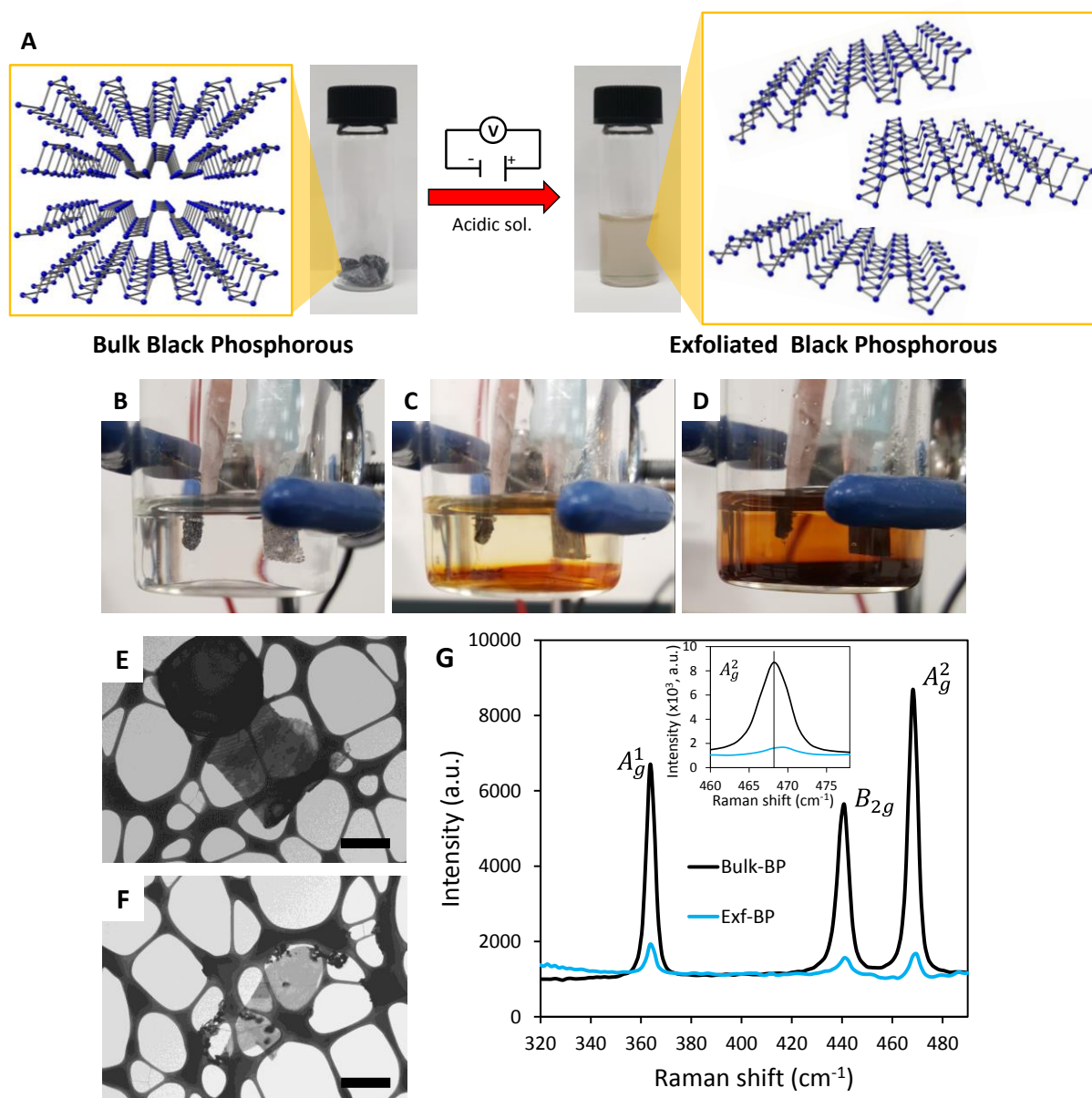


Figure 6. A) Schematic of the exfoliation procedure. The layered crystal structure of black phosphorous is exfoliated in an acidic aqueous solution by the application of a DC voltage. The starting BP crystals (left) and the exfoliated material dispersion in DMF (right) are also shown. The electrochemical setup with the BP-flake anode and Pt-foil cathode, in acidic solution ($0.5 \text{ m H}_2\text{SO}_4$), separated by a fixed distance of 2 cm at B) no potential applied, C) after 20 min applying a voltage of +3 V, and D) after 2 h of applied voltage. STEM images of E) bulk crystal of black phosphorous and F) exfoliated black phosphorous nanosheet. Scale bar=1 mm. G) Raman spectra of crystal BP (black) and electrochemically exfoliated BP (blue). An enlarged section of the spectrum between 460 and 480 cm^{-1} . Inset: Raman shift is presented to highlight the blue-shift of the A_g^2 vibration mode for the exfoliated nanosheets. Reproduced from ref. 43 with permission from Wiley-VCH, copyright 2017.

Several other procedures in anodic conditions and in aqueous or non-aqueous solutions have been proposed for the exfoliation of graphite. In aqueous solution it can be mentioned the work presented by Rao *et al.* who used alkaline conditions with 1 M NaOH and investigate the influence of H₂O₂ addition to the exfoliation efficiency. The presence of H₂O₂ significantly enhanced the exfoliation thank to the formation of highly nucleophilic O₂²⁻ ions which intercalate and expand the graphene layers. This is in addition to the highly reactive radical species such as ·OH and ·O generated by the anodic oxidation of water and which oxidize and open the edge sheets facilitating intercalation of the peroxide ions. The exfoliation process resulted extremely fast (minutes), obtaining low density of defect graphene sheets and low oxygen groups content.⁴⁴ Other anodic exfoliations of graphite were proposed using nitrate, perchloride, carboxylate, and phosphate to name a few.⁴⁵

Table 2. Most significant anodic exfoliation procedures.

Intercalant ion	Solvent	Bulk 2D material	Electrochemical input	Thickness	Yield	Sonication	Refs
R-SO ₃ ³⁻	PSS or SDBS in H ₂ O	Graphite rod	5 V for 4h or 25 V for 6h	1-2 L	15 %	-	33,34
SO ₄ ²⁻	H ₂ SO ₄ or K ₂ SO ₄ in H ₂ O	HOPG or graphite flakes	+10 V	1-7 L	65 %	Yes in DMF for 5 min	35
SO ₄ ²⁻	(NH ₄) ₂ SO ₄ or Na ₂ SO ₄ or K ₂ SO ₄ in H ₂ O	Graphite flakes	+10 V	1-2 L	72 %	Yes in DMF for 10 min	36
SO ₄ ²⁻	(NH ₄) ₂ SO ₄ + TEMPO	Graphite foil	10 V	1-3 L	52 %	Yes in DMF for 15 min	37
SO ₄ ²⁻ , ClO ₄ ⁻	H ₂ SO ₄ or Na ₂ SO ₄ or LiClO ₄ in H ₂ O	Graphite foil	10 V	6-8 L	-	-	38
OH ⁻	NaOH + H ₂ O ₂	Graphite rod	3 V for 3 min	3 L	55 %	Yes in DMF for 10 min	44
SO ₄ ²⁻	H ₂ SO ₄ in H ₂ O	MoS ₂ crystal	10 V	1-3 L	-	Yes in DMF for 15 min	39
SO ₄ ²⁻	Na ₂ SO ₄ in H ₂ O	MoS ₂ crystal	10 V for 2h	1-5 L	75 %	Yes in NMP for 1h	40
SO ₄ ²⁻	Na ₂ SO ₄ in H ₂ O	Bi ₂ Se ₃ and Bi ₂ Te ₃	Alternating +10 V and -10 V for 2 min	-	-	Yes in H ₂ O for 1h	41
SO ₄ ²⁻	H ₂ SO ₄ in H ₂ O	BP crystal	+3 V for 2h	-	-	-	42

PSS: Polystyrene sulfonate; **SDBS:** Sodium dodecylbenzenesulfonates; **TEMPO:** (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl; **DMF:** N,N dimethyl formamide; **NMP:** N-Methyl-2-pyrrolidone; **BP:** Black phosphorous; **HOPG:** Highly oriented pyrolytic graphite.

4. Bipolar electrochemical exfoliation

Bipolar electrochemistry consists in the application of a voltage between two driving electrodes (generally made of Pt) immersed in a conductive electrolyte solution and in the presence of conductive materials (bipolar electrode) suspended in the same solutions. The generation of a uniform electric field across the solution between the electrodes generates asymmetrical polarizations at the extreme edges of the bipolar electrode in a wireless manner as said without the direct contact with the driving electrodes.⁴⁶ A potential difference is thus produced within the material in solution (ΔE_{elec}) and which depends on the distance between the driving electrodes ($l_{channel}$), the size of the bipolar electrode (l_{elec}) and the driving total electric field applied (E_{tot}) according to the equation:

$$\Delta E_{elec} = E_{tot} \left(\frac{l_{elec}}{l_{channel}} \right)$$

The concept of bipolar electrochemistry can be used to drive asymmetrical reactions at the poles of the material in solution such as water splitting with oxygen generation obtained at the anode and hydrogen is produced from the cathodic pole in aqueous solutions when a sufficient driving potential is applied.⁴⁷ In our group, the setup employed for bipolar electrochemistry has been used to reduce the size of suspended particles of layered materials to obtain few-layer thick nanoparticles. Pt driving electrodes have been set at a distance of 2 cm in a Na_2SO_4 electrolyte aqueous solution. The application of a driving voltage of 10 V between the Pt electrodes produced a significant size reduction of WS_2 sheets present in solution and suspended by magnetic stirring (Figure 7).⁴⁸ The produced WS_2 nanoparticles have been used then as electrochemical signaling labels for immunoassay applications obtaining excellent analytical performance in terms of a wide range and high selectivity,

sensitivity and reproducibility of the sensing device. This procedure has been successfully applied for the production also of other nanosized materials such as MoSe_2 ⁴⁹ and black phosphorous⁵⁰ obtaining nanoparticles with average diameter of 100 nm and 70 nm, respectively.

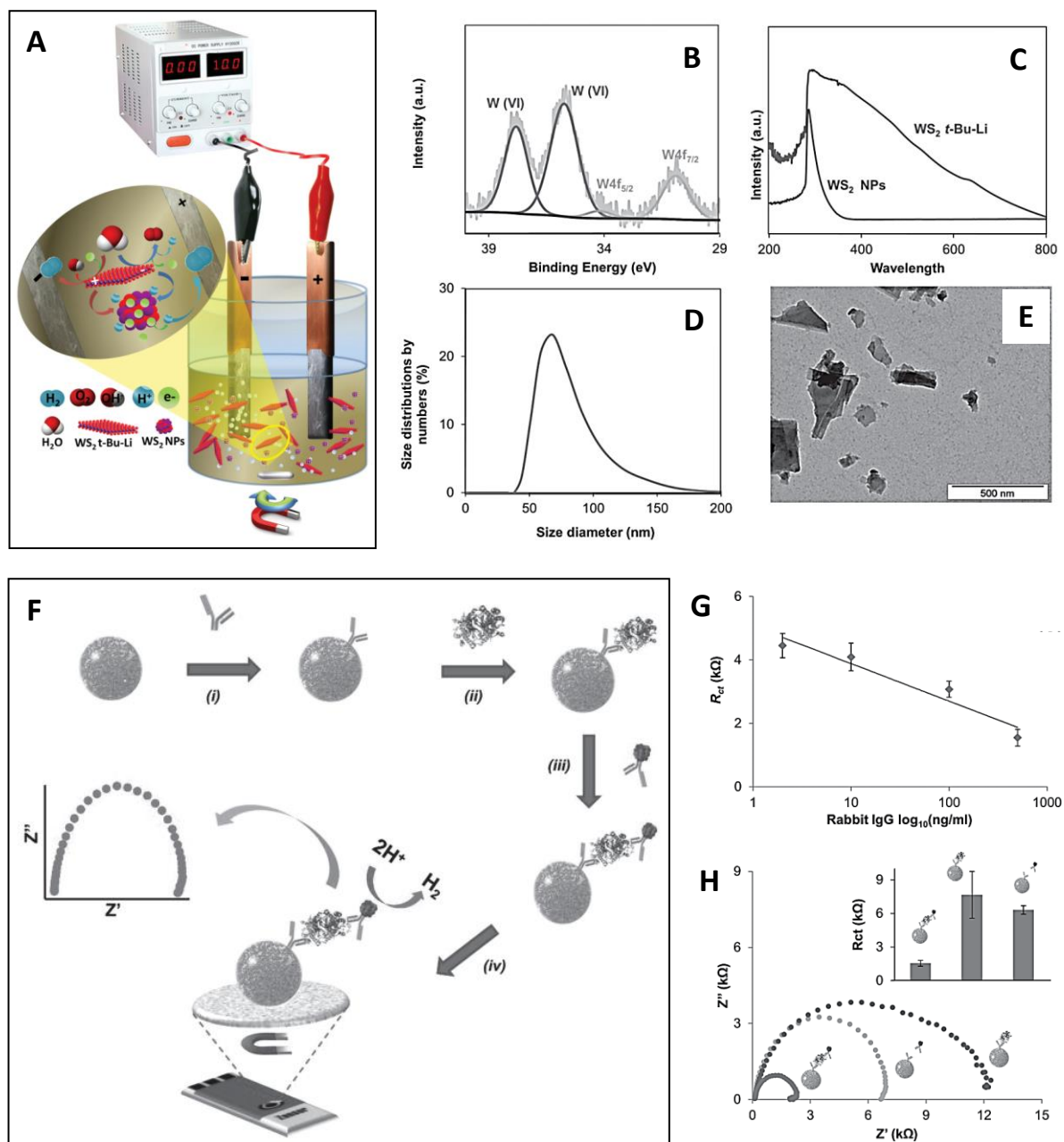


Figure 7. A) Schematic representation of the bipolar electrochemical synthesis of WS₂ NPs. B) High-resolution XPS spectrum of WS₂ NPs. C) UV-vis spectra of WS₂ t-BuLi and WS₂ NPs. D) The particle size distribution measured by DLS of WS₂ NPs. E) TEM image of WS₂ NPs. F) Schematic (not to scale) of preparation of magneto-immunosandwich assay for rabbit IgG detection using

WS₂ nanolabel through HER catalysis and EIS as a transduction method. (i) Incubation with primary anti-rabbit IgG, (ii) incubation with desired concentration of rabbit IgG, (iii) last conjugation of magneto-immunosandwich with anti-rabbit IgG with WS₂ tags, and (iv) electrochemical detection based on HER using EIS. G) Calibration curve obtained by plotting R_{ct} values versus logarithm of different concentrations of rabbit IgG. H) Selectivity evaluation, comparison of the magneto-immunosandwich assay using 500 ng mL⁻¹ rabbit IgG without label and using human hemoglobin instead of rabbit IgG. Reproduced from ref. 48 with permission from Wiley-VCH, copyright 2016.

The mechanism behind the material size reduction is still under investigation. It could be the combination of the bipolar effect on the particles in solution and the direct anodic or cathodic potential produced on the material when it comes into contact with the anode or cathode driving electrodes, respectively. The potential applied is larger enough to produce water splitting reactions with the concomitant gas release (H₂ at cathode or O₂ at anode) which results in a mechanical fragmentation of the material over an extended period of time.

5. Conclusion and future perspectives

The use of electrochemical methods to assist the exfoliation of layered materials holds great promises for large scale production of single or few-layered 2D materials beyond graphene. It has proved to be extraordinarily efficient for the exfoliation of graphite and it is only at its early stages to be a viable route for the production of several other layered materials. Several challenges and limitations have to be taken into account when dealing with materials other than graphite. One for all is that the materials need to be able to conduct electricity and so only conducting and semiconducting materials can be considered for this preparation method. In other cases, structural aspects, stability at ambient conditions, ability to sustain strong anodic/cathodic conditions without significant chemical alterations, etc. need to be considered. Both aqueous and non-aqueous electrolytes have been used for exfoliation of

layered materials but while for the exfoliation of graphite the process in aqueous solutions and anodic conditions is the most widely used due to the higher efficiency compared to the cathodic intercalation of positive ions in organic solvents, for the exfoliation of other layered materials, the process which demonstrated to be the most universal and efficient is based on Li intercalation in organic solvents. Only MoS₂, BP, Bi₂Te₃ and Bi₂Se₃ have been exfoliated electrochemically in aqueous solutions and therefore more efforts are still needed to successfully exfoliate a larger range of layered materials in aqueous electrolytes which represent the most viable route to be industrially implemented for large scale. At the same time a better understanding of the intercalation and exfoliation process/mechanism driven by the application of current is urgently needed and which could facilitate the use of electrochemical means to exfoliate a large number of layered materials with greater efficiencies.

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Biographies



Dr. Adriano Ambrosi received his PhD degree from Dublin City University, Ireland in 2007. As postdoctoral researcher he firstly worked for two years at ICN (Spain), and then, in 2009, at NIMS (Japan). In 2010 he joined the research group of Prof. Martin Pumera at Nanyang Technological University (Singapore) where he currently works as Senior Research Fellow. His research interests include the application of nanomaterials to electrochemical biosensors, synthesis

and fundamental electrochemical studies of graphene and other 2D materials for biosensing and energy storage devices, 3D-printing, and synthetic nanomotors.



Martin Pumera is the Director of the Center for Advanced Functional Nanorobots and a tenured faculty member at University of Chemistry and Technology, Prague. He received his Ph.D. at Charles University, Czech Republic, in 2001. After two postdoctoral stays (in the United States, Spain), he became tenured group leader at the National Institute for Materials Science, Japan, in 2006. In 2010, Martin joined Nanyang Technological University, Singapore, where he worked as tenured associate professor for almost a decade. Prof. Pumera has broad interests in nanomaterials and microsystems, in the specific areas of electrochemistry and synthetic chemistry of 2D nanomaterials, nanotoxicity, micro and nanomachines, and 3D printing. Martin is “2017 Highly Cited Researcher” by Clarivate Analytics. He published over 550 papers which received more than 25,000 citations.

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