7

Two-dimensional nanomaterials via liquid-phase exfoliation: synthesis, properties and applications

M.Mar Bernal^{*}, Domenico Milano

IMDEA Nanociencia, 28049-Madrid, Spain Università degli Studi di Trieste, 34127-Trieste, Italy

Outline

Introduction	160
Liquid-phase exfoliation <i>via</i> sonication	161
Sonication Process	162
Surface Energy	162
Purification	164
Graphene	165
Liquid-phase exfoliation of graphite	166
Properties and Applications	169
Hexagonal Boron Nitride Nanosheets	170
Liquid-phase exfoliation of boron nitride	170
Properties and Applications	172
Transition Metal Dichalcogenides	173
Liquid-phase exfoliation of TMDs	174
Properties and Applications	175
Conclusion	. 177
References	177

Introduction

Two-dimensional (2D) nanosheets, one-atomic thick materials with infinite planar dimensions, have gained worldwide attention in recent years because of their outstanding properties that arise from their structure and dimensionality. [1-3] The advantage of these materials is that they offer in their exfoliated state, as single- or few-layers, promising opportunities for diverse applications at scientific and technological levels. Discovered in 2004, graphene, a one-atom-thick planar sheet of sp^2 -hybridized carbon atoms, is the most widely known 2D layered material. [4] The unique properties of this carbon allotrope, such as high thermal conductivity and Young's modulus, high intrinsic mobility and ballistic transport and large specific surface area, have been reported elsewhere. [5-8] Recently, other 2D layered materials, such as the transition metal dichalcogenides (TMDs), metal oxides and hexagonal boron nitride (*h*-BN) have gained a renewed interest. Their lamellar structure, analogous to that of graphite, can be exfoliated into single- and few-layer nanosheets. Exfoliated TMDs are chemically reactive presenting unique electronic, electrochemical and photonic properties, [9-14] due to their high surface area and quantum confinement effects, [3, 15, 16] not observed in their bulk counterparts. On the other hand, 2D h-BN nanosheets have been used as a dielectric support in graphene-based transistors due to their extraordinary insulating properties and high chemical stability. [15]

The importance of the structure and morphology of exfoliated 2D layered materials strongly influences their later properties. In general, strong in-plane bonds and weak van der Waals interactions between adjacent layers characterize these 2D materials. Consequently, the key issue on their exfoliation into individual layers is based on the disruption of this non-covalent interlayer binding [17, 18] and how to overcome these interactions so as to obtain high quality, basal plane defect free sheets. Thus, the development of different routes to prepare low dimensional individual layers has attracted the interest of the researcher community, since the appearance of the first studies on single-layer graphene. [4] Two main strategies have been developed for the production of atomically thin 2D nanosheets, namely bottom-up and top-down approaches. The former relies on the production of large-area uniform layers by different synthetic methods while the latter is based on the separation/exfoliation of thin flakes of layered materials from their bulk crystals. [19] Thin-layered nanomaterials obtained by *bottom-up* techniques showed large-area high quality sheets with great electronic properties. However, even if the quality of the nanosheets produced by these approaches is in some cases high, the harsh conditions of the transfer methods and the small yield production still, at present, limit their application at a truly industrial scale. On the other hand, top-down strategies include techniques such as mechanical cleavage, liquid-phase exfoliation or ball milling. Although the good-quality and large size of the sheets generated by micromechanical exfoliation, the small yield production and delicate procedure, limit its application to fundamental research. On the contrary, liquid-based synthetic routes yield products in large amounts and do not require the use of extreme conditions, being in some cases environmentally friendly. The interaction through van der Waals forces between the sheets facilitates their separation of these layered solids directly by sonication in appropriate solvents to obtain singlelayer and few-layer sheets (Figure 7.1). Even though, the potential of liquid-phase exfoliation (LPE) is set on its versatility, its scalability besides the possibility of exfoliation in common solvents, the nanosheets obtained present higher degree of disorder. While bottom-up approaches, which are amstrong-level-controlled ordering techniques, or top-down methodologies produce defect-free graphene, finding applications as electronic devices at the nanoscale, nanosheets obtained by LPE can be used to fabricate films or composite materials.



FIGURE 7.1

Schematic representations of 2D and 3D layered compounds produced form liquid-phase exfoliation of their bulk counterparts. Reprinted with permission from ref. [20] Wiley-VCH

This chapter is organized as follows: in the first section, recent progress made on liquid-phase exfoliation of 2D layered materials is presented; in the second section, synthesis of graphene via sonication assisted liquid-phase exfoliation, its properties and applications are reviewed; in the third and fourth sections, the application of this exfoliation method to hexagonal boron nitride and transition metal dichalcogenides, respectively, is reported, while properties and applications of these renewed layered materials are described.

Liquid-phase exfoliation via sonication

The liquid-phase exfoliation methodology to prepare graphene sheets generally involves three steps: i) dispersion of the starting material in a liquid medium, ii) exfoliation via ultrasonication and iii) purification. To achieve an effective exfoliation of layered materials the strategy needs to be scalable and efficient. [19, 21] Ultrasonication processes have been widely exploited to produce 2D layered materials in liquid media. Shear forces and cavitation produced due to the propagation of high amplitude sonication waves act on the surface of bulk materials inducing its exfoliation. [22, 23] In order to stabilize the as-produced 2D sheets, the interfacial tension between the materials and the liquid medium needs to be minimized, thus reflecting the existence of good interactions (Figure 7.2). Hence, the choice of liquid systems for the dispersion of the materials is crucial on the effectiveness of the methodology. [24, 25]



FIGURE 7.2

Sonication of 2D layered materials in liquid media: poor solvents lead to re-stacking of the as-formed sheets while good solvents stabilize the exfoliated state

Sonication process

Ultrasonication has emerged as one of the most powerful strategies to overcome the van der Waals interactions and produce 2D layered structures from 3D crystals. Ultrasound is defined as *a sound wave that is transmitted through any substance (solid, liquid or gas) with elastic properties.* [23] During ultrasonication of materials, physical phenomena, mainly acoustic cavitation, are manifested influencing the related sonochemical events. According to these phenomena, the sonication process has been divided in different steps: i) generation of nuclei on cavitation bubbles; ii) bubble growth due to gas diffusion; iii) damage of bulk materials due to intense shock-waves or high-speed jets; iv) formation of high-velocity interparticle collisions and; v) increase of surface area of solid materials because of their fragmentation. [26-28] Evidently, for an efficient and scalable sonication scheme several parameters should be considered, from sonication time to cavitation intensity.

Surface Energy

In 2D layered materials the mechanism underlying the liquid-phase exfoliation process is based on solution thermodynamics. Assuming that dispersions can be considered as solutions, the free energy of mixing (ΔG_{mix}) is given by

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. As it is well known, large ΔS_{mix} guarantees negative ΔG_{mix} , favouring mixing. However, nanosheets are large and hence their

 ΔS_{mix} is very small. Therefore, good nanosheets dispersions are achieved when the ΔH_{mix} is minimized. [25, 29, 30] Bergin *et al.* [31] developed a thermodynamic model for carbon nanotubes, already applied for graphene and TMDs [25, 30, 32], which describes the enthalpy of mixing per unit volume of mixture as;

$$\Delta H_{mix} \approx \frac{2}{T_{NS}} \left(\sqrt{\gamma_s} - \sqrt{\gamma_{NS}} \right)^2 \phi$$
 Eq.[2]

where γ_s and γ_{NS} are the solvent and nanosheet surface energy, respectively, T_{NS} is the nanosheet thickness and ϕ is the dispersed nanosheet volume fraction. Hence, the enthalpy of exfoliation is minimized when the solvent surface energy (γ_s) is close to that of nanosheets. Coleman and coworkers [25] demonstrated that solvents with surface tensions in the range of 40 - 50 mJm⁻² are the best solvents to obtain a successful liquid exfoliation of layered materials. Solvents with surface energy on that range are summarized in Table 7.1. [32] Unfortunately, these solvents present different inconveniences such as toxicity and cost. Furthermore, their high boiling point is a challenge for characterization and future processing of the dispersions.

While the surface energy of some solvents matches the one required to minimize the enthalpy of exfoliation, the concentration of nanosheets in the final dispersions is very low and thus the surface tension is considered as a crude solubility parameter. [30] For this reason, studies consider the Hildebrand solubility parameter (δ_T), which is related to the total cohesive energy density of a material ($E_{C,T}$), $\delta_T = \sqrt{E_{C,T}/V}$ However, δ_T is related to the total solute-solvent interactions and other specific interactions *i.e.* polar and hydrogen-bonding interactions or dispersions are dismissed. Each of the abovementioned solubility parameters are enclosed in the Hansen parameters framework and represent the square root of the contribution to the cohesive energy density, being the Hildebrand solubility parameter (δ_D) the sum of their squares:

where δ_D , δ_P and δ_H are the dispersive, polar and H-bonding solubility parameters, respectively. Consequently, in order to minimize the enthalpy energy of exfoliation, all three solubility parameters should exhibit values close to those of the solute. Nonetheless, Coleman [33] reported uncertainties on the combination of dispersive, polar and H-bonding solubility parameters to describe the system at a molecular scale.

TABLE 7.1

Best known graphene solvents, characterized by the fraction of graphene remaining after centrifugation. [32]

Solvent	Surface Tension (mJm ⁻²)
Benzyl Benzoate	45.95
NMP (N-methyl pyrrolidone)	40.10
DMSO (dimethyl sulfoxide)	42.98
DMF (dimethyl formamide)	37.10
ODCB (ortho-dichlorobenzene)	37.00
IPA (isopropanol)	21.66

As mentioned above, many serious drawbacks are associated with the organic solvents, principal amongst which is the solvents similar surface tensions as the 2D layered materials. Therefore, water or low boiling point solvents (acetone, chloroform isopropanol, etc.) can be a good alternative to exfoliate graphite, TMDs or *h*-BN. However, while the surface tension of water ($\gamma \sim 72$ mJm⁻²) is too high for the dispersion of layered materials and they are highly hydrophobic, the surface tension of low boiling point solvents is lower ($\gamma \sim 25$ mJm⁻²) compared to the other suitable solvents and the exfoliation yields are too low. [34, 35] In order to exfoliate 2D layered materials in water, the use of linear chain surfactants, salts or polymers is required, as will be explained in the next sections. [34, 36-41] On the other hand, recent studies have focused their efforts on the co-solvency effect by exfoliation of layered materials in low-boiling solvent mixtures that individually are classified as non-effective for LPE. While Zhou *et al.* [42] reported an efficient exfoliation of TMDs in an appropriate composition of ethanol/water mixtures based on the Hansen solubility parameters, Halim *et al.* [43] demonstrated that along with interfacial energy, co-solvent molecular size influences the steric repulsion and hence the stabilization of the nanosheets, due to an increase on the viscosity.

Purification

The preparation of 2D layered materials with well-defined size is of crucial importance for the control of their physico-chemical properties and applications. [44] After sonication, the majority of the material in the dispersions is composed of nanosheets with different size and thickness, which can be separated by different approaches based on differential centrifugation strategies. [35, 45] Among these strategies the most widely used is sedimentation-based separated by sedimentation without a density gradient medium (DGM), where nanosheets are separated by sedimentation after selecting the appropriate range of centrifugal forces.

Coleman and co-workers described a method to separate graphene dispersions, with mean flake size of 1 μ m, into fractions with different sheet sizes by successive centrifugation, separation and redispersion processes. [35] By transmission electron microscopy (TEM) it has been found that centrifugation at higher rates results in a dispersion of small flakes (Figure 7.3). The same group has applied this methodology for the size-separation of *h*-BN and TMDs. [24, 45] Nevertheless, separation by centrifugation is strongly dependent on the concentration of the material in the dispersions.



FIGURE 7.3

TEM images of graphene flakes prepared with a final centrifugation rates of 3000 rpm (A-B) and 500 rpm (C-D). Reprinted with permission from ref.[35] Copyright 2015 American Chemical Society

Graphene

Graphene, a single-layer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice, has emerged as an attractive 2D nanomaterial in many areas of nanoscience and nanotechnology owing to its outstanding physico-chemical properties. [4-8, 46-48] These properties include high thermal electrical conductivity (5000 W m⁻¹ K⁻¹) [5] and high optical transmittance of almost 98 %, [49] large specific surface area (2630 m² g⁻¹) [7] and remarkable mechanical strength and flexibility (Young's modulus ~ 1 TPa). [6]

Graphene can be considered as the fundamental building block of all graphitic materials of different dimensionalities including zero-dimensional (0D) fullerenes, one-dimensional (1D) carbon nanotubes and three-dimensional (3D) graphite. [8, 50, 51] It is noteworthy that by re-stacking of graphene-layers, 3D graphite can be formed while rolled graphene sheets lead to the formation of carbon nanotubes. [52] (Figure 7.4) The intrinsic out-of plane corrugations of graphene determine not only its existence, due to the stabilization of its intrinsic thermal fluctuations, but its unique physicochemical properties. [53] Hence, the importance of the structure and morphology of 2D graphene sheets strongly influences their further properties.

As described in the introduction several strategies have been developed to prepare single-layer, defect free graphene including liquid-phase exfoliation of graphite. Next, a description of the different liquid environments to extract single- and few-layer graphene sheets by this methodology will be described.



FIGURE 7.4

Molecular models of graphitic materials of different dimensionalities: a) C_{60} : buckminsterfullerene (0D); b) carbon nanotube (1D); c) graphene (2D); d) graphite crystal (3D)

Liquid-phase exfoliation of graphite

The most straightforward method of producing graphene remains exfoliation from graphite, a natural and abundant source of carbon. In graphite, graphene flakes are stacked due to strong π - π interactions contributing to the high-thermodynamic stability of graphite. Therefore, the key issue on the exfoliation of graphene into individual layers is based on the disruption of this non-covalent interlayer interaction [17,18] and how to overcome these interactions to obtain high quality and free of basal-plane defects graphene sheets. Liquid phase exfoliation of pristine graphite by ultrasonication in stabilizing solvents, [32] in the presence of surfactants, [36, 37] polymers [39] or even metal atoms [39, 40] appears as an alternative to produce high quality graphene flakes. In this regard, aromatic molecules have proven to be effective adjuvants in the exfoliation of graphite, producing novel hybrids with exciting optoelectronic properties in a single step. [56-60]

Organic Solvents

The successful exfoliation of graphite in organic solvents strongly depends on matching both surface energies. As discussed previously, solvents may have surface tensions between 40 and 50 mJm⁻² to minimize the enthalpic cost of mixing. [29, 32, 61] Coleman and co-workers have sonicated graphite powder in several solvents followed by mild centrifugation. They found that NMP is one of the best solvents to exfoliate graphite obtaining graphene concentrations up to 0.01 mgmL⁻¹ after sonication for 30 min and subsequent centrifugation at 500 rpm for 90 min. By different characterization methods the presence of mono- and few-layer graphene sheets in the dispersions was demonstrated. This group increased the concentration of graphene obtained by this technique, up to 1.2 mgmL⁻¹, in NMP by using low-power sonication for long times of up to 460 hours. Besides of the higher amount of graphene obtained, which is useful for preparation of composites, the number of deleterious defects observed by Raman spectroscopy increased with sonication time (Figure 7.5).



FIGURE 7.5

a) The left axis shows the measured absorbance per cell unit, A/I, while the right axis displays the concentration of graphene calculated using an absorption coefficient of $\alpha = 3620$ mL mg⁻¹ m⁻¹, as function of sonication time. The upper axis shows the total energy output of the bath. The line is a linear fit to $C_{\infty} \propto \sqrt{t}$, while cuvettes contain dispersions after 6 and 180 hours. b) Raman spectra of starting graphite and of thin filtered films prepared at 36 h and 192 h, while the one prepared at 146 h was centrifuged at 500 rpm and 4000 rpm. Inset shows the D to G band intensity ratio at different sonication times. Reprinted with permission from ref. [21] Wiley-CVH

The use of organic solvents is not limited to NMP. Gayathri *et al.* [62] prepared graphene by sonicating graphite in ODCB for 8 hours. They found that the dispersion of graphite in this solvent leads to the formation of sono polymer and as the sonication time increases the formation of polymer bounded graphite sheets and the distance between layers increase, producing single- and few- layer graphene sheets. On the other hand, Bourlinos *et al.* [63] propose alternative solvents belonging to a peculiar class of perfluorinated aromatic molecules: hexafluorobenzene (C_6F_6), octafluorotoluene ($C_6F_5CF_3$), pentafluorobenzonitrile (C_6F_5CN) and pentafluoropyridine (C_5F_5N). The authors optimized the sonication time to 1 hour and depending on the solvent, the final concentrations varied between 0.05 to 0.1 mgmL⁻¹. In this study, the mechanism of solubilization involved charge transfer through π - π stacking from the electron-rich carbon layers to the electron-deficient aromatic molecules that contain strong electron-withdrawing fluorine atoms. Nevertheless, all these solvents still present different drawbacks such as high boiling points or toxicity, limiting the application of the resultant graphene. Zhang *et al.* [64] developed a strategy to disperse graphene in ethanol by a solvent exchange from NMP. The dispersion obtained is relatively stable and the small amount of sedimentation can be redispersed by mild sonication.

Surfactant water solutions

Aqueous-based exfoliation of graphite is one of the most promising alternatives to produce graphene at low cost and with minimal environmental impact. However, the high hydrophobicity of graphite makes necessary the use of surfactant molecules, which can promote the exfoliation of graphite into graphene. The surfactant molecules form a coating over the basal plane of graphene, due to their high energy of adsorption, providing the required steric and electrostatic repulsion to prevent the graphene flakes from aggregating. [19, 65]

Sodium dodecylbenzenesulfonate (SDBS) is the most commonly used ionic surfactant to stabilize the liquid-phase exfoliation of graphite in water to produce defect-free graphene. Lotya *et al.* [37] developed a method to obtain graphene in SDBS-water by ultrasonication leading to multilayer graphene, typically with < 5 layers and small quantities of monolayer graphene. The as-prepared dispersions were relatively stable for at least 6 weeks and were used to prepare films by vacuum filtration with a reasonably conductivity, 35 Sm⁻¹. On the other hand, sodium cholate (SC) has shown to form stable graphene dispersions, which enables solution phase processing of graphene using density gradient ultracentrifugation (DGU). [66] Lotya *et al.* [67] reported concentrations of graphene up to 0.3 mgmL⁻¹ after ultrasonication of graphite in a solution of water/SC followed by centrifugation. Even if concentration of graphene increases with sonication time, high-quality dispersions were obtained for centrifugation rates between 500 and 2000 rpm. This process yields a monolayer number fraction of 10 %. These dispersions can be easily cast into free-standing films with good electrical and mechanical properties.

Smith *et al.* [68] reported the dispersion of graphene in water, stabilized in 12 different ionic and non-ionic surfactants. Besides the similar flake size obtained in all cases, the dispersed concentration varied by a factor of 2-3 from surfactant to surfactant. They shown that for ionic surfactants, the concentration of graphene scales linearly with a repulsive potential barrier that stabilizes surfactant-coated sheets against aggregation. However, for non-ionic surfactants the repulsive potential barrier has steric origins.

High graphene concentrations, up to 1 $mgmL^{-1}$, were obtained with the use of non-ionic surfactants. [69] The dispersions consisted of single- and few-layer, defect-free graphene sheets,

which were subsequently processed as paper-like films with significant values of electrical conductivity. Perhaps most noteworthy of all, [36] reported a different strategy based on the continuous addition of a non-ionic surfactant during the exfoliation process. By continuously replacing the surfactant to lower the surface tension during sonication, the concentration of graphene was significantly increased.

Polyaromatic hydrocarbons systems

The exfoliation of graphite with aromatic intercalating agents has come to the fore as one new possible route in obtaining high quality graphene sheets in liquid media thanks to the similar structure, in some cases, of the aromatic molecules and graphene. The advantage of this simple and scalable exfoliation approach is that small polyaromatic hydrocarbons, such as pyrene, coronene, perylene, etc. manifest as nano-graphenes (NGs) and thus they act as healing agents in case of formation of some defects during the exfoliation procedure. Besides the actuation of NGs as exfoliating agents, the well-known physico-chemical properties of these aromatic molecules makes the non-covalently functionalized graphene nano-hybrids promising materials for applications related to organic light-emitting diodes (OLEDs), organic photovoltaics (OPV) and sensors.

Zhang *et al.* [54] investigated the production of graphene by direct dispersion with the pyrene derivatives, 1-pyrenemethylamine (Py-NH₂) and 1,3,6,8-pyrenetetrasulfonic acid (Py-4SO₃), in water. This exfoliation strategy is simple and scalable, leading to the production of high-quality single-layer graphene sheets used to prepare transparent conductive films. Similarly, Yang *et al.* [70] reported the exfoliation of graphite in water with 1-pyrenesulfonic acid sodium salt (Py-1SO₃). By this approach the authors obtained ~ 70 % few-graphene layers (< 7 layers) and showed that the exfoliation efficiency strongly depends on the number of functional groups by comparing suspensions obtained by Py-1SO₃ and Py-4SO₃. Following this work, Schlierf *et al.* [71] studied the mechanism of surface adsorption of organic dyes on graphene, and successive exfoliation in water of these dye-functionalized graphene sheets. For this reason, they compared four pyrene derivatives with varying number of polar functionalizations for their efficiency as exfoliation agents. The concentration of graphene exfoliated was higher for the derivative having the largest dipole and most asymmetric functionalization.

Other aromatic molecules have been successfully tested to exfoliate graphite in liquid environments. Englert *et al.* [72] presented a simple and efficient method to obtain single- and fewlayer graphene sheets by sonication of graphite powder in the presence of aqueous solutions of perylene-based bolaamphiphile detergent. Sampath *et al.* [73] described the exfoliation of graphite through the exploitation of π - π interactions between the N,N'-dimethyl-2,9-diazopyrenium dication (MP²⁺) and graphene in organic solvents and in aqueous media. The obtained graphene sheets were stable in water for many weeks without aggregation, while the efficient quenching of the molecule with graphene indicates the existence of an energy transfer from MP²⁺ to graphene. Ghosh *et al.* [57] selected an anionic coronene derivative for the exfoliation and non-covalent functionalization of graphene in aqueous solutions. They observed a strong molecular chargetransfer interaction between coronene and graphene and the exfoliation of large quantities of single- and few-layer graphene sheets. Xu *et al.* [74] reported the production of graphene sheets through liquid-phase exfoliation of graphite in organic solvents with addition of naphthalene. They achieved concentrations of graphene in NMP as high as 0.15 mgmL^{-1} after sonication for 90 minutes.

Porphyrins have been widely used to decorate carbon materials such as fullerenes and carbon nanotubes in a supramolecular fashion, because of their strong π - π stacking interactions with them. [75-77] Moreover, the electron-donor character of porphyrins can promote photoinduced electron transfer processes with carbon-based materials for the development of optoelectronic devices. [75-79] Malig *et al.* [78] reported the direct exfoliation of graphite using a free-base porphyrin, yielding stable suspensions of single and few layer graphene/nanographene. Bernal *et al.* [60] developed a simple one-pot process to exfoliate graphite and synthesize nanographene-dimesitylporphyrin hybrids. Despite the bulky mesityl groups, which are expected to hinder the efficient π - π stacking between the porphyrin core and graphene, the liquid-phase exfoliation of graphite is significantly favored by the presence of the porphyrins.

Properties and Applications

The liquid-phase exfoliation method to obtain single- and few-layer graphene sheets maintains the pristine graphitic basal plane of graphene free of defects allowing for the fabrication of devices, which retain the remarkable properties of pristine graphene. Furthermore, large amounts of graphene sheets are obtained using this strategy, which makes it ideal for application in composite materials.

Hernández et al. [32] observed that films prepared by exfoliating graphene in NMP had conductivities of ~ 6500 Sm⁻¹ and optical transparencies of ~ 42 %. Meanwhile, polystyrenegraphene composites showed a conductivity of $\sim 100 \text{ Sm}^{-1}$ for 60 – 80 vol.-% films. Nevertheless, Lotya et al. [37] showed that the presence of residual surfactant in graphene dispersions is detrimental for the optical and electrical properties. Indeed, the as-deposited films had a transmittance of ~ 62 % coupled with sheet resistance of ~ 970 k Ω m⁻¹, which corresponds to a DC conductivity of 35 Sm⁻¹. The same authors reported later the preparation of films, from graphene exfoliated in aqueous surfactant solutions, with average conductivities of 17500 Sm⁻¹ after annealing at 500 °C under an argon/hydrogen atmosphere. [67] On the other hand, Zhang et al. [54] prepared transparent and highly conductive films with graphene/Py-NH₂ (Gr-Py-NH₂) and graphene/Py-SO₃ (Gr-Py-SO₃) with a sheet resistance of $1.9 \times 10^8 \Omega m^{-1}$ and a transmittance of 90 %. After annealing at 1000 °C, the resistance further decreases to 778 Ω per square, corresponding to conductivities of 8400 Sm⁻¹ and 181200 Sm⁻¹ for Gr-Py-NH₂ and Gr-Py-SO₃. Furthermore, Wang et al. [80] reported that dispersions of graphene in solvents display broadband nonlinear optical response when excited by nanosecond pulses, observing how the optical transmission falls from 85 % to 48 % as the pulse energy density is increased to 10 Jcm^{-2} .

An *et al.* [81] fabricated ultrathin electrochemical double layer capacitors (EDLC) or ultracapacitors with graphene film membranes. These EDLC showed high specific capacitance (~ 120 F g⁻¹), power density (~ 105 kW kg⁻¹) and energy density (~ 9.2 Wh kg⁻¹). On the other hand, Keeley *et al.* used exfoliated graphene in DMF as an electrode material for the electrochemical detection of β -nicotinamide adenine dinucleotide (NADH), demonstrating its high performance as sensor. The same DEG-based electrode was tested as sensor for ascorbic acid, displaying a detection limit of 0.12 mM.

Regarding the mechanical properties, Khan *et al.* [21] performed mechanical measurements on graphene films, observing differences depending on the sonication time. They observed that, films prepared from sonicated graphene up to 50 hours showed a Young's modulus in the order of 5 - 11 GPa and strength of 12 - 18 MPa. Nevertheless, graphene films prepared from low sonication times were extremely delicate, being difficult to remove from the membrane.

Coleman and co-workers found that as-prepared liquid-phase exfoliated graphene is a promising reinforcement in polymer-based nanocomposites. [83, 84] Khan *et al.* [83] reported an improvement of the Young's modulus and stress at 3 % strain in polyurethanes filled with graphene, being 1 GPa and 25 MPa, respectively, for mass fractions above 50 wt.-%. Later, it has been observed that the size of graphene influences the final mechanical properties of polyvinylalcohol (PVA), obtaining higher modulus for graphene flakes with large aspect ratio. Nevertheless, a decrease in the strength was observed, due to a failure at the polymer-graphene interface. [84] Recently, Istrate *et al.* [85] reported that polyethylene terephthalate (PET) filled with exfoliated graphene have superior mechanical properties as those observed in neat PET. Indeed, for low loading contents of graphene (0.07 wt.-%) they observed an increase on the elastic modulus of 10 % and an enhancement in the tensile strength of more than 40 % compared to neat PET.

Hexagonal Boron Nitride Nanosheets

Layered hexagonal boron nitride (*h*-BN) consists of a structural lattice similar to graphite in which alternating boron (B) and nitrogen (N) atoms substitute carbon (C) atoms in graphite. Therefore, boron nitride nanosheets (BNNSs) are composed by sheets of sp^2 -hybridized 2D layers, organized in a honeycomb geometry, with an interlayer distance of *ca*. 0.33 – 0.34 nm (Figure 7.6). [15, 41] Recently, BNNSs have emerged as interesting 2D nanomaterials because of their differences/advantages compared to graphene. Besides the unique chemical and thermal stabilities [41, 86] of BNNSs, they present exciting electrical insulating properties (band gap of 5 ~ 6 eV). [87] Therefore, BNNSs have easily found application as promising materials in nanodevices or functional composites.



FIGURE 7.6 Hexagonal boron nitride (*h*-BN) structural model

Liquid-phase exfoliation of h-BN

The strategy used to synthesize h-BN for several years was by ultra-high vacuum (UHV) chemical vapour deposition (CVD) via the decomposition of a borazine precursor on single crystal metallic

substrates. [88-90] This methodology provides single-layer BNNSs but requires extreme conditions of temperature and pressure and, therefore, is widely considered as unsuitable to synthesize BNNSs at larger scales.

On the other hand, *top-down* approaches based on mechanical and liquid-phase exfoliation methods, already reported for graphene, have been successfully used to separate individual sheets of 2D crystals. However, the B-N bond presents a partially ionic character compared to the covalent C-C bonding of graphene, leading to the so-called "lip-lip" interactions between neighbouring BN layers. [41] These forces are stronger than the weak van der Waals interactions between graphene layers and hence it is challenging to exfoliate *h*-BN. Mechanical exfoliation strategies based on micromechanical cleavage [91] produces high quality monolayer BNNSs but in very low quantities. Meanwhile, despite the high efficiency of ball milling [92] to produce BNNSs, it creates a high density of defects.

Liquid-phase exfoliation appears as one excellent alternative to overcome the "lip-lip" interactions of BN layers. [93] Zhi *et al.* [94] reported the exfoliation of BN particles in DMF to obtain pure BNNSs structures with adjusted averaged thickness of nanosheets after centrifugation. The successful exfoliation is attributed to the strong interactions between the DMF and BN surfaces. Nevertheless, Coleman and co-workers, [25] proposed a number of different solvents based on the Hansen solubility theory to exfoliate *h*-BN, being NMP and IPA the most promising. On the other hand, Zhou *et al.* [42] demonstrated that a mixture of poor solvents, such as water and ethanol, can be used to exfoliate BN and to obtain highly stable suspensions of exfoliated materials. Recently, Marsh *et al.* [95] reported a high efficiency co-solvent approach based in 60 wt.-% concentration of *tert*-butanol (tBA) in water. These authors suggested that there is a relationship between surface tension, solvent molecular weight, and structural dependencies on the exfoliation of *h*-BN (Figure 7.7).



FIGURE 7.7

a) TEM image of BNNSs after sonication for 3 hours in 60% tBA (scale bar 100 nm); b) Magnification of the square outline in a) (scale bar 10 nm); c) Image of the scrolling of BNNSs (scale bar 500 nm); d) Diffraction pattern of few-layered BNNSs. Reproduced from ref. [94] with permission from The Royal Society of Chemistry. e) Pictures of dispersions of BNNSs in different organic solvents; f) Previous dispersions irradiated with a laser beam to visually indicate the Tyndall effect; g) Pictures of the same dispersions after 1 week. Reproduced from ref. [93] with permission from The Royal Society of Chemistry

Similar to the case of graphene, BN particles are highly hydrophobic and hence their exfoliation in water is challenging. Lin *et al.* [96] demonstrated that water can be an effective solvent to exfoliate *h*-BN by a sonication-assisted hydrolysis method that promotes cutting of pristine or thicker *h*-BN flakes affording smaller and more exfoliated sheets. On the other hand, the same group proposed a functionalization using lipophilic and hydrophilic amine molecules that induced the exfoliation of layered *h*-BN, resulting in mono- and few-layered BNNSs, which are soluble in organic solvents and water. [97] A different approach to prepare large quantities of BNNSs in water is by adding surfactants. Smith *et al.* [34] reported that aqueous solutions of ionic surfactants, such as sodium cholate, are able to exfoliate a range of layered compounds, including *h*-BN. Guardia *et al.* [98] found that the use of non-ionic surfactants are ineffective in affording high concentrations of *h*-BN platelets, being similar to those obtained in water without surfactants. Hence, the use of surfactants is not sufficient in some cases and their residues are difficult to remove. For this reason, other stabilising agents, such as organic dyes, have recently replaced surfactants. [99]

BNNSs have been prepared also in a 1,2-dichloroethane solution of poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylenevinylene) breaking the *h*-BN crystals into few layer *h*-BN and forming a non-covalent functionalization of BNNSs. [100] Furthermore, large scale preparation of BNNSs have been reported using a protic sulfonic acid, methanesulfonic acid (MSA). [101] The BNNSs obtained by the latter method can be redispersed in different solvents finding a wide range of applications. May *et al.* [35] reported the exfoliation of *h*-BN in a different range of polymer solutions, dissolved in tetrahydrofuran (THF) and cyclohexanone (CXO).

Properties and Applications

h-BN has been widely employed as a high-temperature solid lubricant and, because of its good electrical insulation properties, as charge leakage barrier layers in electronic equipment. [15] However, BNNSs present unique chemical stability and intrinsic insulation as well as high thermal stability compared to their bulk counterparts. As a result, BNNSs are considered promising materials for novel polymer nanocomposites. For example, the in-plane thermal conductivity of BNNSs is 2000 W m⁻¹K⁻¹ [102] while that of h-BN is only ca. 400 Wm⁻¹K⁻¹. [103] Kuang et al. [102] used BNNSs obtained by liquid-phase exfoliation to fabricate elastomeric nanocomposites with high thermal conductivities. They found that increasing the orientation of BNNSs in silicon rubber (SiR) and natural rubber (NR) the thermal conductivity can be significantly enhanced. The mechanical properties of BNNSs are expected to be similar to that of graphitic materials, due to the similar crystal structure. Indeed, the 2D elastic modulus of BNNS is of the order of $200 - 500 \text{ Nm}^{-1}$ for sheet thickness of 1 - 2 nm, [104] indicating that BNNSs could potentially function as a good polymer reinforcement. Zhi et al. [94] prepared transparent PMMA/BNNSs composites observing an improvement of 22 % in the elastic modulus while an increase of 11 % in the strength was obtained with only 0.3 wt.-% of BNNSs. Recently, Liu et al. [105] observed that the size of the BNNSs have a profound effect on the mechanical properties of cellulose acetate (CA). BNNSs with larger aspect ratios obtained by separating nanosheets at lower centrifugation rates, up to 1500 rpm, contributed to the improvement of modulus and break elongation. BNNSs/CA composites, of 2 wt.-% nanosheets, increased the modulus and tensile strength by 12.4 % and 14 %, respectively, compared to pure CA. On the other hand, BNNSs obtained by exfoliation in MSA were used to fabricate poly [2,2'-(p-oxydiphenylene)-5,5'-bibenzimidazole] (OPBI)/BNNSs composites with superior mechanical and thermal properties. [101] Other unique thermal properties have been noted in such composites; for example, it has been observed that BNNSs nanofillers increase the

glass transition temperature (T_g) of polymer composites due to a reduction in chain mobility. [94, 106]

Transition Metal Dichalcogenides

Over the past decade an ever-increasing interest in the remarkable properties of graphene [4-8, 46-48] at the scientific and technological levels has triggered a new wave of attention towards other 2D layered materials, such as the transition metal dichalcogenides (TMDs). The potential of 2D nanostructures arises from their dimensionality as well as the composition and arrangement of the atoms in single layers. [3] TMDs adopt the general formula MX_2 , where M represents a transition metal element (usually Mo, W, Nb, Ti, Ni or V) while X is a chalcogen (S, Se or Te), consist of hexagonal layered structures of the form X-M-X (Figure 7.8). The bulk 3D crystals are formed in different polytypes, varying on the stacked planes, covalently bonded, and the van der Waals interactions between adjacent layers. Hence, the lamellar structure of TMDs, analogous to that of graphite, can be exfoliated into single- and few-layer nanosheets. It is worth noting that exfoliated TMDs are chemically reactive and possess unique electronic, electrochemical and photonic properties, [9-14] due to their high surface area and quantum confinement effects, [3, 15, 16] not observed in their bulk counterparts. Nevertheless, the exceptional properties of exfoliated TMDs show a strong layer dependency. For instance, when MoS_2 is exfoliated, its electronic properties change from an indirect band gap of 1.2 eV in its bulk state, to a direct gap semiconductor of 1.8 eV for a monolayer. [9, 11] As a result of this upshift, a strong photoluminescence in single-layer MoS_2 is observed which was otherwise absent in thicker crystals. [2, 10, 11] One of the main advantages of these layered materials, that have to be remarked, pertains to their functional diversity. Depending on the combination of the transition metal and chalcogen, these materials behave as insulators (HfS₂), semiconductors (MoS₂, WS₂), semimetals (WTe₂, TiSe₂), metals (NbS₂, VSe₂) and superconductors (NbSe₂, TaS₂). [3, 107] As a consequence, the exciting electronic and physicochemical properties of atomically thin 2D TMDs have aroused tremendous research interest for applications in photovoltaic devices, transistors, supercapacitors, lithium ion batteries, heterogeneous catalysis, sensors, and storage devices. [107, 108]





Liquid-phase exfoliation of TMDs

The isolation of high-quality single-layer TMDs has increased the interest of the scientific community since the discovery of the extraordinary properties of single-layer graphene. In TMDs, as the number of layers is reduced, dramatic changes in the electronic structure and properties are observed. As in the case of graphene, two main strategies have been developed for the production of atomically thin 2D TMDs; *bottom-up* and *top-down*.

Bottom-up techniques permit to produce free-defect high quality TMDs with good control of the number of layers (mainly single-layer sheets) and lateral dimensions. 2D TMDs obtained by bottom-up techniques are widely used in nanoelectronics and nanodevices due to the abovementioned features. Several techniques, similar as those mentioned for graphene, have emerged for the obtainment of single-layer TMDs: CVD, [110-115] thermal evaporation, [116, 117] pulse laser deposition [118] or UHV approaches. [119, 120] Amongst all these techniques CVD is the most widely employed to produce high-quality single-layer TMDs and is based on the use of precursors such as sulphur, selenium or transition metals (Mo, W, etc.) which in their vapour form are deposited over a substrate with the help of a carrier gas. However, all these methodologies yields low quantity of nanosheets, being used at the nanoscale level for devices.

On the other hand, top-down strategies include techniques such as mechanical cleavage, [9, 11, 121-123] liquid-phase exfoliation by sonication in appropriate liquids, [20, 25, 42, 124-126] intercalation of TMDs by ionic species followed by liquid exfoliation, [10, 127] electrochemical ionintercalation and exfoliation, [128-130] ball milling [131, 132] and laser thinning technique. [133] Mechanical cleavage ("scotch tape" or "peel off" method) produces high quality and single-layer sheets, an essential feature to achieve the excellent properties desired. Nevertheless, thickness and size of the as-produced sheets cannot be controlled, the low yield production and delicate and time-consuming procedure limits its application to fundamental research. [134] On the contrary, liquid-based synthetic routes afford products in large amounts and do not require the use of extreme conditions, being in some cases environmentally friendly. The van der Waals interactions between the sheets facilitate the separation of these uncharged layered solids directly by sonication in appropriate solvents to obtain single-layer and few-layer sheets. The potential of this methodology is set on its versatility and its scalability, besides the possibility of exfoliation in common solvents. Recently, electrochemical ion-intercalation and exfoliation has become an effective method to increase the mass production of exfoliated 2D TMDs sheets. By this methodology, the electronic structure of TMDs can be electrochemically tuned by the diffusion of intercalated ions (Li^{\dagger} , Na^{\dagger} , K^{\dagger}) by means of a discharge process. [10, 128-130] However, some challenges remain unresolved; control of the ion-intercalation, amount of inserted ions or structural deformations in TMDs and thus alterations of the electronic properties and formation of metal nanoparticles.

Liquid-phase exfoliation of 2D TMDs has emerged as a leading method to obtain mono- and fewlayer nanosheets in a wide range of solvents. Coleman *et al.* [25] described an exhaustive analysis on the exfoliation of MoS₂, WS₂, MoSe₂, MoTe₂, NbSe₂ and NiTe₂ in a number of solvents with different surface tensions. By optical absorption spectroscopy, they demonstrated that the amount of material in the dispersions increases as the surface tension of the solvents is close to that of the bulk materials. Later, they studied how solution thermodynamics and in particular solubility parameters can be used as a framework to understand the dispersion of 2D materials. [30] The same group reported a study on the sonication of MoS_2 in NMP to prepare dispersions based on the initial concentration of bulk materials and sonication time, in this way they could separate the dispersions in fractions with different mean size by controlled centrifugation. [45] At a similar time, Pachauri *et al.* [126] optimized the liquid-phase exfoliation of MoS_2 in acetonitrile obtaining thin layers with sizes of the order of $10 - 60 \ \mu$ m. Acetonitrile is a polar aprotic solvent, which dissolves a wide range of ionic and non-polar compounds, and physisorbs on the surface of MoS_2 , weakening the van der Waals forces between layers. Meanwhile, Zhou *et al.* [42] reported a mixed-solvent strategy in volatile solvents, which offers promising advantages such as low cost, lower toxicity, and easy removal for postprocessing methods. Dong *et al.* [135] developed a spontaneous exfoliation approach to prepare few-layer MoS_2 nanosheets under mild conditions. An exfoliation yield of 60 % was achieved in a mixed solvent of H_2O_2/NMP volume ratio = 1:19 v/v. May *et al.* [35] showed that TMDs can be exfoliated in dissolved polymers - a useful approach for those TMDs that cannot be exfoliated in common solvents. Furthermore, this strategy presents an advantage for the preparation of polymer nanocomposites.

Nevertheless, exfoliation in water is challenging, as similarly observed in other 2D materials, and hence the use of surfactants is required for successful exfoliation of TMDs. Smith *et al.* [34] used sodium cholate and reported the production of thin flakes of different TMDs under ambient conditions. Their production method shows clear advantages for the large-scale preparation of composites (Figure 7.9). On the other hand, Backes *et al.* [24] used the same aqueous-surfactant solution to exfoliate TMDs but, after sonication, they employed a centrifugation technique based on band sedimentation to separate nanosheets by lateral size distribution. Guardia *et al.* [98] have tested non-ionic surfactants to exfoliate MOS₂ and WS₂. Higher concentrations as those obtained with water-sodium cholate were achieved.



FIGURE 7.9

Dispersions of layered compounds. a) Optical photographs of TMDs and BN in aqueous sodium cholate suspensions. b) Absorption spectra of dispersions in a). c) Vacuum filtered thin films of TMDs and BN obtained from the dispersions. d-i) TEM images of nanosheets from dispersion in a). Reprinted with permission from [34]. Copyright 2015 American Chemical Society

Properties and Applications

TMDs show in their bulk state diverse electronic, optical and magnetic properties [9, 15, 134, 136-139] and exhibit some particular phenomena such as superconductivity and charge density wave.

[140-143] However, the potential of TMDs resides in their 2D exfoliated form due to their tunable bandgap and their high chemical and thermal stabilities. [9-13] Therefore, the versatility of single layers of TMDCs, as a function of their composition and structure, offers a broad range of new possibilities in nanotechnology.

The photoluminescence of single- and few-layer MoS_2 has been observed also in liquid-phase exfoliated MoS_2 nanosheets. Wang *et al.* [128] describe a facile strategy to modulate the 2D photoluminescence of exfoliated MoS_2 , by electrochemically manipulating the amount of intercalating Li⁺, Na⁺ and K⁺ ions. Nanosheets obtained by this methodology could be used to fabricate highly photoelectrochemical sensors, high performance optical modulators, or enhanced solar cells. On the other hand, exfoliated MoS_2 in aqueous dispersions of (poly(ethylene glycol)block-poly(propylene glycol)-block-poly-(ethylene glycol)), with a feed ratio of 20:70:20 (EO:PO:EO) has shown photocalytic properties. [124] The effect is based on the photoluminescence properties of single- and few-layer MoS_2 sheets and their large surface area, affording rapid adsorption of the material to the particle surface. This procedure allows for the preparation of semiconducting MoS_2 nanosheets with a useful bandgap of 1.97 eV. Pachauri *et al.* [126] prepared devices using exfoliated MoS_2 flakes to use as chemical sensors based on their photoresponse properties.

Recently, Winchester *et al.* [144] reported on the electrochemical properties of MoS_2 exfoliated into few layers in different electrolytes. The electrochemical charge storage capacity of MoS_2 nanosheets increased by an order of magnitude, compared to their bulk counterpart, and they obtained a maximal specific capacitance of ~ 2.4 mFcm⁻² with BMIM-PF₆ as the electrolyte. The MoS_2 nanosheets and MoS_2 -graphene synthesized by Dong *et al.* [135] showed discharge capacities, at a current density 200 mAg⁻¹, of 866 mAhg⁻¹, and 865 mAhg⁻¹ and after 50 cycles, the Coulombic efficiencies are 98.2 % and 98.6 % for MoS_2 -graphene electrodes, respectively. MoS_2 nanosheets obtained by this method may ultimately find application in energy storage, catalysis, and novel composites.

The mechanical properties of individual MoS_2 monolayers have shown high values of stiffness ($Y \sim 300$ GPa) and tensile strength ($\sigma_B \sim 23$ GPa). Even if these values are lower as those observed in graphene, they are still higher than those displayed by other, more traditional particles and hence, TMDs could be used as reinforcement of polymer nanocomposites. O'Neill *et al.* [42] prepared PVA nanocomposites with 0.25 wt.-% MoS₂ nanosheets obtained directly after exfoliation and with 0.25 wt.-% MoS₂ nanosheets after flake size selection. They observed that using non-selected size flakes both strength and modulus decreased by a factor of 2 while using size selected nanosheets increased *ca.* 15 %. Meanwhile, Eksik *et al.* [145] prepared epoxy nanocomposites with MoS₂ nanosheet weight fractions ranging from 0.1 % to 1.0 %. The mechanical properties were generally enhanced for low loading fractions of up to 0.2 – 0.3 %. However, beyond this weight fractions MoS₂ nanosheets produced a detrimental effect in all mechanical properties due to the formation of agglomerates. Nevertheless, MoS₂ nanosheets are highly effective in strengthening and stiffening epoxy matrices and show much promise in the field.

Finally, Tao *et al.* [146] prepared $MoS_2/PMMA$ nanocomposites, showing low optical limiting thresholds, 0.4 and 1.3 Jcm⁻² when the concentration of MoS_2 was around 0.016 mgcm⁻³. This polymer nanocomposites showed low limiting differential transmittance, 2 % and 3 % under nanosecond pulsed laser exposure, operating at 532 nm and 1064 nm, respectively; $MoS_2/PMMA$

nanocomposites are promising materials for the preparation of solid nonlinear optical materials for optical limiting applications.

Conclusion

Two-dimensional nanomaterials, such as graphene, BNNSs and TMDs, have received significant attention in recent years because of their extraordinary properties. The different strategies to achieve high-quality large surface area nanosheets are classified in *bottom-up* and *top-down approaches*. Liquid-phase exfoliation of layered materials can be enclosed in the *top-down* strategies and is based on the exfoliation of 2D materials by sonication in a liquid environment followed by a purification method. The main advantage of the liquid-phase exfoliation is the production of exfoliated material with high yields under mild conditions without creating high number of defects on the surface of the flakes.

The exfoliation of graphene, BNNSs and TMDs in liquid environments produce single- and few-layer nanosheets in large quantities, thus finding applications as nanofillers in polymers to obtain composite materials for advanced applications. However, an efficient exfoliation in liquid environments requires similar surface tensions between the solvents and the layered materials, which usually occurs in high-boiling point solvents such as NMP. The development of new strategies to exfoliate 2D layered materials in water with the aid of surfactants or in polymer solutions or using polyaromatic hydrocarbons in the case of graphene have opened a great range of possibilities to produce 2D nanosheets not only as nanofillers in composite materials but in applications at the nanoscale for sensors or electronic devices.

References

- 1. Sun Z, Chang H. Graphene and Graphene-like Two-Dimensional Materials in Photodetection: Mechanisms and Methodology. ACS Nano. 2014;8(5):4133-56.
- 2. Butler SZ, Hollen SM, Cao L, Cui Y, Gupta JA, Gutiérrez HR, et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. ACS Nano. 2013;7(4):2898-926.
- 3. Chhowalla M, Shin HS, Eda G, Li L-J, Loh KP, Zhang H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat Chem. 2013;5(4):263-75.
- 4. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Electric Field Effect in Atomically Thin Carbon Films. Science. 2004;306(5696):666-9.
- 5. Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, et al. Superior Thermal Conductivity of Single-Layer Graphene. Nano Letters. 2008;8(3):902-7.
- 6. Lee C, Wei X, Kysar JW, Hone J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science. 2008;321(5887):385-8.
- 7. Stoller MD, Park S, Zhu Y, An J, Ruoff RS. Graphene-Based Ultracapacitors. Nano Letters. 2008;8(10):3498-502.
- 8. Geim AK, Novoselov KS. The rise of graphene. Nat Mater. 2007;6(3):183-91.
- 9. Mak KF, Lee C, Hone J, Shan J, Heinz TF. Atomically Thin MoS2: A New Direct-Gap Semiconductor. Physical Review Letters. 2010;105(13):136805.

- 10. Eda G, Yamaguchi H, Voiry D, Fujita T, Chen M, Chhowalla M. Photoluminescence from Chemically Exfoliated MoS2. Nano Letters. 2011;11(12):5111-6.
- 11. Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim C-Y, et al. Emerging Photoluminescence in Monolayer MoS2. Nano Letters. 2010;10(4):1271-5.
- 12. Fukuda K, Ebina Y, Shibata T, Aizawa T, Nakai I, Sasaki T. Unusual Crystallization Behaviors of Anatase Nanocrystallites from a Molecularly Thin Titania Nanosheet and Its Stacked Forms: Increase in Nucleation Temperature and Oriented Growth. Journal of the American Chemical Society. 2006;129(1):202-9.
- 13. Sakai N, Ebina Y, Takada K, Sasaki T. Electronic Band Structure of Titania Semiconductor Nanosheets Revealed by Electrochemical and Photoelectrochemical Studies. Journal of the American Chemical Society. 2004;126(18):5851-8.
- 14. Nicolosi V, Chhowalla M, Kanatzidis MG, Strano MS, Coleman JN. Liquid Exfoliation of Layered Materials. Science. 2013;340(6139).
- 15. Xu M, Liang T, Shi M, Chen H. Graphene-Like Two-Dimensional Materials. Chemical Reviews. 2013;113(5):3766-98.
- 16. Lv R, Robinson JA, Schaak RE, Sun D, Sun Y, Mallouk TE, et al. Transition Metal Dichalcogenides and Beyond: Synthesis, Properties, and Applications of Single- and Few-Layer Nanosheets. Accounts of Chemical Research. 2014.
- 17. Eigler S, Hirsch A. Chemistry with Graphene and Graphene Oxide—Challenges for Synthetic Chemists. Angewandte Chemie International Edition. 2014;53(30):7720-38.
- 18. Pénicaud A, Drummond C. Deconstructing Graphite: Graphenide Solutions. Accounts of Chemical Research. 2012;46(1):129-37.
- 19. Ciesielski A, Samori P. Graphene via sonication assisted liquid-phase exfoliation. Chemical Society Reviews. 2014;43(1):381-98.
- 20. Srivastava VK, Quinlan RA, Agapov AL, Dunlap JR, Nelson KM, Duranty E, et al. Macroscopic Properties of Restacked, Redox-Liquid Exfoliated Graphite and Graphite Mimics Produced in Bulk Quantities. Advanced Functional Materials. 2014;24(31):4969-77.
- 21. Khan U, O'Neill A, Lotya M, De S, Coleman JN. High-Concentration Solvent Exfoliation of Graphene. Small. 2010;6(7):864-71.
- 22. Suslick KS. Sonochemistry. Science. 1990;247(4949):1439-45.
- 23. Mason TJ, Lorimer JP. Applied Sonochemistry: Uses of Power Ultrasound in Chemistry and Processing: Wiley-VCH Verlag GmbH & Co. KGaA; 2003.
- 24. Backes C, Smith RJ, McEvoy N, Berner NC, McCloskey D, Nerl HC, et al. Edge and confinement effects allow in situ measurement of size and thickness of liquid-exfoliated nanosheets. Nat Commun. 2014;5.
- 25. Coleman JN, Lotya M, O'Neill A, Bergin SD, King PJ, Khan U, et al. Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. Science. 2011;331(6017):568-71.
- 26. Handbook on Applications of Ultrasound: Sonochemistry for Sustainability: CRC Press; 2011.
- 27. Suslick KS, Price GJ. Applications of ultrasound to materials chemistry Annual Review of Materials Science. 1999;29(1):295-326.
- 28. Xu H, Zeiger BW, Suslick KS. Sonochemical synthesis of nanomaterials. Chemical Society Reviews. 2013;42(7):2555-67.
- 29. Coleman JN. Liquid-Phase Exfoliation of Nanotubes and Graphene. Advanced Functional Materials. 2009;19(23):3680-95.

- 30. Cunningham G, Lotya M, Cucinotta CS, Sanvito S, Bergin SD, Menzel R, et al. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly between Compounds. ACS Nano. 2012;6(4):3468-80.
- Bergin SD, Nicolosi V, Streich PV, Giordani S, Sun Z, Windle AH, et al. Towards Solutions of Single-Walled Carbon Nanotubes in Common Solvents. Advanced Materials. 2008;20(10):1876-81.
- 32. Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun Z, De S, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. Nat Nano. 2008;3(9):563-8.
- 33. Coleman JN. Liquid Exfoliation of Defect-Free Graphene. Accounts of Chemical Research. 2012;46(1):14-22.
- 34. Smith RJ, King PJ, Lotya M, Wirtz C, Khan U, De S, et al. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. Advanced Materials. 2011;23(34):3944-8.
- 35. May P, Khan U, Hughes JM, Coleman JN. Role of Solubility Parameters in Understanding the Steric Stabilization of Exfoliated Two-Dimensional Nanosheets by Adsorbed Polymers. The Journal of Physical Chemistry C. 2012;116(20):11393-400.
- 36. Notley SM. Highly Concentrated Aqueous Suspensions of Graphene through Ultrasonic Exfoliation with Continuous Surfactant Addition. Langmuir. 2012;28(40):14110-3.
- 37. Lotya M, Hernandez Y, King PJ, Smith RJ, Nicolosi V, Karlsson LS, et al. Liquid Phase Production of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. Journal of the American Chemical Society. 2009;131(10):3611-20.
- 38. Liang YT, Hersam MC. Highly Concentrated Graphene Solutions via Polymer Enhanced Solvent Exfoliation and Iterative Solvent Exchange. Journal of the American Chemical Society. 2010;132(50):17661-3.
- 39. Vallés C, Drummond C, Saadaoui H, Furtado CA, He M, Roubeau O, et al. Solutions of Negatively Charged Graphene Sheets and Ribbons. Journal of the American Chemical Society. 2008;130(47):15802-4.
- 40. Cheng M-Y, Ye Y-S, Cheng J-H, Yeh Y-J, Chen B-H, Hwang B-J. Defect-free graphene metal oxide composites: formed by lithium mediated exfoliation of graphite. Journal of Materials Chemistry. 2012;22(29):14722-6.
- 41. Golberg D, Bando Y, Huang Y, Terao T, Mitome M, Tang C, et al. Boron Nitride Nanotubes and Nanosheets. ACS Nano. 2010;4(6):2979-93.
- 42. Zhou K-G, Mao N-N, Wang H-X, Peng Y, Zhang H-L. A Mixed-Solvent Strategy for Efficient Exfoliation of Inorganic Graphene Analogues. Angewandte Chemie International Edition. 2011;50(46):10839-42.
- 43. Halim U, Zheng CR, Chen Y, Lin Z, Jiang S, Cheng R, et al. A rational design of cosolvent exfoliation of layered materials by directly probing liquid–solid interaction. Nat Commun. 2013;4.
- 44. Bonaccorso F, Zerbetto M, Ferrari AC, Amendola V. Sorting Nanoparticles by Centrifugal Fields in Clean Media. The Journal of Physical Chemistry C. 2013;117(25):13217-29.
- 45. O'Neill A, Khan U, Coleman JN. Preparation of High Concentration Dispersions of Exfoliated MoS2 with Increased Flake Size. Chemistry of Materials. 2012;24(12):2414-21.
- 46. Du X, Skachko I, Barker A, Andrei EY. Approaching ballistic transport in suspended graphene. Nat Nano. 2008;3(8):491-5.
- 47. Zhang Y, Tan Y-W, Stormer HL, Kim P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. Nature. 2005;438(7065):201-4.

- 48. Novoselov KS, Geim AK, Morozov SV, Jiang D, Katsnelson MI, Grigorieva IV, et al. Twodimensional gas of massless Dirac fermions in graphene. Nature. 2005;438(7065):197-200.
- 49. Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, et al. Fine Structure Constant Defines Visual Transparency of Graphene. Science. 2008;320(5881):1308.
- 50. Terrones M, Martín O, González M, Pozuelo J, Serrano B, Cabanelas JC, et al. Interphases in Graphene Polymer-based Nanocomposites: Achievements and Challenges. Advanced Materials. 2011;23(44):5302-10.
- 51. Rao CNR, Biswas K, Subrahmanyam KS, Govindaraj A. Graphene, the new nanocarbon. Journal of Materials Chemistry. 2009;19(17):2457-69.
- 52. Terrones M, Botello-Méndez AR, Campos-Delgado J, López-Urías F, Vega-Cantú YI, Rodríguez-Macías FJ, et al. Graphene and graphite nanoribbons: Morphology, properties, synthesis, defects and applications. Nano Today. 2010;5(4):351-72.
- 53. Fasolino A, Los JH, Katsnelson MI. Intrinsic ripples in graphene. Nat Mater. 2007;6(11):858-61.
- 54. Zhang M, Parajuli RR, Mastrogiovanni D, Dai B, Lo P, Cheung W, et al. Production of Graphene Sheets by Direct Dispersion with Aromatic Healing Agents. Small. 2010;6(10):1100-7.
- 55. Zhang F, Chen X, Boulos RA, Md Yasin F, Lu H, Raston C, et al. Pyrene-conjugated hyaluronan facilitated exfoliation and stabilisation of low dimensional nanomaterials in water. Chemical Communications. 2013;49(42):4845-7.
- 56. Wang W, Zhang Y, Wang Y-B. Noncovalent $\pi \cdots \pi$ interaction between graphene and aromatic molecule: Structure, energy, and nature. The Journal of Chemical Physics. 2014;140(9):-.
- 57. Ghosh A, Rao KV, George SJ, Rao CNR. Noncovalent Functionalization, Exfoliation, and Solubilization of Graphene in Water by Employing a Fluorescent Coronene Carboxylate. Chemistry A European Journal. 2010;16(9):2700-4.
- 58. Costa RD, Malig J, Brenner W, Jux N, Guldi DM. Electron Accepting Porphycenes on Graphene. Advanced Materials. 2013;25(18):2600-5.
- 59. Luo B, Liu S, Zhi L. Chemical Approaches toward Graphene-Based Nanomaterials and their Applications in Energy-Related Areas. Small. 2012;8(5):630-46.
- 60. Bernal M, Pérez E. One-Pot Exfoliation of Graphite and Synthesis of Nanographene/Dimesitylporphyrin Hybrids. International Journal of Molecular Sciences. 2015;16(5):10704-14.
- 61. Khan U, Porwal H, O'Neill A, Nawaz K, May P, Coleman JN. Solvent-Exfoliated Graphene at Extremely High Concentration. Langmuir. 2011;27(15):9077-82.
- 62. Gayathri S, Jayabal P, Kottaisamy M, Ramakrishnan V. Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study. AIP Advances. 2014;4(2):027116.
- 63. Bourlinos AB, Georgakilas V, Zboril R, Steriotis TA, Stubos AK. Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes. Small. 2009;5(16):1841-5.
- 64. Zhang X, Coleman AC, Katsonis N, Browne WR, van Wees BJ, Feringa BL. Dispersion of graphene in ethanol using a simple solvent exchange method. Chemical Communications. 2010;46(40):7539-41.
- 65. Ricardo KB, Sendecki A, Liu H. Surfactant-free exfoliation of graphite in aqueous solutions. Chemical Communications. 2014;50(21):2751-4.
- 66. Green AA, Hersam MC. Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation. Nano Letters. 2009;9(12):4031-6.

- 67. Lotya M, King PJ, Khan U, De S, Coleman JN. High-Concentration, Surfactant-Stabilized Graphene Dispersions. ACS Nano. 2010;4(6):3155-62.
- 68. Ronan JS, Mustafa L, Jonathan NC. The importance of repulsive potential barriers for the dispersion of graphene using surfactants. New Journal of Physics. 2010;12(12):125008.
- 69. Guardia L, Fernández-Merino MJ, Paredes JI, Solís-Fernández P, Villar-Rodil S, Martínez-Alonso A, et al. High-throughput production of pristine graphene in an aqueous dispersion assisted by non-ionic surfactants. Carbon. 2011;49(5):1653-62.
- 70. Yang H, Hernandez Y, Schlierf A, Felten A, Eckmann A, Johal S, et al. A simple method for graphene production based on exfoliation of graphite in water using 1-pyrenesulfonic acid sodium salt. Carbon. 2013;53(0):357-65.
- 71. Schlierf A, Yang H, Gebremedhn E, Treossi E, Ortolani L, Chen L, et al. Nanoscale insight into the exfoliation mechanism of graphene with organic dyes: effect of charge, dipole and molecular structure. Nanoscale. 2013;5(10):4205-16.
- 72. Englert JM, Röhrl J, Schmidt CD, Graupner R, Hundhausen M, Hauke F, et al. Soluble Graphene: Generation of Aqueous Graphene Solutions Aided by a Perylenebisimide-Based Bolaamphiphile. Advanced Materials. 2009;21(42):4265-9.
- 73. Sampath S, Basuray AN, Hartlieb KJ, Aytun T, Stupp SI, Stoddart JF. Direct Exfoliation of Graphite to Graphene in Aqueous Media with Diazaperopyrenium Dications. Advanced Materials. 2013;25(19):2740-5.
- 74. Xu J, Dang DK, Tran VT, Liu X, Chung JS, Hur SH, et al. Liquid-phase exfoliation of graphene in organic solvents with addition of naphthalene. Journal of Colloid and Interface Science. 2014;418(0):37-42.
- 75. Guo Z, Du F, Ren D, Chen Y, Zheng J, Liu Z, et al. Covalently porphyrin-functionalized singlewalled carbon nanotubes: a novel photoactive and optical limiting donor-acceptor nanohybrid. Journal of Materials Chemistry. 2006;16(29):3021-30.
- 76. Xu H, Wu P, Liao C, Lv C, Gu Z. Controlling the morphology and optoelectronic properties of graphene hybrid materials by porphyrin interactions. Chemical Communications. 2014;50(64):8951-4.
- 77. Aly SM, Parida MR, Alarousu E, Mohammed OF. Ultrafast electron injection at the cationic porphyrin-graphene interface assisted by molecular flattening. Chemical Communications. 2014;50(72):10452-5.
- 78. Malig J, Stephenson AWI, Wagner P, Wallace GG, Officer DL, Guldi DM. Direct exfoliation of graphite with a porphyrin creating functionalizable nanographene hybrids. Chemical Communications. 2012;48(70):8745-7.
- 79. Kiessling D, Costa RD, Katsukis G, Malig J, Lodermeyer F, Feihl S, et al. Novel nanographene/porphyrin hybrids preparation, characterization, and application in solar energy conversion schemes. Chemical Science. 2013;4(8):3085-98.
- 80. Wang J, Hernandez Y, Lotya M, Coleman JN, Blau WJ. Broadband Nonlinear Optical Response of Graphene Dispersions. Advanced Materials. 2009;21(23):2430-5.
- 81. An X, Simmons T, Shah R, Wolfe C, Lewis KM, Washington M, et al. Stable Aqueous Dispersions of Noncovalently Functionalized Graphene from Graphite and their Multifunctional High-Performance Applications. Nano Letters. 2010;10(11):4295-301.
- Keeley GP, O'Neill A, Holzinger M, Cosnier S, Coleman JN, Duesberg GS. DMF-exfoliated graphene for electrochemical NADH detection. Physical Chemistry Chemical Physics. 2011;13(17):7747-50.

- 83. Khan U, May P, O'Neill A, Coleman JN. Development of stiff, strong, yet tough composites by the addition of solvent exfoliated graphene to polyurethane. Carbon. 2010;48(14):4035-41.
- 84. May P, Khan U, O'Neill A, Coleman JN. Approaching the theoretical limit for reinforcing polymers with graphene. Journal of Materials Chemistry. 2012;22(4):1278-82.
- 85. Istrate OM, Paton KR, Khan U, O'Neill A, Bell AP, Coleman JN. Reinforcement in meltprocessed polymer–graphene composites at extremely low graphene loading level. Carbon. 2014;78(0):243-9.
- 86. Chen Y, Zou J, Campbell SJ, Le Caer G. Boron nitride nanotubes: Pronounced resistance to oxidation. Applied Physics Letters. 2004;84(13):2430-2.
- 87. Kubota Y, Watanabe K, Tsuda O, Taniguchi T. Deep Ultraviolet Light-Emitting Hexagonal Boron Nitride Synthesized at Atmospheric Pressure. Science. 2007;317(5840):932-4.
- 88. Corso M, Auwärter W, Muntwiler M, Tamai A, Greber T, Osterwalder J. Boron Nitride Nanomesh. Science. 2004;303(5655):217-20.
- 89. Nagashima A, Tejima N, Gamou Y, Kawai T, Oshima C. Electronic states of monolayer hexagonal boron nitride formed on the metal surfaces. Surface Science. 1996;357–358(0):307-11.
- 90. Ćavar E, Westerström R, Mikkelsen A, Lundgren E, Vinogradov AS, Ng ML, et al. A single h-BN layer on Pt(1 1 1). Surface Science. 2008;602(9):1722-6.
- 91. Pacilé D, Meyer JC, Girit ÇÖ, Zettl A. The two-dimensional phase of boron nitride: Fewatomic-layer sheets and suspended membranes. Applied Physics Letters. 2008;92(13):133107.
- 92. Li LH, Chen Y, Behan G, Zhang H, Petravic M, Glushenkov AM. Large-scale mechanical peeling of boron nitride nanosheets by low-energy ball milling. Journal of Materials Chemistry. 2011;21(32):11862-6.
- 93. Lin Y, Connell JW. Advances in 2D boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene. Nanoscale. 2012;4(22):6908-39.
- 94. Zhi C, Bando Y, Tang C, Kuwahara H, Golberg D. Large-Scale Fabrication of Boron Nitride Nanosheets and Their Utilization in Polymeric Composites with Improved Thermal and Mechanical Properties. Advanced Materials. 2009;21(28):2889-93.
- 95. Marsh KL, Souliman M, Kaner RB. Co-solvent exfoliation and suspension of hexagonal boron nitride. Chemical Communications. 2015;51(1):187-90.
- 96. Lin Y, Williams TV, Xu T-B, Cao W, Elsayed-Ali HE, Connell JW. Aqueous Dispersions of Few-Layered and Monolayered Hexagonal Boron Nitride Nanosheets from Sonication-Assisted Hydrolysis: Critical Role of Water. The Journal of Physical Chemistry C. 2011;115(6):2679-85.
- 97. Lin Y, Williams TV, Connell JW. Soluble, Exfoliated Hexagonal Boron Nitride Nanosheets. The Journal of Physical Chemistry Letters. 2010;1(1):277-83.
- 98. Guardia L, Paredes JI, Rozada R, Villar-Rodil S, Martinez-Alonso A, Tascon JMD. Production of aqueous dispersions of inorganic graphene analogues by exfoliation and stabilization with non-ionic surfactants. RSC Advances. 2014;4(27):14115-27.
- 99. Huafeng Y, Freddie W, Elias G, Edward L, Liam B, Alexandre F, et al. Dielectric nanosheets made by liquid-phase exfoliation in water and their use in graphene-based electronics. 2D Materials. 2014;1(1):011012.
- 100. Han W-Q, Wu L, Zhu Y, Watanabe K, Taniguchi T. Structure of chemically derived monoand few-atomic-layer boron nitride sheets. Applied Physics Letters. 2008;93(22):223103.

- 101. Wang Y, Shi Z, Yin J. Boron nitride nanosheets: large-scale exfoliation in methanesulfonic acid and their composites with polybenzimidazole. Journal of Materials Chemistry. 2011;21(30):11371-7.
- 102. Kuang Z, Chen Y, Lu Y, Liu L, Hu S, Wen S, et al. Fabrication of Highly Oriented Hexagonal Boron Nitride Nanosheet/Elastomer Nanocomposites with High Thermal Conductivity. Small. 2015;11(14):1655-9.
- 103. Sichel EK, Miller RE, Abrahams MS, Buiocchi CJ. Heat capacity and thermal conductivity of hexagonal pyrolytic boron nitride. Physical Review B. 1976;13(10):4607-11.
- 104. Song L, Ci L, Lu H, Sorokin PB, Jin C, Ni J, et al. Large Scale Growth and Characterization of Atomic Hexagonal Boron Nitride Layers. Nano Letters. 2010;10(8):3209-15.
- 105. Liu L, Shen Z, Zheng Y, Yi M, Zhang X, Ma S. Boron nitride nanosheets with controlled size and thickness for enhancing mechanical properties and atomic oxygen erosion resistance. RSC Advances. 2014;4(71):37726-32.
- 106. Yu J, Huang X, Wu C, Wu X, Wang G, Jiang P. Interfacial modification of boron nitride nanoplatelets for epoxy composites with improved thermal properties. Polymer. 2012;53(2):471-80.
- 107. Li H, Wu J, Yin Z, Zhang H. Preparation and Applications of Mechanically Exfoliated Single-Layer and Multilayer MoS2 and WSe2 Nanosheets. Accounts of Chemical Research. 2014;47(4):1067-75.
- 108. Gao M-R, Xu Y-F, Jiang J, Yu S-H. Nanostructured metal chalcogenides: synthesis, modification, and applications in energy conversion and storage devices. Chemical Society Reviews. 2013;42(7):2986-3017.
- 109. Zeng H, Cui X. An optical spectroscopic study on two-dimensional group-VI transition metal dichalcogenides. Chemical Society Reviews. 2015.
- 110. Lee Y-H, Zhang X-Q, Zhang W, Chang M-T, Lin C-T, Chang K-D, et al. Synthesis of Large-Area MoS2 Atomic Layers with Chemical Vapor Deposition. Advanced Materials. 2012;24(17):2320-5.
- 111. Lee Y-H, Yu L, Wang H, Fang W, Ling X, Shi Y, et al. Synthesis and Transfer of Single-Layer Transition Metal Disulfides on Diverse Surfaces. Nano Letters. 2013;13(4):1852-7.
- 112. Wang X, Feng H, Wu Y, Jiao L. Controlled Synthesis of Highly Crystalline MoS2 Flakes by Chemical Vapor Deposition. Journal of the American Chemical Society. 2013;135(14):5304-7.
- 113. Zhan Y, Liu Z, Najmaei S, Ajayan PM, Lou J. Large-Area Vapor-Phase Growth and Characterization of MoS2 Atomic Layers on a SiO2 Substrate. Small. 2012;8(7):966-71.
- 114. Liu K-K, Zhang W, Lee Y-H, Lin Y-C, Chang M-T, Su C-Y, et al. Growth of Large-Area and Highly Crystalline MoS2 Thin Layers on Insulating Substrates. Nano Letters. 2012;12(3):1538-44.
- 115. Najmaei S, Liu Z, Zhou W, Zou X, Shi G, Lei S, et al. Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. Nat Mater. 2013;12(8):754-9.
- Balendhran S, Ou JZ, Bhaskaran M, Sriram S, Ippolito S, Vasic Z, et al. Atomically thin layers of MoS2via a two step thermal evaporation-exfoliation method. Nanoscale. 2012;4(2):461-6.
- 117. Lin Y-C, Zhang W, Huang J-K, Liu K-K, Lee Y-H, Liang C-T, et al. Wafer-scale MoS2 thin layers prepared by MoO3 sulfurization. Nanoscale. 2012;4(20):6637-41.

- 118. Zabinski JS, Donley MS, Prasad SV, McDevitt NT. Synthesis and characterization of tungsten disulphide films grown by pulsed-laser deposition. Journal of Materials Science. 1994;29(18):4834-9.
- 119. Kibsgaard J, Lauritsen JV, Lægsgaard E, Clausen BS, Topsøe H, Besenbacher F. Cluster–Support Interactions and Morphology of MoS2 Nanoclusters in a Graphite-Supported Hydrotreating Model Catalyst. Journal of the American Chemical Society. 2006;128(42):13950-8.
- 120. Lauritsen JV, Kibsgaard J, Helveg S, Topsoe H, Clausen BS, Laegsgaard E, et al. Sizedependent structure of MoS2 nanocrystals. Nat Nano. 2007;2(1):53-8.
- 121. RadisavljevicB, RadenovicA, BrivioJ, GiacomettiV, KisA. Single-layer MoS2 transistors. Nat Nano. 2011;6(3):147-50.
- 122. Mak KF, He K, Lee C, Lee GH, Hone J, Heinz TF, et al. Tightly bound trions in monolayer MoS2. Nat Mater. 2013;12(3):207-11.
- 123. Lee C, Yan H, Brus LE, Heinz TF, Hone J, Ryu S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS2. ACS Nano. 2010;4(5):2695-700.
- 124. Quinn MDJ, Ho NH, Notley SM. Aqueous Dispersions of Exfoliated Molybdenum Disulfide for Use in Visible-Light Photocatalysis. ACS Applied Materials & Interfaces. 2013;5(23):12751-6.
- 125. Shmeliov A, Shannon M, Wang P, Kim JS, Okunishi E, Nellist PD, et al. Unusual Stacking Variations in Liquid-Phase Exfoliated Transition Metal Dichalcogenides. ACS Nano. 2014;8(4):3690-9.
- 126. Pachauri V, Kern K, Balasubramanian K. Chemically exfoliated large-area two-dimensional flakes of molybdenum disulfide for device applications. APL Materials. 2013;1(3).
- 127. Zheng J, Zhang H, Dong S, Liu Y, Tai Nai C, Suk Shin H, et al. High yield exfoliation of twodimensional chalcogenides using sodium naphthalenide. Nat Commun. 2014;5.
- 128. Wang Y, Ou JZ, Balendhran S, Chrimes AF, Mortazavi M, Yao DD, et al. Electrochemical Control of Photoluminescence in Two-Dimensional MoS2 Nanoflakes. ACS Nano. 2013;7(11):10083-93.
- 129. Zeng Z, Yin Z, Huang X, Li H, He Q, Lu G, et al. Single-Layer Semiconducting Nanosheets: High-Yield Preparation and Device Fabrication. Angewandte Chemie International Edition. 2011;50(47):11093-7.
- Zeng Z, Sun T, Zhu J, Huang X, Yin Z, Lu G, et al. An Effective Method for the Fabrication of Few-Layer-Thick Inorganic Nanosheets. Angewandte Chemie International Edition. 2012;51(36):9052-6.
- 131. Kouroupis-Agalou K, Liscio A, Treossi E, Ortolani L, Morandi V, Pugno NM, et al. Fragmentation and exfoliation of 2-dimensional materials: a statistical approach. Nanoscale. 2014;6(11):5926-33.
- 132. Yao Y, Lin Z, Li Z, Song X, Moon K-S, Wong C-p. Large-scale production of two-dimensional nanosheets. Journal of Materials Chemistry. 2012;22(27):13494-9.
- 133. Castellanos-Gomez A, Barkelid M, Goossens AM, Calado VE, van der Zant HSJ, Steele GA. Laser-Thinning of MoS2: On Demand Generation of a Single-Layer Semiconductor. Nano Letters. 2012;12(6):3187-92.
- 134. Wang QH, Kalantar-Zadeh K, Kis A, Coleman JN, Strano MS. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat Nano. 2012;7(11):699-712.
- 135. Dong L, Lin S, Yang L, Zhang J, Yang C, Yang D, et al. Spontaneous exfoliation and tailoring of MoS2 in mixed solvents. Chemical Communications. 2014;50(100):15936-9.

- 136. Johari P, Shenoy VB. Tuning the Electronic Properties of Semiconducting Transition Metal Dichalcogenides by Applying Mechanical Strains. ACS Nano. 2012;6(6):5449-56.
- 137. Yoon Y, Ganapathi K, Salahuddin S. How Good Can Monolayer MoS2 Transistors Be? Nano Letters. 2011;11(9):3768-73.
- 138. Chen J-R, Odenthal PM, Swartz AG, Floyd GC, Wen H, Luo KY, et al. Control of Schottky Barriers in Single Layer MoS2 Transistors with Ferromagnetic Contacts. Nano Letters. 2013;13(7):3106-10.
- 139. Osada M, Sasaki T. Two-Dimensional Dielectric Nanosheets: Novel Nanoelectronics From Nanocrystal Building Blocks. Advanced Materials. 2012;24(2):210-28.
- 140. Wilson JA, Di Salvo FJ, Mahajan S. Charge-density waves and superlattices in the metallic layered transition metal dichalcogenides. Advances in Physics. 1975;24(2):117-201.
- 141. Castro Neto AH. Charge Density Wave, Superconductivity, and Anomalous Metallic Behavior in 2D Transition Metal Dichalcogenides. Physical Review Letters. 2001;86(19):4382-5.
- 142. Kam KK, Parkinson BA. Detailed photocurrent spectroscopy of the semiconducting group VIB transition metal dichalcogenides. The Journal of Physical Chemistry. 1982;86(4):463-7.
- 143. Podzorov V, Gershenson ME, Kloc C, Zeis R, Bucher E. High-mobility field-effect transistors based on transition metal dichalcogenides. Applied Physics Letters. 2004;84(17):3301-3.
- 144. Winchester A, Ghosh S, Feng S, Elias AL, Mallouk T, Terrones M, et al. Electrochemical Characterization of Liquid Phase Exfoliated Two-Dimensional Layers of Molybdenum Disulfide. ACS Applied Materials & Interfaces. 2014;6(3):2125-30.
- 145. Eksik O, Gao J, Shojaee SA, Thomas A, Chow P, Bartolucci SF, et al. Epoxy Nanocomposites with Two-Dimensional Transition Metal Dichalcogenide Additives. ACS Nano. 2014;8(5):5282-9.
- 146. Tao L, Long H, Zhou B, Yu SF, Lau SP, Chai Y, et al. Preparation and characterization of fewlayer MoS2 nanosheets and their good nonlinear optical responses in the PMMA matrix. Nanoscale. 2014;6(16):9713-9.