Supercritical Fluid-Facilitated Exfoliation and Processing of 2D Materials

Zhenyu Sun,* Qun Fan, Mingli Zhang, Shizhen Liu, Hengcong Tao, and John Texter*

Since the first intercalation of layered silicates by using supercritical CO2 as a processing medium, considerable efforts have been dedicated to intercalating and exfoliating layered two-dimensional (2D) materials in various supercritical fluids (SCFs) to yield single- and few-layer nanosheets. Here, recent work in this area is highlighted. Motivating factors for enhancing exfoliation efficiency and product quality in SCFs, mechanisms for exfoliation and dispersion in SCFs, as well as general metrics applied to assess quality and processability of exfoliated 2D materials are critically discussed. Further, advances in formation and application of 2D material–based composites with assistance from SCFs are presented. These discussions address chemical transformations accompanying SCF processing such as doping, covalent surface modification, and heterostructure formation. Promising features, challenges, and routes to expanding SCF processing techniques are described.

1. Introduction

Nanosheet materials are creating much excitement in advanced materials research because of their essentially 2D sheet structures and diversity of chemical characteristics. We briefly discuss their compositional diversity and approaches being taken for their syntheses and processing. Supercritical fluids (SCFs) are introduced, and their properties are reviewed. Various applications of SCFs to exfoliation are presented with emphasis on opportunities to process without chemically modifying 2D materials, as well as examples where a chemical change (such as redox chemistry, sheet scission) is a natural outcome of using particular SCFs.

Following this introduction, we focus on briefly articulating the predominant SCF-based or -assisted processing methods

1.1. Nanosheets and Breadth of 2D Materials

2D materials are referred to as nanosheets with atomic thickness and significantly larger lateral sizes. Thinning of layered materials down to a single layer or few layers can lead to enhanced or unusual electronic, optical, and mechanical properties as well as large specific surface area and chemical reactivity due to electron confinement in two dimensions.

The past decade has witnessed a rapid development of 2D compounds in terms of variety and number of materials following the discovery of graphene in 2004. To date, a wide variety of 2D layered materials have been reported, which include: 1) monoelements: i) group III (borophene), ii) group IV (graphene and its derivatives such as GO, doped graphene, and graphane as well as silicone, germanane, and stanine), and iii) group V (phosphorene, 2D arsenic, antimony, and bismuth) elements; 2) metal chalcogenides: i) dichalcogenides with the formula MX2, where M consists of one or two transition metals from groups 4–10 (Ti, Hf, V, Nb, Re, Ta, Zr, Mo, W, Rh, Fe, Ni, Pd, Pt), X comprises one or two chalcogens (S, Se, Te); trichalcogenides (Bi2Te3, Sb2Te3, NbSe3, TaSe3); ii) group III (GaS, GaSe, InSe) and IV (SnSe, SnS, GeS, GeSe) monochalcogenides, and iii) others (SnS2); 3) metal oxides, such as PbO, MnO2, α-MoO3, V2O5, and perovskites (LaNb2O7, LaMnO3); 4) metal hydroxides, such as β-Ni(OH)2, layered double hydroxides (LDHs); 5) transition metal halides, such as PbI2, BiBr2; 6) nitrides, such as hexagonal boron nitride (h-BN or white graphene), graphitic

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carbon nitride (g-C₃N₄), and metal nitrides; 7) transition metal carbides; 8) transition metal hydrides; 9) transition metal phosphides (Li₂MnP₄, MnP₄); 10) transition metal phosphates and phosphonates; 11) ternary bismuth tellurohalides BiTeX (X = I, Br, Cl); 12) MXenes derived from carbides and nitrides (Mₓ+1AXₓₙ, [MAX] where n = 1 to 3, M is an early transition metal, A is an A-group element [mostly IIIA and IVA, or groups 13 and 14] and X is either carbon, nitrogen, or both); 13) covalent organic frameworks.

These emerging 2D crystals range from insulators to semimetals and further to superconductors, thus providing utility for diverse applications. Note that there are still a large number of possible 2D materials (about 1700 compounds) that remain to be examined.[1] Combining different 2D crystals enables the formation of lateral or van der Waals (vdW) (in one vertical stack) heterostructures exhibiting vertical stacking, affording exotic properties and functionalities due to charge transfers and synergistic effects between layers. Furthermore, 2D materials allow for alloying, doping, intercalation of ions and molecules, and chemical functionalization, offering flexibility in material design with tailored properties for expanding applications.[2-4]

1.2. Current Synthesis Methods

Two methodologies can produce 2D materials: 1) bottom-up (atom by atom growth); and 2) top-down (isolation from bulk) strategies. The former mainly include physical vapor deposition, (modified) chemical vapor deposition, molecular beam epitaxy, growth on SiC (to make graphene), and wet chemical syntheses.[5] Most of these methods require harsh reaction conditions (high temperature, high vacuum), rigorous control of substrate interactions, and complex post-treatment steps (such as transfer and cleaning). Chemical synthesis can be performed at a relatively lower temperature (<200 °C) and allows better control at an atomic level. However, syntheses of large-area 2D nanosheets by such bottom-up routes need further development. Respectively, accompanying mechanisms underlying 2D crystal growth processes are still not sufficiently understood.

Top-down approaches involve micromechanical cleavage (such as Scotch tape methods),[6] anodic bonding (a variant of micromechanical cleavage),[7] chemical exfoliation,[8] and liquid-phase exfoliation.[9] Parent crystals suitable for exfoliation are composed of chemically bonded manifolds held together by weak vdW interactions with interlayer cohesive energies less than 130 meV Å⁻².[1] However, both micromechanical cleavage and anodic bonding are labor intensive with low yield and slow throughput. Also, they are not industrially scalable. Chemical exfoliation can be achieved either by alkali ion intercalation (Li⁺) followed by forced hydration (to release H₂)[10] or through oxidation using Brodie’s, Staudenmaier’s, or Hummers’ methods or their variations. These routes have benefits of low cost and scalability. However, irreversible alteration of structure and properties occurs after chemical exfoliation. Additionally, interfering impurities originating from intercalants, oxidizing or reducing reagents may be covalently bound or strongly physisorbed to exfoliated flakes, complicating further processing.

To circumvent these problems, direct exfoliation of layered materials in suitable liquids (solvents or co-solvent mixtures, surfactant or polymer solutions, biomolecules, ionic liquids) appears to be a promising route for mass production of 2D nanosheets. This strategy is simple, flexible, versatile, readily scalable, and insensitive to environmental conditions. It also does not require expensive growth substrates. Chemically and colloidal stable flakes consisting of fewer than ten layers that can be obtained by such top-down exfoliation can be further...
sorted and separated according to lateral dimensions and thickness via separation in centrifugal fields or in combination with density gradient ultracentrifugation. These suspension-processable nanosheets allow for further blending, casting, and functionalization for a broad array of applications. Note that in some cases, a high yield of exfoliated flakes is obtained with accompanying flake scission and formation of defects and disorder. Quantification of such defects and disorder is an area of research offering important opportunity.

Ultrasonication-assisted exfoliation is a simple method with proven scalability. However, unintended surface modification of nanosheets is introduced due to radicals formed by sonolysis in various solvents (water, alcohols, N-methylpyrrolidone (NMP), and most solvent molecules). Hydroxyl radicals, HO·, tend to form in both oxygenated and deoxygenated water. Such hydroxyl radicals attack graphene’s π system, for example. Basal plane carbon atoms can undergo addition reactions to produce covalent bonds, leading to hybridization transformations of them from sp² hybridization to sp³ hybridization, with a slight out-of-plane puckering. Each surface hydroxyl group can coordinate up to three hydrogen-bonded water molecules in such a way that can provide a satisfactory dispersion of graphene in pure water. This scenario is reminiscent of dissolution of graphene in chlorosulfonic acid owing to reactions of chlorosulfonic acid with conjugated rings resulting in covalent additions of sulfonate groups to graphenic six-rings. NMP radicals resulting from sonolysis have also been demonstrated to contribute to MoS₂ exfoliation.

1.3. Applicability of SCFs in Processing 2D Materials

An SCF is a substance at conditions above its critical temperature (Tₖ) and pressure (Pₖ), which was first recognized by Baron Charles Cagniard de la Tour in 1822. Figure 1a shows a generalized temperature–pressure phase diagram which illustrates how Tₖ and Pₖ define the supercritical region. SCFs have both vapor- and liquid-like physicochemical properties, such as near zero surface tension, low viscosity, high diffusion coefficients, excellent wetting of surfaces, and strong solvating power (Figure 1b–d). The density of an SCF is about two orders of magnitude higher than that of its corresponding gas state, albeit less than half that of a conventional liquid (Table 1). Viscosity and diffusivity are temperature and pressure dependent and are approximately an order of magnitude lower and higher, respectively, compared to a subcritical liquid. We emphasize that the physical properties of SCFs such as density, viscosity, and dielectric constant are tunable by altering temperature, pressure, or both, or addition

![Figure 1. a) Schematic of a pressure–temperature phase diagram showing a triple point, a critical point, and a supercritical region. b) Carbon dioxide density versus pressure and temperature. Reproduced with permission. Copyright 2004, American Chemical Society. c) Surface tension of liquid CO₂ versus pressure. These data points are labeled with their respective saturation temperatures at specific pressures. In a two-phase region, the surface tension of a condensed phase decreases when its state approaches supercritical conditions. In a supercritical phase region, surface tension vanishes. Reproduced with permission. Copyright 2012, American Chemical Society. d) Solubility enhancement with SCF over ideal gas. Reproduced with permission. Copyright 2014, Royal Society of Chemistry.](image_url)
of a co-solvent. Figure 1d shows that typical solubilities in an SCF and an ideal gas differ. Solubilities of solutes (up to nearly six orders of magnitude) in SCFs are substantially enhanced in comparison with an ideal gas. These features make SCFs useful for both chemical reactions and materials synthesis that are impossible or difficult to be realized using traditional solvents. Also, using SCFs appears to apply to current industrial processing practices and is less damaging to equipment and contacting-material structure.

### 1.4. Overview of Available SCFs

Common SCFs that are considered for processing of 2D materials are listed in Table 2, along with their critical temperatures, pressures, and densities. SCFs that are gaseous at ambient conditions offer an advantage of evaporation after decompression to ambient conditions. This aspect obviates any need for drying and results in minimal solvent residues on nanosheet surfaces.

ScCO$_2$ is a well-known SCF with a readily accessible critical point (Table 2). It has been used for exfoliating 2D crystals because it is cheap, abundant, nontoxic, nonflammable, recyclable, and environmentally friendly. ScCO$_2$ can provide a repulsive free energy barrier to inhibit exfoliated sheets from restacking, affording good stability while maintained in a supercritical state. However, scCO$_2$ alone usually produces thick sheets (more than ten layers), though such thicknesses still offer advantageous applications. This limitation in exfoliation is probably due to CO$_2$’s nonpolar nature and reversible rapid escape after insertion into bulk layers on deprosudization. Despite this limitation, flake thicknesses can be reduced further by cycling into and out of supercritical states. Alternatively, exfoliation of layered structures can be extended and accelerated by using scCO$_2$ mixed with various solvents.

ScN$_2$ (supercritical nitrogen) is another SCF in which exfoliation of graphene and clays has been done. Yields and detailed characterizations of such exfoliated sheets have not been extensively reported.

ScNH$_3$ (supercritical ammonia) has been used for exfoliation of natural graphite. A product yield of ~3 wt% was reported, and about 40% of exfoliated sheets had less than five layers upon treatment (200 °C, 15 MPa) for 1 h. Lateral dimensions ranged from 5 to 8 µm, in contrast to less than 3 µm reported in most liquid-phase exfoliation methods. Interestingly, scNH$_3$ also provides simultaneous nitrogen doping of graphene layers during exfoliation, which suggests an intrinsic chemical modification.

ScCHClF$_2$ (supercritical chlorodifluoromethane) and an scCO$_2$-CH$_2$Cl$_2$ (dichloromethane) mixture can assist in exfoliation of fluorinated clays and promote good dispersion of exfoliated clays in polymer matrices for the preparation of polymer/clay nanocomposites. Perfluorinated polymers and surfactants are often found to be soluble in scCO$_2$ and offer several advantages when designing scCO$_2$-based processing procedures.

### Table 1. Comparison of selected properties of SCFs to those of liquids and gases.

|                | Gas | SCF | Liquid |
|----------------|-----|-----|--------|
| Density, ρ [g cm$^{-3}$] | 10$^{-3}$ | 0.1–1.0 | 1.0   |
| Dynamic viscosity, g [mPa s] | 0.01–0.3 | 0.01–0.03 | 0.2–3 |
| Kinematic viscosity, μ [10$^{-6}$ m$^2$ s$^{-1}$] | 5–500 | 0.02–0.1 | 0.1–5 |
| Diffusivity, D [cm$^2$ s$^{-1}$] | 10$^{-5}$ | 10$^{-3}$ | 10$^{-5}$ |
| Thermal conductivity, λ $[10^3 \text{ W m}^{-1} \text{ K}^{-1}]$ | 4–30 | 28–80 | 80–250 |
| Surface tension, σ [dyn cm$^{-1}$] | 0 | 0 | 20–50 |

### Table 2. Critical data for some fluids that may be useful in processing 2D materials.

| Fluid        | $T_c$ [°C] | $P_c$ [MPa]$^4$ | $ρ_c$ [g cm$^{-3}$] | Ref. |
|--------------|------------|-----------------|---------------------|------|
| N$_2$        | -147.0     | 3.4             | 0.3109              | [21] |
| CH$_4$       | -82.6      | 4.6             | 0.16                | [22] |
| C$_2$H$_4$   | 9.5        | 5.1             | 0.218               | [23] |
| CO$_2$       | 31.0       | 7.4             | 0.469               | [17] |
| C$_2$H$_6$   | 32.5       | 4.9             | 0.203               | [17] |
| C$_3$H$_6$   | 91.9       | 4.62            | 0.23                | [23] |
| Chlorodifluoromethane | 96.0   | 4.9             | 0.524               | [24] |
| C$_2$H$_4$   | 133.0      | 11.4            | 0.244               | [17] |
| n-C$_6$H$_{14}$ | 152.0  | 3.7             | 0.228               | [26] |
| Diethyl ether | 194.3     | 3.6             | 0.193               | [26] |
| C$_2$H$_2$   | 197.0      | 3.4             | 0.237               | [23] |
| C$_2$H$_4$   | 234.1      | 3.0             | 0.233               | [17] |
| 2-ProOH, IPA (2-propanol) | 234.9    | 4.8             | 0.273               | [17] |
| Acetone      | 235.0      | 4.8             | 0.269               | [19] |
| Dichloromethane | 236.7  | 6.1             | 0.440               | [27] |
| MeOH         | 239.5      | 8.1             | 0.272               | [17] |
| EtOH         | 240.9      | 6.1             | 0.276               | [17] |
| Chloroform   | 261.8      | 5.3             | 0.491               | [28] |
| 1-ProOH (1-propanol) | 263.5  | 5.2             | 0.275               | [17] |
| Acetonitrile (ACN) | 272.3 | 4.8             | 0.225               | [17] |
| 1,4-Dioxane (1-butanol) | 274.6  | 4.3             | 0.232               | [29] |
| CCl$_4$      | 283.3      | 4.5             | 0.557               | [17] |
| Benzene      | 288.9      | 4.9             | 0.302               | [30] |
| 1,4-Dioxane (1-butanol) | 289.3 | 4.4             | 0.270               | [17] |
| Toluene      | 319.0      | 4.1             | 0.292               | [23] |
| p-xylene (PX) | 343.0    | 3.5             | 0.286               | [31] |
| H$_2$O       | 374.0      | 22.1            | 0.322               | [17] |
| N,N-dimethylformamide (DMF) | 376.5  | 4.4             | 0.293               | [17] |
| N-methyl-2-pyrrolidone (NMP) | 450.9  | 4.8             | 0.318               | [17] |

$^4$1 MPa = 10 bar.
subcritical or near critical physical states. In such cases, we refer to such near critical conditions, for example, as applied to NMP: ncNMP; scNMP conditions are: $T_c \approx 450.9 \degree C$, $P_c \approx 4.8 \text{ MPa}$ (Table 2). It is also important to note that many mixed gas and liquid systems are investigated, wherein criticality is claimed, but authoritative references or experimentation are not provided to confirm supercriticality for a given mixture. We attempt to distinguish these cases for readers when they arise in our discussions below.

1.5. Initial Exfoliation Applications

Since Gulari et al. demonstrated the first intercalation of layered silicates by using supercritical CO$_2$, scCO$_2$, as a processing medium, these extensive efforts have been devoted to intercalating and exfoliating layered 2D materials in various SCFs to yield single- and few-layer nanosheets (Figure 2a, the SCF intercalation and expansion pictured are discussed at length later). SCFs possess easily tunable solvation strength and favorable interfacial tensions, wetting, and transport properties, making them unique and potentially superior solvent media for rapid exfoliation of 2D nanosheets.$^{[39]}$ Compared with liquid-phase exfoliation via ultrasonication, an SCF exfoliation strategy requires shorter processing time and tends to produce highly crystalline single and few layers with lower defect levels and larger flake sizes. Indeed, Raman data have indicated that D-band to G-band intensity ratios ($I_D/I_G$) are “sufficiently low” of only 0.03 for stabilized graphene by poly(2,2,2-trifluoroethyl methacrylate)-block-poly(4-vinylpyridine) in scCO$_2$ (Figure 2b–d)$^{[40]}$. Fluorinated polymers and surfactants are well-established stabilizers for use in scCO$_2$-based dispersion, suspensions, and complex fluids.$^{[41]}$

These $I_D/I_G$ ratios are important because they are a common metric for graphene “quality” or “pristineness.” The Raman scattering intensities at 1330 to 1370 cm$^{-1}$ and 1540 to 1590 cm$^{-1}$$^{[42–44]}$ respectively, are ascribed to D-band and G-band. This D transition in pristine graphene is forbidden (has zero intensity)$^{[45]}$ but ratios up to 0.3 have been claimed to demonstrate “pristine” character. Therefore, one must be critical in evaluating claims of quality based on Raman measurements. When defects are introduced into graphene sheets by chemical reactions that disrupt the aromatic 2p$_z$ electron density of individual carbon atoms, carbon–carbon bonds are distorted from planarity, and the carbon centers associated with such defects acquire sp$^3$ hybridization. Such chemical effects result in increasing $I_D$ intensity. The G-band is due to C–C bond stretching and is an allowed Raman transition in pristine graphene, and its intensity, $I_G$, is used to “normalize” D-band intensity, via the $I_D/I_G$ ratio. The so-called 2D band is a

![Figure 2.](image-url)

Figure 2. a) Schematic of SCF exfoliation of graphite crystals into few-layer graphene. b) Molecular structure of PTFEMA-b-PVP amphiphilic fluorinated block copolymer. c) Schematic of PTFEMA-b-PVP stabilized graphene exfoliated in scCO$_2$. d) Raman spectra for precipitates of graphite nanoplatelet (GP) and exfoliated graphene samples stabilized by PTFEMA-b-PVP copolymers with low (L) and high (H) molecular weights. Sample ID digits indicate the number in weight percentages of block copolymer. Reproduced with permission.$^{[40]}$ Copyright 2017, Elsevier Inc.
two-phonon band whose shape and position depend somewhat on excitation wavelength. Its intensity variation has not yet succumbed to a simple structural interpretation useful for quantifying defect formation in graphene.

Particularly, in comparison to liquid-phase exfoliation that often, unfortunately, relies on centrifugation and generates high waste, SCF technology does not rely on centrifugation. Avoiding centrifugation is attractive to extend dispersion manufacturing processes. We should note that a direct comparison of SCF exfoliated sheets and those obtained by liquid-phase exfoliation remains an issue because of differences in analysis techniques and procedures, initial bulk concentration, and how raw materials and layered materials are obtained. Also, some workers include centrifugation processing in their SCF exfoliation studies, conflating exfoliation and sedimentation effects. Some care must be exercised in reviewing exfoliation claims obtained by SCF processing, in order to ascertain whether or not centrifugation has also been included in the processing described.

SCFs are proving advantageous for processing and functionalization of 2D materials. However, SCF approaches have received less attention than expected. Only two earlier reviews summarize exfoliation and processing of graphene in SCFs.[17,46] Discussions of supercritical processing of other 2D crystalline materials undergoing rapid application development are lacking. Roles played by SCFs in functionalization, phase transformation, and composite formation of 2D materials remain to be systematically examined. We focus on these aspects in this progress report and also highlight some fundamentals underlying SCF technologies to gain insight for optimization of SCF conditions. Further, applications of 2D materials and composites derived by SCF processing are summarized. We also describe prospects for future developments for processing 2D materials in SCFs.

2. SCF-Assisted Processes

Along with progress in understanding associated phase equilibria and fluid properties, various processes for using SCFs are being developed for 2D materials. In this section, we briefly discuss six SCF-based processing methods that have been applied to 2D inorganic crystals and hybrids. All of these techniques have previously been applied in other aspects of particle technology, and are beginning to be used with layered materials.

2.1. Rapid Expansion from Supercritical Suspensions

Traditional rapid expansion from supercritical suspension (RESS) processes were used for producing particles as a result of precipitation of dissolved materials at a very high rate of supersaturation due to sudden expansion upon depressurization. This process was also applied to exfoliate layered materials (Figure 3A).[49] The RESS process illustrated in Figure 3A involves an SCF and an optional co-solvent.[47] On pressurization to a supercritical state, the layered material is enveloped by SCF and intercalated by SCF and cosolvent. Depressurization leads to expansion and layer separation due to pressure gradients, and the SCF reverts to a subcritical state.

Gulari and coworkers first reported an scCO2-processing technique for intercalating and exfoliating layered silicates[38] and graphite.[50] Following this pioneering work, a variety of 2D crystals have been exfoliated using similar or modified SCF technology, including graphene,[17,47] fluorographene,[51] BN,[52–54] TMDs (MoS 2, WS 2, MoSe 2, etc.),[52,55–58] black phosphorus,[59] NH 4MPO 4 (M = Fe, Mn, Co, Ni),[60] titanate,[61,62] V 2O 5,[63] MoO 3,[64,65] Mn 3O 4,[66] 2H-WS 2/2H-MoS 2,[67] and BN-MoS 2 heterostructures,[19] among others. In SCF-assisted exfoliation, a layered material is initially added to a solvent or solvent mixture and then sealed in a high-pressure reactor. Temperature and pressure are increased to drive any solvent to a critical state. A good solvent intercalates between nanosheet layers under critical conditions. This intercalation causes expansion of the layered material. After incubation for a while, a high-pressure reactor is abruptly depressurized to induce expansion. This expansion causes large pressure gradients between material interlayer regions and ambient conditions, and these gradients push layers apart with formation of mono-, few-, and multi-layer sheets.

To promote SCF intercalation and exfoliation, methods such as stirring,[40] ultrasonication (cavitation),[12,68,69] mechanical shear mixing by a rotor stator,[53,70–72] or ball milling[73] have been used. These mechanical and sonochemical methods may or may not also induce edge or basal plane surface modification chemistry that might aid exfoliation. Addition of co-solvent during an SCF process, such as NMP,[74] or a stabilizer such as pyrene and pyrene-derivatives,[74,75] or poly(2,2,2-trifluoroethyl methacrylate)-block-poly(4-vinylpyridine)[49] can enhance interactions with nanosheet surfaces and further improve exfoliation efficiency. Coupling stirring, rotor-stator, and ultrasonication approaches to providing shear along with SCF depressurization, while such multiphase mixtures are in a supercritical state, appear to provide synergistic effects. Some reports of sequential processing, with an SCF process followed by a sub-critical mechanical shear or ultrasonication process,[48,72,76] often do not offer real advantages and rely upon nanosheet selection by centrifugation to obtain useful but very dilute samples. Moreover, when auxiliary chemomechanical processing steps are included (high shear, ultrasonication), one must be very circumspect in assigning causality in any hypothesized exfoliation mechanistic discussion. Presumably, SCF intercalation can greatly facilitate shear-induced exfoliation prior to reductions in pressure and loss of criticality.

2.2. Complex Fluid Processing

CO2-in-water emulsions and microemulsions stabilized by PFPE, a perfluoropolyether, are formed at a relatively low CO2 pressure (8 MPa), while reverse emulsions and microemulsions of water-in-CO2 are induced at elevated CO2 pressure (>12 MPa) as shown in Figure 3B.[77] ScCO2 serves as a “switch” to tune surfactant molecular aggregation, which is reversible and can be realized by pressurization and depressurization. ScCO2 pressure variations tune such microemulsion-reverse microemulsion continuous phase transitions.
A microemulsion-based process has been claimed to facilitate exfoliation of layered materials. Polyvinylpyrrolidone (PVP) outperformed Pluronics F127 and P123, Tween 20, hexadecyltrimethylammonium bromide (CTAB), and sodium dodecylbenzenesulfonate (SDBS) for exfoliation in scCO$_2$ mixed solvent solutions. The pyrrolidone groups of PVP have a strong affinity for nanosheet surfaces in these layered materials, providing stabilization against re-aggregation. However, no evidence of microemulsion formation was provided, and an actual process described more closely resembled aqueous ethanol ultrasonication followed by centrifugation and afforded meager yields. After discarding most of the graphene mass, the sediment, remaining dispersion concentrations obtained were less than 0.2% by weight and comprised graphene that exhibited an optical absorption coefficient less than 20% that of pristine graphene.

Figure 3. A) Schematic of rapid expansion from supercritical suspensions. Reproduced with permission. Copyright 2014, Royal Society of Chemistry. See text for expanded discussion. B) Phase behavior of emulsion in CO$_2$/PVP/H$_2$O system (upper part) and photographs of the system with different CO$_2$ pressures (lower part). Reproduced under the terms of the Creative Commons Attribution 4.0 International License. Copyright 2015, the Authors, Published by Springer Nature. C) Schematic illustration of supercritical fluid chemical deposition. D) Schematic of antisolvent precipitation in SCF. E) Schematic representation of supercritical drying: The solvent is pressurized and heated beyond the critical point (P$_c$, T$_c$) via one of two pathways either path ABC or path AC. This is followed by depressurization (path CD). In this way, the interface of gas and liquid is circumvented. S–L, L–V, and S–V denote solid–liquid, liquid–vapor, and solid–vapor equilibrium curves, respectively. Reproduced with permission. Copyright 2012, American Chemical Society. F) Schematic of supercritical foaming.
Water-in-SCCO2 microemulsions in scCO2 also provide unique media for uniform decoration of 2D materials with polymer, metal, or metal oxide particles. Aqueous micelle cores with nanometer dimensions allow for solubility of precursors (such as metal salts that are insoluble in CO2) and act as nanoreactors to compartmentalize precipitation. In microemulsions, there is no phase boundary between co-dissolved immiscible liquids. It is challenging to capture nanoscale dimensions of metal and metal oxide nanoparticles in reverse microemulsions unless one can promote these nanoparticle formation kinetics to make them competitive with surfactant reorganization kinetics in swollen microemulsion systems. Interfaces of scCO2 and water can also be used to synthesize hollow oxides (such as silica, titania).

2.3. Supercritical Fluid Chemical Deposition

Supercritical fluid chemical deposition (SFCD) techniques allow one to deposit particles and films (Figure 3C) including metal nanoparticles in polymer matrices and in alumina membrane pores, conformal Pd films on Si and polyimide substrates, ruthenium nanoparticles on carbon nanotube (CNT) surfaces, and ZrO2 films on CNTs. Compared to conventional solvents, SCFs can promote conformal coverage of complex surfaces and poorly wettable substrates (such as graphene or other 2D materials) with dissolved precursors (such as chelate or metal β-diketone complexes) more readily. After reaction at specific temperature and pressure, the formed species from adsorbed compounds tend to nucleate, grow, and deposit on any available support.

These SFCD processes can overcome obstacles of high interfacial tension and viscosity in graphene oxide colloids, which are challenging for most existing methods. Porous graphene decorated with multimetallic nanoparticles (NPs) with small size and tunable loading has been fabricated in scCO2. Some co-solvents such as methanol, ethanol, or tetrahydrofuran can be employed to modify the polarity of CO2 and enhance dissolution of precursors in scCO2. Mechanistically, an SCF wets both substrate and particle materials and makes it feasible to form uniformly distributed dispersions at SC conditions and to then deposit these materials as pressure and temperature are decreased.

2.4. Antisolvent Precipitation in SCFs

This supercritical technique involves a mixed solvent system with a solute compound dissolved in an organic solvent but insoluble in the SCF or with solute dissolved in an SCF but insoluble in an organic solvent, where the organic solvent and SCF are miscible. When a solvent, acting as an antisolvent, is combined with scCO2 in which a solute is soluble, this mixture becomes supersaturated. This saturation induces nucleation of small particles and their precipitation when expanded into an antisolvent as illustrated in Figure 3D. This supercritical antisolvent strategy offers a route for preparing 2D material composites.

Conversely, as scCO2 is introduced into a solvent dispersion containing few-layer nanosheets and a solute compound soluble in this solvent, solute solubility decreases if it is not soluble in scCO2, causing supersaturation and particle condensation. This process routinely uses the SCF to also extract organic solvents for production of dry particle powders useful in pharma. However, this saturation may also lead to nucleation of nanoparticles and their deposition onto nanosheet surfaces. A further chemical or physical treatment rendering such nanoparticles insoluble in the solvent would provide an alternative pathway to a 2D material composite. However, absent such a chemical passivation step, such particles would be expected to redissolve in the solvent.

Both of these approaches use an SCF to drive exfoliation during and after precipitation of particles. However, while both approaches have been used to make particles for various applications, they have not yet been applied to make particle composites with 2D materials.

2.5. Supercritical Drying

Supercritical drying provides advantages for processing of 2D materials and hybrids, such as drying of graphene-based aerogels. Conventional solvent evaporation by heating leads to large capillary forces and causes microstructure collapse, resulting in low specific surface areas. This type of problem can be solved by using a supercritical drying protocol. Meanwhile, supercritical drying can avoid the formation of any liquid-gas interface, resulting in smaller particles with increased specific surface areas and higher homogeneity (Figure 3E).

2.6. Supercritical Foaming

Polymer foams or scaffolds can be obtained by using SCF as a physical blowing agent, provided there exists a sufficient pressure-dependent solubility of the blowing agent in the polymeric prefoam (Figure 3F). This scheme can be applied to make 2D material-based porous polymer composites. Specifically, 2D crystal–polymer composites are first swollen and plasticized with dissolved SCF (such as scCO2) for some periods. After rapid pressure reduction, CO2 solubility in a composite decreases, causing nucleation and growth of oversaturated CO2 to generate bubbles. As a result, 2D nanosheets coated with a porous polymer network are formed. Such porous structures encompass closed cell pores, open-cell pores (interconnected cells), macropores, and mesopores. Foam inner morphology relies on SCF saturation level that is associated with several parameters such as SCF pressure and temperature, dynamics of nucleation and bubble growth (due to pressure drop and interfacial stabilization by nanosheets), and SCF pressure reduction rate. Supercritical CO2 has been used to affect graphene exfoliation in polypropylene (PP)/G composites.

Graphene nanoplatelets (GNP) were mixed with high-density polyethylene (HDPE) in a tandem extruder assembly at about 1.1% by volume. CO2 was used as a blowing agent and SCF to produce foams having a high permittivity and low dielectric loss. The GNP had nominal dimensions of 50 µm in diameter and 20 nm in thickness. A temperature range of 130–215°C in this extrusion system resulted in good dispersion and partial
exfoliation. CO₂ was injected into the first extruder and dissolved under thermal and pressure conditions therein. When exiting a second extruder, a drop in pressure and temperature resulted in foaming to produce a nanocomposite with a permittivity, ε', of about 77.5 and a dielectric loss, ε'', of about 0.233 at 10⁵ Hz. This foaming action resulted in a positive synergistic effect to produce parallel GPNPs that were very polarizable in applied fields. A low density of about 0.15 g cm⁻³ that is very difficult to achieve when formulating high dielectric inorganic nanoparticles (e.g., BaTiO₃) in polymer matrices is another positive attribute of this advanced dielectric material.

Polyvinyl alcohol/GO nanocomposite foams have been evaluated using scCO₂. In one study, pan milling to prepare a PVA/GO nanocomposite was followed by melt extrusion with varying amounts of PVA, followed by scCO₂-based blowing to create foam materials at various temperatures and depressurization rates. A foam prepared at 80 °C containing 2.5% GO resulted in pores of 17.9 μm in average diameter compared to 29.1 μm for a PVA-only control. This GO nanocomposite in compression to 50% strain exhibited a maximum stress of 178% relative to that of the PVA-only control. These improved mechanical properties and decreased pore diameters were attributed to the incorporation of GO in the pore walls. In a related process, aqueous PVA/GO dispersions were partially dried to produce hydrated mixtures and then compression molded into thin plates at 165 °C. These plates were then infused with scCO₂ at 100 °C and 15 MPa followed by decreasing the pressure at 5 MPa s⁻¹. GO contents of 0%, 0.1%, 0.5%, and 2.5% showed that pore diameter decreased and compressive strength increased with increasing GO content to 0.2%: the 2.5% GO content showed no improvement over the 0.5% GO level. A significant physical aspect of these studies is the stabilization of smaller pores by the GO sheets. This stabilization can be understood in terms of a Pickering stabilization effect as recently reviewed for G and GO.

Another useful material was obtained by using scN₂ to induce exfoliation and foaming in graphene mixtures with HDPE. Foaming degrees of 7%, 16%, and 26% were obtained, and a transient plane source hot disk thermal constant analyzer was used for conductivity analysis. These analyses yielded a solid-phase conductivity of 4 W m⁻¹ K⁻¹ according to a Maxwell–Eucken model. Moderate foaming (7%) gave the highest bulk conductivity that increased with GNP from 0.8 W m⁻¹ K⁻¹ (4.5 vol%) to 3.75 W m⁻¹ K⁻¹ (18 vol%). Further increases in foaming decreased bulk conductivity.

3. Exfoliation and Chemical Processing in SCFs

We discuss features of critical solvent parameters and other orthogonal processes that affect exfoliation, which appear essential for using SCF-based and SCF-assisted processes. It is always appropriate to consider how additives, co-solvents, and mechanicochemical treatments may impact nanosheet surface chemistries.

3.1. Exfoliation Facilitated by SCFs

Before initiating exfoliation, SCFs are considered to first intercalate into galleries or nanosheet interlayers to expand interlayer separation and swell these materials. Increasing pressure can promote such SCF intercalation and expansion of spaces between interlayers. Increasing pressure results in a higher free energy barrier and reduced interlayer attraction, which also enhances colloidal stability of exfoliated sheets in dispersion. Two parameters are critical to this process: 1) any pretreatment of bulk materials; and 2) SCF type. Using pretreated sample such as surfactant (e.g., alkyl-based quaternary ammonium surfactants)-modified natural clays or nitric acid–treated graphite as a starting material facilitates nanosheet-solvent interaction as well as intercalation of SCF molecules and expansion of these interlayer gallery spacings due to physical and chemical modifications. As a consequence, exfoliated sheet yields are improved. However, a significant increase in exfoliation efficiency by oxidation pretreatments is often accompanied by a degradation in a sample’s quality. These effects need to be considered when designing further processing and applications. A summary of 2D materials exfoliated in various SCFs is provided in Table 3.

A fundamental aspect of SCF-assisted exfoliation is that 1) intercalation of SCFs and often other solvents, polymers, and stabilizers occurs under supercritical conditions, and 2) when high pressure is released, expansion of SCF within interlayers drives sheets apart to yield exfoliation that is stabilized or not, depending on the conditions and environment of pressure release. Gulari and Serjatkulu showed in their early studies of graphite exfoliation using PDMS solutions in scCO₂ that X-ray powder diffraction peaks at 20 values over 26° to 27° were significantly attenuated and broadened as a result of such intercalation and expansion. Similarly, intersheet spacings in layered silica (Na⁺ Cloisite) were shown to substantially expand on scCO₂ treatment with galactose-based stabilizers.

While most reports of SCF-driven exfoliation have not included corroborating X-ray diffraction evidence that intercalation by SCFs and stabilizers when present occurs, past SCF expansion data unequivocally demonstrate that exfoliation has occurred. Exfoliation in the absence of intercalation can only occur if an external adhesive force is applied, or a sufficiently high shear force is applied. It can, therefore, be concluded that intercalation driven by SCF is a starting point for exfoliation, at least in processes without high shear fields or ultrasonication. It would be useful to quantify intercalation by specific SCFs, particularly in situ if possible. In view of diverse applications of powder X-ray diffraction to particle and materials synthetries in SCFs, such valuable studies are feasible.

### 3.1.1. High-Boiling Solvents

Efforts have been made to study interactions between solvent molecules and 2D materials, in searching for appropriate solvents for effective exfoliation. Exfoliation appears to occur when van der Waals forces that are sufficiently small between adjacent nanosheets are overcome. Texter claimed that the best solvents from a wetting perspective are those that satisfy the inequality: γ₂D > γ₂D/sol + γ₂D/sol, where γ₂D is the Gibbs surface energy of a 2D material, γ₂D/sol is the surface energy (surface tension) of a solvent (a Gibbs free energy that can be readily measured), and γ₂D/sol is the interfacial energy of the solvent/2D...
### Table 3. Summary of 2D materials exfoliated in SCFs.

| 2D materials | SCF | Exfoliation condition | Yield | Dimension |
|---------------|-----|-----------------------|-------|-----------|
| Silicate      | NcCO₂, ScCO₂, sugar acetate | 11.7 MPa, 40 °C, 24 h (dense gas solution, DGS); 7.9 MPa, 40 °C, 24 h (gas-expanded liquid, GEL) | N/A | Thickness: 3.2 layers (DGS); 2.9 layers (GEL) |
| Graphene      | ScCO₂ | 10 MPa, 45 °C, 30 min | 30 to 40 wt% | Thickness: 10 layers |
|               | ScCO₂ | 8 MPa, 40 °C under ultrasonication (0, 60, 120, or 300 W), 30 min, then CF: 1500 rpm, 60 min | N/A | Lateral size: a few micrometers |
|               | ScCO₂ | 10 MPa, 45 °C, 30 min | ≈ 30 to 40 wt% | Thickness: 1–10 layers |
|               | ScCO₂ | 8 MPa, 40 °C under ultrasonication (0, 60, 120, or 300 W), 30 min, then CF: 1500 rpm, 60 min | N/A | Lateral size: 5–100 µm, 2–15 µm, 0.5–10 µm, 50–100 nm (corresponding to 0, 60, 120, and 300 W, respectively) |
|               | ScCO₂ | 10 MPa, 45 °C, 30 min | N/A | Lateral size: 0.5–20 µm |
|               | ScCO₂ | 10 MPa, 50 °C, 24 h, then magnetic stirring, 1 h and ultrasonication (250 W), 30 min in ethanol/water solution | 32 wt% | Presence of monolayer |
| Reduced graphene (rGO) | ScEtOH/scMeOH/ scPrOH and scBuOH | Ultrasonication: 1 h, 12.9–36.5 MPa, 40 °C, 2 h | N/A | N/A |
| N doped graphene | ScACN | 310 °C, 2–24 h | N/A | N/A |
| N-doped graphene | ScNH₃ | 15 MPa, 200 °C, 1–2 h, then CF: 1000 rpm, thrice | 3 wt% | Thickness: <5 layers (40%) |
| BN            | ScCO₂ | 10 MPa, 45 °C under ultrasonication (60 W), 40 min | N/A | Thickness: <5 layers (90%), 1 layer (20%), 2 layers (40%) |
| MoS₂, MoSe₂   | ScDMF | Ultrasonication (160 W): 5 min, then 400 °C, 1 h, CF: 2000 rpm, 15 min | N/A | Lateral sizes: 0.5–2 µm |
| MoS₂          | ScCO₂ | 16 MPa, 75 °C under shearing (1200 rpm), 3 h, then ultrasonication, 30 min in ethanol, CF: 2000 rpm, 40 min | N/A | Thickness: <10 layers (95%), 1–4 layers (50%) |
| MoS₂          | ScCO₂ | 16 MPa, 75 °C under shearing (1200 rpm), 3 h, then ultrasonication, 30 min in ethanol, CF: 2000 rpm, 40 min | N/A | Thickness: predominantly 3–5 layers |
| BP            | ScCO₂–NMP | Ultrasonication (150 W): 1 h, then 15 MPa, 40 °C, 3 h, and ultrasonication: 1 h | N/A | Thickness: predominantly 3–5 layers |
| LiFePO₄/C, LiMnPO₄/C, LiCoPO₄/C, LiNiPO₄/C | ScEtOH–PVP | 10 MPa, 400 °C, 2 h | N/A | Thickness: 4.3, 1.6, 2.1, and 1.7 nm |
| Titania       | ScDMF | 400 °C, 15 min, CF: 3000 rpm, 3 min, then 8000 rpm, 20 min | N/A | Thickness: 1 layer (>8%) |
material interface (that can be estimated from contact angle measurement). This inequality guarantees a positive spreading coefficient and spontaneous wetting by the solvent. Over 70 solvents have been examined for exfoliation, and some apparently good solvents have been identified for various 2D crystals. However, only a few of these solvents such as high-boiling-point NMP and DMF have been employed under supercritical and near critical conditions for exfoliating graphite,[131–133] layered titanate,[61] NH4MPO4·H2O (M = Fe, Mn, Co, Ni),[80] MoS2,[56,143] MoSe2,[56] BN,[144] and BN-MoS2 heterostructure.[39] Compared to gaseous molecules, such high-boiling-point solvents have a stronger affinity for surfaces of 2D materials. This affinity seemingly enables higher exfoliation efficiency and better stabilization to prevent re-stacking. For instance, after a short processing time of 15 min in ncNMP (near critical NMP) and scDMF (supercritical DMF), natural graphite exfoliation into few-layer sheets in which 90% to 95% are 10-layer or thinner flakes and 5–9% were monolayers was claimed.[133] Stable and dilute dispersions with a concentration up to 2–4 mg mL−1 were claimed. Such yields contrast with a very low (nearly zero) yield of monolayer graphene in both scCO2 and scNH3. However, both NMP and DMF unequivocally present processing challenges due to their high boiling points.

Mixed solvents such as NMP/water,[145] NMP/N-octylbenzene,[146] and DMF/N-butyl alcohol[147] have been shown to enhance nanosheet yield through ultrasonication-based exfoliation. Nevertheless, there are only a few reports on using such supercritical mixtures for exfoliation, and it seems unequivocal that ultrasonication of water-containing mixtures produces hydroxyl radicals that undergo addition reactions with basal planes of graphite and graphene.[142]

3.1.2. Low-Boiling (Mixed) Solvents

In order to address issues of high cost, toxicology, and vapor pressure for some good solvents with high boiling points, using low-boiling-point solvents would be preferred, if sufficiently concentrated dispersions could be obtained. As an alternative, supercritical alcohols such as scEtOH (supercritical ethanol),[61,131,133,148] scACN (supercritical acetonitrile),[138] and a mixture of scIPA (supercritical isopropanol)[54] or scEtOH[148] and water have been studied. These alternative solvents apparently provide sufficient penetration and intercalation to yield exfoliation of mono- and few-layer sheets. Higher supercritical density provides a stronger repulsive free energy barrier to sheet re-aggregation and, therefore, enhanced exfoliation efficiency.[129,148] Tuning the Hansen solubility parameters of SCFs by controlling process conditions was claimed to promote enhancement of exfoliation yield.[148] Other potential low-boiling solvents such as acetone, chloroform, and mixtures remain to be investigated for different 2D crystals by using SCF exfoliation processing.

3.1.3. Cavitation and Shear Force–Assisted Exfoliation in SCFs

Cavitation occurs during rarefaction cycles of ultrasound waves to create transient microbubbles, which collapse and form microjets and shock waves. Shock waves can break bulk flakes into thin layers and also cause scission in lateral dimensions. Meanwhile, microturbulence (or microconvection) and pitting effects stemming from bubble collapse provide mechanical energy (mostly in the form of tensile stress) to overcome attractive interactions between the layers, inducing exfoliation. Increasing fluid pressure was reported to decrease a cavitation threshold, thus suppressing any creation of cavitation bubbles. Nevertheless, a sufficiently large increase in applied ultrasound intensity could induce cavitation, even at high overpressures. A collapse of such transient cavities leads to a higher intensity and consequently enhanced sonolysis effects. Intensive cavitation in a pressurized reactor can substantially enhance exfoliation efficiency in RESS.[52,128,149] Cavitation was claimed to be unlikely in scCO2 due to an absence of phase boundaries, but loading with bulk layered materials provides phase boundaries. Although insoluble impurities in scCO2 might serve as sites where nucleation of cavitation bubbles can take place, resulting cavitation intensity is believed to be small and not significant in aiding exfoliation. Under such circumstances, shear stress and pressure fluctuations generated by ultrasound were conjectured to be mainly responsible for enhanced exfoliation yields in scCO2.[69] Computational fluid dynamics (CFD) simulation showed that the maximal shear stress along with the amount of active area increased with ultrasonic power from 12 to 240 W, which may contribute to graphite exfoliation in scCO2 (Figure 4a). Meanwhile, exfoliation yield was linked to differences of pressure, system pressure, and density contrast (Figure 4b–d). Yields increased when the pressure was raised from 8 to 12 MPa but started to decrease above 12 MPa. Such a decrease might be a result of reduction in the density contrast, which weakens volume expansion of scCO2 caused by ultrasound, adversely affecting exfoliation efficiency. Alternatively, coupling micro-jet with scCO2 was also demonstrated to facilitate exfoliation of graphene with a mechanism similar to ultrasonication.[150]
As an alternative to ultrasound, mechanical shear also can help accelerate exfoliation of layered materials in SCFs.\cite{53,72,151,152} High rotation speeds of a shear mixer usually mean large shock velocities of SCF molecules parallel to the sheets. As a consequence, these SCF molecules can be wedged into interlayer spaces more readily with large kinetic energy to overcome interlayer vdW attraction. Jet cavitation and collisions that occur during shear mixing may also improve exfoliation in SCFs.\cite{70} As a proof of this concept, coupling shear force with scCO₂ appeared to support a claim of high exfoliation yield of graphene of up to 63.2%. About 79% of the flakes were less than five layers, of which monolayer, bilayer, and trilayer represented 27%, 25%, and 14%, respectively. Combining mechanical shear with ultrasound allowed Zhao and co-workers to increase this claim to a cumulative yield of 80%.\cite{153}

Such rotor–stator devices are popular in industrial fluid processing for formulating emulsions and for small-scale manufacturing. Other high shear manufacturing methods such as homogenization are used at much higher scales in industrial manufacturing and have yet to be extensively investigated in SCF processing. Homogenization can be envisaged as sequential (cyclical) pressurization to a supercritical state followed by depressurization in a flow that impinges on a mechanical barrier (plate). A very recent paper has addressed an example of this kind of processing.\cite{154} The homogenization system used is similar to units used in industry to disperse very small batch volumes and imparts shear by driving a graphite–scNMP multiphase-fluid through a 3 cm steel capillary (200 µm inner diameter) with cycling fluid flow. Unfortunately, details of this system, other than a cartoon drawing and the capillary dimensions, were not provided. However, similar capillary-based systems have proven themselves in emulsification for many decades in industry for bench-top formulation and research.

The results of this small batch study appear promising. Gravimetric yields, obtained by drying and weighing a particular volume of supernatant after 30 min of centrifugation at 3000 rpm, up to 15% were obtained.\cite{154} These yields, at least, do not depend on visible absorption coefficient. It should be mentioned, however, that yields 800% higher and 33% more concentrated (50 mg mL⁻¹) have been reported using sonication in water.\cite{155} One inconsistency that is difficult to resolve in this study is that TEM of multisheet platelets exhibit the standard and well established intersheet spacing of about 0.35 nm, while the AFM data of exfoliated sheets were interpreted assuming a sheet thickness of 0.8 nm. Such a thickness is consistent with graphene oxide and reduced graphene oxide, but not with pristine graphene. However, the Raman I_D/I_G band ratios of about 0.54 were seen in the starting graphite material and in the exfoliated graphene multisheets. Therefore, pristine graphene appears not to have been available in this study. Further process development using such homogenization and related methods seem to offer promise.
We believe that shear forces derived from fluidic dynamics in SCFs seem a possibly better approach than ultrasound, in light of an absence of sonochemically generated radicals and associated perturbation in nanosheets quality. Although such SCF approaches are thought to produce pristine graphene, an absorption coefficient at 660 nm used to evaluate dispersed graphene of only 16.39 cm² mg⁻¹ is only 18% of the absorption coefficient of graphene measured by Nair and co-workers as discussed by Ager and co-workers. The experimental results of Nair and co-workers agree with the fine structure constant-based value, 91 cm² mg⁻¹ in dispersion (2/3 the value for light polarized parallel to a graphene plane), for randomly oriented nanosheets. This means that these estimates of yield are fivefold too high.

However, it is reasonable to presume there are many features that affect absorption coefficients of graphite and graphene samples obtained by different methods and from different sources. Some of these variations are manifested in edge and basal plane defects of various types, and their impact on electronic structure, particularly with respect to electronic absorption coefficients (dipole allowed photon absorption probabilities) have yet to be thoroughly evaluated theoretically and experimentally. A more universally accepted means of ascertaining “pristineness” is needed in order to extend our understanding of positive and negative aspects of nanosheet exfoliation processing.

3.2. Modification of 2D Materials in SCFs

SCF processing in 2D materials processing has mainly been considered in terms of high-pressure changes that physically affect interlayer attraction. Additionally, SCFs behave as all solvents behave by modifying distributions of solutes in solution, by causing partitioning among multiple liquid phases, and in modifying chemical equilibria and reaction kinetics. In this section, we focus on reactions of this last type that involve covalent bond formation and scission.

3.2.1. Reduction of GO Using SCFs

Currently, the reduction of GO with hydroxyl, carboxyl, or epoxide groups appears to be the most commonly used route to make graphene-like materials, that is, reduced graphene oxide (rGO). These modifications can be done through thermal, chemical, electrochemical, or combined thermal–chemical treatments. Thermal methods usually involve high temperatures up to 1000 °C. Chemical reductions can be induced at relatively lower temperatures (less than 100 °C) by using reducing agents. While most strong reductants such as hydrazines and hydrides are highly toxic and explosive, some non-toxic alternatives such as l-ascorbic acid, sugar, protein, and green tea require long processing times. It is often difficult to effectively restore C = C π-conjugation of graphene sheets. Additionally, interfering substances arising from reducing reagents may be strongly physisorbed to rGO, complicating further processing.

SCFs have been demonstrated to be capable of converting GO into rGO, taking advantage of their unique properties (low density and viscosity and diminishing surface tension) and showing efficiency for such conversion provided the treatment temperature and time are no less than 200 °C and 3 h, respectively. Indeed the GO films annealed in scCO₂ at ≥200 °C displayed a significant increase in electrical conductivity, which reached almost 3 S cm⁻¹ in the film treated at 300 °C (10 MPa, 5 h) dramatically higher than that in the original GO films (<10⁻² S cm⁻¹). A mechanistic understanding of deoxygenation of GO in scCO₂ remains to be established. ScEtOH exhibited a larger reduction activity under similar conditions. Electrical conductivity was further improved up to 2.5 S cm⁻¹ by using scEtOH (with inherent hydrogen donating ability in the form of molecular hydrogen, hydride, or protons) at 250 °C (10 MPa, 5 h).

Of the five different alcohols (methanol [MeOH], ethanol [EtOH], 1-propanol [PrOH], 2-propanol [IPA], and 1-butanol [BuOH]) used at supercritical conditions, scEtOH was found to afford an rGO with the highest carbon-to-oxygen ratio of 14.4 and the largest surface area of 203 m² g⁻¹ (Figure 5a–g). The powder conductivity of the resulting rGO in scEtOH was up to 27 500 S m⁻¹, 2.5 times higher than that of the rGO treated in scMeOH (10000 S m⁻¹), both of which outperform the electrical conductivity of the rGO sample reduced by hydrazine (10000 S m⁻¹). After treatment in scIPA for 1 h, double-oxidized GO with an O 1s/C 1s ratio of 0.73 and an H/C molar ratio of 7.07 was reduced to an rGO with increased carbon to oxygen ratio (C 1s/O 1s = 12.33) and decreased hydrogen to carbon ratio (H/C = 2.27). This result compares favorably with a thermally annealed sample which showed a lower C 1s/O 1s (10.67) and H/C (0.82). Such hydrogen-enriched rGO facilitated Li binding and resulted in high Li⁺ ion uptake, highlighting the importance of this SCF processing. The effective removal of the oxygen functionalities of GO in supercritical alcohols was attributed to a combination of thermal and chemical reduction. The former may involve decarboxylation and hydrodeoxygenation pathways. The latter may be associated with a de-epoxidation mechanism.

ScH₂O offers a green alternative to toxic reducing agents. A higher degree of deoxygenation of GO was attained in supercritical H₂O and scH₂O (473–653 K) compared to moderate temperature (373 K) treatment. Spectroscopic results suggested that the deoxygenation of GO in subcritical H₂O and scH₂O could be due to several pathways including hydrogen ion–initiated dehydration by inter- or intramolecular reactions, reduction of highly strained epoxide groups, decarboxylation, and generation of conjugated π-network, as shown in Figure 5h. The addition of glycerol in scH₂O was found to also enhance GO oxygen removal by up to 59%, resulting from an in situ hydrogen generation. A very high C/O ratio of 28.2 was obtained by scH₂O gasification of glycerol to reduce GO sheets (with a C/O ratio of 2.5), outweighing those reported for hydrazine-based methods.

3.2.2. Nitrogen Doping of Graphene (or GO) via SC Reaction

N-doping of graphene induces polarization in the carbon network due to the higher electronegativity of N (3.04) relative to C.
A band gap is opened upon N-doping, resulting in new properties for catalysis and device applications. SCFs provide unique processing media for chemically doping graphene (or GO) owing to their tunable transport properties. For example, GO was N-doped by employing N-containing compounds such as ethylenediamine, melamine, or hexamethylenetetramine\(^{[168]}\) in supercritical ethanol and water solutions (400 °C, 20–25 MPa), with doping levels (at%) of about 4.7, 2.0, and 5.3%, respectively. Using urea,\(^{[169]}\) dimethylglyoxime,\(^{[170]}\) or glycine\(^{[171]}\) as a dopant, similar doping results were obtained in scH\(_2\)O (400 °C). At milder conditions (310 °C), N-doped few-layer graphene was obtained in scACN without any addition of other N precursors,\(^{[138]}\) Cyclotrimerization of cyano groups in acetonitrile was inferred to form a 1,3,5-triazine ring, facilitating the formation of C–N bond primarily at the edges of graphene at high temperature and pressure. The doping content was tuned from approximately 1.6 to 4.6 at% by prolonging reaction time from 2 to 24 h. An even higher N doping level of 6.4 at% was achieved in scNH\(_3\) (200 °C, 15 MPa) by using graphite as a starting material (Figure 6).\(^{[37]}\) The resulting N configurations were dominated with pyrrolic N (45.9%) followed by graphitic N in the basal plane (32.5%) and also at the edge (10.1%), and pyridinic N (11.5%). However, there was no contribution from oxidized N\(^+\)O\(^-\) which contrasts the formation of 13.9% pyridinic N\(^+\)O\(^-\) by doping in ammonia solution under ultrasonication. When using GO instead of graphite in scNH\(_3\), the doping level was improved to 10.8 at%, comparable to the value obtained by annealing (220 °C) with ammonia gas. Graphene doping types...
can be changed by adjusting scNH3 pressure and by introducing a second phase like CH4. SCFs can promote the doping of many other materials such as TiO2. Nevertheless, relevant studies regarding doping such 2D materials in SCFs are lacking.

3.2.3. Etching of Graphene (or Carbon Flakes) in ScH2O

Crystallographic etching of graphene can be achieved based on 1) catalytic (preferably armchair) carbon gasification,174,175 and 2) oxidative catalytic etching in scH2O.134,176

As early as 1955, a variety of metal particles have been investigated for the catalytic graphite–water vapor reaction.174,175 Metallic particles move on the surface of graphite during a reaction, leading to the formation of trenches which with the smallest catalyst particles were found to orient mostly in the <1120> directions.175 Fe, Co, and Ni were reported as active catalysts for the reaction between 600 and 1000 °C.175,177 V and Mo were shown to be weak catalysts under these conditions, while Cu, Zn, Ca, Cr, Mn, and Pb were inactive. Although graphite gasification hardly occurred by Ag NPs in scH2O, catalytic carbon oxidation with oxygen was shown to be significantly accelerated by the metallic NPs in scH2O.175 The etching rate was observed to increase with water density above 0.1 g mL−1. Such enhancement of carbon oxidation in scH2O was attributed to the efficient removal of adsorbed gaseous products (CO, CO2) from the catalyst surface and the formation of hydroxyl (OH) and hydroperoxyl (HO2) radicals. This anisotropic etching in combination with exfoliation in scH2O allows the scalable production of zigzag-edge-rich graphene nanosheets for electrochemical devices.176

ScH2O treatment of anthracite coal (400 °C, 25 MPa, 120 min) was observed to result in single-layer graphene oxide quantum dots (GQDs).178 ScH2O cutting down of large anthracite flakes started as early as 10 min. The depolymerization of coal was hypothesized to result from cleavage of ether and carbon–carbon (C–C) bonds induced by the nonpolar scH2O. In contrast to commonly used oxidizing agents, the scH2O oxidation was selective and did not bring about severe aromatic ring degradation. Exfoliation occurred at the same time, which led to a significant reduction in the number of layers for the GQDs upon extension of treatment.

3.2.4. SCF-Induced Phase Engineering

Phase transformations of layered materials have been realized in SCFs. It has been reported that scDMF boosts oxygen release in layered MnO2, enabling a phase change from MnO2 to Mn3O4 in short periods (400 °C, <10 min) and further to MnO after extended processing times (>10 min).179 In scDMF, a chemical phase change occurs, and morphology (nanocrystal habit) transformations occur in kinetic competition with one another. MnO2 to Mn3O4 to MnO changes show that a reduction occurs from Mn4+ to mixed Mn3+ and Mn2+ to Mn2+, respectively.180 Accompanying oxidation processes were not identified. Starting nanosheet layers are transformed into nanocrystals of various shapes. This diversity is driven by phase change and by Ostwald ripening. Ripening is promoted by solvation of chemical units (ions, complexes, molecules) in scDMF (or other solvents in other 2D material systems).

Compared to scDMF which exfoliates titanate without phase change, scH2O was found to trigger a phase transformation of H12[Si2O5(OH)]·H2O into anatase above 200 °C.62 This was presumably due to dissolution and recrystallization (Ostwald ripening) caused by H+ that was supplied by scH2O, as illustrated in Figure 7.

Protonation often increases solubility in polar solvents, and can then expected to promote Ostwald ripening.

SCFs also offer external stimuli to facilitate the formation of 2D lateral heterostructures for enhanced photocatalysis.35,65,67,78,181–184 For example, scCO2-ethanol-water mixed solvents provided benefits for the production of 2H-WS2 nanosheets with abundant edges.35 Those exfoliated monolayers were readily oxidized by the air remaining in the system to form WO3, yielding 2D WS2/WO3 lateral heterostructures. High-resolution transmission electron microscopy (HRTEM) revealed irregular holes or vacancies on the basal planes of WO3·H2O nanosheets.182 The presence of oxygen deficiency on the surface was further confirmed by X-ray photoemission spectroscopy. The formed H3O+ originating from

Figure 6. a) Schematic of graphite exfoliation and N doping simultaneously in scNH3. b) ID/IG value relative to N doping level of graphene reported by other methods to those of present study. Reproduced with permission.137 Copyright 2016, American Chemical Society.

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the reaction of water and CO2 may initiate defect generation via an electrophilic attack.

SCCO2 was also found to induce a phase transition of semiconducting (trigonal prismatic) 2H-MoS2 to metallic (octahedral) 1T-MoS2 ([Figure 8]).[181,184,185] No defects or deformation of the lattice structure of MoS2 were observed during the process ([Figure 8c–f]). The adsorption energy of CO2 on the 1T-MoS2 (−0.62 eV) was calculated to be more than three times stronger than that on the 2H-MoS2 (−0.18 eV) ([Figure 8i]). This difference in CO2 adsorption strength was assumed to cause such phase conversion. The obtained 1T MoS2 nanosheets were speculated to be stabilized by the adsorbed CO2. However, how to control the yield of 1T-MoS2 has not been addressed. A similar concept has been demonstrated to be effective in the construction of amorphous MoO3 nanosheets with the help of scCO2.[65,186] The coexistence of metastable h-MoO3 and stable α-MoO3 resulting from the oxidation of exfoliated MoS2 likely played a role.[65] Such conjecture was based on the finding that starting from pure MoO3 nanosheets only yielded an orthorhombic crystalline structure rather than an amorphous structure after scCO2 treatment. The stronger adsorption of CO2 on an amorphous surface than on crystal surface was supposed to favor stabilization of the amorphous MoO3.[187,188] It may also induce diffusive atomic disordering of MoO3 nanosheets.

### 3.3. Molecular Modeling of SCF-Assisted Exfoliation

Wu and Yang provided some significant molecular dynamics simulation results where scCO2 was examined as a solvent for two model graphene sheets at a critical density, \( \rho_c \) (0.468 g cm\(^{-3}\)), and at 2\( \rho_c \), at three temperatures, 45, 90, and 135 °C.[129] These thermal variations were inconsequential, but density (pressure) was found to have a significant effect, with intersheet repulsion increasing with density. They quantitatively examined free energy solvent effects through a calculated potential of mean force (PMF) by partitioning it into a sheet–sheet component and an scCO2-induced component. This second component accounts for density effect and arises from the formation of molecular layers of scCO2 on the sheet surfaces.[129] These authors found that as density increased additional solvent layers preferentially formed on the sheets, and this sheet solvation accounts for stabilizing maxima in the intersheet repulsion at separations greater than 6.5 Å. They also concluded that intersheet solvent intercalation is a critical step in exfoliation. This layer-solvation effect was discussed by Israelachvili and co-workers many years ago in terms of a “solvation force.” These workers explored specific solvation effects between crossed cylinders in initial versions of a surface forces apparatus. Intersheet repulsion forces were found to exhibit periodic maxima corresponding to solvent layer thicknesses.[189,190] They also found a similar periodic variation in repulsion when they examined C\(_{60}\) fullerene multilayers on clay surfaces.[191] We can thereby understand graphene stability in scCO2 in terms of fundamental colloid science, Israelachvili’s multilayer solvation force. Similar MD (molecular dynamics) studies of other supercritical solvents will be very useful, particularly if solvents exhibiting overlapping \( \pi \) binding to graphene’s \( sp^2 \) surfaces can be modeled.

An initial examination of such \( \pi \) binding solvation under near-critical and supercritical conditions has been described by Xu and co-workers[192] in steered molecular dynamics (SMD)[31] simulations as a function of sheet separation for a polyethylene glycol-pyrene (Py-PEG) polymeric conjugate. These SMD simulations included subcritical and supercritical conditions; they included mixtures of CO2, PX (p-xylene), and Py-PEG, as well as examinations of CO2 and PX alone. The scCO2-alone simulations corroborated some of Wu and Yang’s finding[129] that initial separations less than 6.5 Å evolved to an exclusion of CO2 and de facto association of graphene sheets with an interlayer separation of about 4 Å (because of an
scCO₂-induced intersheet repulsive barrier at about 6.5 Å). Initial separations of 10 Å also evolved to an average separation of about 4 Å (first to about 6.5 Å and then to 4 Å) at a density of 0.912 g cm⁻³, above \( \rho_c \) and only slightly lower (2.6%) than 2\( \rho_c \) (0.936 g cm⁻³). This discrepancy was not discussed by Xu and co-workers but may be a consequence of their nanosheet constraints. A conclusion that scCO₂ cannot stabilize graphene nanosheets appears contrary to many experimental observations. The detailed discussion of Wu and Yang describes a step-wise wedge-opening effect followed by surface solvation by scCO₂.\(^{[129]}\) We emphasize that this repulsive barrier at about 6.5 Å was also observed at only 0.468 g cm⁻³ (\( \rho_c \)). The only PMTs provided by Xu and co-workers\(^{[192]}\) were expressed in terms of a “sliding distance.” It is unclear whether this coordinate corresponds to nanosheet separation (which happens along the \( y \)-coordinate, normal to nanosheets) or to sliding of one sheet past the other at an imposed velocity of 2.5 Å ns⁻¹ in the \( x \)-coordinate direction. Values of PMF ranged from 0 to about 25.6 kJ mol⁻¹ nm⁻²\(^{[192]}\), which is only a 25% potential energy change calculated between the nanosheet aggregation state energy minimum at about 4 Å separation to a primary maximum at 7.5 Å separation, and an energy difference of about 100 kJ mol⁻¹ nm⁻² (23.9 kcal mol⁻¹ nm⁻²).\(^{[129]}\) Whatever these calculated\(^{[192]}\) PMFs are, the “sliding distance” cannot be nanosheet separation along a \( y \)-coordinate because the energies of these PMFs go to zero as “sliding distance” goes to zero. Additionally, in neither case is a ceiling to a steadily increasing barrier shown, since the maximum sliding distance illustrated is 6 Å.

Xu and co-workers also examined mixtures of CO₂ and PX and CO₂, PX, and Py-PEG. They found that PX alone was not effective in initiating exfoliation with initial layers spaced 6 Å apart, but at an initial separation of 10 Å, the sheets evolved to a 7.4 Å separation, indicating that at least a monolayer of PX separates the respective sheets. Mixed CO₂/PX solutions were useful when the [CO₂]/[PX] ratio was higher than 2.5. At such higher concentration ratios, the nanosheet spacing evolved to about 7.5 Å when starting from 6 Å, and to 10.5 Å when starting from a 10 Å interlayer spacing. Unfortunately, PMF was not calculated for these solvent compositions. A qualitatively significant advance was in analyzing stabilization by Py-PEG, when mixed CO₂/PX solvents initiated exfoliation. These simulations showed that the pyrene head groups provided \( \pi-\pi \) binding that survived venting of CO₂.\(^{[192]}\) This same kind of binding can be obtained for many pyrene derivatives of varying charges.\(^{[31]}\) Essentially, any conjugated ring system is a suitable candidate for \( \pi-\pi \) adsorption or anchoring to graphene surfaces. Suitably strong binding moieties for 2D material surfaces somewhat dissimilar from graphene must be found empirically.

Figure 8. a) SEM image of bulk MoS₂ powder. b) TEM and c) HRTEM images of MoS₂ nanosheets. Inset: FFT of the region enclosed by the yellow square. d) HRTEM image of MoS₂ heterostructure. Inset: Schematic structures of the unit cells of 1T and 2H MoS₂. e,f) Filtered images of the regions enclosed by white squares shown in (d). g) Intensity distribution along the red dashed line in (e,f). h) Schematic of the 1T@2H-MoS₂ heterostructure formation mechanism. i) Adsorption of CO₂ on a single-layer MoS₂ (2×2) surface: CO₂ is adsorbed on one side of I) 1T-MoS₂ and II) 2H-MoS₂, and on two sides of III) 1T-MoS₂ and IV) 2H-MoS₂. j) Schematic of the top and side views of MoS₂ with strained S vacancies on the basal plane by using scCO₂. Reproduced with permission.\(^{[181]}\) Copyright 2016, American Chemical Society.
3.4. Process Opportunities

It appears that simple RESS processing can induce exfoliation and that cyclical repeating of such processing has an additive effect resulting in progressively increased exfoliation extents. SCFs with mild critical properties that are gases under ambient conditions offer important processing advantages. Using co-solvents with some of these “mild” SCFs provides some apparent advantages, including formation of complex fluids (using co-solvents immiscible with SCFs that form emulsions, polymer solutions). Also, coupling shearing-generating processing methods with SCF processing appears to be a very useful area for process development.

Further work is needed in understanding and characterizing covalent bond formation accompanying extant solvent processing of 2D materials, and this need is also a development opportunity for many SCF processes applied to such materials. Shear-induced bond breaking, sonolysis-induced solvent radical formation, reactions of radicals with 2D sheets in SCF and SCF-co-solvent mixtures, and redox reactions in SCF are examples of chemistries that would benefit from further understanding in connection with 2D material processing in SCFs.

More physical and chemical modeling and simulation on different length scales are needed. CFD helps us understand microscopic fluid dynamics and how macroscopic waves and shear-fields can be generated and transmitted in multiphase suspensions. Molecular dynamics simulations have also advanced so that nanoscopic processes can be examined and correlated with macroscopic supercritical parameters. One of these studies has provided a clear picture of how SCF molecules produce free energy potentials that promote exfoliation.

4. Formation and Applications of 2D Materials Processed by SCFs

Applications of nanosheets prepared or processed with SCF assistance are mirroring those of nanosheets created by other top-down and bottom-up approaches. Catalysis and energy account for a large majority of these applications and analytical applications such as imaging and sensors represent another primary focus. Sasikala and co-workers have recently discussed supercritical fluid applications of graphene in conductive films and field effect transistors, batteries, capacitors, solar cells, fuel cells, biological and environmental applications, sensors, catalysis (an Mo2C/rGO material obtaining hydrocarbons from glycerides), and microwave absorption devices. A novel heterostructured material composed of graphene nanosheets encapsulated with MoS2 is a noteworthy advance in superhydrophobicity.

Sathish and co-workers noted that coatings of these encapsulated sheets exhibited superhydrophobicity (water contact angle of 166°). The component nanosheets BN and MoS2 separately yielded contact angles of 125°. This synergism is most likely due to a “lotus” effect that often accompanies a very rough surface topography, a property that often accompanies 3D heterostructures. However, a key property of these mixed sheet materials is obtaining heterojunction contacts of basal planes.

In many of these applications (Table 4), 2D materials are major components of electrodes, and their electrical conductivity is a necessary property. We also discuss some particular types of composite materials, wherein 2D nanosheets provide flame retardancy. Lubricants compose a type of multiphase materials, sometimes multiphase fluids, and we discuss those containing nanosheets.

4.1. Catalysis

Catalysis with 2D nanosheets has gained increasing research interest because of their remarkable properties and flexibility in surface and structure modification by diverse methods. By using SCFs, the surfaces of graphene, rGO, or GO have been decorated with a variety of metal (such as Pt, Ru, Pd, Ag, Au, Fe, N, PtRu, PtFe, PtFeCo, metal oxide (such as ZnO, TiO2, CoO, SnO2, TiO2, MoO2, MnO2, Al2O3, and SnO2), and metal sulfide (such as CdS)) with tunable sizes, loadings, and compositions. These supported catalysts hold promise for many different catalytic processes. For example, rGO supported Pt NPs of 3.5–5.4 nm and Ru NPs of 2.5–4.4 nm were demonstrated to be active for limonene hydrogenation in scCO2 with a selectivity of ~90% for p-menthene. Both catalysts exhibited higher conversions (~78% at 60 min) than commercial Ru/C (42%) and rGO (38%). The Ru/rGO catalyst was reused four times with only a minor loss of performance. Such good activity and selectivity may be related to the 2D open structure of the rGO support, which favors adsorption of reactants and desorption of intermediate products.

RGO-supported Mo2C NPs were synthesized using a supercritical alcohol route, which was followed by carothermal hydrogen reduction. This composite could be used as a catalyst for oleic acid deoxygenation to produce hydrocarbons with ~85% yield and ~90% hydrocarbon selectivity. This value is higher than those (yields = 18.5–50.3%) obtained for the Mo2C catalysts using other carbon substrates, including glassy spherical carbon, activated carbon, and mesoporous carbon. The high hydrocarbon yield for the Mo2C/rGO composite was attributed to the uniform distribution of Mo2C NPs on the 2D support as well as efficient transport of reactants imparted by the large pore size (~9.7 nm) and slit-like pore structure of the catalyst. The superior role of rGO as a catalyst support compared to other carbon materials (carbon nanotubes, activated carbon, and carbon black) has also been observed in the catalytic dehydrogenation of LiAlH4.

CoO4 NPs of 3.2–8.8 nm were attached on the surface of GO resulting from decomposition of cobalt nitrate in scCO2-ethanol mixtures. This CoO4/GO composite could catalyze the decomposition of ammonium perchlorate (AP) with lower decomposition temperature (297 °C) and enhanced exothermic heat (1591 J g−1) as compared to the values of 308 °C and 1448 J g−1, respectively, for pure CoO4. Despite these preliminary results, mechanistic understanding of the catalytic decomposition of AP using CoO4/GO is still unclear.

Local electronic structures of graphene and GO are easily modified by chemical doping with heteroatoms to yield metal-free electrocatalysts. ScN(NH)2 was reported to facilitate the...
Table 4. Summary of SCF-processed 2D materials reported for various applications.

| 2D materials and hybrid | Precursor | Experimental condition | (Application) Performance | Ref. |
|-------------------------|-----------|------------------------|----------------------------|------|
| Pt (or Ru)–rGO          | C10H18Pt, C30H50O4Ru, rGO | ScCO2, 13 MPa, 60 °C, 24 h | (Limonene hydrogenation) Conversion: 57% (Pt–rGO) and 54% (Ru–rGO) and 87% (Ru–rGO) Yield: 48% (Pt–rGO) and 47% (Ru–rGO) TOF: 43 × 10⁻³ h⁻¹ (reaction time: 30 min) | [105] |
| Pt–rGO                  | Pt(C14H18O2)2, rGO          | ScCO2, 12 MPa, 200 °C, 3 h | (Methanol electro-oxidation) Onset potential: 0.17 V (vs Ag/AgCl) ECSA: 41.5 m² g⁻¹ | [195] |
| Pt–rGO                  | C12H18Pt, rGO               | ScCO2, 24.5 MPa, 70 °C, 6 h | (Methanol electro-oxidation) ECSA: 44.3 m² g⁻¹ | [196] |
| Pd (or Fe, Ni, Pd, and Au)–rGO | Pd(C10H18O2)2, Fe(C14H18O2)2, Ni(C14H18O2)2, AuCl2, GO | ScCO2–methanol, 10 MPa, 50 °C, 2 h, dimethyl amineborane as reductant | 4.5 wt% hydrogen desorption time: 0.3 h (2.5 wt% of Fe–rGO) and 6 min (10 wt% of Fe–rGO) | [100] |
| Pd–graphene             | Pd(C14H18O2)2, graphene     | ScCO2–NMP/methanol, 18 MPa, 50 °C, 5 h, dimethyl amine borane as reductant | (Formic acid electro-oxidation) ECSA: 103.8 m² g⁻¹ | [102] |
| Pd–rGO                  | Pd(C14H18O2)2, rGO          | ScCO2–H₂, 4000 psi, 45 °C, 24 h | (Suzuki reaction) Yield: 98.5% (100 °C, 5 min, 5.1 wt% Pd–rGO) Recyclability: 79.1% (yield) after 10 cycles | [197] |
| Ag–GO                   | AgNO3, GO                   | ScCO2–ethanol, 12 MPa, 65 °C, 3 h, glucose as reductant | (Photocatalytic dye degradation) Rhodamine 123 dye degradation efficiency: 82% Acetaldehyde degradation efficiency: 93% (after 60 min of visible light illumination) | [198] |
| PtRu–rGO                | Pt(C14H18O2)2, Ru(O2C5H7)3, rGO | ScCO2–H₂-methanol, 12 MPa, 200 °C, 1.5 h, then 16 MPa, 30 min | (Methanol electro-oxidation) Onset potential: 0.12 V (vs Ag/AgCl) I_f/I_r: 6.75, 3.45, and 2.64 (first, fifth, and tenth cycles) | [199] |
| PtFe–graphene           | Pt(C14H18O2)2, Fe(C14H18O2)2, honeycomb-structured graphene (HSG) | ScCO₂–tetrahydrofuran (THF), 30 MPa, 333 K, 2 h, then 15 MPa, 333 K, 30 min, borane-THF as reductant | (Oxygen reduction reaction, ORR) ECSA: 110 m² g⁻¹ | [107] |
| PtFeCo–graphene         | Pt(C14H18O2)2, Co(C14H18O2)2, honeycomb-structured graphene (HSG) | ScCO₂–tetrahydrofuran (THF), 30 MPa, 333 K, 2 h, then 15 MPa, 333 K, 30 min, borane-THF as reductant | (Oxygen reduction reaction, ORR) ECSA: 110 m² g⁻¹ | [200] |
| ZnO–rGO                 | Zn(NO3)2·6H2O, GO           | ScCO2–ethanol, 9 MPa, 300 °C, 6 h | (Photocatalytic hydrogen production) Activity: 28.9 μmol g⁻¹ (2 h) | [101] |
| Co3O4–GO                | Co(NO3)2·6H2O, GO           | ScCO2–ethanol, 9 MPa, 150 °C, 24 h | (Ammonium perchlorate decomposition) Decomposition temperature: 297 °C Exothermic heat: 1591 J g⁻¹ | [96] |
| Fe–TiO2–rGO             | (C12H28O4)Ti, FeCl2, rGO   | ScCO2–IPA/acetic acid, 5000 psig, 60 °C, 24 h | (E2 photodegradation) Half-life of E2: 41 min (1 sun intensity) | [201] |
| TiO2–graphene           | (C12H28O4)Ti, graphene     | ScCO2–ethanol/H₂O, 23 MPa, 350 °C, 8 h | (Methyl orange dye photodegradation) Efficiency: 100% (180 min) | [202] |
| Mo2C–rGO                | C12H30MoO10, GO            | SC 2-methyl-1-propanol, 400 °C, 30 min | (Oleic acid deoxygenation) HC selectivity: ≥90% HC yield: ≥85% | [193] |
| 2D materials and hybrid | Precursor | Experimental condition | (Application) Performance | Ref. |
|------------------------|-----------|------------------------|--------------------------|-----|
| Cds−rGO                | C$_2$H$_5$CO$_2$H, H$_2$O, Na$_2$S$_2$O$_5$, H$_2$O, rGO, glutathione | ScCO$_2$−H$_2$O, 12.5 MPa, 75 °C, 90 min | (Photoelectrochemical water splitting) Photocurrent densities: at least three times higher than pristine Cds NPs | [103] |
| N−doped graphene (NG)  | Graphite  | ScNH$_3$, 15 MPa, 200 °C, 1−2 h | (ORR) Reduction peak: −0.30 V (vs Ag/AgCl) Electron transfer number: 3.62 | [17] |
| 1T@2H MoS$_2$          | MoS$_2$ nanosheets | ScCO$_2$−ethanol/H$_2$O, 353.2 K, 6 h | (Photoelectrochemical water splitting) Photocurrent densities: −1400 µA cm$^{-2}$ (at −0.6 V) Photocurrent response: 1.2 × 10$^{-5}$ A cm$^{-2}$ | [181] |
| 2H−/1T−MoS$_2$−graphene| Graphene, 2H-MoS$_2$ nanosheets | ScCO$_2$−ethanol/H$_2$O, 20 MPa, 433.2 K, 6 h | (Photocatalytic hydrogen evolution) Photocurrent response: 51.0 µA cm$^{-2}$ | [184] |
| 2H@1T−MoS$_2$−graphene | Graphite, MoS$_2$ powder, PVP | ScCO$_2$−ethanol/H$_2$O, 16 MPa, 40 °C, 3 h | (Photoelectrochemical hydrogen evolution) Photocurrent response: 5.5 × 10$^{-5}$ A cm$^{-2}$ Activity: 19.82 mmol g$^{-1}$ h$^{-1}$ | [78] |
| WS$_2$−WO$_3$/H$_2$O/1T−2H MoS$_2$ | WS$_2$ powder, MoS$_2$ powder | ScCO$_2$−ethanol/H$_2$O, 313.2 K, 3 h | (Photoelectrochemical hydrogen evolution) Photocurrent response: 10.6 × 10$^{-5}$ A cm$^{-2}$ | [67] |
| WS$_2$/MoS$_2$/H$_2$O | WS$_2$ powder | ScCO$_2$−ethanol/H$_2$O, 16 MPa, 313.2 K, 3 h | (Methyl orange photodegradation) Degradation: 90% (40 min, UV irradiation or 240 min, visible-light irradiation) Photocurrent response: 6 × 10$^{-4}$ A cm$^{-2}$ | [35] |
| rGO                    | GO        | ScMeOH, 30 MPa, 400 °C, 15 min−2 h | (Anode in LIBs) Discharge capacity: 652 mA h g$^{-1}$ at 50 mA g$^{-1}$ after 40 cycles | [161] |
| Hydrogen-enriched rGO  | GO        | ScIPA, ultrasonication: 1 h, then 400 °C, 1 h | (Anode in LIBs) Reversible capacity: 1331 mAh g$^{-1}$ at 50 mAg$^{-1}$ after 100 cycles Rate-performance: 328 mAh g$^{-1}$ at 5 A g$^{-1}$ Cycling stability: 1000 cycles at 10 A g$^{-1}$ | [164] |
| Si nanowire−graphene  | Diphenylsilane, GO | SC hexane, 360 °C, 1 h | (Anode in LIBs) Reversible capacity: 1400 mA h g$^{-1}$ for the 30th cycle at 420 mA g$^{-1}$ | [203] |
| Hydrogen-enriched porous carbon nanosheets | Natural graphite, KMnO$_4$, H$_2$O$_2$, H$_2$SO$_4$ | ScIPA, ultrasonication: 1 h, then 400 °C, 1 h | (Anode in sodium ion batteries) Reversible capacity: 300 mAh g$^{-1}$ at 50 mAg$^{-1}$ Cycling stability: 2000 cycles at 1−5 A g$^{-1}$ | [204] |
| 1-Pyrene sulfonic acid sodium salt modified graphene | Graphite powder, 1-pyrene sulfonic acid sodium salt | ScEtOH/H$_2$O, 450 °C, 2 h | (Anode in LIBs) Saturated reversible capacity: 301.25 mA h g$^{-1}$ at 0.01 mA g$^{-1}$ | [74] |
| SnO$_2$−rGO            | Tin(II) acetate, GO | ScMeOH, 400 °C, 30 min | (Anode in LIBs) Reversible discharge capacity: 776 mA h g$^{-1}$ after 70 cycles at 0.1 A g$^{-1}$ Rate-performance: 147 mA h g$^{-1}$ at 5 A g$^{-1}$ Cycling performance: 531 mA h g$^{-1}$ after 1000 cycles at 1 A g$^{-1}$ | [205] |
| CoCO$_2$−rGO           | Co(CH$_3$COO)$_2$, rGO | ScCO$_2$−ethanol, 50 °C, 10 MPa, 2 h | (Anode in LIBs) Reversible discharge capacity: 745 mA h g$^{-1}$ at 6 A g$^{-1}$ Coulombic efficiency: >95% after 2 cycles (Anode in NIBs) Reversible discharge capacity: 370 mA h g$^{-1}$ at 50 mA g$^{-1}$ | [206] |
| LiFePO$_4$−graphene     | Graphite powder, LiFePO$_4$ particles | ScCO$_2$, 40 °C, 8 MPa, 30 min, CF: 1500 rpm, 60 min | (Cathode in LIBs) Discharge capacity: 160 mA h g$^{-1}$ at 0.1 C over 15 cycles | [32] |
| LiFePO$_4$/C, LiMnPO$_4$/C, LiCoPO$_4$/C, LiNiPO$_4$/C | (NH$_4$)$_2$PO$_4$·3 H$_2$O, FeSO$_4$·7H$_2$O, MnSO$_4$·H$_2$O, CoSO$_4$·7H$_2$O, NiSO$_4$·6H$_2$O, CH$_3$COOLi·H$_2$O | ScEtOH−PVP, 10 MPa, 400 °C, 2 h | (Cathode in LIBs) Discharge capacity: 70 mA h g$^{-1}$ at 80 C (LiFePO$_4$/C), 40 mA h g$^{-1}$ at 30 C (LiMnPO$_4$/C); 53 mA h g$^{-1}$ at 20 C (LiCoPO$_4$/C) | [60] |
| V$_2$O$_5$              | V$_2$O$_5$ powder | ScEtOH, 250 °C, 12 h | (Cathode in LIBs) Initial capacity: 90 mA h g$^{-1}$ at 15 C 100% capacity retention after 200 cycles | [63] |
| Li$_2$MnSiO$_4$ (M = Fe, Mn)−multiwalled carbon nanotubes (MWNTs) | FeCl$_3$·4H$_2$O, Si(OCl)$_3$H$_4$ | LiOH·H$_2$O, ascorbic acid, MWNTs | (Cathode in LIBs) Discharge capacity: 340 mA h g$^{-1}$ at 45 ± 5°C Cycle ability: 20 cycles | [207] |
Table 4. Continued.

| 2D materials and hybrid | Precursor | Experimental condition | (Application) Performance | Ref. |
|-------------------------|-----------|------------------------|--------------------------|------|
| MoS₂, MoSe₂            | Bulk MoS₂ and MoSe₂ | ScDMF, ultrasonication (160 W): 5 min, then 400 °C, 1 h, CF: 2000 rpm, 30 min and 30 000 rpm, 1 h | (Cathode in Mg–Li ion batteries) Discharge capacities: 81 mAh g⁻¹ (MoS₂) and 55 mAh g⁻¹ (MoSe₂) at 20 mA g⁻¹ | [56] |
| Graphene aerogel        | GO        | ScCO₂ drying followed by H₂ reduction at 1100 °C for 1 h | (Supercapacitor) Specific capacitances: 153 (ionic liquid [EMIM][TF₂N]) and 90 F g⁻¹ (1 μM MeEt₃NBF₄ in PC) at 100 mA g⁻¹. Energy density: 21.4 Wh kg⁻¹ at 100 mA g⁻¹ ([EMIM][TF₂N]) | [208] |
| Nitrogen-doped graphene oxide (NGO) | GO, ethylenediamine or melamine or hexamethylenetetramine | ScH₂O ethanol, ultrasonication: 30 min, then 20–25 MPa, 400 °C, 30 min | (Supercapacitor) Specific capacitances: 280 F g⁻¹ in aqueous 1 M H₂SO₄ (0.9 V) and 104 F g⁻¹ in ionic liquid EMITFSA (3.6 V). Energy densities: 8 (1 M H₂SO₄) and 40 W h kg⁻¹ (EMI-TFSA) | [168] |
| Nitric acid treated–NGO | GO, urea, HNO₃ | ScH₂O, ultrasonication: 30 min, 200 °C, 20–25 MPa, 1 h | (Supercapacitor) Specific capacitance: 261 F g⁻¹ at 0.5 A g⁻¹ | [169] |
| NGO                    | GO, dimethylglyoxime | ScH₂O, 400 °C, 2 h | (Supercapacitor) Maximum specific capacitance: 286 F g⁻¹ at 0.5 A g⁻¹. Cycling results: 98% specific capacity retention, 100% coulombic efficiency over 1000 cycles at 5 A g⁻¹ | [170] |
| NGO                    | GO, glycine | ScH₂O, 400 °C, 1 h | (Supercapacitor) Specific capacitance: 270 F g⁻¹ at 0.5 A g⁻¹. Capacitance retention: 90% over 10 000 cycles at 10 A g⁻¹. Symmetric supercapacitor cell energy density: 4.1 and 36 Wh kg⁻¹ in aqueous and ionic liquid electrolytes, respectively | [171] |
| ZnO–rGO                | Zn(NO₃)₂·6H₂O, GO | ScCO₂–ethanol, 9 MPa, 300 °C, 6 h | (Supercapacitor) Specific capacitance: 303 F g⁻¹ at 10 A g⁻¹. Cycling stability: 1000 cycles at 10 A g⁻¹ | [99] |
| MnO₂–graphene          | KMnO₄, graphene | ScCO₂–ethanol, 12 MPa, 50 °C, 30 min | (Supercapacitor with ionic liquid EMI-TFSA additive) Specific capacitances: 230 (at 50 mV s⁻¹) and 207 F g⁻¹ (at 500 mV s⁻¹). Cycling stability: 98% of capacitance retained after 10 000 cycles at 30 mV s⁻¹ | [209] |
| Polypyrrole-coated GO–carbon nanofiber films (GC–SC/PPy) | GO, carbon nanofiber, pyrrole polymerization in the presence of HCl and ammonium persulfate (APS) | ScCO₂, 16 MPa, 40 °C, 3 h, then | (Supercapacitor) Specific capacitances: 144.6 F g⁻¹ at 10 mV s⁻¹. Cycling stability: 89% of initial capacitance after 5000 cycles at 1 A g⁻¹ | [210] |
| GO–polyaniline         | GO, aniline | ScCO₂–ethanol/H₂O, ultrasonication: 30 min, then 12 MPa, 40 °C, 3 h in the presence of HCl and APS | (Supercapacitor) Specific capacitance: 425 F g⁻¹ at 0.2 A g⁻¹. Cycling stability: 83% of initial capacitance after 500 cycles at 1 A g⁻¹ | [211] |
| Graphene               | Graphite crystals | ScNMP/scEOH/ScDMF, ultrasonication (160 W): 10 min, then 38–40 MPa, 300–400 °C, 3 min | (Electronic devices) Sheet resistance: 2–6 kΩ | [133] |
| Graphene               | Graphite powder | ScCO₂, 40 °C, 12 MPa under ultrasonication (120 W), 60 min | (Conductive films) Electrical conductivity: 6.6×10² S m⁻¹ (37 nm film thick) and 2.8×10³ S m⁻¹ (>300 nm film thick) | [128] |
| NG                     | Expanded graphite, acetonitrile | ScACN, 310 °C, 2–24 h | (Electronic devices) Sheet resistance: =300 Ω/Ω | [138] |
| MoS₂                   | Bulk MoS₂ | ScDMF, ultrasonication: 5 min, then 400 °C, 1 h | (Electronic devices) Charge carrier mobility: =1530 cm² V⁻¹ s⁻¹ | [55] |
| Eu³⁺ doped CaTiO₃      | Ca(NO₃)₂·4H₂O, Eu(NO₃)₃·6H₂O, Ti(OC₂H₅)₄ | ScN₂, 1 MPa, 250 °C, 4 h, then 265 °C, 1.5 h, then calcination in air, 800 °C, 4 h | (Luminescence imaging) Red emission at 616 nm (excited at 466 nm) | [212] |
formation of N-doped graphene, which enables a 4e⁻ transfer oxygen reduction reaction (ORR) process in alkaline electrolyte. Such nonmetallic catalyst exhibited a more positive ORR potential (~0.3 V vs Ag/AgCl) and larger current density than the one prepared in NH₄OH. This result may be explained by the relatively higher N content of the N-doped G obtained in scCO₂ than in NH₄OH.

In addition to abundance and environmentally friendly nature, graphene-based materials possess outstanding electrical conductivity and high mechanical strength and stability, which are beneficial when used as catalyst supports in electrocatalysis. A recent study by Lin et al. reported the synthesis of a series of Pt-based/3D graphene composites by using an scCO₂ technology. The as-prepared Pt₄₀Fe₆₀/3D graphene delivered impressive ORR activities with 14.2-fold enhancement in mass activity (1.70 A mgPt⁻¹ at 0.9 V vs RHE), and higher durability compared with commercial Pt/C catalyst (Figure 9c–e). Such high performance was correlated with the use of the scCO₂ approach which afforded highly dispersed and small metallic NPs in close contact with the 3D porous graphene support. Trimeatallic PtFeCo/graphene cellular monolith (GCM) catalysts were derived using a similar SCF strategy. Improved ORR activities were obtained relative to bimetallic PtFe/GCM.

### Table 4. Continued.

| 2D materials and hybrid | Precursor | Experimental condition | (Application) Performance | Ref. |
|-------------------------|-----------|------------------------|---------------------------|-----|
| MoS₂                    | MoS₂ powder | ScCO₂–ethanol/H₂O, ultrasonication: 2 h, then 16 MPa, 313.2 K, 3 h, and ultrasonication: 3 h, CF: 3000 rpm, 15 min | (Luminescence imaging) Emission peaks at 395 and 572 nm (excited in the range 300–550 nm) | [79] |
| MoS₂                    | MoS₂ powder | ScDMF, ultrasonication: 5 min, then 400 °C, 30 min, CF: 2000 rpm, 20 min | (Luminescence imaging) Blue emission peak at 420 nm (excited at 360 nm) | [143] |
| Pd–rGO                  | (C₆H₅F₂O₂)Pd, rGO | ScCO₂–methanol, 10 MPa, 50 °C, 2 h, dimethylamine borane as a reductant | (Sensors) Detection of 1 μM ascorbic acid (AA), 2 μM dopamine (DA), and 50 μM uric acid | [97] |
| Ionic liquid modified   | (C₆H₅F₂O₂)Pd, rGO, butylimidazolium hexafluorophosphate (BMI–PF6) | ScCO₂–methanol, 10 MPa, 50 °C, 2 h | (Sensors) Selective detection of glucose or AA from their mixture. BMP–TFSI is selective for glucose detection; BMP–DCA is selective for AA detection | [104] |
| Ionic liquid modified   | (C₆H₅F₂O₂)Pd, GO, 1-butyl-3-methylimidazolium hexafluorophosphate (BMI–PF6) | ScCO₂–methanol, 10 MPa, 50 °C, 2 h | (Sensors) DA detection selectivity: 3.28 μA μM⁻¹ DA detection limit: 0.12 μM | [213] |
| Au–rGO                  | HAuCl₃•3H₂O, rGO | ScCO₂–methanol, 10 MPa, 50 °C, 2 h | (Sensors) Glucose detection sensitivities: 16.3 μAM μM⁻¹ cm⁻² and 97.8 μAM μM⁻¹ cm⁻² (with ionic liquid additive) Detection limits: 0.183 μM and 0.062 μM (with ionic liquid additive) | [214] |
| RGO–Prussian blue       | GO, K₁[Fe(CN)₆], FeCl₃, L-ascorbic acid | ScCO₂ drying | (Sensors) H₂O₂ detection limit: 5 nm A wide linear range (0.005–4 μM) | [115] |
| Al₂O₃–rGO               | Al(NO₃)₃•9H₂O, rGO | ScCO₂, 20 MPa, 300 °C, 30 min | (Sensors) Chemical sensing ethanol concentration: 1.5 μg mL⁻¹ at 200 °C Response time: about 10 s Recovery time: <100 s | [215] |
| Ag–rGO                  | AgNO₃, GO | ScCO₂–ethanol, 15 MPa, 80 °C, 1 h in the presence of glucose and NH$_3$·H$_2$O | (Lubricants) Friction coefficient: 30.4% Wear scar diameter: 27.4% | [84] |
acetaldehyde by rGO (GO) also led to enhanced photocatalytic degradation of organic pollutants.[198]

ScCO₂ was shown to enable phase conversion of 2H-MoS₂ into 1T-MoS₂ to form 2D 1T@2H MoS₂ heterostructures.[181] An electrode with such heterostructure displayed a photocurrent response of $1.2 \times 10^{-5}$ A cm$^{-2}$ for water splitting under visible light excitation, three times higher than that of 2H-MoS₂. Such enhancement was ascribed to the suppression of charge recombination due to the presence of metallic 1T-MoS₂. An even higher photocurrent response ($10.6 \times 10^{-5}$ A cm$^{-2}$ in visible light) was achieved by using a 2D lateral WS₂-WO₃·H₂O/1T-2H MoS₂ heterostructure obtained in scCO₂.[67] The addition of graphene could further promote this phase transfer.[78,184] The resultant triphasic 1T@2H-MoS₂/graphene hybrid catalyzed H₂ evolution reaction with H₂ production rate reaching 19.82 mmol g$^{-1}$ per hour under visible light irradiation in the presence of TEOA as a sacrificial donor.[78] Alternatively, 2D lateral WS₂/WO₃·H₂O heterostructures were fabricated with the assistance of scCO₂. The potential of WS₂ at the conduction band (CB) minimum (0.42 eV vs the normal hydrogen electrode [NHE]) is lower than that of WO₃·H₂O (1.26 eV), while the valence band (VB) maximum level of WO₃·H₂O (3.51 eV) is higher than that of WS₂ (1.81 eV). Hence photogenerated electrons and holes accumulated at the CB of WO₃·H₂O and the VB of WS₂, respectively. This response resulted in enhanced photocatalytic activity toward the degradation of methyl orange under irradiation with visible light.[35]

**4.2. Batteries**

Rechargeable batteries such as Li-ion batteries (LIBs) and Na-ion batteries (SIBs) store chemical energy with an ability to deliver electrical energy response by repeated charging–discharging processes. 2D nanosheets are showing promise in rechargeable batteries with better rate capability and higher cycling stability than bulk counterparts.

The use of graphene as either a cathode or an anode permits fast electron and ion transport in electrodes, enabling
fast charge and discharge. As an anode material for LIBs, graphene exhibits a theoretical specific capacity of 744 mAh g\(^{-1}\), provided that lithium is bound on both sides of graphene to form Li\(_2\)C\(_6\).[223] RGO (initial discharge capacities of 540–1600 mAh g\(^{-1}\) at 50 mA g\(^{-1}\))[163,224] modified RGO,[74,164] and RGO-based composite materials (such as graphene/Si,[201] graphene/CoCO\(_3\),[206] and graphene/LiFePO\(_4\)) may be promising alternatives for high-performance LIBs. For example, hydrogen-enriched rGO derived by reduction of double-oxidized GO in scIPA exhibited a rather high reversible discharge capacity of 1331 mAh g\(^{-1}\) even after 100 cycles at a current rate of 50 mA g\(^{-1}\), which outperformed thermally reduced GO and scIPA reduced single-oxidized GO electrodes.[164] A large irreversible capacity decay was observed during the first cycle with an initial coulombic efficiency of 45.4%, as in the case of GO and other RGO samples, which was attributable to the formation of a solid electrolyte interphase (SEI) layer due to the presence of defects and reactions between oxygenated functional groups and lithium ions. The electrode showed both good rate and cycling performances with charge capacities of 193 and 167 mAh g\(^{-1}\) after 1000 cycles at 5 and 10 A g\(^{-1}\), respectively. The abundance of hydrogen-terminated groups in rGO was suggested to be beneficial for the high Li-ion-storage capacity. Likewise, the hydrogen-terminated groups and defects on the carbon sheets were also proposed to contribute to enhancement in Na ion uptake.[204] A reversible capacity of 300 mAh g\(^{-1}\) at 50 mA g\(^{-1}\) and cycling stability up to 2000 cycles at 1–5 A g\(^{-1}\) were demonstrated for hydrogen-enriched porous carbon nanosheets in Na ion batteries. Modification of graphite with 1-pyrene sulfonic acid sodium salt (1-PSA) in scH\(_2\)O improved Li-ion charge–discharge properties of exfoliated graphite by providing more active sites (sulfonate groups) for adsorbing lithium ions.[74]

One of the major issues when using metal and metal oxide NPs as electrode materials in LIBs is the significant volume change during charge/discharge, limiting cyclability. This issue can be alleviated by combination with conductive graphene materials with high surface areas.[225] Indeed, Si nanowires–graphene composites prepared in supercritical hexane showed improved specific capacities (1400 mAh g\(^{-1}\) at 240 mA g\(^{-1}\)) and cycling stability (up to 50 cycles) as compared to pure Si NWs (about 1030 mAh g\(^{-1}\) during the 30th cycle).[203] This stability can be explained by the possibility that graphene in the hybrid accommodated the volume changes of Si nanowires during the lithiation/delithiation. Similarly, SnO\(_2\)-rGO composites synthesized in scMeOH also provided high cycling stability (531 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) after 1000 cycles), showing potential as an anode material in LIBs.[205]

Olivine-type LiMPO\(_4\) (M = Fe, Mn, Co, Ni) nanosheets with exposed (010) surface facets were fabricated by employing a solvothermal lithiation process in SC ethanol–water solution (Figure 10a–f).[160,226] These nanosheets exhibited better cycling stabilities as cathodes than their bulk materials in LIBs (Figure 10g–i). During the 50th cycle at 0.2 C, the LiFePO\(_4\)/C, LiMnPO\(_4\)/C, and LiCoPO\(_4\)/C nanosheets (thickness: 3.7–4.6 nm) showed reversible discharge capacities of 163, 147, and 136 mAh g\(^{-1}\), corresponding to a capacity retention of 99.4%, 93.6%, and 88.3%, respectively.[60] Perhaps more interestingly, the ultrathin nanosheet features facilitated fast lithium transport, affording high-energy densities and excellent rate capabilities (e.g., 18 kW kg\(^{-1}\) and 90 Wh kg\(^{-1}\) at an 80 C rate for LiFePO\(_4\)/C nanosheets) (Figure 10j), which are promising for energy storage and conversion devices with both high-power and high-energy densities. Li\(_2\)MnSiO\(_4\) nanosheets of a few atom thick were also prepared in SC ethanol–water solution.[207] This nanosheet structured cathode material showed two lithium extraction/insertion performances (a discharge capacity of ≈340 mAh g\(^{-1}\) at 45 ± 5 °C) with good cycle ability without any structural instability up to 20 cycles. V\(_2\)O\(_5\) nanosheets that were prepared via an SCF route are another cathode alternative for LIBs.[83] The nanosheets displayed a capacity of 90 mAh g\(^{-1}\) at 15 C and an almost 100% capacity retention after 200 cycles.
A recent report of preparing nanoparticulate SnO₂ and depositing 1 nm SnO₂ particles on graphene sheets exfoliated in scCO₂ was developed for SIB anode applications.[227] The reported synthesis was not entirely clear about whether nanoparticle synthesis was done before attempting to reach a supercritical state. The reaction purportedly contained 50 mL of ethanol, and this reaction was pressurized at 40, 60, and 80 °C in different preparations, and no mention of whether or not the critical conditions of their EtOH/CO₂ mixture were exceeded was made.[227] Critical parameters for ethanol/CO₂ solutions have been determined.[228] A mixture of 50 mL of ethanol in a 500 mL reactor pressurized to 10 MPa yields a mole fraction of CO₂ of 0.86. The specific parameters of such a mixture of solvents are Tₚ = 77 °C and Pₚ = 12.6 MPa. These parameters were not attained in these experiments, so this processing should be termed “subcritical” or “near critical.” However, a better dispersity of nanoparticles obtained by pressurization was shown in TEM. Also, the specific capacity (mAh g⁻¹) at “high” discharge rates up to 0 1 A g⁻¹, was twice that measured for the “air” control as well as for CNT controls made with “ncCO₂.”[227] Therefore, these gas expanded “near critical, GA-ncCO₂-ncEtOH, mixtures” were beneficial and should be so recognized.

### 4.3. Supercapacitors

Supercapacitors (or ultracapacitors), including electrical double layer capacitors and pseudocapacitors, are promising short-term high power density storage devices for applications in between those requiring electrolytic capacitors and others requiring batteries. Graphene-based materials obtained in SCFs have been exploited as supercapacitor electrode materials. Graphene aerogels prepared by scCO₂ drying and H₂ reduction provided a specific capacitance of 153 F g⁻¹ and an energy density of 21.4 Wh kg⁻¹ at a current density of 0.1 mA g⁻¹ in an ionic liquid electrolyte (1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide) at 60 °C.[208] The specific capacitance reached 90 F g⁻¹ in an organic electrolyte (1 M MeEt₃NBF₄/PC). Graphene exfoliated in scNMP by a small scale homogenization process was used to make supercapacitors with a specific capacitance of 135 F g⁻¹ in aqueous 6 M KOH.[154] This capacitance dropped to about 100 F g⁻¹ at current densities of 5 to 50 A g⁻¹ with good cycling stability.

Nitrogen-doped graphene sheets obtained in near-critical fluids and SCFs[158–171] were used to obtain a maximum specific capacitance of about 290 F g⁻¹ at 0.5 A g⁻¹ in aqueous 1 M H₂SO₄.[170] Capacitance retention of 98% with 100% coulombic efficiency was achieved over 1000 cycles of charge–discharge at 5 A g⁻¹.[170] It is not sure yet whether dimethylglyoxime-saturated water is critical at only 400 °C, the maximal treatment temperature used with this oxide source. The functional groups and defects/edge sites were proposed to be more active in an acidic medium for pseudocapacitor reactions than in both alkaline and neutral media. The capacitive performance may be further improved by nitric acid treatment to generate pores.[169] A fabricated symmetric supercapacitor cell using N-doped graphene showed an energy density of 8 and 40 Wh kg⁻¹ in aqueous 1 M H₂SO₄ and ionic liquid electrolyte, respectively. Note that supercritical reaction conditions and N-precursors have a direct impact on the N-content, N-type doping, conductivity, and specific surface area, which profoundly affect capacitive behavior.

Incorporating metal oxides, such as MnO₂,[98] ZnO,[99] and conducting polymers of polyaniline[211] and polypyrrole[210] into rGO with the assistance of scCO₂ was shown to be capable of delivering high specific capacitances of 200 (based on cyclic voltammetry at 50 mV s⁻¹ in 3 M KCl), 303 (based on galvanostatic charge–discharge at 10 A g⁻¹ in 2 M KOH), 280 (at 1 A g⁻¹ in 1 M H₂SO₄), and 144.6 F g⁻¹ (based on cyclic voltammetry at 50 mV s⁻¹ in 1 M H₂SO₄), respectively. High cycling stability was also claimed with a capacitance retention ratio of 98% for the ZnO/rGO composite electrode after 1000 cycles.[99] This excellent performances of rGO hybrid electrodes can be attributed to a synergism between each single phase. RGO provides ample surface area and high electrical conductivity as well as superior mechanical and chemical stability. The oxide or polymer acts as a spacer to suppress graphene restacking and help create electrolyte-accessible channels within the electrode. It is believed that SCF processing favors the formation of intimate contact between the oxide (or polymer) and graphene, which benefits enhancement of supercapacitor performance.[220]

ScCO₂ has also been used to facilitate exfoliation of GO in aqueous dispersions for supercapacitor applications.[230] The GO produced, in addition to being exfoliated, also acquired pores that provide active sites for charging and ion diffusion. Electrical double layer capacitances of 253 and 210 F g⁻¹ were obtained at 1 and 16 A g⁻¹, respectively.

### 4.4. Conductive Films and Electronic Devices

Direct exfoliation of graphite in SCFs obtained graphene films with high conductivity.[128,133] Current-voltage (I–V) curves for vacuum-dried graphene samples (at 200 °C) showed resistance in the range of 2–6 kΩ.[133] An ohmic behavior was observed in a low voltage range, while nonlinear symmetric behavior and conduction increase in a high-bias region were identified in the large voltage range. The current density was estimated to be over 1.0 × 10⁸ A cm⁻². No annealing process is required using this SCF approach, which is quite useful for the fabrication of films on various substrates. The SCF method also showed advantages for the preparation of MoS₂ thin films with remarkably better electrical transport performance (≈1530 cm² V⁻¹ s⁻¹) than those obtained by many other techniques.[35] A non-linear I–V characteristic was reported for MoS₂ devices. Such non-linearity was assigned to various charge transport mechanisms such as space-charge-limited conduction, Fowler–Nordheim tunneling, and Poole–Frenkel conduction.

N-doped graphene produced in scACN was demonstrated to display an n-type behavior, in contrast to the p-type field-dependent behavior for pristine graphene.[130] The sheet resistance of the N-doped graphene was ~300 Ω/□, indicating its good quality and high electrical conductivity.

### 4.5. Luminescence and Cellular Imaging

A diverse band structure among various 2D materials provides for many variations in optical properties in absorption and
emission. Reviews of bulk and nanoscale luminescent materials,\textsuperscript{[233]} tuning luminescence in LDH materials,\textsuperscript{[234]} boron nitride nanomaterial luminescence,\textsuperscript{[235]} graphene-based chemiluminescence sensors,\textsuperscript{[236]} layered rare-earth hydroxides,\textsuperscript{[237]} and luminescence and associated mechanisms in graphene and related materials\textsuperscript{[238]} have been provided. Applications of nanosheets in cellular imaging have also been reviewed.\textsuperscript{[239]} Advantages that accompany SCF processing of 2D materials, mainly lack of chemical surface modification, are expected but have not yet been extensively realized.

More basic luminescence studies of nanosheets produced by SCF-aided processing have begun but are not numerous. Yang and Hu doped CaTiO\textsubscript{3} nanosheets with Eu\textsuperscript{3+} and found a maximum in emission intensity at a doping level of 0.2\%\textsuperscript{[212]} These sheets were prepared from ethanol solution of Ca(NO\textsubscript{3})\textsubscript{2} solvo-thermally with Ti(OCH\textsubscript{3})\textsubscript{4} in scN\textsubscript{2} at 1 MPa and 265 °C, and doping was done by including Eu(NO\textsubscript{3})\textsubscript{3} in the reaction. After venting, the nanosheets were collected and calcined in air for 4 h at 800 °C. A growth process that transformed nanoparticles into nanosheets was found that was driven by Ostwald ripening. Excitation of the resulting nanosheets at 466 nm produced a red emission at 616 nm.

Thangasamy and Sathish examined blue luminescence from nanosheets (nanoscrolls) of MoS\textsubscript{2}.\textsuperscript{[143]} This synthesis was done by sonicating powdered MoS\textsubscript{2} in DMF, placing this reaction mixture in an autoclave at 400 °C for 30 min, and then quenching at 5 °C. The supernatant was collected and centrifuged to obtain the MoS\textsubscript{2} nanosheets. The scCO\textsubscript{2} process driven to minimize surface free energy. This minimization is a pervasive force in nature where Gibbs surface free energy is decreased by minimization of surface area to volume ratios and is a consequence of MoS\textsubscript{2} units being constrained to a sheet structure after exfoliation. These authors noted a strong optical absorption band at 328 nm tailing into the visible as far as 500 nm. Their reported excitation spectrum indicated a peak in excitation at 360 nm and a blue emission peak at 420 nm. It was also mentioned that increasing the wavelength of excitation resulted in more extended wavelength emission, and some of these effects are dependent on particle size.\textsuperscript{[143]}

Interestingly, Xu and co-workers reported a novel scCO\textsubscript{2} exfoliation process for MoS\textsubscript{2} that produces stable nanosheets that are not scCO\textsubscript{2} at 40 °C, and stirred to form Pickering emulsions of scCO\textsubscript{2} and ethanol in an aqueous ethanol continuous phase, with scCO\textsubscript{2} and ethanol solution droplets. These emulsion droplets are stabilized by MoS\textsubscript{2} flakes that gradually exfoliate to stabilize more droplet interfacial area. The stability of the resulting MoS\textsubscript{2} nanosheets, relative to the scCO\textsubscript{2} process discussed above, can be rationalized by the much lower SCF temperature of this scCO\textsubscript{2} process compared to the scDMF process. Xu and coworkers noted that such MoS\textsubscript{2} nanosheets likely would be useful for cellular bioimaging applications, but did not report any.\textsuperscript{[79]} These dispersed nanosheets are prevented from restacking tightly following CO\textsubscript{2} removal by the adsorbed Pd NPs. Electrochemical sensing of ascorbic acid, dopamine, and uric acid was superior to graphene and “conventionally prepared” Pd/graphene electrodes using both cyclic voltammetry (CV) and differential pulse voltammetry.\textsuperscript{[97]} In this context, superior means higher sensitivity (1× to 4×).

Similar Pd–graphene composites prepared by scCO\textsubscript{2}-assisted exfoliation and NP deposition were used to also examine effects
of ionic liquids (ILs).\textsuperscript{[104,213]} In a comparative study of graphene (G) and mult walled carbon nanotubes (MWCNTs), Pd NPs were deposited with assistance from scCO$_2$ (10 MPa, 50 °C). Electrodes were prepared as pastes by combining respective nanocarbon materials with isopropl alcohol/Nafion solutions and depositing onto glassy carbon electrodes. IL-containing examples were prepared with 1-butyl-3-methylimidazolium hexafluorophosphate adsorbed into Pd/nanocarbon pastes. For ascorbic acid, dopamine, and uric acid, the electrodes without added IL, the Pd-MWCNT electrodes were slightly to significantly more sensitive than the Pd-G electrodes. However, the added ILS significantly increased sensitivities for both nanocarbons, relative to the IL-free electrodes, and the G electrodes out-performed the MWCNT electrodes by 2× to 3×.\textsuperscript{[213]} In a related study, it was demonstrated that both glucose and ascorbic acid could be detected by such electrodes prepared with scCO$_2$ processing and augmented with IL.\textsuperscript{[104]} Butylmethylpyrrolidinium-bis(trifluoromethanesulfonyl)imide (BMP–TFSI) IL was found to be beneficial for detecting glucose and butylmethylpyrrolidinium-dicyanamide (BMP–DCA) IL worked well for detecting ascobic acid. These were the first demonstrations of detecting these analytes in the presence of each other without using an enzyme-based detection system.\textsuperscript{[104]} A glucose sensor based on Au nanoparticle–decorated graphene and activated with an IL is also an example of a useful heterostructure produced using scCO$_2$ processing.\textsuperscript{[214]} This sensor was made at 50 °C and incubated at 10 MPa, and contained an MeOH/CO$_2$ mixture at least 20% MeOH (T$_e$ = 239 °C) by weight. Such a mixture is 74% mole fraction CO$_2$ (relative to CO$_2$ and MeOH) and has critical parameters of 71 °C and 13 MPa.\textsuperscript{[228]} Therefore, the results reported\textsuperscript{[214]} must be attributed to sub-critical CO$_2$. Ionic liquids have been found to be most beneficial in electrocatalysis as well.\textsuperscript{[251]}

4.7. Flame Retardants

Fire resistance benefitting from incorporating nanosheet materials into polymers and composite materials has been recognized, and multiple reviews are available for graphene,\textsuperscript{[252-257]} metal dichalogenides,\textsuperscript{[258-260]} phosphates,\textsuperscript{[261]} layered double hydroxides,\textsuperscript{[262]} and phosphonates.\textsuperscript{[263,264]} Only a few studies have utilized SCFs in purposely formulating fire retardancy in composite materials, but all composites incorporating inorganic nanosheets will have increased flame retardancy if their matrix or continuous phase is a combustible polymer. This generality can fail if the nanosheets, such as MnO$_2$, discussed below, catalyze thermal decomposition.

Poly(styrene-co-acrylonitrile) nanocomposites with nanoclay were prepared by melt blending in an extruder to provide nanocomposite sheets. These sheets were then subjected to scCO$_2$ and allowed to expand at sub-critical 110 °C to produce foamed sheets. Nanoclay-containing nanocomposites yielded decreased peaks of heat release rate, demonstrating efficacy in flame resistance relative to polymer-only foam controls.\textsuperscript{[112]} More recently Hu and coworkers reported using scDMF to exfoliate graphite and MnO$_2$ to produce graphene nanosheets and exfoliated MnO$_2$ nanosheets.\textsuperscript{[265]} The scDMF also promoted redox changes and mixed valence Mn oxide formation in the form of mixed shape nanocrystals.\textsuperscript{[179]} These nanocrystals formed mixed suspensions with graphiche sheets to finally form heterostructured epoxy nanocomposites comprising heterojunctions of graphene–graphene and Mn oxide–graphene contacts. These same mixtures of nanofil lers were subsequently used to formulate flame-retardant epoxy nanocomposites.\textsuperscript{[266]} Relative to separate graphene-epoxy and MnO$_2$-epoxy materials, mixed graphene/MnO$_2$ epoxy resins exhibited a synergistic and increased degradation with increasing heating relative to separate nanofil lers. However, a mixed graphene/MnO$_2$ epoxy resin that also contained a phosphate amine component, DAP (diphenylamido phosphate), provided synergistically improved flame retardation. This combination incorporating phosphate resulted in increased “over char” retaining larger amounts of filler at up to 700 °C.\textsuperscript{[266]} The graphene-only epoxy nanocomposite without DAP performed nearly as well as the mixed filler plus DAP system.

4.8. Lubricants

Graphite’s long-known efficacy as a lubricant has made examining nanosheets as lubricants a natural application for investigation. Batteas and co-workers have reviewed using nanosheets of graphene, graphite, fluorographene, MoS$_2$, WS$_2$, h-BN, and α-Zr(PO$_3$)$_2$ to control interfacial friction.\textsuperscript{[267]} Updated mechanistic and wear analyses have recently been provided,\textsuperscript{[268]} and interactions of such nanosheets with various functionalization at fluid-fluid interfaces have been reviewed.\textsuperscript{[269]} NiCl$_2$ was combined with citrate and surfactant (sodium dodecyl sulfate) in ethanol and then with GO and reducing agent (dimethyl borane, DMAB), and then this suspension was infused with scCO$_2$ at 18 MPa and 100 °C. Controlled depressurization after 2 h yielded Sc-Ni/GO nanosheets uniformly covered with nickel nanoparticles. These nanosheets were used as an additive to liquid paraffin (LP), lubricant, as were nickel nanoparticles, GO, and nickel nanoparticle–covered GO (Ni/GO) controls. The performance of the Sc-Ni/GO as an additive resulted in a lower coefficient of friction (COF) and smaller wear scar diameters (WSDs)\textsuperscript{[270]} than any of the controls.\textsuperscript{[83]} Decreases in COF were 17% and 32%, respectively, relative to Ni/GO and LP controls, and decreases of 24% and 43% in WSD were reported, respectively, for these same controls. These improvements are highly significant for what is mostly a solvent effect.

A similar study by Su and co-workers addressed lubrication by scCO$_2$-processed Ag nanoparticles dispersed on GO in 10W40 engine oil.\textsuperscript{[84]} Their tribology improvements for their Sc-Ag/GO material, in 10W40, were not as significant as in the Sc-Ni/GO-LP case discussed above. A COF decrease of 7% relative to Ag/GO was not distinguishably greater than experimental uncertainties, but an improvement of 32% was seen relative to a 10W40 control. WSD decreases of 6% and 26%, respectively, were obtained relative to Ag/GO and 10W40 controls. These results, however, are more practically meaningful because 10W40 is a widely used engine oil. Another particularly useful aspect of using SCF-generated nanosheets for lubrication and wear applications is that SCFs generally do not chemically modify nanosheet surfaces (in comparison to sonolysis chemistries that covalently attach solvent fragments to basal planes).\textsuperscript{[141,142]}
Table 5. Summary of patenting activity for SCF-processed 2D materials.

| Product 2D material | Source or starting materials | Role of SCF | Ref. |
|---------------------|-----------------------------|-------------|------|
| Graphene            | Expanded graphite           | Exfoliation agent | [105,271] |
| Graphene            | Graphite and “coating agent” (polymeric binder) | Intercalation and exfoliation | [287] |
| Graphene (oxidized) | Graphite                    | Intercalation and exfoliation | [272–277] |
| Graphene            | Graphite, solvent, surfactant | Intercalation and exfoliation | [278] |
| Graphene            | Coke, coal                  | Intercalation and exfoliation | [279,280,283,284] |
| Graphene            | Reduced graphene oxide, alcohol | Exfoliation and drying | [281] |
| Graphene            | Graphite                    | Intercalation and exfoliation | [282] |
| Graphene            | Graphite, intercalant        | Exfoliation | [285,286] |
| Graphene-polymer composite | Graphite, intercalant | Intercalation and exfoliation | [288] |
| Graphene-VO aggregate | Graphene fluoride, graphene oxide | Intercalation and exfoliation | [289] |
| Graphene-containing porous carbon | Graphite, water, H2O2, organic carbon precursors | ScH2O facilitates oxidation | [290] |
| Graphene and MoS2 containing aerogels | Graphite, graphene, MoS2, metal oxides, metal nanoparticles, carbon nanotubes | Supercritical drying | [291] |
| BN-containing aerogels | BN, boron oxide, carbon | Supercritical drying | [292,293] |
| Surface-functionalized 2D materials | 2D material, SF6, O2, BX3 | ScCO2 used as reaction medium, intercalation, and exfoliation | [294] |

4.9. Patent Activity Overview

The Gulari and co-workers patent documents discussed earlier[38,48] serve as a prominent reference for ensuing patenting activity for using SCFs to process 2D materials. The major focus has been on extending and refining the use of SCF to convert graphite and other graphene precursors to graphene powders and dispersions.[271–286]

Several of these efforts disclosed using intercalation driven by agents other than SCF.[271,285,286,288] ScH2O was used as a reaction medium for controlling oxidation,[290] and scCO2 was used as a medium in which to do surface functionalization with SF6, O3, and BXn.[294] Their use in composites are also being explored,[288–290] including aerogel formulation and drying.[291–293] These studies and other processing patent disclosures are very briefly summarized in Table 5.

5. Summary and Perspective of Future Developments

Experimental process development, introductory dynamical modeling, and several application reports show that SCF processing of 2D materials offers advantages and possibilities of overcoming some limitations that accompany subcritical shear processing. Greater exfoliation, so far, can be obtained by exfoliation in subcritical liquids, and applications such as RFID fabrication, thermal absorption, dispersion stability, and coloration likely cannot be improved by SCF processing. More highly value-added applications that seek defect density minimization, larger sheets, and higher electrical conductivity likely will benefit from advanced SCF processing, but more process development is needed. It has become apparent that the existence of defects depends a great deal on the source and process by which a particular type of 2D material is prepared. This is particularly evident for graphene.

It appears that some synergistic effects can be realized by formulating SCFs with immiscible co-solvents to make emulsification a process component. Certain other SCFs provide useful chemical effects with some 2D materials. The importance of chemical surface modification in promoting and stabilizing exfoliation cannot be overemphasized.

Some SCFs with mild (low) critical parameters provide exfoliation without any chemical effects, and for the case of scCO2, molecular dynamics simulations have provided some mechanistic understanding of scCO2 graphenic sheet interactions.[38] Critical pressures must be sufficiently large to separate sheets by about a nanosheet thickness in order to develop a sufficient free energy barrier to reaggregation in the absence of additional stabilizers.

It is important to distinguish exfoliation processing of “non-reactive” SCFs from SCF processing that concomitantly uses chemomechanical activation such as ultrasonication and externally applied high shear (small media milling). X-ray powder diffraction measurements should be taken at intermediate stages in between distinct processing regimens in order to better quantify intercalation and exfoliation events.

When sedimentation or centrifugation steps are included in a process, the amount of material removed should be quantified gravimetrically. This will allow more meaningful tracking of dispersion efficiency, and allow more meaningful yields to be tracked and reported. Obviously, processing that obviates any need for centrifugation separation of large fractions of 2D materials is preferred when possible and when economically accessible.

5.1. Promising Features

Supercritical fluids provide excellent mass transfer, gas-like diffusion coefficients, and very low viscosities.[83] Besides, they
exhibit negligible surface tension, and this property ensures excellent wetting of all solid and liquid phases with which they contact. We are used to thinking in terms of thermal activation, and we have become skilled at analyzing Arrhenius behaviors to estimate activation energies. Activation volumes may also be significant and can be derived from supercritical high-pressure measurements.\textsuperscript{[295]} It has been suggested that SCFs jam themselves into interlayer spaces to initiate exfoliation. A slightly more refined explanation is to consider activated separation of adjacent nanosheets along edges that is followed by adsorption of solvent molecules on nanosheet surfaces. When such adsorption or wetting occurs, it facilitates further exfoliation. Graphically, this process has been depicted for a case of polymer stabilization exfoliation,\textsuperscript{[296]} and it has been noted that adsorbed solvent acts as a temporal barrier to vdW re-aggregation of separated nanosheets.\textsuperscript{[129]}

A general discussion about using activation volumes for mechanistic studies has been provided by Wu and co-workers.\textsuperscript{[297]} Such an approach is deemed particularly appropriate when various reaction properties vary significantly with pressure, and such a situation exists when SCFs are used to intercalate and exfoliate 2D materials or to surface modify such materials. We have discussed how simulation studies have shown that scCO\textsubscript{2} stabilization of graphenic sheets depends on supercritical density,\textsuperscript{[129,192]} and it seems that such a pressure-dependent property is ideally suited for volume activation analysis.

The most crucial role for a solvent in multiphase suspensions and dispersions is not solubility per se but wetting. For many highly dispersed systems, lack of solubility is preferred because it blocks unwanted growth through Ostwald ripening. When such growth is desired, it is a simple matter to include co-solvents that will promote solubility and ripening.

Solvation of nanosheet surfaces is another significant feature, and the vanishing of surface tension above a solvent’s critical point makes spontaneous wetting of all available surfaces favorable. This wetting facilitates formation of physical mixtures of nanosheets and particles. Such mixtures also experience rapid interdiffusion of components because of low viscosity and high diffusion coefficients.

Using SCFs because they do not chemically transform nanosheets is motivating for their use, and SCFs that are unreactive indeed are good candidates. Some SCF processing of 2D materials, wherein critical parameters are “mild”, offer a promise of facilitating exfoliation without leaving surfactant, polymeric, or solvent residues that interfere and thwart essential transport properties such as electrical and thermal conductivities. In cases of chemically reactive SCFs that vary with SCF and nanosheet composition, specific chemistries can be induced. In these cases, chemical modifications of 2D nanosheets by some SCFs are intrinsic under critical conditions and promote ripening, redox chemistries, heterostructure formation and Ostwald ripening, and doping. Also, when sonolysis forces are present, untoward or advantageous surface modification can be induced.

Multiple studies of incorporating ultrasonication into high-pressure SCF reactors have shown synergistic results. Coupling these two processing methods is very amenable to existing chemical processing technology. Coupling shear with SCF reactors has been demonstrated so far using different shearing approaches, and for SCFs with “mild” critical parameters have performed satisfactorily.

5.2. Challenges

A continuing challenge in SCF applications to dispersing 2D nanosheets is to know analytically how much nanosheet material has been dispersed. It is more difficult to do simple UV-visible absorption measurements of supercritical\textsuperscript{[298]} nanosheet suspensions, than doing such measurements in a laboratory at ambient conditions, but cells suitable for such measurements are available. A particular limitation is to agree on what reference absorption coefficient is applicable for single sheet materials. A related challenge is to articulate what constitutes pristine single and few-sheet layered materials. Wet chemical tests for particular types of surface functionality that can quantify effects based on Avogadro’s number, \( N_0 \), of species, or even \( (N_0)^{1/10} \) will be helpful in characterizing defects per gram of material. Selected sampling by AFM or by HRTEM is much less statistically significant.

Mixed solvent systems are becoming more important, including pairs of immiscible solvents as well as pairs of miscible solvents. Even in cases of immiscible solvents, there is finite co-solubility of each in the other, so care must be taken in learning how a second solvent affects a mixture’s supercritical parameters. We have discussed two examples wherein significant synergisms cause mixtures of SCFs (CO\textsubscript{2} and MeOH, CO\textsubscript{2} and EtOH) to become subcritical at conditions thought to be critical. Process development should be done with solvent combinations where \( T_c \) and \( P_c \) have been determined as a function of mole fraction of each solvent component, so that criticality can be tuned with confidence.

All reactors operating at elevated temperature and pressure pose safety concerns, and these concerns are particularly justified when working with SCFs. An explosion of pressurized reactors and vessels can cause catastrophic injury.\textsuperscript{[299,300]} Necessary safety awareness, training, and precautions should be used in such experimentation.\textsuperscript{[101–104]}

5.3. Future Developments

A coupling of shear forces using homogenization technology\textsuperscript{[305–308]} with SCF processing has just been reported,\textsuperscript{[154]} and likely will become increasingly important. Homogenization is the most widespread emulsification technology used in industry and offers many design and implementation opportunities. Such processing involves impinging a multiphase fluid against a target or plate or through a rigid and porous material of high tortuosity, wherein a substantial pressure drop occurs before target impingement or across the porous material.

Advances in using co-solvents that will serve as a useful continuous phase solvent post depressurization and is using suitable stabilizers useful in post depressurization will make particular dispersion applications more practical. These
include applications wherein such stabilizers do not thwart any nanosheet–nanosheet interactions needed (such as electrical and thermal conductivity). Ultrasonication will be used to have more significant advantages in inducing designed surface modification[12,14,309] by solvent radicals to facilitate stabilizing dispersions in desired co-solvents.

Pressurization[114,310,311] and depressurization processing steps will be coaxially coupled with particular subcritical liquids to produce uniform dispersions suitable for forming coatings and monolithic materials before thermally initiated free radical polymerization, UV photoinitiated polymerization, and condensation polymerization. Such processes will facilitate producing more advanced composite materials than are currently accessible by extruder-based technologies.

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Conflict of Interest
The authors declare no conflict of interest.

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