Combustion/micropyretic synthesis of atomically thin two-dimensional materials for energy applications
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In recent years progress in the materials research field has been associated with the discovery of graphene and other two-dimensional atomic crystals. Those materials uniquely combine many exceptional properties, which make them highly attractive for a variety of applications. Despite significant advancement in synthesis and processing, the relevance of those materials is essentially driven by progress in their production. In the past 3 years, several unique inexpensive combustion-based approaches have been developed to prepare the nanomaterials. This article specifically aims to be an overview of current trends and as a perspective of combustion synthesis of 2D-crystals. We summarized the benefits of extreme combustion conditions for atomic-scale processing and integration of these materials for advanced energy applications.

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Introduction
Two-dimensional (2D) solids are defined as atomically thin, layered materials that have strong bonding in one crystal plane, while neighboring atomic planes are held together by much weaker van-der-Waals forces. Such dimensionality leads to a unique variety of properties, which makes those crystals promising candidates for the next-generation of flexible and transparent nanodevices [1,2]. Graphene, a carbon honeycomb with only one-atom thickness isolated from graphite, is an example of 2D single-layer atomic crystal. Its exceptional properties, such as half-integer quantum Hall effect, extremely high carrier mobility, high thermal conductivity and the highest strength ever measured, provide great possibilities for the implementation of graphene for a large variety of applications [3]. Since the discovery of graphene, other 2D layered materials, such as hexagonal boron nitride (h-BN), transition metal dichalcogenides (MoS2, WS2, NbSe2, etc.), carbides (TiC, NbC), metal oxides, hydroxides, have also been fabricated [3,4*]. Being structurally related to graphene but having their own distinctive properties, they offer the possibility of fine-tuning the material characteristics and devices to better fit a particular technology or to be used in combination with graphene.

The applications of 2D materials are essentially driven by progress in their production. Currently, there are numerous different methods to prepare individual 2D materials, which can be classified into several groups, such as mechanical or liquid phase exfoliation techniques, as well as surface-assisted growth [3,5]. However, a search for new synthesis routes is still a field of immense research activity with focus on inexpensive and scalable methods to produce 2D materials.

During the past decade, significant progress has been achieved in synthesis of nanomaterials using low cost combustion methods, which are based on self-sustained exothermic reactions [6]. In general those approaches are often referred as combustion synthesis (CS). There are different types of CS methods. If the initial reaction system involves gasless exothermic chemical reactions to prepare inorganic materials it is also called micro-pyretic synthesis (MPS) [7], or self-propagating high temperature synthesis (SHS) [6]. A modification of SHS, so-called gas-solid infiltration synthesis, utilizes rapid exothermic reaction between solid reactants (e.g. metals) and gases, where reaction occurs on the surface of the condensed precursors, resulting in nitrides, hydrides, and so on [6]. Another modification of the SHS process, termed a solid state metathesis (SSM), uses highly exothermic reactions between a metal pnictide, chalcogenide, silicide or boride with a metal halide and combustion reaction takes place primarily between gasified precursors [8]. Solution combustion synthesis (SCS) was developed to prepare complex nanostructured oxides, as well as metals, by self-sustained reactions in aqueous solutions of water-soluble metal nitrates and fuels (amines, acids and aminoacids) [9,10*]. Finally, flame synthesis (FS) has a long history and has developed separately from other combustion-based techniques. In this method, typically the pyrolysis of the initial precursors (metal organic compounds), which are injected directly into the flame, leads to the...
formation of oxide nanoparticles [11]. A common feature of all above approaches is that they involve rapid high temperature self-sustained reactions, which may result in the fabrication of solid nanomaterials.

More specifically, in past 3 years, many unique CS approaches have been reported for preparation of a variety of 2D materials. In general, the next paradigm in combustion synthesis is shifting toward processing the atomic scale crystals. In order to have a unified vision of the field, this review summarizes the state-of-art knowledge and prospective of using rapid exothermic self-sustained combustion reactions for synthesis of atomically thick 2D materials for energy applications.

Combustion synthesis of graphene

A variety of 2D crystals, including hexagonal boron nitride (h-BN), molybdenum sulfide (MoS2) and tungsten oxide (WO3) were synthesized by using different combustion-based approaches. However, most works are devoted to CS of graphene.

SHS of graphene materials

Single-layer and few-layer graphene sheets were prepared by SHS in the ceramic (SiC) — polymer (polytetrafluoroethylene, PTFE) system under the argon environment [12**]. In this case both precursors are in solid state. It was shown that, in the preheating zone, C2F4 gas forms due to decomposition of the polymer, followed by an exothermic reaction with SiC particles in the reaction front. As a result silicon is transferred to the gas phase (SiF4) by the following reaction:

\[ \text{C}_2\text{F}_4(\text{g}) + \text{SiC}(\text{s}) \rightarrow \text{SiF}_4(\text{g}) + \text{C}(\text{s}) \]  

with formation of carbon as the only solid product. Microstructural characterization indicated that the combustion product consists of mesoporous carbon nanoparticles. It is more important that these nanoparticles have folded ‘native’ graphene layers on their surface, which serve as nucleation cites for growth of ‘free standing’ graphene sheets. A schematic of the reaction mechanism is shown in Figure 1a.

It was also proved that ~70% of observed carbon sheets (Figure 1b) were single or bilayer graphene and the rest were multilayer graphene. It is worth noting that the synthesized graphene contains less than 1 wt.% of oxygen. This hybrid structure of graphene sheets and mesoporous carbon particles combines the merits of electrical properties of graphene and large specific surface areas (500–950 m²/g) for porous carbon. Those nanomaterials are promising candidates for a variety of applications including batteries, super-capacitors, and catalysis.

Several publications were devoted to gas-solid SHS of graphene. It is an interesting approach that includes the combustion of metals (Mg, Li, Ca, Ti, Al, Zr) in carbon dioxide, followed by the acid-purification of the solid product that was used to produce the multilayer graphene [13,14]. It was shown that Li, Mg and Ca facilitate formation of ordered carbon sheets, while other metals predominantly form mixtures of corresponding oxides and carbides. It was shown that graphene materials prepared by magnesium combustion in CO₂ adsorb 0.85 wt.% of H₂ at 6.5 MPa and 77 K [15]. High surface area (1270 m²/g) graphene foams prepared from the combustion of sodium ethoxide in air showed even higher hydrogen storage capacity (2.1 wt.%) at 1 MPa and 77 K [16*]. It should be noted that the storage capacity of commercially available graphene materials was nearly twice lower, which may be explained by their significantly lower specific surface area (∼650 m²/g).

Figure 1

The reaction route in SiC + PTFE combustion wave (a); graphene sheet-amorphous carbon hybrids structure (b), selected area diffraction (SAD) patterns and Raman spectrum are inserted in Figure 1b.
An interesting phenomenon, that is, the self-propagating deoxygenation of graphene oxide (GO) to prepare graphene materials was reported in [17]. GO is water dispersive graphene layers containing hydroxyl, epoxy and carboxyl functionalized groups [18]. Highly energetic and thermally unstable GO can readily undergo exothermic disproportionation reactions to produce reduced graphene oxide (r-GO). It was shown that the energy released during a short (1 ms) flash of light is sufficient to initiate the rapid (∼10 cm/s) self-propagation deoxygenation of GO foam in air (or inert gas) resulting in a crystalline layered carbon material [17]. Since the exothermic decomposition of GO can be easily triggered, the heat released from GO self-decomposition may be used as a more efficient ignition source for different fuels. For example, it was demonstrated that upon flashing, ethanol soaked GO sample readily combusts [17].

Similar deoxygenating combustion approaches were used to produce nanoparticle-decorated r-GO materials [19,20**]. In this case GO solid films were loaded by chloroauric acid (HAuCl4) or ruthenium(III) chloride (RuCl3) and the combustion was triggered by localized short-term heating. It is important that the reduction of HAuCl4 (or oxidation of RuCl3 to RhO2) occurs simultaneously with the deoxygenation of GO. Such a process enables the uniform distribution of Au (or RhO2) nanoparticles with diameter of 5 nm on r-GO sheets. Cyclic voltammetry tests indicated that the specific capacitance measured for combustion synthesized RuO2/r-GO electrode was 228 F g⁻¹, which is much higher than that (162 F g⁻¹) for r-GO.

Solution combustion synthesis of graphene
Several groups have reported a one-step synthesis of nanoparticle-decorated graphene materials by solution combustion route. In those cases, GO was dispersed in solutions of metal nitrates and fuels (e.g. glycine, urea), which are then uniformly heated to produce gels. For example, to produce hybrid materials of nitrogen doped r-GO/Ag a gel containing GO, silver nitrate and glycine was heated to ~220°C to initiate the exothermic reaction [21†]. Relatively high reaction temperatures (~500°C) and presence of NH₃ and NOₓ facilitates simultaneous nitrogen doping of r-GO. A similar approach was used to prepare r-GO/TiO₂ materials by combustion of gels containing GO, titanyl nitrate and urea [22,23]. It was shown that produced material exhibits enhanced photo-degradation performance for methyl orange, due to the effective transfer of electron from the TiO₂ to r-GO. CdS/r-GO composites were also synthesized by SCS method and showed improved visible-light photo-degradation performance of methylene blue [24].

Co₃O₄/r-GO-based composites were fabricated by SCS and used as an anode material for a secondary lithium ion battery or as a magnetically recyclable photocatalyst [25,26]. For example, combustion-derived Co₃O₄ nanoparticles (25–50 nm) uniformly deposited on the graphene sheets showed better electrochemical performance than pure Co₃O₄ [25]. The Co₃O₄/r-GO electrode delivered an initial charge capacity of 890 mAh g⁻¹ and exhibited 90% capacity retention after 30 cycles. The pure Co₃O₄ nanoparticle electrode showed an initial capacity of 878 mAh g⁻¹, which quickly fades to 67% after 30 cycles.

Flame synthesis of graphene
Recent advancements in flame synthesis have allowed the fabrication of a variety of oxygen-free nanomaterials. For example, a few-layer graphene-encapsulated metal (Cu, Fe) and carbide (Fe, C) nanoparticles were successfully synthesized under a nitrogen atmosphere [27,28]. Precise control over the fuel (methylene, acetylene) to oxygen ratio allowed the surface coverage of metal nanoparticles by graphene thus stabilizing them against oxidation in air (up to 200°C). The graphene encapsulation of Fe₃C allowed covalent surface functionalization of nanoparticles, which make them attractive for biotechnological and medicinal applications, for example, as nanomagnets.

The first attempt to produce large area thin carbon films by flame synthesis were made by inserting a copper foil into a low temperature (500–700°C) region of ethanol flame [29]. A carbon-enriched atmosphere of inner flame enabled the growth of a uniform transparent layer of amorphous carbon deposited on the metal substrate. Later, the dual-flame approach was introduced to prepare graphene films on metal substrate [30].

Recently, graphene nanoballs were also produced by FS of sunflower oil using cotton wick coated with iron acetylacetonate [31]. The combustion of oil usually produces nanoparticles of amorphous soot with broad size distribution. The addition of the iron acetylacetonate formed an iron oxide(s) nucleus, which acts as a catalyst to promote the formation of graphene nanoballs.

A novel flame synthesis configuration, based on a multiple inverse-diffusion (non-premixed) flame burner, where the post-flame hydrocarbon fragments can be directed to a metal substrate to grow graphene in open atmosphere, was also developed [32,33**,34,35]. In this case, methane was introduced into the hydrogen flame and it was directed to a metal (Ni, Cu, Co, Fe, Cu–Ni) substrate for a short (minutes) time period. After that, the oxygen supply was turned off, which extinguishes the flame, while the fuel continued to flow, cooling the substrate. Crystalline carbon films were formed on the substrate, but the growth was shown to be non-uniform, and wrinkles appeared along the metal grain boundaries.
Flame synthesis of graphene-coated h-BN hybrid materials was reported in [36]. The h-BN sheets (20–50 μm in size) were dispersed in a solution of polymethylmethacrylate (PMMA) and dried in a vacuum to obtain the PMMA-coated h-BN sheets. The materials were then placed in evacuated quartz tubes, heated at 1200°C for 20 s by hydrogen flame. Few-layer graphene sheets were observed on h-BN from the thermal decomposition of PMMA. The hydrogen flame was the only heating source and had no direct influence on chemistry, but it provided rapid heating and cooling of materials, which is difficult to accomplish by any other technique.

Combustion synthesis of other 2D materials

Synthesis of 2D h-BN and WO₃ crystals

Synthesis of other 2D crystals by combustion approaches was also reported. One of such attempts was aimed at preparation of 2D h-BN crystals by combustion of gels containing boric acid (H₃BO₃), urea ((NH₂)₂CO), sodium azide (NaN₃) and ammonium chloride (NH₄Cl) [37]. However, because of the low exothermic effect of the process, BN appeared to be amorphous, and a post-synthesis annealing under nitrogen atmosphere at 1000–1400°C was used. Note that the long-time annealing results in the formation of relatively thick (~25 nm) nanoplates.

Tungsten oxide (WO₃) attracted great interest as an n-type semiconductor catalyst due to its photosensitivity, good charge transport properties, and stability against photo-corrosion [38]. Some theoretical studies [39] showed that doping of WO₃ by hafnium, zirconium or titanium results in a shift of both valence and conduction bands to higher energies and a reduction of the band gap. As a result, such materials could have an important application in devolving of efficient solar water splitting devices.

Recently, we prepared pure and doped WO₃ nano-sheets using SCS method (unpublished). A two-stage process has been suggested. On the first stage, calcium tungstate (CaWO₄) was synthesized by combustion of a solution that contains tungsten peroxo-complexes, calcium and ammonium nitrides and citric acid. The size of particles (range 0.1–5 μm) was controlled through fine-tuning of the ammonium nitrate quantity. On the second stage, CaWO₄ powders were subjected to a short-term (30 min) sonication in a diluted HCl solution in the presence of surfactants (sodium dodecylsulfate). Such a treatment allowed selective etching of calcium oxide resulting in formation of exfoliated layers of tungstic acid (H₂WO₄) as follows:

\[
\text{CaWO}_4(s) + \text{HCl}(l) = \text{CaCl}_2(l) + \text{H}_2\text{WO}_4(s)
\]  

Figure 2

XRD pattern (a) and SEM images (b–d) of WO₃ thin crystals.
Dehydrogenation of tungstic acid at mild conditions (~250°C) enabled the preparation of highly crystalline WO₃ sheets (Figure 2a) with thickness of ~3–5 nm. It is important that the size of WO₃ sheets may be easily controlled from 50 to 5000 nm (Figure 2b–d) by changing the size of CaWO₄ precursors. Such process also allows the production of transition metal (Zr, Hf) doped WO₃ sheets via formation of doped CaWO₄.

A similar approach was used to produce WO₃/W composites by combustion of the Na₃WO₄ + 3Mg + CaF₂ system [40]. The ability of calcium fluoride to change the reaction pathway enables the formation of an intermediate CaWO₄ phase. Some quantities of the non-reduced CaWO₄ phase in the combustion product allowed for obtaining unique WO₃/W core–shell nanostructures with 2D oxide flakes assembled on metallic particles. The average thickness of 2D tungsten oxide crystals was estimated to be in the range 4–8 nm.

SSM of 2D MoS₂ crystals
Molybdenum sulfite (MoS₂) is a promising electrocatalyst for the electrochemical hydrogen evolution reaction. Both computational and experimental results confirmed that the hydrogen evolution reaction activity stemmed from the sulfur edges of MoS₂ plates while their basal planes were catalytically inert [41–43]. Thus 2D MoS₂ with controlled thickness and exposed edges should be more active in the hydrogen evolution reaction electrocatalysis than the materials in bulk forms. It is known [44] that MoS₂ could be synthesized by the solid state metathesis (SSM) reaction as follows:

\[ 2\text{MoCl}_5 + 5\text{Na}_2\text{S} = 2\text{MoS}_2 + 10\text{NaCl} + \text{S} \] (3)

An analogous SSM reaction between tungsten hexachloride and sodium subsulfide may also be applied for preparation of WS₂ layered material [45]. However, due to low ignition temperatures, SSM reactions often uncontrollable in terms of precise tuning of the synthesis conditions. To overcome this obstacle, we suggest the application of mild ball milling of the precursors in an inert gas atmosphere, which leads to the self-ignition of the mixture and production of MoS₂ phase (unpublished). The Raman spectrum of MoS₂ prepared under optimal inert gas pressure (0.05 MPa) exhibits two peaks at 405 and 385 cm⁻¹ (Figure 3a). It is known that the Raman spectrum of bulk MoS₂ has two prominent peaks: an in-plane (E₂g) mode centered at 383 cm⁻¹ and an out-of-plane (A₁g) mode located at 407 cm⁻¹ [46]. As MoS₂ becomes single-layer the in-plane mode upshifts to 386 cm⁻¹ and the out-of-plane downshifts to 404 cm⁻¹ [46]. Thus, Raman spectrum of combustion-derived MoS₂ indicates the presence of few-layered MoS₂ sheets. The results of electron-energy loss spectroscopy revealed that the thickness of the sheets changing in the range 3–5 nm, which corresponds to 4–7 S–Mo–S layers and high resolution TEM analysis indicates crystalline nature of these sheets (Figure 3b).

Conclusions
The combustion-based methods for synthesis of thin 2D crystals do not require any external energy source, as they occur in a self-sustained synergetic manner. Unique combustion conditions (e.g. high temperatures, rapid self-heating and cooling) facilitate formation of highly crystalline materials with tunable morphology and properties. Those approaches are flexible in terms of the control of the synthesis conditions, and allow easy scale-up of materials production. Combustion processes enable the preparation of individual 2D materials, composites and hybrid structure in form of powder, films and coatings. CS also provides environmentally friendly routes for materials processing. For example, graphene oxide reduction to r-GO does not require toxic reducers (e.g. hydrazine), which are currently used for liquid-phase processing of graphene. Other advantages of combustion
processing are related to the possibility of simultaneous synthesis of complex structures, for example, nanoparticle-decorated nitrogen-doped graphene sheets.

Those materials show great potential to be integrated into electrochemical energy storage devices (batteries and super-capacitors), solar-water splitting technologies and to be used as hydrogen storage materials. Combustion-derived semiconductor-decorated graphene materials also show great promise for photocatalytic degradation of water pollutants in environmental applications. Finally, the self-sustained nature of those reactions may be used for a variety of energetic application (in fuel ignition systems, high-energy density materials, etc.).

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

● of special interest

** of outstanding interest


This review article summarizes synthesis of new class of 2D materials (MXenes) for energy applications.


The article describes the mechanism of solution combustion synthesis of nanostructured metals.


A novel way to growth free-standing graphene sheet using combustion synthesis is reported.


The authors describe a combustion synthesis of a three-dimensional graphene network with high surface area that able to store hydrogen material with a capacity of 2.1 wt%.


The article highlights the challenges and opportunities associated with GO’s thermal instability and new syntheses using GO as an in situ power source to make nanoparticle decorated graphene composites for energy storage and catalysts.


It opens a new possibility for the synthesis of nitrogen-doped graphene decorated with various metallic nanoparticles.


The article provides a synthesis pathway of hybrid graphene-based nanomaterials for energy storage applications.


Large scale graphene films were grown first time in open-atmosphere on metal substrates using a multiple inverse-diffusion flame burner with methane as fuel.


