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 (MoS_2, WS_2, $NbSe_2$, etc.), carbides (Ti_2C, Nb_2C), 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-sold 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.
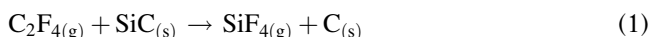
More specifically, in past 3 years, many unique CS approaches have been reported for preparation of a variety of 2D materials. In general, the next paradigm in combustion synthesis is shifting toward processing the atomic scale crystals. In order to have a unified vision of the field, this review summarizes 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 (MoS_2) and tungsten oxide (WO_3) 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, C_2F_4 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 (SiF_4) by the following reaction:

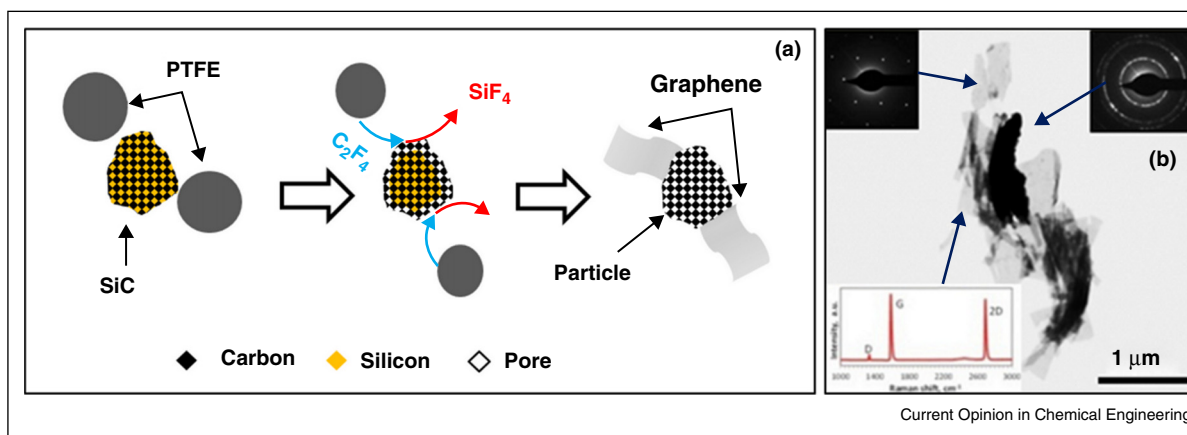$$C_2F_{4(g)} + SiC_{(s)} \rightarrow SiF_{4(g)} + C_{(s)} \tag{1}$$

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 m^2/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 CO_2 adsorb 0.85 wt.% of H_2 at 6.5 MPa and 77 K [15]. High surface area (1270 m^2/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 m^2/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 dispersible 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 ($\sim$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 ($HAuCl_4$) or ruthenium(III) chloride ($RuCl_3$) and the combustion was triggered by localized short-term heating. It is important that the reduction of $HAuCl_4$ (or oxidation of $RuCl_3$ to RhO_2) occurs simultaneously with the deoxygenation of GO. Such a process enables the uniform distribution of Au (or RhO_2) nanoparticles with diameter of 5 nm on r-GO sheets. Cyclic voltammetry tests indicated that the specific capacitance measured for combustion synthesized RuO_2/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 $\sim$220°C to initiate the exothermic reaction [21•]. Relatively high reaction temperatures ($\sim$500°C) and presence of NH_3 and NO_x facilitates simultaneous nitrogen doping of r-GO. A similar approach was used to prepare r-GO/TiO_2 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 TiO_2 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].

Co_3O_4/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 Co_3O_4 nanoparticles (25–50 nm) uniformly deposited on the graphene sheets showed better electrochemical performance than pure Co_3O_4 [25•]. The Co_3O_4/r-GO electrode delivered an initial charge capacity of 890 mAh g^{-1} and exhibited 90% capacity retention after 30 cycles. The pure Co_3O_4 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_3C) nanoparticles were successfully synthesized under a nitrogen atmosphere [27,28]. Precise control over the fuel (methane, 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 Fe_3C 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 WO_3 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 (H_3BO_3), urea ((NH_2)$_2$CO), sodium azide (NaN_3) and ammonium chloride (NH_4Cl) [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 (WO_3) 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 WO_3 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 WO_3 nano-sheets using SCS method (unpublished). A two-stage process has been suggested. On the first stage, calcium tungstate ($CaWO_4$) 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, $CaWO_4$ 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 (H_2WO_4) as follows:
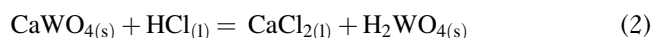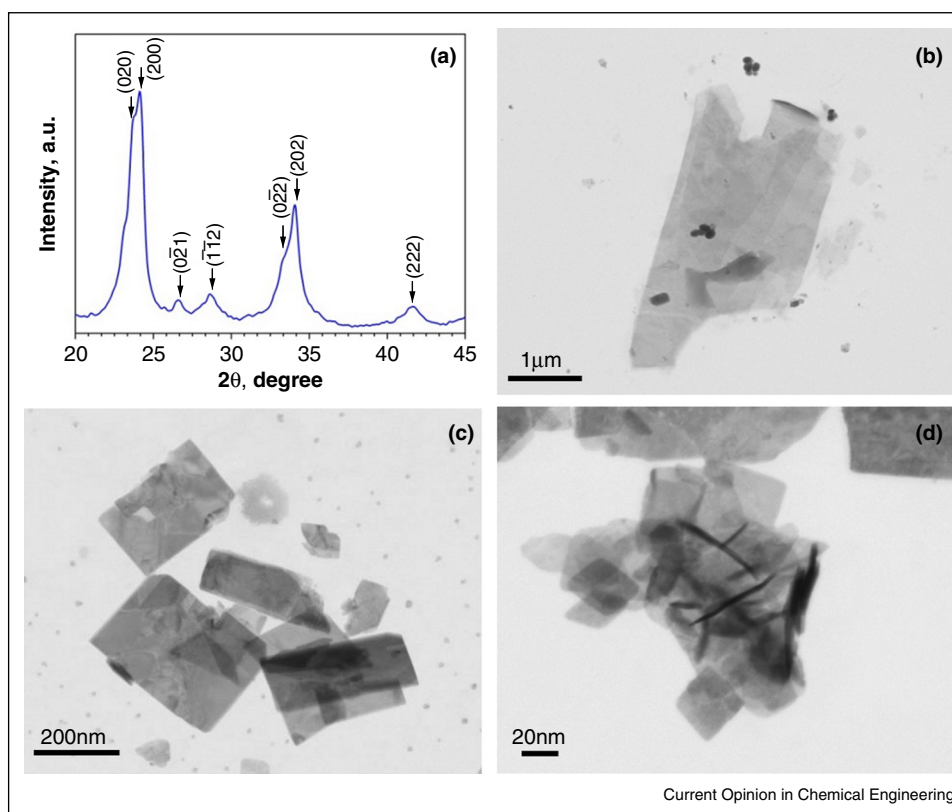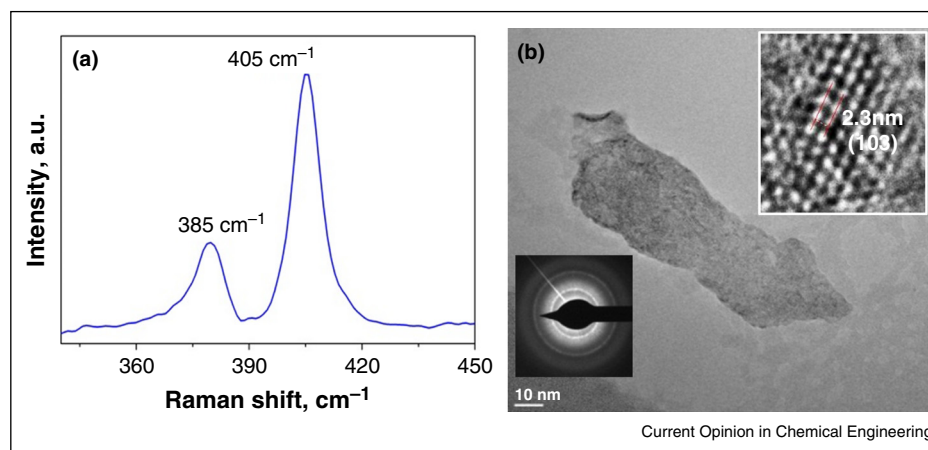
$$CaWO_{4(s)} + HCl_{(l)} = CaCl_{2(l)} + H_2WO_{4(s)} \quad (2)$$

Figure 2

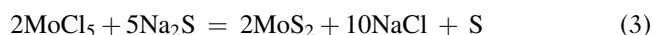XRD pattern **(a)** and SEM images **(b–d)** of WO_3 thin crystals.

Figure 3

Raman spectrum **(a)** and TEM image **(b)** of MoS₂, selected area diffraction pattern and high resolution TEM image are inserted in Figure 3b.

Dehydrogenation of tungstic acid at mild conditions (~250°C) enabled the preparation of highly crystalline WO_3 sheets (Figure 2a) with thickness of ~3–5 nm. It is important that the size of WO_3 sheets may be easily controlled from 50 to 5000 nm (Figure 2b–d) by changing the size of $CaWO_4$ precursors. Such process also allows the production of transition metal (Zr, Hf) doped WO_3 sheets via formation of doped $CaWO_4$.

A similar approach was used to produce WO_3/W composites by combustion of the $Na_2WO_4 + 3Mg + CaF_2$ system [40]. The ability of calcium fluoride to change the reaction pathway enables the formation of an intermediate $CaWO_4$ phase. Some quantities of the non-reduced $CaWO_4$ phase in the combustion product allowed for obtaining unique WO_3/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 (MoS_2) is a promising electrocatalyst for the electrochemical hydrogen evolution reaction. Both computational and experimental results confirmed that the hydrogen evolution activity stemmed from the sulfur edges of MoS_2 plates while their basal planes were catalytically inert [41–43]. Thus 2D MoS_2 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 MoS_2 could be synthesized by the solid state metathesis (SSM) reaction as follows:

$$2MoCl_5 + 5Na_2S = 2MoS_2 + 10NaCl + S \qquad (3)$$

An analogous SSM reaction between tungsten hexachloride and sodium subsulfide may also be applied for preparation of WS_2 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 MoS_2 phase (unpublished). The Raman spectrum of MoS_2 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 MoS_2 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 MoS_2 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 MoS_2 indicates the presence of few-layered MoS_2 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.).

Acknowledgement

References and recommended reading

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

- • of special interest
- •• of outstanding interest

1. Novoselov KS, Jiang D, Schedin F, Booth TJ, Khotkevich VV, Morozov SV, Geim AK: **Two-dimensional atomic crystals**. *Proc Natl Acad Sci U S A* 2005, **102**:10451-10453.

2. Allen MJ, Tung VC, Kaner RB: **Honeycomb carbon: a review of graphene**. *Chem Rev* 2010, **110**:132-145.

3. Mas-Ballesté R, Gómez-Navarro C, Gómez-Herrero J, Zamora F: **2D materials: to graphene and beyond**. *Nanoscale* 2011, **3**:20-30.

4. Naguib M, Mochalin VN, Barsoum MW, Gogotsi Y: **25th
•• anniversary article: MXenes: a new family of two-dimensional materials**. *Adv Mater* 2013, **26**:992-1005.
This review article summarizes synthesis of new class of 2D materials (MXenes) for energy applications.

5. Novoselov KS, Fal'ko VI, Colombo L, Gellert PR, Schwab MG, Kim K: **A roadmap for graphene**. *Nature* 2012, **490**:192-200.

6. Merzhanov A: **The chemistry of self-propagating high-temperature synthesis**. *J Mater Chem* 2004, **14**:1779-1786.

7. Li H, Sekhar J: **The influence of the reactant size on the micropyretic synthesis of NiAl intermetallic compounds**. *J Mater Res* 1995, **10**:2471-2480.

8. Parkin I: **Solid state metathesis reaction for metal borides, silicides, pnictides and chalcogenides: ionic or elemental pathways**. *Chem Soc Rev* 1996, **25**:199-207.

9. Aruna ST, Mukasyan AS: **Combustion synthesis and nanomaterials**. *Curr Opin Solid State Mater Sci* 2008, **12**:44-50.

10. Manukyan KV, Cross A, Roslyakov S, Rouvimov S, Rogachev AS,
• Wolf EE, Mukasyan AS: **Solution combustion synthesis of nano-crystalline metallic materials: mechanistic studies**. *J Phys Chem C* 2013, **117**:24417-24427.
The article describes the mechanism of solution combustion synthesis of nanostructured metals.

11. Strobel R, Pratsinis SE: **Flame aerosol synthesis of smart nanostructured materials**. *J Mater Chem* 2007, **17**:4743-4756.

12. Manukyan KV, Rouvimov S, Wolf EE, Mukasyan AS: **Combustion
•• synthesis of graphene materials**. *Carbon* 2013, **62**:302-311.
A novel way to growth free-standing graphene sheet using combustion synthesis is reported.

13. Chakrabarti A, Lu J, Skrabutenas JC, Xu T, Xiao Z, Maguire JA, Hosmane NS: **Conversion of carbon dioxide to few-layer graphene**. *J Mater Chem* 2011, **21**:9491-9493.

14. Dąbrowska A, Huczko A, Dyjak S: **Fast and efficient combustion synthesis route to produce novel nanocarbons**. *Phys Status Solidi* 2012, **249**:2373-2377.

15. Cunning BV, Pyle DS, Merritt CR, Brown CL, Webb CJ, Gray EMA: **Hydrogen adsorption characteristics of magnesium combustion derived graphene at 77 and 293 K**. *Int J Hydrogen Energy* 2014, **39**:6783-6788.

16. Lyth SM, Shao H, Liu J, Sasaki K, Akiba E: **Hydrogen adsorption
• on graphene foam synthesized by combustion of sodium ethoxide**. *Int J Hydrogen Energy* 2014, **39**:376-380.
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%.

17. Gilje S, Dubin S, Badakhshan A, Farrar J, Danczyk SA, Kaner RB: **Photothermal deoxygenation of graphene oxide for patterning and distributed ignition applications**. *Adv Mater* 2010, **22**:419-423.

18. Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruof RS: **Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide**. *Carbon* 2007, **45**:1558-1565.

19. Kim F, Luo J, Cruz-Silva R, Cote LJ, Sohn K, Huang J: **Self-propagating domino-like reactions in oxidized graphite**. *Adv Funct Mater* 2010, **20**:2867-2873.

20. Krishnan D, Kim F, Luo J, Cruz-Silva R, Cote LJ, Jang HD, Huang J:
•• **Energetic graphene oxide: challenges and opportunities**. *Nano Today* 2012, **7**:137-152.
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.

21. Mayavan S, Sim J-B, Choi S-M: **Easy synthesis of nitrogen-
• doped graphene–silver nanoparticle hybrids by thermal treatment of graphite oxide with glycine and silver nitrate**. *Carbon* 2012, **50**:5148-5155.
It opens up a new possibility for the synthesis of nitrogen-doped graphene decorated with various metallic nanoparticles.

22. Gao Y, Pu X, Zhang D, Ding G, Shao X, Ma J: **Combustion synthesis of graphene oxide–TiO₂ hybrid materials for photodegradation of methyl orange**. *Carbon* 2012, **50**: 4093-4101.

23. Pu X, Zhang D, Gao Y, Shao X, Ding G, Li S, Zhao S: **One-pot microwave-assisted combustion synthesis of graphene oxide–TiO₂ hybrids for photodegradation of methyl orange**. *J Alloys Compd* 2013, **551**:382-388.

24. Liu J, Pu X, Zhang D, Seo HJ, Du K, Cai P: **Combustion synthesis of CdS/reduced graphene oxide composites and their photocatalytic properties**. *Mater Res Bull* 2014, **57**:29-34.

25. Rai AK, Gim J, Anh LT, Kim J: **Partially reduced Co₃O₄/graphene
• nanocomposite as an anode material for secondary lithium ion battery**. *Electrochim Acta* 2013, **100**:63-71.
The article provides a synthesis pathway of hybrid graphene-based nanomaterials for energy storage applications.

26. Zhang D, Pu X, Gao Y, Su C, Li H, Li H, Hang W: **One-step combustion synthesis of CoFe₂O₄–graphene hybrid materialsfor photodegradation of methylene blue**. *Mater Lett* 2013, **113**:179-181.

27. Athanassiou EK, Grass RN, Stark WJ: **Large-scale production of carbon-coated copper nanoparticles for sensor applications**. *Nanotechnology* 2006, **17**:1668-1673.

28. Herrmann IK, Grass RN, Mazunin D, Stark WJ: **Synthesis and covalent surface functionalization of nonoxidic iron core–shell nanomagnets**. *Chem Mater* 2009, **21**:3275-3281.

29. Li Z, Zhu H, Wang K, Wei J, Gui X, Li X, Li C, Fan L, Sun P, Wu D: **Ethanol flame synthesis of highly transparent carbon thin films**. *Carbon* 2011, **49**:237-241.

30. Li Z, Zhu H, Xie D, Wang K, Cao A, Wei J, Li X, Fan L, Wu D: **Flame synthesis of few-layered graphene/graphite films**. *Chem Commun* 2011, **47**:3520-3522.

31. Kumar N, Shukla A, Singh J, Patra MK, Ghosal P, Vadera SR: **Simple route for synthesis of multilayer graphene nanoballs by flame combustion of edible oil**. *Graphene* 2013, **1**:63-67.

32. Memon NK, Tse SD, Al-Sharab JF, Yamaguchi H, Goncalves A.-M.B., Kear BH, Jaluria Y, Andrei EY, Chhowalla M: **Flame synthesis of graphene films in open environments**. *Carbon* 2011, **49**:5064-5070.

33. Memon NK, Tse SD, Chhowalla M, Kear BH: **Role of substrate,**
•• **temperature, and hydrogen on the flame synthesis of graphene films**. *Proc Combust Inst* 2013, **34**:2163-2170.
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.

34. Memon NK, Kear BH, Tse SD: **Transition between graphene-film and carbon-nanotube growth on nickel alloys in open-atmosphere flame synthesis**. *Chem Phys Lett* 2013, **570**:90-94.

35. Memon NK, Xu F, Sun G, Dunham SJB, Kear BH, Tse SD: **Flame synthesis of carbon nanotubes and few-layer graphene on metal-oxide spinel powders**. *Carbon* 2013, **63**:478-486.

36. Lin T, Wang Y, Bi H, Wan D, Huang F, Xie X, Jiang M: **Hydrogen flame synthesis of few-layer graphene from a solid carbon source on hexagonal boron nitride**. *J Mater Chem* 2012, **22**:2859-2862.

37. Zhao Z, Yang Z, Wen Y, Wang Y: **Facile synthesis and characterization of hexagonal boron nitride nanoplates by two-step route**. *J Am Ceram Soc* 2011, **94**:4496-4501.

38. Zheng H, Ou JZ, Strano MS, Kaner RB, Mitchell A, Kalantar-zadeh K: **Nanostructured tungsten oxide — properties, synthesis, and applications**. *Adv Funct Mater* 2011, **21**:2175-2196.

39. Wang F, Di Valentin C, Pacchioni G: **Doping of WO$_3$ for photocatalytic water plitting: hints from density functional theory**. *J Phys Chem C* 2012, **116**:8901-8909.

40. Manukyan KV, Voskanyan AA, Rouvimov S, Mukasyan AS, Kharatyan SL: **W and two-dimensional WO$_3$/W nanocrystals produced by controlled self-sustaining reduction of sodium tungstate**. *J Mater Res* 2013, **28**:2611-2621.

41. Hinnemann B, Moses PG, Bonde J, Jørgensen KP, Nielsen JH, Horch S, Chorkendorff I, Nørskov JK: **Biomimetic hydrogen evolution: MoS$_2$ nanoparticles as catalyst for hydrogen evolution**. *J Am Chem Soc* 2005, **127**:5308-5309.

42. Jaramillo TF, Jørgensen KP, Bonde J, Nielsen JH, Horch S, Chorkendorff I: **Identification of active edge sites for electrochemical H$_2$ evolution from MoS$_2$ nanocatalysts**. *Science* 2007, **317**:100-102.

43. Li Y, Wang H, Xie L, Liang Y: **MoS$_2$ nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction**. *J Am Chem Soc* 2011, **133**:7296-7299.

44. Wiley JB, Kaner RB: **Rapid solid-state precursor synthesis of materials**. *Science* 1992, **255**:1093-1097.

45. Bonneau P, Jarvis R, Kaner RR: **Rapid solid-state synthesis of materials from molybdenum disulphide to refractories**. *Nature* 1991, **349**:510-512.

46. Lee C, Yan H, Brus L, Heinz T, Hone J, Ryu S: **Anomalous lattice vibrations of single-and few-layer MoS$_2$**. *ACS Nano* 2010, **4**:2695-2700.