Combustion synthesis and nanomaterials

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Abstract

The recent developments and trends in combustion science towards the synthesis of nanomaterials are discussed. Different modifications made to conventional combustion approaches for preparation of nanomaterials are critically analyzed. Special attention is paid to various applications of combustion synthesized nanosized products.

1. Introduction

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an effective, low-cost method for production of various industrially useful materials. Today CS has become a very popular approach for preparation of nanomaterials and is practiced in 65 countries. Recently, a number of important breakthroughs in this field have been made, notably for development of new catalysts and nanocarriers with properties better than those for similar traditional materials. The extensive research carried out in last five years emphasized the SHS capabilities for materials improvement, energy saving and environmental protection. The importance of industrialization of the SHS process is also realized. All these aspects were adequately brought out and discussed in the international conference devoted to the 40th anniversary of SHS, which was held at ISMAN (Chernogolovka, Russia) in October 2007.

Several books [1–4] and reviews [5–11] have been published on this subject in recent years. The book on chemistry of nanocrystalline oxide materials gives the recipes for the preparation of different nanosize oxide materials [1]. In the monograph [2] authors discuss the wide scope of fundamental issues related to the diagnostics and mechanisms of CS process. Several chapters in the other book are devoted to nanomaterials synthesis by using SHS method [3]. Specific directions for SHS nanosynthesis were reviewed by Merzhanov et al. [8]. The criteria for distinguishing the homogeneous and discrete combustion waves based on the analysis of local and global behaviour of the reaction systems was suggested in recent review [9], where the different theoretical models that account the discrete nature of the combustion process have been also discussed and compared with experimental results. The recent papers on the mechanisms of internal electromagnetic fields generation during combustion in heterogeneous systems, as well as the influence of external electromagnetic fields on SHS process has been critically reviewed in [10]. The specifics of solution combustion (SC) method for the synthesis of lamp phosphor materials has also been well documented [11]. An analysis of the combustion parameters for different SC reaction modes is briefly presented in [12].

In prior review on CS of advanced materials published in 2002, the developments in the combustion synthesis with special emphasis on the preparation of catalysts by solid state and solution combustion were discussed [7]. It was concluded that the conventional solid state SHS being a gasless combustion process typically yield much coarser particles than solution combustion approach. One of the goals of this review is to discuss the various modifications made to conventional solid state SHS for preparing nanomaterials. Another important aim is to critically evaluate the recent progress and novel trends in solution combustion synthesis of nanomaterials as well as their application and scaling-up aspects. The review also focuses on the current status of studies on combustion synthesis of nanomaterials concentrating mainly on the publications, which have appeared in the last 1-year. Thus the...
results on CS of nanomaterials are discussed using the processes classification that is based on the physical nature of the initial reaction medium:

- **Conventional SHS** of nanoscale materials, i.e. initial reactants are in solid state (condensed phase combustion).
- **Solution–combustion synthesis** (SCS) of nanosized powders, i.e. initial reaction medium is aqueous solution.
- **Synthesis** of nanoparticles in flame, i.e. gas-phase combustion.

The last approach has a long history and was recently overviewed by Dr. P. Roth [13]. This method is not directly related to SHS and thus not deliberated in this work. It should be noted that the specific feature of gas-phase synthesis is the ability of producing non-agglomerated fine particles [14]. However, the list of materials produced by this method is relatively short and low effectiveness of this technology currently dictates high cost of the final products.

2. **Conventional SHS: condensed phase combustion**

It is not an easy task to produce nanomaterials by conventional SHS, where the typical scale of heterogeneity for the initial solid reactants is on the order of 10–100 μm. This feature, coupled with high reaction temperatures (>2000 K), makes it difficult to synthesize nanosize structures with high surface area. However, several methods were suggested for synthesis of nanomaterials by using this approach: (i) SHS synthesis, followed by intensive milling; (ii) SHS + mechanical activation (MA); (iii) SHS synthesis followed by chemical treatment, so-called chemical dispersion; (iv) SHS with additives; (v) carbon combustion synthesis (CCS). Since the first method is common and well known [15], and different combinations of SHS and MA have already been well documented [16], the abilities of three other methods are briefly discussed below.

The process of etching SHS-powders in an appropriate dilute acid (e.g. HNO₃ or H₂SO₄) solution, thus dissolving the defect-rich layers between the crystallites and removing impurities, followed by ball milling, is termed as chemical dispersion. This approach was suggested by the group from Institute of Structural Macrometallurgy and Materials Science, Russian Academy of Sciences [17].

A variety of fine powders including boron, aluminium and silicon nitrides were produced by this technique. Fig. 1 shows the changes in the specific surface area as a function of grinding time for different BN powders without (curve 1) and with chemical dispersion (curve 2). The analysis of products microstructures confirmed that chemical treatment in acid significantly facilitated the increase of powder surface area and reduced the particle size to nanoscale. Chemical dispersion appears to be an attractive approach compared to milling of the as-synthesized powders for producing nanopowders as it results in pure product and consumes less energy. But it is not obvious that this approach can be effectively used for wide range of SHS-products, hence it is desirable to produce nanomaterials directly in the combustion wave, avoiding post-synthesis treatments.

The SHS method with additives for nanomaterials synthesis is known as alkali metal molten salt assisted combustion [18,19]. In this process, the reducing metal, (e.g. Mg) reacts with transition metal oxide (Me₂O₃) in the melt of alkali metal salt (e.g. NaCl) to form fine reduced metal particles (Me). Due to the heat generated by combustion reaction, salt melts at ~1083 K and further nucleation of metal particles occurs in the molten NaCl, which protects them from agglomeration and growth (see Fig. 2). Note that the by-product, i.e. MgO, can be easily leached out by washing powder in acid (HCl or HNO₃) solution.

Current leader in SHS synthesis of nanopowders by using alkali metal molten salt assisted combustion is Materials Research Centre at Chungnam National University (Korea). Recently, scientists from this group showed that by this method one could synthesize not only nanopowders of pure metals such as titanium (e.g. by reaction TiO₂ + Mg → Ti + 2MgO [3]), molybdenum [19] or tungsten [20], but also different carbides (e.g. TiC [3]; WC [21]) and complex compositions like WC-Co [21]. Fig. 3 shows the microstructures of as-synthesized titanium and titanium carbide powders. These compounds can be used for the production of cemented carbides for cutting tools and wear parts. Also, the nanograined WC-Co composites (50–200 nm) have a potential to replace standard materials for tools and dies, and wear parts because of their extremely higher hardness. Relatively low final product yield, owing to formation of MgO and different salts, is a drawback of this approach.

**Carbon combustion synthesis of oxides** (CCSO) is a novel and economical technology for production of micron and nanostructured particles of complex oxides for advanced device applications. As the name suggests, carbon is used as the reaction fuel instead of pure metals used in conventional SHS and thereby making the reaction gaseous [22,23]. The high rate of CO₂ release facilitates synthesis of highly porous (~70%) powders having particle size in the range of 50–800 nm. Martirosyan and Luss from University of Houston (USA) reported the synthesis of variety of advanced fine oxide powders by this method [22,23]. The materials include ferroelectrics (BaTiO₃, SrTiO₃, LiNbO₃, mullite), transition metal oxides, complex oxides (La₂O₃, La₂O₃·2ZrO₂·3MnO₃), battery electrode material (LiMn₂O₄), hard/soft ferrites (BaFe12O19, CoFe₂O₄), Ni–Zn, Mn–Zn–ferrites, Y₃Fe₅O₁₂), and diesel emission removal catalysts (LaCrO₃, LiCrO₃) [22,23]. These products are not only economical

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**Fig. 1.** Specific surface area as a function of grinding time for different powders: (1) as-synthesized; (2) after chemical dispersion. From Ref. [17].

**Fig. 2.** Schematic illustration of metal reduction by magnesium in the molten NaCl. From Ref. [3].
but also some of their properties (e.g. magnetic/dielectric) are superior to those produced by conventional methods. This approach also enables the synthesis of oxides such as CaSnO₃ and LaGaO₃ that cannot be produced by conventional SHS from elements due to the pyrophoric nature of metals (La, Li) or metals with low melting point (e.g. Ga, Hg, Cs).

3. Solution combustion synthesis

Solution combustion synthesis (SCS) is a versatile, simple and rapid process, which allows effective synthesis of a variety of nano-size materials. This process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Depending on the type of the precursors, as well as on conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields nanosize oxide materials but also allows uniform (homogeneous) doping of trace amounts of rare-earth impurity ions in a single step. Among the gamut of papers published in recent years on SCS, synthesis of luminescent materials and catalysts occupy the lion share. The latest developments in SCS technique are discussed based on the materials applications. The synthesis of nanophosphors is currently a hot topic in the field of CS. The range of nanophosphor-based materials prepared by SCS [24–32] is listed in Table 1. From the table, it is evident that urea continues to be the preferred fuel for phosphor materials synthesis.

In the field of electrocatalysis and power applications, a large number of papers on materials preparation for fuel cells, supercapacitors, batteries and dye-sensitized solar cells have been published. More specifically, many papers are focused on the synthesis of various materials for application in solid oxide fuel cells (SOFC) and direct methanol fuel cells (DMFC). For example, microstructure, chemical compatibility and electrochemical performance of SC-synthesized Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋ₓ (BSCF)–La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₋ₓ (LSGM) composite for SOFC cathode have been investigated [33]. The specific resistance and the activation energies of this composite appeared to be very low, which demonstrates the suitability of combustion synthesized BSCF as a cathode material for LSGM electrolyte. The group at Bhabha Atomic Research Centre (India) is also working on preparation of SOFC related nanosize oxides for cathode (La₁₋ₓSrₓMnO₃) and interconnect (CaO doped LaCrO₃) [34,35]. Nanocrystalline (Ni/NiO)-YSZ powders have been prepared by microwave-assisted combustion method [36]. Composite perovskite–Pt catalysts synthesized directly by SCS exhibit superior performance compared to the standard Pt-Ru in conditions close to that in DMFC [37]. It is believed that perovskite-based catalysts may hold a key to a low-cost solution for synthesis of effective catalysts for DMFC. Combustion-synthesized oxygen-lean doped wüstite (AₓZn₁₋ₓFe½₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋ₓ₋_x yO powders exhibited better water-splitting activity, hydrogen yield and regeneration capability in comparison to conventionally synthesized samples of the same composition due to the higher concentration of structural defects [38].

Single step SCS has been used for the preparation of nanosized ZnO/carbon composite for supercapacitor application, which showed higher specific capacitance, compared to micron sized ZnO powder [39]. Layer structure of LiCoO₂ formed during SCS

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**Table 1**

<table>
<thead>
<tr>
<th>Phosphor material</th>
<th>Fuel used</th>
<th>Crystallite size from XRD (nm)</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂SiO₅:Ce, Lu₂SiO₅:Ce, Gd₂SiO₅:Ce</td>
<td>Hexamine</td>
<td>20–80</td>
<td>Detection of ionizing radiation and dense scintillators</td>
<td>[24]</td>
</tr>
<tr>
<td>SrAl₂O₄:Eu⁺⁺⁺, Dy⁺⁺⁺, Tb⁺⁺⁺</td>
<td>Urea; urea + boric acid flux</td>
<td>50–80</td>
<td>Long lasting phosphorescence materials</td>
<td>[25]</td>
</tr>
<tr>
<td>Eu⁺⁺⁺ activated YAlO₃ and LaAlO₃</td>
<td>Ammonium nitrate + urea</td>
<td>80</td>
<td>Red phosphors</td>
<td>[26]</td>
</tr>
<tr>
<td>GdPO₄:Eu⁺⁺⁺</td>
<td>Glycine</td>
<td>40</td>
<td>Red phosphor</td>
<td>[27]</td>
</tr>
<tr>
<td>CaWO₄:Eu⁺⁺⁺</td>
<td>Citric acid</td>
<td>50–100 (TEM)</td>
<td>Fluorescent lamps, colored lightning for advertisement industries and other optoelectronic devices.</td>
<td>[28]</td>
</tr>
<tr>
<td>M₃Al₂O₆:Eu⁺⁺⁺, R⁺⁺⁺ (M = Sr, Ba, Ca; R = Dy, Nd and La)</td>
<td>Ammonium nitrate</td>
<td>21–40</td>
<td>Long persistent luminescent material</td>
<td>[29]</td>
</tr>
<tr>
<td>Pr⁺⁺⁺, Tm⁺⁺⁺ doped Gd₃Ga₅O₁₂</td>
<td>Urea</td>
<td>30–00</td>
<td>Magneto optical films and materials for solid state lasers</td>
<td>[30]</td>
</tr>
<tr>
<td>Y₂O₃:Eu⁺⁺⁺</td>
<td>Sucrose</td>
<td>30–50</td>
<td>Red emitting phosphor used in CRT screens, plasma displays, fluorescent lamps</td>
<td>[31]</td>
</tr>
</tbody>
</table>
was found to be suitable and beneficial for lithium ion battery fabrication [40]. It is important to note that SC synthesized nanotitania applied as a thin film in dye-sensitized solar cells showed a high light-to-electricity conversion yield [41]. Technologically important Giant magneto resistant materials have also been prepared by SCS and their properties studied [42].

The recent references on solution combustion synthesized catalysts for air and water pollutants remediation (e.g., noble metal doped ceria and titania) have proved that the doping in these oxides is not mere metal substitution but instead it is ionic substitution [43]. Also uniform adherent coating of Pd-substituted ceria (Ce0.98Pd0.02O2−δ) on cordierite monolith (Fig. 4) has been demonstrated at the Indian Institute of Science (India) for the first time in a single step by SCS of cericammonium nitrate, oxalyl dihydrazide and PdCl2 redox mixture at 500°C [44]. This material is used as a three-way catalyst in automobiles. Also, LaCoO3 catalyst deposited by in situ SCS directly over a ceramic honeycomb monolith and tested in a lab-scale test rig gave 90% of N2O conversion performance for Gas Hourly Space Velocity values of industrial interest (10,000–30,000 h−1) [45]. These simple and inexpensive processes for preparation of the supported catalysts hold a great promise for automobile exhaust remediation. Other catalysts prepared by SCS [46–53] along with their particle size and applications are listed in Table 2. Among these materials let us outline the SCS-synthesized WO3 that removes ~90% of the initial dye like methylene blue from the aqueous solution after 30 min of equilibration, while a popular commercial photocatalyst, i.e. Degussa P-25 TiO2, shows only little proclivity for dye adsorption even after 24 h [51]. This clearly demonstrates the versatility and energy efficiency of SC synthesized WO3. Similarly, SC synthesized nanoTiO2 (10 nm) has shown higher rate for carcinogenic hexavalent chromium Cr(VI) reduction compared to commercial Degussa P-25 TiO2 [52]. This may immensely benefit the metal plating and metal finishing industries. Also, SCS derived porous nanocrystalline MgO with surface area of 107 m2/g has proved to be an eco-friendly and non-toxic adsorbent which could remove 97% of fluoride present in water as compared to 76% by regenerated MgO and 17% by commercial grade MgO [53].

Metal matrix composites is the other area where the SCS-nanopowders have found a variety of new applications. Aruna et al. for the first time incorporated SCS nanosize powders such as zirconia, alumina, ceria, yttria doped ceria, alumina–zirconia etc., into the metal (e.g. Ni) matrix during electrodeposition [54–56]. It was found that the nanoparticles enhanced the matrix properties including microhardness, wear resistance and corrosion resistance [54,55]. A patent has been filed for the preparation of Ni–Y3Al5O12 composite coating exhibiting a synergistic combination of improved microhardness, higher corrosion resistance and wear resistance with a lower friction coefficient [56]. However, the agglomeration of nanosize particles in the Ni matrix has to be overcome.

Luo et al. used a combinatorial synthesis technique based on SCS [57]. A luminescent library of terbium doped yttrium aluminium garnet, Y3Al5O12:Tb+, was synthesized to demonstrate the applicability of the parallel SCS technique to high-temperature materials (Fig. 5). This approach holds promise for combinatorial studies of metastable and nanoscale materials with large specific surface area.

It is well recognized that the fuel is an important component for the preparation of oxides by SCS. Urea and glycine are the most popular and attractive fuels for producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry. The glycine nitrate process (GNP) has been billed as ‘environmentally compatible’. But the recent study by Pine et al. has shown CO and NOx as the products of incomplete combustion in GNP [58]. Hence for GNP technique to be used on an industrial scale, the potential for producing and emitting hazardous nitrogen oxides and

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**Table 2**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fuel used</th>
<th>Crystallite size from XRD (nm)</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaBO3 B = Cr, Mn, Fe and Co</td>
<td>Urea</td>
<td>55–75 (FESEM)</td>
<td>Decomposition of N2O to N2 and O2</td>
<td>[45]</td>
</tr>
<tr>
<td>CuO/Cu</td>
<td>Urea</td>
<td>–</td>
<td>Selective CO oxidation</td>
<td>[46]</td>
</tr>
<tr>
<td>Ce0.98Pd0.02O2−δ</td>
<td>Oxalyl dihydrazide</td>
<td>30–40</td>
<td>Oxidative hydrogen production from methanol</td>
<td>[47]</td>
</tr>
<tr>
<td>Cu/ZrO2/ZrO2/Pd</td>
<td>Glycine</td>
<td>7–14</td>
<td>Partial oxidation of methane to syn-gas</td>
<td>[48]</td>
</tr>
<tr>
<td>Ni</td>
<td>Glycine</td>
<td>24</td>
<td>Solvent-free synthesis of coumarins</td>
<td>[49]</td>
</tr>
<tr>
<td>TiO2</td>
<td>Glycine, urea, thiourea</td>
<td>12–59</td>
<td>Carcinogenic hexavalent chromium reduction</td>
<td>[51]</td>
</tr>
<tr>
<td>MgO</td>
<td>Glycine</td>
<td>12–23</td>
<td>Fluoride removal from drinking water</td>
<td>[52]</td>
</tr>
</tbody>
</table>

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Fig. 4. Uncoated and Pd-substituted ceria coated cordierite monolith. From Ref. [44].

Fig. 5. Composition map and luminescent photograph of the YAG/Tb library under 254-nm UV excitation. From Ref. [57].
CO must be addressed seriously [58]. It is surprising to note that researchers worldwide have shown reluctance to use hydrazine-based fuels in recent years.

Use of different organic compounds such as: (i) alanine [59] (ii) asparagine, serine [60] (iii) methyl cellulose [61] (ii) ammonium acetate, ammonium citrate and ammonium tartarate have been explored as fuels [62]. After the publication of the first paper on the concept of mixture of fuels [63], large numbers of papers have been published on the use of combination of fuels such as citric and succinic acids [64]; citric acid and glycine [65], urea, monoethanolamine, alanine [66], etc. Although complex fuels favour formation of nanosize particles, in many cases a further calcination is required to form organic free pure nanocrystalline powders.

It is important to note that researchers are focusing their efforts towards the up scaling of SCS and also finding new applications of combustion synthesized nanosize powders. For example, a patent on an apparatus for continuous synthesis of nanopowders by SCS with a yield of 0.5–2 kg/h (Fig. 6) has been filed [67]. This is a first step towards the scaling-up of SCS. A method for making high purity, multiphase calcium carbonate powders using an auto-ignition combustion synthesis of calcium and phosphate salts has been reported and patented [68]. It is worth noting that two patents on Pt doped ceria (Ce1-xPtO2) catalyst for use in sealed lead acid batteries have been filed and transferred to industry. Similarly, combustion synthesized Ba/Sr hexa-aluminates doped with Eu3+ phosphors found industrial application in signage products (labels, toys, paints, plastics and electronics). Badini et al. hold patent for their work on single step solution combustion based ceria coatings [69] and TBC coatings [70]. Patent on synthesis of MgO and ZnO for defluoridation and arsenic removal has also been filed [71].

4. Future scope/conclusions

The year 2008 is a landmark year in SCS marking two decades of the first publication on SCS of alumina and related oxides [72], while the year 2007 marked the 40th anniversary of SHS origin. It is gratifying to note that SHS and SCS waves have crossed the borders and propagated to various parts of the world. Many new CS-groups have emerged in Brazil, Greece, China, Korea, France and other countries. The profound interest in combustion synthesis is due to the simplicity and cost effectiveness of the process followed by the superior nature of the particulate properties of the products. Despite of above success, it is important to outline that although extensive work has been reported on the modelling and mechanism of conventional (solid state) SHS, there is still a lacuna of modelling and mechanism aspects in case of SCS. Also, special attention has to be focused towards the preparation of agglomeration free nanosize particles with pre-designed morphology.

In recent years, CS has not only opened new vistas for the preparation of various novel nanosize oxides and composites, but also succeeded in continuous synthesis methods of nanopowders and development of various supported catalysts and coatings. As a result, conditions are mature for breakthroughs in these areas over the next several years. Promoters of nanotechnology, an approach defined on the basis of a length scale, have done a great job of selling the idea that ‘smaller is better’. Similarly, now it is time to commercialize SC method by selling the reality of ‘simpler is smarter and better’.

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

* Of special interest;
** Of outstanding interest.