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Novel Method for Synthesis of Nano-Materials: Combustion of Active Impregnated Layers**

By *Alexander S. Mukasyan** and *Peter Dinka*

Nanomaterials with characteristic structural dimensions on the order of few nanometers (1–100 nm) attract wide attention owing to their unique properties. They found a variety of applications in different branches of science and industry including catalysis, micro and biotechnologies, energy storage and conversion devices, such as fuel cells.

Different techniques have been developed for nanomaterial preparations, solid-state, wet-type and CVD methods, mechano-, plasma- and combustion synthesis. A combination of combustion and reactive solution approaches leads to so-called *solution (aqueous) combustion synthesis (SCS)* method.[1–3] Typically SCS involves a self-sustained reaction in solutions of metal nitrates and different fuels, which can be classified based on their chemical structure, i.e. type of reactive groups (e.g. amino, hydroxyl, carboxyl) bonded to the hydrocarbon chain.[4] The reaction between fuel and oxygen containing species provides high temperature rapid interaction. In self-sustained propagation mode after local initiation the combustion front steadily moves along the sol-gel media forming extremely fine solid products with tailored composition.[3,5]

Several distinctive features of SCS contribute to the unique properties of the synthesized products. First, the initial reaction media being a liquid solution allows mixing the reactants on the *molecular* level thus permitting precise and uniform formulation of the desired composition on *nano scale*. Second, the *high* combustion *temperatures* ensure the formation of the desired phase composition *directly* in SCS wave. This feature allows one to skip additional step, i.e. high-temperature product calcination, which typically follows the conventional sol-gel approach. Third, short process duration (seconds) and formation large amount of gases during SCS, inhibit solid particle size growth and favor synthesis of *nano-size* powders with high specific surface area. Forth, almost no external energy is required to produce materials, since SCS occurs owing solely to the self-sustained highly exothermic reactions. Finally, simple equipments are typically used for this process. A wide variety of nano-materials was synthesized by the SCS approach, including unique pigments and catalysts, materials for SOFC and lithium batteries, oxygen sensors and storages, novel dielectric and piezoelectric compositions.[1,2]

Recently we reported method for synthesis of high surface area supported catalysts by reactive solution impregnation to the *inert* porous solid support, followed by initiation of the combustion reaction in such complex heterogeneous media.[6] An unusual effect was found. By using this, so-called Impregnated Support Combustion (ISC) method, materials with very high specific surface area (> 200 m^2/g) were synthesized.

However, not every material can be obtained by above techniques. Many *low exothermic systems*, which allow synthesize of valuable compositions, do not provide self-sustained reaction mode. To overcome this obstacle a novel, so-called, *Impregnated Active Layer Combustion* (IALC) method was developed and described below. IALC allows not only one step high yield production of powders with high surface area but also suggests an approach for continuous synthesis of such materials.

Impregnated Active Layer Combustion

The concept of IALC has some similarity with ISC approach,[6] however in the former case the reaction solution is impregnated to the porous media, which is also *reactive* and thus can *assist* in propagation of combustion reaction. In order to control composition of the synthesized fine particles it is convenient that the reaction products of active layer do not contribute to the final structure of nano-material. This effect can be achieved if all layer related products are in gas phase. Also, for synthesis of nano-particles the combustion temperature should be relatively low and process duration as short as possible. All above requirements suggest using a thin porous layer of carbon-based combustible support, e.g. cellulose paper. Indeed such a media has excellent infiltration characteristics and can be easily impregnated with liquid reactive solution. Also the experiments show that residual ash after burning of the paper in air is less than 0.2 wt.%. Finally, burning of thin layer, owing to a large heat loss, leads to so-called

[*] ■*Please check title and addresses of authors!*■
Dr. A. S. Mukasyan, Dr. P. Dinka
Department of Chemical and Biomolecular Engineering
Center for Molecularly Engineered Materials
University of Notre Dame
Notre Dame, IN 46556, USA
E-mail: ■

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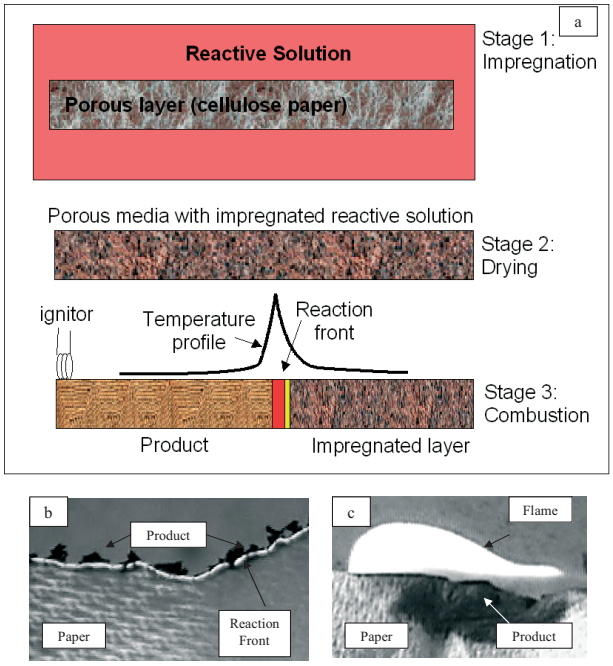

Fig. 1. Stages of Impregnated Active Layer Combustion (a) and different IALC modes: smoldering (b); flame (c).

"quenching" effect, i.e. rapid temperature drop after the reaction front, which favors the formation of fine powders.

The scheme for Impregnated Active Layer Combustion is presented in Figure 1(a). On the first stage the desired aqueous solution of fuels and oxidizers is impregnated into the thin layer of porous media (e.g. cellulose paper, carbon nanotubes, etc). Next step assumes drying of thus formed complex reaction system to decrease the amount of water. This component, which plays a constructive role on the stage of solution preparation, while hinders the process on the stage of reaction propagation. Ignition is an important part of the method, because two different combustion modes can be accomplished (Fig. 1(b) and (c)), i.e. slow smoldering (b) and rapid flame (c) combustion waves. Smoldering mode can be initiated by electrically heated metal wire with relatively low temperature (~ 500 K), while applying higher temperatures results in flame combustion mode. Slowly propagating (0.1–1 mm/s) smoldering mode leads to higher product yield and larger surface area of the synthesized powders. During IALC the final product forms as agglomerates of nano-particles. It is important that chemical analysis shows small (0.01–0.15 wt. %) free carbon content in a variety of thus synthesized products.

IALC of $SrRuO_3$ Perovskite

Let us consider IALC approach in more details on the example of synthesis of $SrRuO_3$ perovskite, which is a valuable catalyst for direct alcohol fuel cells.[7] This system, because of a high melting point of strontium nitrite, $Sr(NO_3)_2$ and low exothermicity of ruthenium nitrite reduction, does not allow self-propagating modes described above. In addition, the conventional, so-called volume solution combustion mode, because of its thermal explosion nature, provides only 30 % of product yield.

In this work, chromium nitrate, $Sr(NO_3)_3$, ruthenium nitrosyl nitrate, $Ru(NO)(NO_3)_3$, and glycine ($C_2H_5NO_2$) (all from Alfa Aesar) were used to synthesize different perovskite-based catalysts. In general, under equilibrium conditions, the combustion reaction in such systems can be represented as follows:

$$Me^{\nu}(NO_3)_{\nu} + (\frac{5}{9}\nu\cdot\phi)\,CH_2NH_2CO_2H + \nu\cdot\frac{5}{4}(\phi-1)\,O_2 \Rightarrow$$
$$MeO_{\nu/2}^{(s)} + (\frac{10}{9}\nu\cdot\phi)\,CO_2^{(g)} + \frac{25}{18}\phi\,H_2O^{(g)} + \nu\cdot(\frac{5}{9}\phi+1)/2\,N_2^{(g)} \quad (1)$$

where Me^{ν} is a metal with valence ν, ϕ is a fuel to oxidizer ratio. $\phi = 1$ means that the initial mixture does not require atmospheric oxygen for complete oxidation of the fuel, while $\phi > 1$ (< 1) implies fuel-rich (lean) conditions. Specifically for synthesis of the $SrRuO_3$ perovskite the following stoichiometric (ϕ=1) reaction is considered:

$$Sr(NO_3)_3 + Ru(NO)(NO_3)_3 + 32/5\cdot C_2H_5NO_2 \Rightarrow$$
$$SrRuO_3 + 32/5\cdot CO_2\uparrow_g + 16H_2O\uparrow_g + 67/10\cdot N_2\uparrow_g \quad (2)$$

Decomposition rates and temperatures for all precursors are shown in Figure 2(a). It can be seen that glycine ($CH_2NH_2CO_2H$), rapidly decomposes in the range of 523–566 K. Calculation shows that the weight decrease of 46 % (T = 566 K) corresponds to the removal of ammonia and water. Note that this reaction is endothermic. Initial (T = 468 K) decrease of weight (~ 9 %) during decomposition of $RuNO(NO_3)_3$ occurs owing to release of NO. Next relatively sharp drop occurs in the temperature range 470–650 K leading to formation of RuO_2. Endothermic decomposition of $Sr(NO_3)_2$ takes place at high temperature $T > 870$ K and results in formation of SrO at T= 1020 K.

Cellulose $(C_6H_{10}O_5)_n$ is a long-chain polymeric polysaccharide of beta-glucose. It was shown that the cellulose paper (SCOTT® Hard Roll Towel) used in this study as an active support media almost completely burn in air, i.e. weight of residual ash (T = 647 K) is less than 0.2 wt % (see Fig. 2(b)). Note that a rapid highly exothermic oxidation reaction starts at relatively low temperature ~ 556 K.

Results of DT/TG analysis for $Sr(NO_3)_3$+$Ru(NO)(NO_3)_3$+$32/5\cdot C_2H_5NO_2$ reaction solution (Fig. 3(a)) indicates two exothermic peaks. First, relatively weak peak coincides with decomposition temperature of the glycine (~ 525 K) and is a result of its interaction with ruthenium (III) nitrosyl-nitrate. The second large exothermic peak starts at T ~ 650 K is related to the reduction of solid $Sr(NO_3)_2$ by carbon-containing phase, which formed during the glycine decomposition. Thus, because of the high decomposition temperature for strontium nitrite, to initiate a reaction one has to preheat system to relatively high temperature (~ 650 K). But even under such conditions reaction occurs not in the homogeneous

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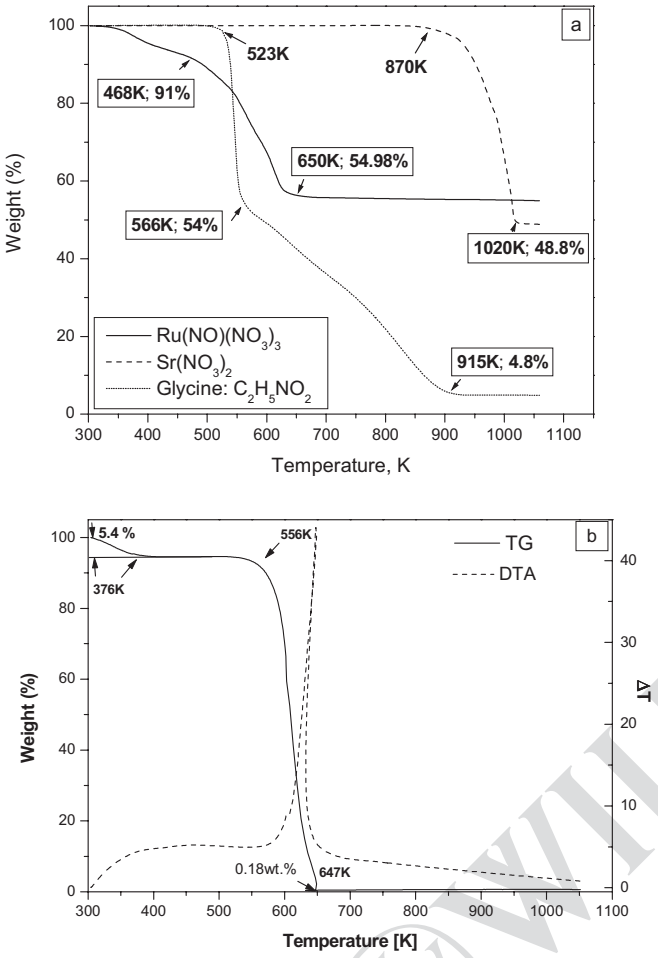

Fig. 2. DTA for: (a) reactive precursors; (b) cellulose (20 °C/min, oxygen atmosphere. 50 ml/min).

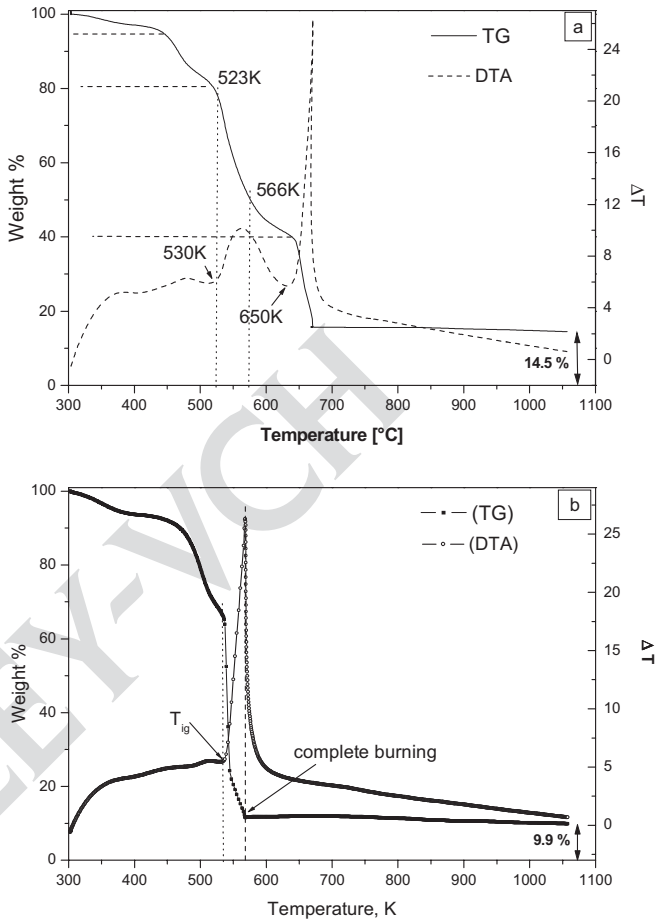

Fig. 3. DTA-TG of: (a): $Sr(NO_3)_3$+$Ru(NO)(NO_3)_3$+32/5·$C_2H_5NO_2$ solution (b) cellulose impregnated by $Sr(NO_3)_3$+$Ru(NO)(NO_3)_3$+32/5·$C_2H_5NO_2$ solution (20 °C/min, oxygen atmosphere. 50 ml/min).

solution, but in the heterogeneous mixture of ruthenium oxide- carbon-based phase and $Sr(NO_3)_2$. The latter make it difficult direct synthesis of desired perovskite structure and an additional calcination step is required. Also after preheating to 650 K the system explodes, giving only ~ 30 % of theoretical product yield.

The TGA-DTA date of the cellulose impregnated by glycine- $RuNO(NO_3)_3$ – $Sr(NO_3)_2$, solution is shown in Figure 3(b). It can be seen that in this case only one exothermic peak presents and reactions starts at T ~ 525 K, which correspond to ignition temperature of such complex media in air. Note that this temperature is below decompositions temperatures of all precursors (see Fig. 2(a)) and as a result the reaction leads to one step formation of the desired perovskite.

It is more important that reaction in such media can be easily initiated at room temperature without any preheating. For this, reactive solution was prepared by mixing above mentioned nitrites and glycine in stoichiometric ratio (ϕ = 1), and was impregnated into the bulk of a thin (~ 0.3 mm) layer of cellulose paper with paper/solution ratio 1:1. By using low temperature (T_{ig} = 500 K) ignition device, smoldering mode was accomplished and reaction propagated steadily with velocity ~ 5 mm/s along the impregnated media.

A typical temperature time profile for such combustion front propagation is shown in Figure 4(a) (Profile 1). Two distinctive temperature peaks, corresponding to two reaction fronts, can be resolved. XRD measurements of the quenched products reveal that the first stage is primarily carbon oxidation by atmospheric oxygen, while on the second stage the desired perovskite formed (see Fig. 4(b)) owing to metal nitrites – glycine interaction.

It is interesting that pure cellulose cannot burn in smoldering mode: initiated by low temperature source this reaction quickly extinguishes owing to large heat loss. Also the combustion temperature for pure paper (Profile 2; Fig. 4) is much higher than the first peak for smoldering mode of complex solution-cellulose system. This effect can be explained taking into account the suppression of carbon oxidation reaction by evaporation of water constrained in metal nitrites. Finally, note that for highly exothermic solutions (e.g. iron nitrite/glycine) the sequence of reactions in the smoldering wave can be reverse, i.e. first the solid oxide is formed, followed by carbon burning (Profile 3; Fig. 4).

The initial microstructure of this conventional paper towel is shown in Figure 5(a, b). It can be seen (Fig. 6(a)) that it consists of long yarns with diameters of ~ 50 μm and large pores

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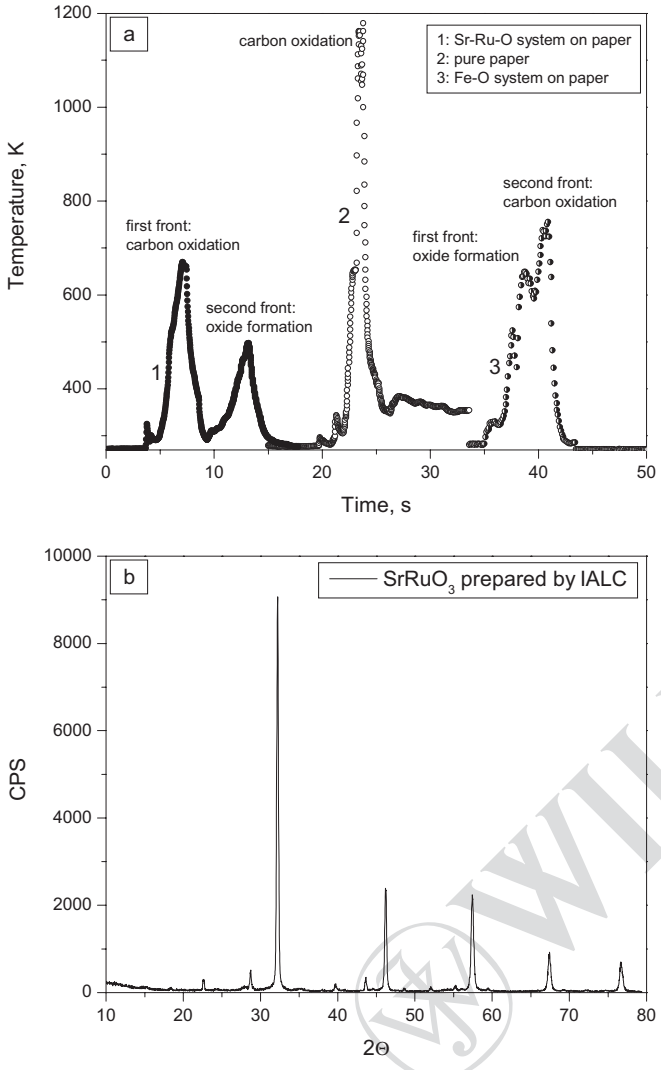

Fig. 4. Typical temperature profiles for IALC in different systems (a) and XRD-patterns for as-synthesized product in Sr-Ru-O_3 system (b).

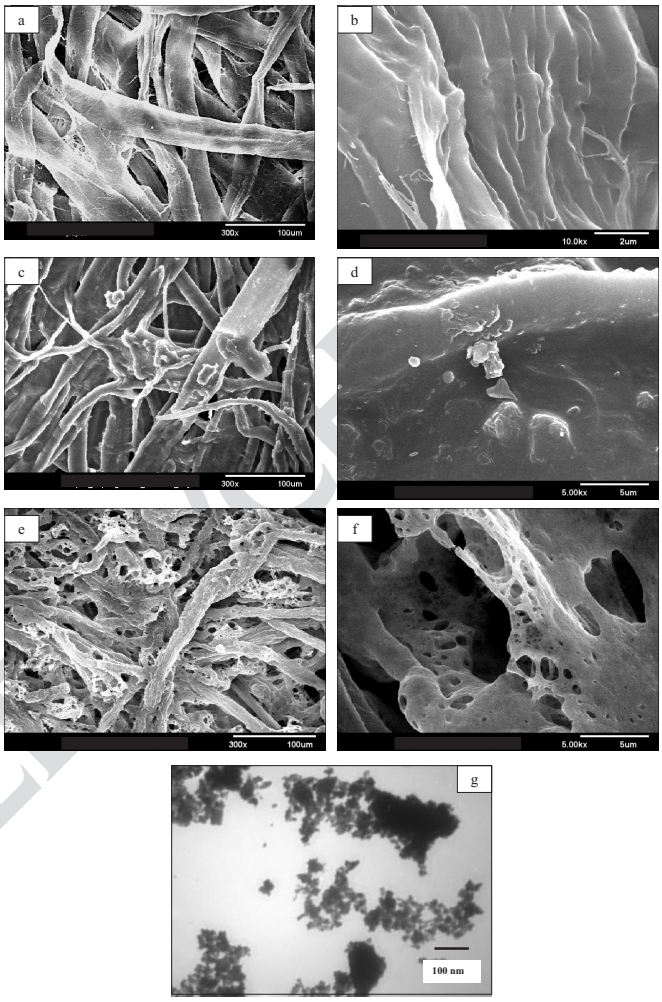

Fig. 5. Typical microstructures of the reactive media and combustion products: (a), (b) cellulose; (c) (d) impregnated layer; (e), (f) as synthesized product (g) product after milling (1 minute).

(100 μm). More close inspection shows that yarns surfaces (Fig. 6(b)) are well developed with characteristic scale of heterogeneity on the order of 1 μm. Microstructure of the cellulose paper impregnated by reaction solution after drying is shown in Figure 5(c,d). It is interesting that formed sol-gel type media does not occupy the large pores of the cellulose structure, but uniformly distributed along the surface of the cellulose yarns, making thin (~ 1 μm) reactive layers (compare Fig. 6(b) and 6(d)). Microstructure of as-synthesized product is shown in Figure 5(e–f). It can be seen that on the scale of 100 μm the product structure exactly "mimic" those for cellulose (compare Fig. 6(a) and 6(e)). However, the micrographs with higher magnification (Fig. 5(f)) indicate that "yarns" are hollow, with thin walls, which in turn are very porous. This porosity is a result of combustion/"evaporation" of the cellulose, leading to the formation of media with high surface area (~ 16 m^2/g) for this type of perovskites Also because the produced agglomerates are very porous just one minute of conventional solid milling (powder: ball ratio = 3:1, rotation speed 15 min^{-1}) leads to development of nano-particles with the average size on the order of 20 nm (see Fig. 5g).

Table 1. Some properties for various complex-oxides synthesized by IALC method.

Composition	Surface area*, BET (m^2/g)	C content as synthesized [wt.%]
Fe_2O_3	40.5	0.07
$CaRuO_3$	18.5	0.19
$SrRuO_3$	16.0	0.10
$LaRuO_3$	20.2	0.08
$La_{0.6}Ce_{0.4}Fe_{0.8}Ni_{0.2}O_{3-d}$	21.5	0.15
$La_{0.6}Ce_{0.4}Fe_{0.68}Ni_{0.2}K_{0.12}O_{3-\delta}$	15.2	0.17
$CuO/ZnO/ZrO_2$	20.5	0.1

all presented values were measured for as-synthesized products, i.e. without milling

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The IALC method was used to produce a variety of materials with high specific surface area (see Tab. 1). For example, by this approach several compositions were synthesized and tested as catalysts in direct ethanol and methanol fuel cells,[8] as well as for reforming of kerosene-type fuels to produce hydrogen.[9] It was demonstrated that these catalysts possess high catalytic activities and currently they are under long-term testing in different leading industrial companies. Finally, it is important to note that IALC method allows continuous method for synthesis of nano-powders. In this scheme the active layer also serves as a career of the reactive media.[9]

Conclusion

A novel effective method, i.e. Impregnated Active Layer Combustion, for synthesis of oxide-based nano-materials is described. The unique future of considered approach includes high surface area and crystallinity of the synthesized powders, exceptionally high product yield and opportunity for continuous technology. It is also important that method allows synthesis of complex metal-oxide nano-materials for low exothermic systems, which can not be otherwise produced by combustion approach.

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[1] K. Patil, S. Aruna, S. Ekambaram, *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 158.
[2] K. Patil, S. Aruna, T. Mimani, *Curr. Opin. Sol. State Mater. Sci.* **2002**, *6*, 507.
[3] A. S. Mukasyan, P. Epstein, P. Dinka, *Proc. Combus. Inst.* **2007**, *31*, 1789.
[4] A. Varma, A. S. Mukasyan, K. Deshpande, P. Pranda, P. P. Erii, *Mater. Res. Soc. Symp. Proc.* **2003**, *800*, 113.
[5] K. Deshpande, A. S. Mukasyan, A. Varma, *Chem. Mater.* **2004**, *16*, 4896.
[6] P. Dinka, A. S. Mukasyan, *J. Phys. Chem.* **2005**, *109*, 21627.
[7] A. Lan, A. S. Mukasyan, *ECS Trans.* **2007**, *2*, 1.
[8] P. Dinka, A. S. Mukasyan, *J. Power Source* **2007**, *167*, 472.
[9] A. S. Mukasyan, P. Dinka, *PCT Appl. No. PCT/US2006/030486*, Filed: August 4, **2006**.

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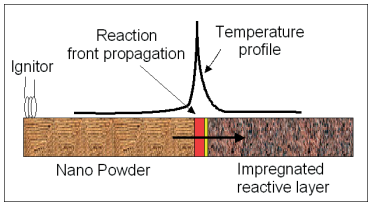
Novel Method for Synthesis of Nano-Materials: Combustion of Active Impregnated Layers

A. S. Mukasyan, P. Dinka*

Solution Combustion of Active Impregnated Layer is a novel method for synthesis of nano-materials. It combines features of impregnation and combustion approaches and allows production of nano-powders using low exothermic reaction systems, which cannot be accomplished by conventional solution combustion method.



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