



*Dedicated to Nicolae I. Ionescu PhD
on the occasion of his 85th anniversary*

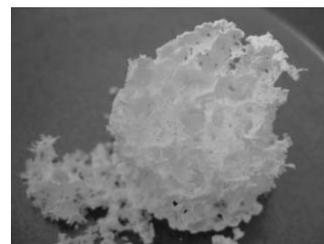
CARBOHYDRATE BASED COMBUSTION SYNTHESIS: A PROMISE OF GREENING MATERIALS SYNTHESIS

Oana CARP*

“Ilie Murgulescu” Institute of Physical Chemistry, Roumanian Academy, 202 Splaiul Independenței, 060021 Bucharest, Roumania

Received November 14, 2017

Currently, the environment protection represents one of the most important task force of Science and Society, determining the remarkable development of the Green Chemistry, as an alternative chemistry that seeks to minimize risk by minimizing hazard. The design/synthesis of nanomaterials must also circumscribe to the present environment requirements. A simple but efficient approach is to “green” the existing synthetic procedures by introducing as raw materials, benign, bio-renewable compounds as carbohydrates. This review is focused on carbohydrate-mediated combustion synthesis of the metal oxides, analysing critically the results of the research undertaking during the last years on this topic.



INTRODUCTION

An effective synthesis methodology must respond to multiple demands: applicability in a cost-effective manner for a broad range of high-quality materials, straightforwardness, flexibility, predictability, scalability and a minimal impact upon the environment.

Combustion synthesis is a worldwide adopted technique to synthesize nanomaterials, providing several attractive advantages over the other methods, such as simplicity of the experimental set-up, surprisingly short time between the preparation of precursors and the availability of the final product, high-yield, and low-cost due to the inexpensive raw materials and energy savings.^{1,2} It should be also noted its general character, because of the easiness with which it can be applied either

to simple or multicomponent oxides (including doped or mixed oxides) with various structures. The synthetic procedure is based on a redox reaction between a fuel (an organic molecule which ignites the reaction) and an oxidizer (usually nitrates)³ that produces the exothermicity necessary for nucleation and growth of the oxide powders. The properties of the resulting oxides (phase, degree of crystallinity, crystallite size, specific surface and associated porosity, *etc.*) are strongly influenced by the adopted experimental parameters, being mainly governed by the enthalpy/temperature of the flame generated during the combustion, which in turn is dependent on the thermochemical characteristics of the fuel and fuel to oxidant ratio.⁴⁻⁷

The conventional organic compounds used as fuels are high-temperature flame ones,⁸ mostly

* Corresponding author: ocarp@icf.ro

containing nitrogen, being largely circumscribed to urea and its derivatives,⁹⁻¹² different amino acids as glycine,¹³⁻¹⁵ alanine,¹⁶ α - and γ - amino butyric acid,¹⁷ hydrazine and its derivatives.¹⁸⁻²⁰ Citric acid is the most used fuel that does contain nitrogen.^{21,22}

In the early stages of the synthesis are developed conjugated and competing dynamic intra- and inter-associations with different nuclearities *via* coordinative, supramolecular and electrostatic linkages between the metal cations and fuels, so from the perspective of coordination/supramolecular chemistry, the fuels have to possess good linking capabilities. The homogeneous distribution of the metallic cations built up in these assemblies makes possible the completion of nucleation process through only short distance diffusion of nearby atoms even during their energetical ignition. On the other hand, the high combustion reaction rate does not provide enough time and energy for the long-distances diffusion of atoms, and obvious for the growth of the crystallites.

The environmental protection enforces the development of materials in a green context. A bridge between "classical", more or less polluting synthetic procedures, and the environmentally friendly alternative can be brought by the use in chemical synthesis of renewable raw materials such as carbohydrates, from mono- to polysaccharides, natural compounds that have a unique combination of eco-friendly features (non-toxicity, biocompatibility, biodegradability, bioactivity, renewability, widely availability, low cost) and functional beneficial properties. Till now, besides their food applications, carbohydrates are used in extremely low quantities for obtaining petrochemical-based materials substitutes (mainly polysaccharides).²³ Their involvement in materials synthesis (metals, metals-oxide, metal/metal oxide-carbohydrate and metal/metal oxide-carbon composites) is till now scarce investigated but with interesting and promising results.²⁴⁻²⁷ The replacement of the traditional fuels with biofuels as carbohydrates may be considered at a first sight a rather exotic option (although the mixture between a sugar fuel and KNO_3 oxidizer is a type of rocket propellant known as "rocket candy" utilized for model rockets²⁸), several arguments, besides their eco-friendly distinctiveness argue in favour of their use in this type of synthesis.

Firstly, the diversity and abundance in terms of chemical functionality ($-\text{OH}$, $-\text{COOH}$, *etc.*) permits on the one side different linkages with a wide range of metal cations, and on the other, various molecular intra/inter-associations. Secondly, the

gelling properties of several carbohydrates allows a distinctive combination of the chemical gelation processes with the combustion ones, that have as result an increased homogeneity of the final products because the segregation during the crystallization of a particular metal is avoided (or reduced). Due to the immobilization into a gel matrix, the metal ions react with each other with a minimum diffusion, being possible, therefore, to synthesize homogeneous and stoichiometrical oxides. The behaviour is especially important in the synthesis of the multicomponent metal oxides. Thirdly, the replacement of the traditional fuels with carbohydrates shifts the combustion from a high-temperature flame toward a low-temperature one, reducing implicitly the exothermicity of the reaction, while almost an equal number of mole gases are released. As a result, the combustion proceeds in a more controllable way and the obtained materials present often a higher surface area/porosity.^{29,30} Fourthly, the varied reducing ability of the carbohydrates suitably exploited, may fine tunes the oxidation states of metal cations (in the case of cations with different oxidation states)³¹ but also the nature and concentration of the lattice defects.³² Last but not least, carbohydrate-assisted combustion follows a more environmentally friendly route due to a reduced evolving of toxic nitrogen oxides (derived only from nitrate anions if nitrate salts are used as metal source), the main gaseous products being CO_2 and H_2O .^{7,12,13}

CARBOHYDRATES AS CO-FUELS IN A MIXTURE OF LOW- AND HIGH-TEMPERATURES FLAME FUELS

A mixture of two or more fuels characterized by different heat of formation with low- and high-temperature flames, could modulate and control the flame temperature, and implicitly important characteristics of the final materials like structure (if the material is allotropic), crystallite size, surface area/porosity and agglomeration.³³⁻³⁵

Several examples concerning the oxide systems synthesized and the specific benefits brought by the use of a carbohydrate additional fuel are given in the following. The analysis is restricted only to urea and its derivatives and amino acids conventional fuels.

Thus, the addition to urea of glucose greatly alleviated the agglomeration of $\text{Cr}^{3+}\text{-Al}_2\text{O}_3$,³³ whereas the sucrose addition to same fuel induces the formation of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ rhombohedral perovskite with larger specific surface area and a

smaller crystallite compared with the oxide obtained when only urea is used as fuel (34.9/13.2 m² g⁻¹ respectively 18/26 nm).³⁶

The vigorous and explosive nitrate–glycine combustion reaction was mitigated by the addition of sucrose, in the synthesis of high-purity nanosized LiMn₂O₄ powders. Compared to the sample obtained using only glycine, the yields of the mixed fuels syntheses were remarkably improved, from around 50% to over 90%. The highest discharge capacity at 1 C was obtained for the sample with 2% added sucrose, which retained a capacity of 116.6 mAh g⁻¹ after 80 cycles.³⁷

Al₂O₃–ZrO₂ nanocomposites with crystallite sizes of ~20 nm were synthesized through a combustion that takes advantage of a urea–starch mixture.³⁴ The use of starch as an additive to urea fuel has a significant effect on the specific surface area of the produced powder and causes it increase from 3.56 to 13.16 m² g⁻¹.

The hydrodesulfurization activity of Al₂O₃-supported Ni–Mo catalysts prepared by a urea–starch combustion synthesis is markedly affected by the starch amount.³⁸ Thus, up to a starch: Al³⁺ molar ratio equal with 2.5, porosity is developed, and catalysts' reducibility and sulfidability is improved due to a lesser interaction of Mo and Ni with the Al₂O₃ support.

Single spinel phase of the oxide zinc aluminate, ZnAl₂O₄, has been obtained through the N-methylurea (NMU) and starch two-fuels combustion method.³⁹ The phase crystallization temperature is strongly related with the starch amount in the fuels mixture, lower values being recorded for the higher values of the starch/NMU ratio. The use of a two-fuels mixture (25% starch and 75% NMU) and a stoichiometric fuel/oxidant ratio determines an extension of the surface area from 9.52 up to 20.69 m² g⁻¹, increase explained by a complete decomposition of the organic/carbonaceous residue.

A glycine–starch mixtures gel-combustion is efficient in the synthesis of MgAl₂O₄ spinel. The ignition and physical–chemical characteristics of the powders depend on the starch content. The purity of the powder increases upon adding 10 wt% starch, but its specific surface area decreases. The gel structure is the dominant factor affecting particles dissipation, which affects specific surface area. The optimum potato starch content for achieving pure spinel nanoparticles is 40 wt%.⁴⁰

Nanosize-necked structure α - and γ -Fe₂O₃ with a particle size and surface area in the ranges of 45–55 nm respectively 61–68 m²g⁻¹ have been

prepared from ferric nitrate by the combustion method using as fuel a mixture of glycine, ammonium nitrate and starch. Both Fe₂O₃ materials have shown good photocatalytic activity for hydrogen generation from H₂S under visible light irradiation.⁴¹ Also superparamagnetic Fe₃O₄ with applications in drug delivery, bio-separation and magnetic resonance imaging were obtained using a glycine, ammonium nitrate and starch mixture.⁴²

Nanoscale MgAl₂O₄ powders were successfully synthesized *via* a microwave-assisted solution combustion process using various mixtures of urea, glycine and starch as fuel. Addition of starch noticeably altered the combustion type, from flame combustion to smoldering combustion and lowered the combustion temperature. The specific surface area of the powders is significantly increased as the starch addition level is raised up to 35.6 wt.%, while it is slightly decreased with starch addition level further rising to 54.7 wt.%. The crystallite size of the MgAl₂O₄ spinel is also slightly decreased with increasing of the starch.³⁵

The combustion synthesis using cellulose as fuel (single or in combination with other fuels) is based on the self-propagated combustion of metal nitrates trapped into various form of nanometer cellulose pores and capillaries (fiber). This particular combustion method is known as impregnated layer combustion synthesis (ILCS). This alternative has two major advantages over the previously mentioned combustion methods. First, it eliminates the preheating stage, since once ignited, the combustion front propagates without requiring any additional energy. Second, a fast cooling rate in the thin reaction front in contact with the surface holding the sol layer decreases the temperature and thus sintering, yielding a product with even finer particle size and thus higher specific surface area.⁴³

Well crystallized multi-component oxides containing copper, zinc, zirconium, and palladium highly active and selective catalysts for oxidative reforming of methanol were prepared by impregnated layer combustion synthesis using cellulose paper and glycine as co-fuel.⁴⁴ The oxides are characterized by higher surface area than co-precipitation because the crystallization occurs simultaneously with the extensive gasification of carbon as CO₂, not in a post-synthesis separate calcination step.

Nanostructured La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} (LSCF) oxide powder was synthesized by an autocombustion process based on a modified glycine-nitrate (GN) process and cellulose fiber.⁴⁵ The more homogeneous

dispersion of the metal ions in cellulose–GN precursor determines a decrease of SrCO₃ impurity (from 4.3 wt% in normal glycine-nitrate process to 1.3 wt% in cellulose–assisted process). The crystallite size of the LSCF is between 15–20 nm. Since the cellulose was combusted after the LSCF formation (GN reaction), its fiber structure effectively blocked the contact of the forming oxide particles, therefore successfully suppressed their grain growth. The temperature reached by the cellulose combustion process is much lower than the glycine-nitrate combustion, and as a result no significant growth of the oxides grains during the combustion removal of cellulose was observed.

Pure, well-crystallized Li₄Ti₅O₁₂ with quasi-sphere shaped crystallites were obtained through a cellulose-glycine-nitrate combustion process at 750°C, using anatase type TiO₂.⁴⁶ The sequence of impregnation has a determinant effect on the phase formation and on the electrochemical performance of oxides. The optimal succession involves first the cellulose impregnation with a mixed solution of LiNO₃ and glycine followed by TiO₂ and HNO₃ impregnation. The oxides exhibit a better electrochemical behaviour at high charge/discharge rates than similar oxides obtained in solid state.

CARBOHYDRATES AS SINGLE LOW-TEMPERATURES FLAME FUELS

By far, the most used biofuel is sucrose. The disaccharide is readily soluble in water, and under acidic conditions (H⁺ from nitric acid) gets hydrolysed to glucose and fructose, which are further oxidized into saccharic acid, glycolic acid and trihydroxybutyric acid with numerous –COOH and –OH groups.⁴⁷ Especially the –COOH groups can easily form linkages with metal ions.⁴⁸ The process is quite similar to the citric acid complexation mechanism, resulting a polymeric resin precursor. The sucrose-mediated synthetic procedure was used for synthesis of simple oxides as NiO,⁴⁷ Bi₂O₃ (with good catalytic activity for the synthesis of heteroaryls using Suzuki coupling reactions in aqueous medium),⁴⁹ α-Al₂O₃ ceramic powders with a high specific surface area higher than 190 m² g⁻¹ and an average pore size between 18 and 25 nm,⁵⁰ as well doped simple oxides among which we mention yttria stabilized zirconia,⁵¹ one of the most versatile ceramic materials, useful across a range of industries and Gd₂O₃ : Eu phosphors with red luminescence of about 85% of the commercial powders.⁵²

The sucrose gel-combustion proved to be very successful in the synthesis of mixed oxides with advanced applications. A great interest was given to the materials with enhanced electrochemical properties, being obtained single spinel ZnMn₂O₄,⁵³ double substituted spinel as LiNi_yCo_{1-2y}Mn_{1+y}O₄,⁵⁴ LiNi_yMn_{2-y}O₄ (0 < y < 0.5),⁵⁵ LiMn_{1.99-y}Li_yM_{0.01}O₄ (M=Al³⁺, Ni²⁺, Cr³⁺, Co³⁺; y = 0.01 and 0.06),⁵⁶ LiNi_{0.5}Mn_{1.5}O₄,⁵⁷ LiCr_{0.2}Ni_{0.4}Mn_{1.4}O₄,⁵⁸ LiCr_xMn_{2-x}O₄ (0.2 < x < 0.8),⁵⁹ and also layered families of oxides like Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂⁶⁰ and Li[Li_{(1-x)/3}Mn_{(2-x)/3}Ni_{x/3}Co_{x/3}]O₂ (0 < x < 1)⁶¹ and oxides with perovskite structure as La_{0.7}Sr_{0.3}Co_{0.5}Fe_{0.5}O₃.⁶² A special mention for the 3D network-like porous MnCo₂O₄ nanostructures fabricated through a sucrose-assisted combustion route followed by a calcination treatment. The 3D architectures present large specific surface area (one of the largest mentioned by the literature, respectively 216.15 m² g⁻¹), abundant mesoporosity (2–50 nm) and high specific capacitance (647.42 F g⁻¹ at a current density of 1 A g⁻¹), remarkable capacitance retention rate (70.67% at current density of 10 A g⁻¹ compared with 1 A g⁻¹), and excellent cycle stability (only 6.32% loss after 3000 cycles).²⁹

Single-phase BiFeO₃ that exhibited either efficient catalytical properties (in acetylation of various amines, alcohols and phenols) or unusual ferromagnetic characteristics which were obtained by sucrose gel-template combustion route⁶³ respectively solid state combustion one.⁶⁴

Several metal oxide based composites were also obtained by sucrose-assisted gel-combustion. An example is Al₂O₃–CeO₂ composite with particle size between 20 and 50 nm, platelet morphology with an aspect ratio of 1.5 and high surface area (281 m² g⁻¹).⁶⁵ Another interesting example is the extension of the gel-autocombustion sucrose-mediated procedure to the synthesis of metal oxide/carbon composites, as the case of nano-sized Li₂FeSiO₄/C one.⁶⁶ The amount of Li₂SiO₃ and Fe_{1-x}O impurities increases with the increase of sucrose amount. Among the synthesized cathode materials, Li₂FeSiO₄ obtained with 1.5 mol of sucrose, showed the best electrochemical performance in terms of discharge capacity, cycling stability and rate capability.

Pure, single phase nickel spinel ferrite (NiFe₂O₄)⁴⁷ and Co-Zr doped hexaferrites (SrCo_xZr_xFe_{12-2x}O₁₉)⁶⁷ have been successfully prepared by applying sucrose as a fuel under gel conditions. In the case of hexaferrites, sucrose series, compared with the oxides obtained in the

absence of the carbohydrate, present more symmetrical structures with lower average particle size. The materials calcinated at 900°C possess the best magnetic characteristics.

A relative large range of oxides (simple, doped, mixed) were obtained using starch gel combustion procedure. Starch has not sucrose's water solubility, but in aqueous solution at temperatures ranging between 50 and 90°C the natural polysaccharide forms a gel, which could incorporate and disperse in a uniform fashion the incipient centres of nucleation of the nanoparticles.

Multifunctional NiO materials with electrochemical, antimicrobial and photocatalytic activity were obtained using different amounts of cassava starch as fuel.⁶⁸ It is concluded that the oxide obtained with a lower fuel to oxidizer ratio, has lesser volume expansion (higher concentration of oxygen vacancies), smaller size, higher negative zeta potential and hence smaller polydispersity index. The same product showed improved capability (955 comparative with 785 mA hg⁻¹) and a retained capacity of 59% and 47% up to 50 cycles in battery studies and behaved as a better antimicrobial/antifungal agent. The product prepared from equal weight ratio of fuel to oxidizer was a better photocatalyst in degrading methylene blue (94%), while the one obtained with higher fuel to oxidizer ratio presents a better photocatalytic efficiency in sunlight because of a visible light-active band gap (2.3 comparative with 2.98 eV).

ZnO nanoparticles, synthesized by a tapioca pearl starch gel-combustion method, exhibited good photocatalytic efficient in sunlight due to band gap reduction to visible region, but its antibacterial activity is moderate.⁶⁹

Spherical shaped cerium oxide nanoparticles (8.1 to 12.7 nm) were synthesized using native cassava starch as a size limiting chelating agent and fuel in a gel-combustion synthesis.³² The Ce⁴⁺ → Ce³⁺ reduction during synthesis process caused an increase of oxygen vacancies molar fraction, which resulted in a higher lattice constant expansion for successively smaller CeO₂ nanoparticles.

Starch-mediated gel combustion route proves its power in the synthesis of mixed oxides. An important class is the multifunctional spinel oxides, among which we mention NiFe₂O₄,^{70,71} CoFe₂O₄,^{71,72} Co_{0.5}Zn_{0.5}Fe₂O₄,⁷¹ CoFe_{2-x}Dy_xO₄ (x = 0 – 0.1 in a step of 0.025),⁷³ MAl₂O₄ (M = Co²⁺, Ni²⁺),⁷⁴ Ni_xZn_{1-x}Al₂O₄ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1).⁷⁵ Ca₃Co₄O₉ p-type semiconductor with a band gap of 2.10 eV was also successfully

obtained by starch-gel assisted combustion route.⁷⁶ Another application of the method is the synthesis of layered structured oxides as Sn-doped LiCoO₂,⁷⁷ LiMn_{0.4}Ni_{0.4}Co_{0.2}O₂ and LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂.⁷⁸

Cellulose represents one of the most promising variants of carbohydrate-assisted combustion, applied either to simple or mixed oxides. So, a mixture of monodisperse α- and γ-Fe₂O₃ nanoparticles using porous structured cellulose films as fuel and sacrificial templates was obtained.⁷⁹ The as-synthesized nanoparticles, with a saturation magnetization value of 98.39 emu g⁻¹ and coercivity about 32.68 Oe could be well-dispersed in water and kept in suspension state for more than 3 months with trace organic surfactant. High phase purity MgO with particle size varying in the range of 3–7 nm were obtained by a high yield combustion synthesis, starting from magnesium nitrate and cellulose fibers.⁸⁰ The material shows a good fluoride adsorption capacity that does not vary in the pH range usually encountered in groundwater. The combustion of the impregnated cellulosic fibres with copper, zinc, zirconium, and palladium nitrates gives two reaction zones upon ignition.⁸¹ The first one provides an amorphous metal oxide layer, converted further into a crystalline nano-sized product (ca. 10 nm) after passing through the second region. These oxides are active and selective catalysts for hydrogen production by the oxidative reforming of methanol.

An interesting example of cellulose-assisted combustion technique is the synthesis at reduced temperature of high rate performance Li₄Ti₅O₁₂ pure spinel, adopting anatase,⁸² rutile,⁸³ and Ti(C₄H₉O)₄⁸⁴ as the titanium source. The resulted oxides show a reversible discharge capacity near the theoretical value. The same synthesis method was applied to the synthesis of Sn-Li₄Ti₅O₁₂ / composites, potential anodes for lithium-ion batteries.⁸⁵ Sucrose was applied for the formation of Li₄Ti₅O₁₂ / carbon composite, since it has been often adopted as an organic carbon source for the *in situ* creation of carbon coating because of its low pyrolysis temperature.⁸⁶ Two routes were investigated. The first is to mix sucrose with phase-pure Li₄Ti₅O₁₂, prepared from the cellulose-assisted combustion synthesis after the calcination at 700°C for 5 h, followed by thermal processing at 700°C in an inert atmosphere to allow the thermal decomposition of sucrose to solid carbon. In the second, the powder obtained from the cellulose-assisted combustion synthesis pre-fired at 400°C instead of 700°C was mixed with sucrose and

calcined at 700°C in nitrogen for 5 h for the decomposition of sucrose to solid carbon.⁸⁷

Glucose is also used as fuel both in solid state and solution combustion routes. Honeycomb Ag / ZnO mesoporous heterostructures exhibiting high photocatalytic activity were prepared *via* simple solution glucose combustion synthesis. The average crystal size of Ag/ZnO heterostructures is about 20 ± 1.0 nm.⁸⁸ LiMn_2O_4 was rapidly synthesized by solid-state combustion synthesis using glucose as fuel. It was demonstrated that the amount of glucose greatly affected the purity of the mixed oxides, in terms of Mn_3O_4 content, which decreased at first and then increased with increasing glucose content. At a glucose content of 10 wt%, no Mn_3O_4 is identified and the material presents the best electrochemical performance.⁷⁸ CoFe_2O_4 -graphene hybrid materials were also synthesized by a one-pot combustion method using glucose as fuel.⁸⁹ The composites consist in anchored ferrite on the surface of graphene sheets. Interesting is the fact that after combustion, grapheme oxide sheets were not oxidized, but reduced. The composites exhibit ferromagnetic characteristics, and compared with pure CoFe_2O_4 , improved photocatalytical performance.

The disaccharide maltose is another attractive biofuel, not so frequently used, but with interesting results, especially with regard to mixed oxides. Thus were obtained single-phase multiferroic BiFeO_3 ferrites,⁹⁰ $\text{BaFe}_{18}\text{O}_{27}$ W-type ferrite nanostructures,⁹¹ various hexaferrites as bean-shaped copper $\text{CuFe}_{12}\text{O}_{19}$,⁹² $\text{PbFe}_{12}\text{O}_{19}$ nanoplates,⁹³ interlaced $\text{BaFe}_{12}\text{O}_{19}$ morphology.⁹⁴ For $\text{BaFe}_{12}\text{O}_{19}$ was investigated the influence of different carbohydrates fuels (glucose, fructose, maltose, starch), being demonstrated that the size, adopted morphology, phase purity and implicit the magnetic properties are fuel-carbohydrate dependent. The best magnetic characteristics (specific saturation magnetization and coercivity of 48 emu g^{-1} and 5000 Oe , respectively) were obtained using maltose biofuel. Spherical clusters of BaAl_2O_4 spinel with good electrochemical properties were also synthesized *via* a combustion method using maltose as a fuel.⁹⁵

Interesting results were obtained in the investigation of the combustion synthesis of Fe_3O_4 using as fuel sucrose, citric acid or glucose.⁹⁶ Depending on the utilized fuel, the specific surface area of the magnetite powders varied between 56 (citric acid) and $106 \text{ m}^2 \text{ g}^{-1}$ (glucose), while the saturation magnetization ranged between 55.3 (glucose) and 59.4 emu g^{-1} (sucrose). The properties of the resulted powders have been discussed in

relation to reaction atmosphere (air/absence of air) and used fuel. Air combustion reactions caused the rapid oxidation of Fe^{2+} to Fe^{3+} under the influence of the atmospheric oxygen, therefore the final reaction product was a mixture of α - and γ - Fe_2O_3 . In air absence, the oxidation of Fe^{2+} is avoided, being obtained only Fe_3O_4 , with crystallite size varying from 10 (glucose) to 18 nm (citric acid).

Three carbohydrates, sorbitol, sucrose, and glucose serve as efficient fuels for indium-gallium tin oxide (IGZO) film combustion synthesis to yield high-performance thin-film transistors (TFTs).⁹⁷ The unique self-generating energy characteristics significantly enhance carrier mobility and operational stability of the TFTs product, with clear correlations between the enthalpy of combustion, microstructural densification, M-O-M lattice content, and IGZO electron mobility.

Strontium aluminium oxides ($\text{Sr}_3\text{Al}_2\text{O}_6$), metal oxides with Ruddlesden-Popper (RP) complex structures, with narrow size distribution of the particles (20 - 35 nm) and good energy storage properties were obtained *via* glucose or maltose combustion synthesis.⁹⁸

Lactose disaccharide is less utilized as fuel, CoAl_2O_4 ⁹⁹ and $\text{CuFe}_{2-x}\text{Ce}_x\text{O}_4$ ¹⁰⁰ nanoparticles with photocatalytical properties are among the oxide materials synthesized *via* lactose-mediated combustion route.

A somewhat exotic (or “sweet”) synthesis is the honey-mediated one for obtaining CoFe_2O_4 .¹⁰¹ Honey, mainly composed of glucose and fructose, has the role of fuel, protecting agent and natural reductant agent.

CONCLUSIONS

The review gathers some general considerations and several illustrative examples regarding the carbohydrates interferences in combustion synthesis of metal oxides or related composite materials, underlining some of the special features of this peculiar synthesis route.

Besides its environmentally benign attributes in terms of sustainability issues of oxide synthesis, carbohydrate-assisted combustion brings an added value to the so synthesized materials. The superior homogeneity, higher surface area and porosity, particular morphology and a lower crystallites size of the obtained materials are preliminary properties that significantly influence other of their characteristics (like optical, (photo)catalytical, magnetical, etc.).

In summary, carbohydrate-mediated combustion synthesis route opens the gates toward an alternative

and less toxic chemistry of nanomaterials, which lucratively compete the classic procedure.

Acknowledgements. This work was financially supported by the research project 234PED-2017 of the Roumanian National Authority for Scientific Research (CNCS - UEFISCDI).

REFERENCES

1. A. Varma, A.S. Mukasyan, A.S. Rogachev and K.V. Manukyan, *Chem. Rev.*, **2016**, *116*, 14493.
2. W. Wen and J.-M. Wu, *RSC Adv.*, **2014**, *4*, 58090.
3. S.R. Jain, K.C. Adiga, and V. Pai Verneker, *Combust Flame*, **1981**, *40*, 71.
4. T. Mimani, *J. Alloys Compd.*, **2001**, *315*, 123.
5. S. Saha, S. Ghanawat and R. Purohet, *J. Mater. Sci.*, **2006**, *41*, 1039.
6. B. Jurca, C. Paraschiv, A. Ianculescu and O. Carp, *J. Therm. Anal. Calorim.*, **2009**, *97*, 91.
7. O. Carp, L. Patron L and A. Reller, *Mater. Chem. Phys.*, **2007**, *101*, 142.
8. A. S. Prakash, A. M. A. Khadar, K. C. Patil and M. S. Hegde, *J. Mater. Synth. Process.*, **2002**, *10*, 135.
9. A. Manikandan, L. J. Kennedy, M. Bououdina and J. J. Vijaya, *J. Magn. Magn. Mater.*, **2014**, *349*, 249.
10. O. Carp, L. Patron and M. Brezeanu, *J. Therm. Anal. Cal.*, **1999**, *56*, 561.
11. O. Carp, L. Patron and A. Reller, *J. Therm. Anal. Cal.*, **2003**, *73*, 867.
12. O. Carp, L. Patron, L. Diamandescu and A. Reller, *Thermochim. Acta*, **2002**, *390*, 169.
13. D. Gingasu, I. Mindru, L. Patron, O. Carp, D. Matei, C. Neagoe and I. Balint, *J. Alloys Compd.*, **2006**, *425*, 357.
14. C. Paraschiv, B. Jurca, A. Ianculescu and O. Carp, *J. Therm. Anal. Calorim.*, **2008**, *94*, 411.
15. R. Epherre, E. Duguet, S. Mornet, E. Pollert, S. Louguet, S. Lecommandoux, C. Schatz and G. Goglio, *J. Mater. Chem.*, **2011**, *21*, 4393.
16. D. Berger, C. Matei, F. Papa, V. Voicu and V. Fruth, *Prog. Solid State Chem.*, **2007**, *35*, 183.
17. S. Jaenicke, G. K. Chuah and S. T. Koe, *Thermochim. Acta*, **1993**, *216*, 285.
18. B. N. Sivasankar and J. R. Sharmila, *J. Therm. Anal. Calorim.*, **2003**, *73*, 271.
19. K. Desphande, A. Mukasjan and A. Varma, *Chem. Mater.*, **2004**, *16*, 4896.
20. C. C. Chen and K. T. Huang, *J. Mater. Res.*, **2005**, *20*, 424.
21. J. Yang, X. Li, J. Zhou, Y. Tang, Y. Zhang and Y. Li, *J. Alloys Compd.*, **2011**, *509*, 9271.
22. R. E. Vizhi, V. Harikrishnan, P. Saravanan and D. R. Babu, *J. Crystal Growth*, **2016**, *452*, 117.
23. F. W. Lichtenhaler and S. Peters, *C.R. Chimia*, **2004**, *7*, 65.
24. A. Stan, C. Munteanu, A. M. Musuc, R. Birjega, R. Ene, A. Ianculescu, I. Raut, L. Jecu, M. Badea Doni, E. M. Anghel and O. Carp, *Dalton Trans.*, **2015**, *44*, 7844.
25. G. Patrinoiu, J. M. Calderón-Moreno, C. M. Chifiriuc, C. Saviuc, R. Birjega and O. Carp, *J. Colloid Interface Sci.*, **2016**, *462*, 64.
26. O. Carp, D. Visinescu, G. Patrinoiu, A. Tirsoaga, C. Paraschiv and M. Tudose, *Rev. Roum. Chim.*, **2010**, *55*, 705.
27. O. Carp, A. Tirsoaga, B. Jurca, R. Ene, S. Somacescu and A. Ianculescu, *Carbohydr. Polym.*, **2015**, *115*, 285.
28. X. Mei, H. Yang, X. Li, Y. Li and Y. J. Cheng, *J. Therm. Anal. Calorim.*, **2015**, *120*, 1749.
29. T. Huang, C. Zhao, L. Wu, X. Lang, K. Liu and Z. Hu, *Ceram. Int.*, **2017**, *43*, 1968.
30. D. Visinescu, G. Patrinoiu, A. Tirsoaga and O. Carp, in "Environmental Chemistry for a sustainable World", E. Lichtfouse, J. Schwarbauer and D. Roberts (Eds.), Springer, 2013, p. 119–172.
31. D. Visinescu, C. Paraschiv, A. Ianculescu, B. Jurca, B. Vasile and O. Carp, *Dyes Pigments*, **2010**, *87*, 125.
32. N. S. Ferreira, R. S. Angélica, V. B. Marques, C. C. O. de Lima and M. S. Silva, *Mater. Lett.*, **2016**, *165*, 139.
33. X. Mi, X. Zhang, X. Ba, Z. Bai, L. Lu, X. Wang and Q. Liu, *Adv. Powder Technol.*, **2009**, *20*, 164.
34. K. Tahmasebi and M. H. Paydar, *Mater. Chem. Phys.*, **2008**, *109*, 156.
35. J. Bai, J. Liu, C. Li, G. Li and Q. g Du, *Adv. Powder Technol.*, **2011**, *22*, 72.
36. D. P. Tarragó, C. de Fraga Malfatti and V. C. de Sousa, *Powder Technol.*, **2015**, *269*, 481.
37. C.-G. Han, C. Zhu, G. Saito and T. Akiyama, *Adv. Powder Technol.*, **2015**, *26*, 665.
38. W. Lai, W. Song, L. Pang, Z. Wu, N. Zheng, J. Li, J. Zheng, X. Yi and W. Fang, *J. Catal.*, **2013**, *303*, 80.
39. D. Visinescu, B. Jurca, A. Ianculescu and O. Carp, *Polyhedron*, **2011**, *30*, 2824.
40. A. Motevalian and S. Salem, *Particuology*, **2016**, *24*, 108.
41. S. K. Apte, S. D. Naik, R. S. Sonawane and B. B. Kale, *J. Am. Ceram. Soc.*, **2007**, *90*, 412.
42. S. A. Kulkarni, P. S. Sawadh, P. K. Palei and K. K. Kokate, *Ceram. Int.*, **2014**, *40*, 1945.
43. A. S. Mukasyan and P. Dinka, *Adv. Eng. Mater.*, **2007**, *9*, 653.
44. A. Kumar, A. S. Mukasyan and E. E. Wolf, *Appl. Catal. A*, **2010**, *372*, 175.
45. W. Zhou, Z. Shao, R. Ran, H. Gu, W. Jin and N. Xu, *J. Am. Ceram. Soc.*, **2008**, *91*, 1155.
46. T. Yuan, K. Wang, R. Cai, R. Ran and Z. Shao, *J. Alloys Compd.*, **2009**, *477*, 665.
47. E. A. Souza, J. G. S. Duque, L. Kubota and C. T. Meneses, *J. Phys. Chem. Solids*, **2007**, *68*, 594.
48. M. Milde, S. Dembski, A. Osvet, M. Batentschuk, A. Winnacker and G. SEXTL, *Mater. Chem. Phys.*, **2014**, *148*, 1055.
49. S. Anusha, B. S. Anandakumar, C. D. Mohan, G. P. Nagabhushana, B. S. Priya, K. S. Rangappa and G. T. Chandrappa, *RSC Adv.*, **2014**, *4*, 52181.
50. R. N. Das, A. Bandyopadhyay and S. Bose, *J. Am. Ceram. Soc.*, **2001**, *84*, 2421.
51. K. Prabhakaran, A. Melkeri, N. M. Gokhale and S. C. Sharma, *Ceram. Int.*, **2007**, *33*, 1551.
52. L. Xu, B. Wei, W. An, Z. L□, H. Gao, Y. Zhanga and Z. Zhang, *J. Alloys Compd.*, **2008**, *460*, 524.
53. T. Huang, C. Zhao, Z. Qiu, J. Luo and Z. Hu, *Ionics*, **2017**, *23*, 139.
54. R. M. Rojas, J. M. Amarilla, L. Pascual, J. M. Rojo, D. Kovachevab and K. Petrov, *J. Power Sources*, **2006**, *160*, 529.
55. M. G. Lazarraga, L. Pascual, H. Gadjov, D. Kovacheva, K. Petrov, J. M. Amarilla, R. M. Rojas, M. A. Martin-Luengo and J. M. Rojo, *J. Mater. Chem.*, **2004**, *14*, 1640.
56. J. M. Amarilla, K. Petrov, F. Picó, G. Avdeev, J. M. Rojo and R. M. Rojas, *J. Power Sources*, **2009**, *191*, 591
57. J. M. Amarilla, R. M. Rojas and J. M. Rojo, *J. Power Sources*, **2011**, *196*, 5951.

58. M. Aklalouch, J. M. Amarilla, R. M. Rojas, I. Saadoune and J. M. Rojo, *Electrochem. Commun.*, **2010**, *12*, 548.
59. R. M. Rojas, K. Petrov, G. Avdeev, J. M. Amarilla, L. Pascual and J. M. Rojo, *J. Therm. Anal. Calorim.*, **2007**, *90*, 67.
60. L. A. Riley, S. V. Atta, A. S. Cavanagh, Y. Yan, S. M. George, P. Liu, A. C. Dillon and S.-H. Lee, *J. Power Sources*, **2011**, *196*, 3317.
61. G.-Y. Kim, S.-B. Yi, Y. J. Park and H.-G. Kim, *Mater. Res. Bull.*, **2008**, *43*, 3543.
62. L. da Conceição, A. M. Silva, N. F. P. Ribeiro and M. M. V. M. Souza, *Mater. Res. Bull.*, **2011**, *46*, 308.
63. S. Farhadi and M. Zaidi, *J. Mol. Catal. A: Chem.*, **2009**, *299*, 18.
64. T. Li, J. Shen, N. Li and M. Ye, *J. Alloys Compd.*, **2013**, *548*, 89.
65. S. Bose and Y. Wu, *J. Am. Ceram. Soc.*, **2005**, *88*, 1999.
66. M. Dahbi, S. Urbonaitė and T. Gustafsson, *J. Power Sources*, **2012**, *205*, 466.
67. P. Kaur, S. K. Chawla, S. S. Meena, S. M. Yusuf and S. B. Narang, *Ceram. Int.*, **2016**, *42*, 14475.
68. A. K. Ramasami, M. V. Reddy and G. R. Balakrishna, *Mater. Sci. Semicond. Process.*, **2015**, *40*, 194.
69. A. K. Ramasami, H. R. Naika, H. Nagabhushana, T. Ramakrishnappa, G. R. Balakrishna and G. Nagaraju, *Mater. Charact.*, **2015**, *99*, 266.
70. R. S. Yadav, J. Havlica, J. Masilko, L. Kalina, J. Wasserbauer, M. Hajdúchová, V. Enev, I. Kuřitka and Z. Kožáková, *J. Mag. Mater.*, **2015**, *394*, 439.
71. R. S. Yadav, J. Havlica, M. Hnatko, P. Šajgalík, C. Alexander, M. Palou, E. Bartoňčková, M. Boháč, F. Frajkorová, J. Masilko, M. Zmrzlý, L. Kalina, M. Hajdúchová and V. Enev, *J. Magn. Magn. Mater.*, **2015**, *378*, 190.
72. R. S. Yadav, J. Havlica, J. Masilko, L. Kalina, M. Hajdúchová, V. Enev, J. Wasserbauer, I. Kuritka and Z. Kozakova, *J. Supercond. Nov. Magn.*, **2015**, *28*, 1851.
73. R. S. Yadav, J. Havlica, I. Kuritka, Z. Kozakova, M. Palou, E. Bartoňčková, M. Boháč, F. Frajkorova, J. Masilko, L. Kalina, M. Hajdúchová, V. Enev and J. Wasserbauer, *J. Supercond. Nov. Magn.*, **2015**, *28*, 2097.
74. A. Tirsoaga, D. Visinescu, B. Jurca, A. Ianculescu and O. Carp, *J. Nanopart. Res.*, **2011**, *13*, 6397.
75. D. Visinescu, F. Papa, A. C. Ianculescu, I. Balint and O. Carp, *J. Nanopart. Res.*, **2013**, *15*, 1456.
76. K. Agilandeswari and A. Ruban Kumar, *J. Mag. Mater.*, **2014**, *364*, 117.
77. S. Valanarasu and R. Chandramohan, *Cryst. Res. Technol.*, **2010**, *45*, 835.
78. D. Gangulibabu, D. Bhuvaneshwari and N. Kalaiselvi, *J. Solid State Electrochem.*, **2013**, *17*, 9.
79. S. Liu, D. Tao and L. Zhang, *Powder Technol.*, **2012**, *217*, 502.
80. S. M. Maliyekkal, A. K. R. Antony and T. Pradeep, *Sci. Total Env.*, **2010**, *408*, 2273.
81. A. Kumar, A. S. Mukasyan and E. E. Wolf, *Appl. Catal. Gen.*, **2010**, *372*, 175.
82. T. Yuan, K. Wang, R. Cai, R. Ran and Z. P. Shao, *J. Alloys Compd.*, **2009**, *477*, 665.
83. T. Yuan, R. Cai, P. Gu and Z. Shao, *J. Power Sources*, **2010**, *195*, 2883.
84. T. Yuan, R. Cai, K. Wang, R. Ran, S. M. Liu and Z. P. Shao, *Ceram. Int.*, **2009**, *35*, 1757.
85. R. Cai, X. Yu, X. Liu and Z. Shao, *J. Power Sources*, **2010**, *195*, 8244.
86. K. Wang, R. Cai, T. Yuan, X. Yu, R. Ran and Z. P. Shao, *Electrochim. Acta*, **2009**, *54*, 2861.
87. T. Yuan, X. Yu, R. Cai, Y. Zhou and Z. Shao, *J. Power Sources*, **2010**, *195*, 4997.
88. Y. Cai, H. Fan, M. Xu and Q. Li, *Colloids Surf., A*, **2013**, *436*, 787.
89. D. Zhang, X. Pu, Y. Gao, C. Su, H. Li, H. Li and W. Hang, *Mater. Lett.*, **2013**, *113*, 179.
90. T. Wang, S.-H. Song, T. Xu and M. Wang, *J. Sol-Gel Sci. Technol.*, **2016**, *80*, 675.
91. S. Mandizadeh, M. Sadri and M. Salavati-Niasari, *Int. J. Hydrogen Energy*, **2017**, *42*, 12320.
92. F. Ansari, A. Sobhani and M. Salavati-Niasari, *J. Mag. Mater.*, **2016**, *401*, 362.
93. F. Ansari, A. Sobhani and M. Salavati-Niasari, *RSC Adv.*, **2014**, *4*, 63946.
94. S. Mandizadeh, F. Soofivand and M. Salavati-Niasari, *Adv. Powder Technol.*, **2015**, *26*, 1348.
95. A. Salehabadi, M. Salavati-Niasari and F. Sarrami and A. Karton, *Renew. Energ.*, **2017**, *114*, 1419.
96. R. Ianoş, A. Tăculescu, C. Păcurariu and I. Lazău, *J. Am. Ceram. Soc.*, **2012**, *95*, 1.
97. B. Wang, L. Zeng, W. Huang, F. S. Melkonyan, W. C. Sheets, L. Chi, M. J. Bedzyk, T. J. Marks and A. Facchetti, *J. Am. Chem. Soc.*, **2016**, *138*, 7067.
98. A. Salehabadi, M. Salavati-Niasari and T. Gholami, *J. Clean. Prod.*, **2018**, *171*, 1.
99. S. Khademolhoseini and R. Talebi, *J. Mater. Sci: Mater. Electron.*, **2016**, *27*, 2938.
100. M. Rahimi-Nasrabadi, M. Behpour, A. Sobhani-Nasab and M.R. Jeddy, *J. Mater. Sci: Mater. Electron.*, **2016**, *27*, 11691.
101. R. S. Yadav, I. Kuřitka, J. Vilcakova, J. Havlica, J. Masilko, L. Kalina, J. Tkacz, J. Švec, V. Enev, M. Hajdúchová, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **2017**, *8*, 045002.