



GREEN SYNTHETIC STRATEGIES OF OXIDE MATERIALS: POLYSACCHARIDES-ASSISTED SYNTHESIS.

I. POLYSACCHARIDES ROLES IN METAL OXIDES SYNTHESIS

Oana CARP,^{a*} Diana VISINESCU,^a Greta PATRINOIU,^a Alina TIRSOAGA,^{a,b}
Carmen PARASCHIV^c and Madalina TUDOSE^a

^aRoumanian Academy, Institute of Physical Chemistry "Ilie Murgulescu", Coordination and Supramolecular Chemistry Laboratory, Splaiul Independenței 202, 060021 Bucharest, Roumania

^bUniversity of Bucharest, Faculty of Chemistry, Physical Chemistry Department, Bd. Elisabeta 4-12, 030018 Bucharest, Roumania

^cNational Institute for Research and Development in Electrical Engineering, ICPE-CA, Advanced Research, Splaiul Unirii 313, 030138 Bucharest, Roumania

Received April 30, 2010

Natural polysaccharides have received more and more attention in the field of material synthesis, particularly in metal oxides based materials. Polysaccharides are valuable bioresources which combine their functional properties with eco-friendly features, characteristics that natural fit in various green chemistry approaches. Taking the advantage provided by their diversity regarding the chemical functionality and structural specific features, several polysaccharides-assisted strategies of materials were developed recently. The paper here, the first of a series that reviews the involvement of polysaccharides in oxide materials (simple, mixed and composites) synthesis, presents some generalities of the polysaccharides as well as their main roles (stabilizing, template, assembling, functionalizing and combustible agent) played in nanomaterials synthesis.

INTRODUCTION

Polysaccharides, known also as glycans, represent a large family of natural carbohydrates which include both compounds assembled from glycosidically linked sugar residues and also molecules that contain polymeric saccharide structures bonded to amino acids, peptides, proteins and lipids. Polysaccharides are special raw materials being very abundant (called also biopolymers), widely available in many countries, inexpensive and renewable. They have also biological and chemical properties such as non-toxicity, biocompatibility, biodegradability, polyfunctionality, hydrophilicity, high chemical reactivity, chirality, chelation and adsorption abilities. Their benign water-solubility is a crucial property in "green chemistry" methods and opens large possibilities in aqueous solution routes for the synthesis of nanomaterials.

The involvement of polysaccharides in metal oxide synthesis is a new, interesting and promising application in materials science. The solution and low-temperature procedures (co-precipitation, sol-gel, metal-organic precursors or combustion methods) developed especially in the last decades, have proved to be suitable routes to achieve nanosizes (1-100 nm), specific shapes and surfaces for metal oxides particles. The multiple effects of polysaccharides in wet and/or low-temperature methods (as assistant in heterogeneous nucleation, as complexing agent, to control the growth step or as surface capping agent, to avoid nanoparticles agglomeration) have recommended them as appealing additives in chemistry of materials.

Fusing the above-mentioned important topics, new advanced oxide nanomaterials could be pre-designed using polysaccharides-assisted green synthetic routes. Indeed, along with their abundance, the combination between the eco

* Corresponding authors: carp@acodarom.ro

friendly attributes with their chemical features transform the polysaccharides into a promising source of raw material for green nanochemistry of materials with a wide range of applications. Polysaccharides are active ingredients in non-polluting strategies and play a double role: as a tool to complete and control material synthesis and as a component of material itself, alone or as a part of a composite.

The aim of this series of papers is to review some of the most important polysaccharide-directed synthesis of oxide nanoparticles. The paper here, the first in a series, presents the key features of polysaccharides, a survey of their potential applications and includes also an analysis of the main effects of these carbohydrates in oxide materials synthesis, namely stabilizer, template, assembler, functionalizing and combustible agent. The following papers of the series will examine the potential applications of each particular polysaccharide in oxides synthesis, highlighting the advantages of the developed approaches, but also mark the unexplored areas of this new green chemistry topic.

POLYSACCHARIDES IN OUR WORLD

Every year the nature produces 175 billion tons of biomass materials, three quarters from the total amount being represented by carbohydrates. Most of the natural carbohydrate materials occurs in the form of polysaccharides ($\approx 90\%$ from carbohydrate) but only a very small percentage is currently used by man.¹ The polysaccharides origin is varied, which explains the richness of their structures and corresponding properties: from plants (*e.g.* starch, cellulose, pectin, guar gum), algal (*e.g.* alginate agar, carrageenans), microbial (*e.g.* dextran, xanthan gum), and animal (*e.g.* chitosan, chondroitin).²⁻⁴

They are essentially natural macromolecules build up from monosaccharides units (200 and 3000 units) connected through glycosidic bonds. Each sugar residue carries multiple hydroxyl groups, able to act as acceptor of glycosyl substituents, leading to branched or mixed linear-branched polysaccharides structures. The most common constituent of polysaccharides is D-glucose, but D-fructose, D-galactose, L-galactose, D-mannose, L-arabinose, and D-xylose are also frequent units. Some monosaccharide derivatives found in polysaccharides include the amino sugars (D-glucosamine and D-galactosamine) as well as

amino acids (*N*-acetylneuraminic acid and *N*-acetylmuramic acid), and simple sugar acids (glucuronic and iduronic acids). Homopolysaccharides are often named after the constituent sugar monomer, for example glucose-containing homopolysaccharides are called glucans, while mannose homopolysaccharides are known as mannans.

Polysaccharides carries a large number of reactive groups, have a wide range of molecular weight, with different chemical composition, resulting in a variety of structures and functionalities, consistent with their corresponding roles (mainly structural and energy storage) in biological systems.

Several characteristics differentiate the polysaccharides: the nature of the constituent monosaccharides building-blocks, the length of the polymeric chain and the amount of the chain branching. The large variety of polysaccharides makes very difficult a classification of these biopolymers. One criterion is their functionality in biological systems: storage polysaccharides (*e.g.* starch in plants) and structural polysaccharides (*e.g.* cellulose, which is the most abundant biopolymer in the world).^{5,6} The two polysaccharides categories have similar compositions, but their properties are very distinct and could be related with their structural differences, for example the mixed linear-branched and flexible structure of starch *versus* the linear and rigid skeleton of cellulose.

Polysaccharides are divided into polyelectrolytes and nonpolyelectrolytes, the former class being further parted into positively (chitosan) and negatively charged polysaccharides (*e.g.* alginate, heparin, hyaluronic acid, pectin). From rheological standpoint, some of the polysaccharides form gels as the temperature is rising (starch), or under very mild conditions upon contact with cations (alginate and carrageenan) and anions (chitosan).

Polysaccharides are used not only for materials fabrication (excepting cellulose), but also in water-soluble polymers domain, where they act as thickening, gelling emulsifying, hydrating and suspending polymers. The biocompatible and non-toxic polysaccharide-based compounds are a class of materials with potential applications in medicine, pharmacy, biology, agriculture, on waste water and water treatment. For example, polysaccharides-based materials adsorbents have demonstrated exceptional abilities for decontamination of effluents (removal of dyes and

metal ions pollutants) for separation processes (recovery of valuable metals), and also for analytical purposes (solid phase extraction), offering promising benefits for commercial purpose in the future.⁸

Polysaccharides biomaterials based on alginate, dextran and chitosan⁹ are good candidates for tissue engineering, drug vehicles, controlled release of drugs, cell culture, cancerous cell treatment, separation of biomolecules, immobilization of enzymes.¹⁰

The most widely used oxide-polysaccharides materials are the magnetic hydrogels, as magnetite (Fe_3O_4) or maghemite ($\gamma\text{-Fe}_2\text{O}_3$)-polysaccharide composites. These hybrid materials are biocompatible, with quick response and sensitivity to an external stimulus, for example an applied magnetic field,^{7f,g} and are very useful in many biomedical applications, several commercial products (monocrystalline aggregates, *i.e.* Endorem[®], or polycrystalline ones Sinerem[®], etc) being already available.

THE ROLES OF POLYSACCHARIDES IN METAL OXIDES SYNTHESIS

The biocompatible and non-toxic polysaccharide-based materials represent a special class of which characteristics may have potential applications in medicine, pharmacy, biology, agriculture, on waste water and water treatment. Polysaccharides biomaterials were used specially for tissue engineering, drug vehicles, controlled release of drugs,^{10a} cell culture, cancerous cell treatment, separation of biomolecules or immobilization of enzymes.^{7f, 8b, 10b}

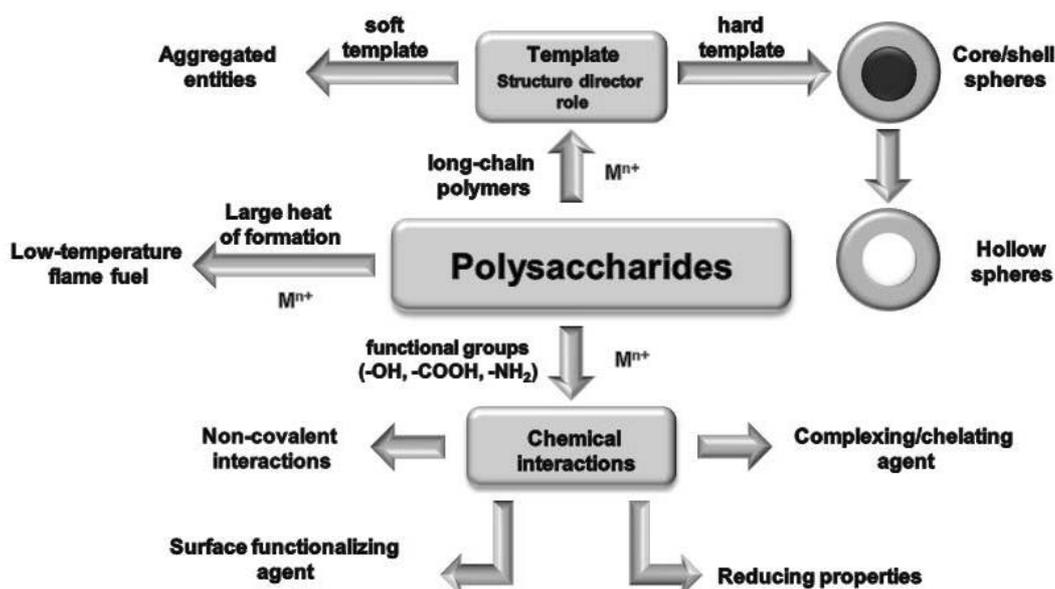
The metal-oxides chemistry has encountered the ideal non-polluting organic additives in polysaccharides. Along with their already known biocompatibility, the polymeric structure of polysaccharides is suitable in solution chemical procedures^{11,12} to achieve and tune the size, morphology and structure of the oxides or oxides-composites nanoparticles: (*i*) stabilizers to control particle size, preventing the spontaneous agglomeration of nanoparticles, (*ii*) templates, directing particles structure and (*iii*) as surface functionalizing agents of the metal oxides, allowing their covalent attachment and self-assembly on surfaces, an indispensable property for loading desired biomolecules (for functional nanomaterials used in different pharmaceutical and biomedical products¹³).

The primary association between a polysaccharide and a metal ion affords usually an intermediary precursor which, depending of several factors (the chemical composition and structure of the polysaccharide, the nature of the metal cation and the solution environment such as pH, raw materials concentration, and the presence of a auxiliary ligand) could be: a colloid, a gel or a mixture of raw materials.

Polysaccharides interference in oxides synthesis takes place in various stages of the synthesis. Scheme 1 resumes some of the remarkable effects of polysaccharides in material synthesis. The organic additive, in our case the polysaccharide, dispersed in the liquid media, behaves like an organic matrix, binding many metal cations, through their functional groups (hydroxylic, carboxylic or amino groups). The initial binding of the metal ions to the polysaccharide determines a homogenous dispersion of the cation in well confined spaces. After the change of the initial reaction conditions, in the presence of a precipitation agent, these binding positions provide preferred nucleation and growth sites for the hydrolyzed M^{n+} -containing particles, due to the high local suprasaturation of metal cations. The conversion oxide precursor \rightarrow oxide needs heating treatments. Since, some of the polysaccharide are decomposed at temperature lower than 300°C ,¹⁴ the combustion of their organic scaffolds can be expected to form dispersed oxides only in conditions in which the sintering is not favored. The homogeneously dispersion of the cations in the polysaccharide and the low temperature of thermal degradation of the organic parts shifts the balance between the nucleation and growth towards the formation of a larger number of smaller crystals of oxide material.

The metal cation binding, both in the incipient stages and after oxide/hydroxide formation, is complicated because involves the presence of different physico-chemical interactions that can act individually or simultaneously (at least some of them)¹⁴ namely coordination/chelation, ion-exchange, electrostatic interactions, acid-base interactions, hydrogen bonds, hydrophobic interactions or physical adsorption.

During the precipitation/maturation stages, the polysaccharides act also as “nanoreactor” templating and stabilizing nanoparticles: the heterogeneous nucleation and subsequent controlled growth occurs in these well-defined sites. A surface coating/functionalization is additionally obtained.



Scheme 1 – Effects of polysaccharides in chemistry of materials.

Polysaccharides may function either as hard or soft template to form 1D and/or hierarchical structures. It is known that the soft templates (long chain polymers¹⁵) will self-assemble, under certain kinetic conditions, into well-defined aggregating entities which restrict and direct the growth of the guest molecules. The growth of these molecules has led to 1D nanostructures, and if these are metastable, they can further organize into hierarchical structures in liquid media.^{16,17} A beautiful example is the nanofabrication of functional ZnO architectures in the presence of sodium alginate.¹⁸

A special role is played by the polysaccharides as ‘hard’ templates on the synthesis of core/shell and hollow nanostructures.¹⁹ The synthetic strategies are straightforward, involving two/three main steps: (i) the preparation of the original template by dehydrating the polysaccharide under hydrothermal conditions; (ii) the deposition of the target shell material onto the surface of the template with the formation of the core-shell composite either by direct surface reactions or by controlled precipitation²⁰ and (iii) the removal of the original template (following calcinations treatments or selective etching) with formation of the hollow structures.

The great advantage of the polysaccharide template route is the formation of functional layers with integral and uniform surface which assures the homogeneity of the shell without the surface modification. The carbonaceous template determines the shape and the structure of the final products. On the other hand, the characteristics of the polysaccharide template could be tuned controlling

the experimental conditions (concentration of the starting material, reaction time and temperature²⁰).

The polysaccharides-assisted strategies are also based on the reducing abilities of these biopolymers, which arise mainly from their high content of hydroxyl groups: as the temperature is rising, the oxidation of C-OH groups into the carboxylic ones may occur simultaneously with the reducing of M^{n+} cations to M^{m+}/M^0 ($n > m$).²¹ This property was used in magnetite, Fe_3O_4 (starting only from Fe^{3+} metal salts) and metals synthesis.²²

Another important feature of the polysaccharides, assembled from glucose repeating units, is the large heat of formation, a characteristic which is very useful in combustion reactions. It is well-known that the flame temperature in combustion method is a critical parameter in reaching a certain morphology, crystalline phase and other specific properties of the final oxide products. The mixture of fuels (high flame temperature fuels, as urea or hydrazine, with low flame temperature fuels) is highly recommended to achieve the control of this parameter and, as consequence of the size distribution, surface area and agglomeration of the particles in the final product.²³ Polysaccharides biopolymers could successfully replace a percent of the classic fuels (urea, for example) the result being a reduced exothermicity and thus, the flame temperature of the combustion reaction, while almost an equal number of mole gases are released.

The multiple and various roles of polysaccharides in the controlled synthesis of oxide materials have unveiled an unknown and spectacular eco-friendly

chemistry, of which further development is crucial in materials sciences.

CONCLUSIONS

The work here gathers some general considerations regarding the polysaccharides and also several illustrative examples of the polysaccharides interferences in different synthesis of oxide-based materials (or related composite materials), highlighting the great versatility of carbohydrates in the classical soft chemistry approaches [(co)-precipitation, sol-gel, combustion or hydrothermal synthesis]: coating, protecting, (bio)-template with structure-directing role, complexing, assembling and fuel agent.

The following papers of the series will examine, one by one, several important natural polysaccharides, namely starch, dextran and cellulose along with some recent published data regarding their specific behaviours in several well-known wet and low-temperature chemistry approaches of nanosized metal oxide materials.

REFERENCES

- J. Thoen and R. Busch, in "Biorefineries-industrial Processes and Products" Eds. B. Kamm, P. R. Gruber, K. Kamm, Wiley-VCH GmbH & Co KGaA, 2006.
- V. R. Sinha and R. Kumria, *Int. J. Pharm.*, **2001**, *224*, 19-38.
- M. Rinaudo, R. Auzely and K. Mazeau "Polysaccharides and carbohydrate polymers. In: Encyclopedia of Polymer Science and Technology", John Wiley, New York, 2004, vol. 11, p. 200-261.
- R. Geremia and M. Rinaudo "Biosynthesis, structure, and physical properties of some bacterial polysaccharides". In S. Dimitriu (Ed.) "Polysaccharides: Structural Diversity and Functional Versatility", Marcel Dekker, New York, 2005, vol. 15, p. 411-430.
- M. N. Anglès and A. Dufresne, *Macromolecules*, **2001**, *34*, 2921-2931.
- F. Cima, L. Ballarin, G. Bressa, G. Martinucci and P. Burighel, *Ecotoxicol. Environ. Safety*, **1996**, *35*, 174-182.
- (a) A. T. Paulino, J. I. Simionato, J. C. Garcia and J. Nozaki, *Carbohydr. Polym.*, **2006**, *64*, 98-103; (b) M. R. Guilherme, A. V. Reis, A. T. Paulino, A. R. Fajardo, E. C. Muniz and E. B. Tambourgi, *J. Appl. Polym. Sci.*, **2007**, *105*, 2903-2909; (c) A. V. Reis, M. R. Guilherme, O. A. Cavalcante, A. F. Rubira and E. C. Muniz, *Polymer*, **2006**, *47*, 2023-2029; (d) M. R. Guilherme, R. Silva, E. M. Giroto, A. F. Rubira and E. C. Muniz, *Polymer*, **2003**, *44*, 4213-4219; (e) X. Liu, V. Novosad, E. A. Rozhkova, H. Chen, V. Yefremenko, J. Pearson, M. Torno, S. D. Bader and A. J. Rosengart, *IEEE Trans. Magn.*, **2007**, *43*, 2462-2464; (f) N. Kato, Y. Takizawa and F. J. Takahashi, *J. Intelligent Mater. Syst. Struct.*, **1997**, *8*, 588-595; (g) D. Paneva, O. Stoilova, N. Manolova and I. Rashkov, *E-Polymers*, **2004**, *060*, 1-11.
- (a) G. Crini, *Prog. Polym. Sci.*, **2005**, *30*, 38-70; (b) A. Gupta, V. S. Chauhan and N. Sankaramakrishnan, *Water Res.*, **2009**, *43*, 3862-3870.
- (a) M. Rinaudo, *Polym. Int.*, **2008**, *57*, 397-430; (b) G. Gomez d'Ayala, M. Malinconico and P. Laurienzo, *Molecules*, **2008**, *13*, 2069-2106.
- (a) Z. Liu, Y. Jiao, Y. Wang, C. Zhou and Z. Zhang, *Adv. Drug Deliv. Rev.*, **2008**, *60*, 1650-1662; (b) S. Dumitriu, "Polysaccharides as biomaterials", in "Polymeric Biomaterials", ed. by S. Dumitriu, Marcel Dekker, New York, 2002, p. 1-61.
- M. Rinaudo, *Macromol. Symp.*, **2006**, *245-246*, 549.
- (a) D. Rabelo, E. C. D. Lima, A. C. Reis, W. C. Nunes, M. A. Novak, V. K. Garg, A. C. Oliveira and P. C. Morais, *Nano. Lett.*, **2001**, *1*, 105-108; (b) S. Qu, H. Yang, D. Ren, S. Kan, G. Zou, D. Li and M. Li, *J. Colloid Interf. Sci.*, **1999**, *215*, 190-192; (c) S. Si, A. Kotal, T. K. Mandal, S. Giri, H. Nakamura and T. Kohara, *Chem. Mater.*, **2004**, *16*, 3489-3496; (d) A. Ditsch, P. E. Laibinis, D. I. C. Wang and T. A. Hatton, *Langmuir* **2005**, *21*, 6006-6018; (e) T.-Y. Liu, S.-H. Hu, T.-Y. Liu, D.-M. Liu and S. -Y. Chen, *Langmuir*, **2006**, *22*, 5974-5978; (f) T. M. Cocker, C. J. Fee and R. A. Evans, *Biotechnol. Bioeng.*, **1997**, *53*, 79-87; (g) H. Lin, Y. Watanabe, M. Kimura, K. Hanabusa and H. Shirai, *J. Appl. Polym. Sci.*, **2003**, *87*, 1239-1247; (h) M. Breulmann, H. Colfen, H.-P. Hentze, M. Antonietti, D. Walsh and S. Mann, *Adv. Mater.*, **1998**, *10*, 237-241.
- (a) H. Honda, A. Kawaba, M. Shinkai and T. J. Kobayashi, *Ferment. Bioeng.*, **1998**, *86*, 191-196; (b) A. K. Gupta and M. Gupta, *Biomaterials*, **2005**, *26*, 3995-4021; (c) D. K. Kim, W. Voit, W. Zapka, B. Bjelke, M. Muhammed and K. V. Rao, *Mat. Res. Soc. Symp. Proc.* **2002**, *676*, Y.8.32.1-Y.8.32.6.
- (a) K. S. Khairou, *J. Therm. Anal. Calorim.*, **2002**, *69*, 583-588; (b) M. J. Zhouriaan and F. Schokrolai, *Polym. Test.*, **2004**, *23*, 575-579.
- (a) M. N. V. Ravi Kumar, *React. Funct. Polym.*, **2000**, *46*, 1-27; (b) S. T. Lee, F. L. Mi, Y. J. Shen and S. S. Shyu, *Polymer*, **2001**, *42*, 1879-1882; (c) J. H. Fendler, *Chem. Rev.*, **1987**, *87*, 877-899.
- (a) H. Wang, C. Xie, D. Zeng and Z. Yang, *J. Colloid Interf. Sci.*, **2006**, *297*, 570-577.
- (a) L. Dong, Y. C. Liu, Y. H. Tong, Z. Y. Xiao, J. Y. Zhang, Y. M. Lu, D. Z. Shen and X. W. Fan, *J. Colloid Interf. Sci.*, **2005**, *283*, 380-384; (b) E. W. Seelig, B. Tang, A. Yamilov, H. Cao and R. P. H. Chang, *Mater. Chem. Phys.*, **2003**, *80*, 257-263; (c) A. P. A. Oliveira, J.-F. Hochepped, F. Grillon and M.-H. Berger, *Chem. Mater.*, **2003**, *15*, 3202-3207; (d) V. Privman, D. V. Goia, J. Park and E. Matijevic, *J. Colloid Interf. Sci.*, **1999**, *213*, 36-45; (e) J. Park, V. Privman and E. Matijevic, *J. Phys. Chem. B*, **2001**, *105*, 11630-11635.
- S. Gao, H. Zhang, X. Wang, R. Deng, D. Sun and G. Zheng, *J. Phys. Chem. B*, **2006**, *110*, 15847-15852.
- F. Caruso, R. A. Caruso and H. Mohwald, *Science*, **1998**, *282*, 1111-1114.
- W. Wang and Z. Zhang, *J. Disp. Sci. Technol.*, **2007**, *28*, 557-561.
- S. Gao, S. Zhang, K. Jiang, S. Yang, W. Lu, *Curr. Nanosci.*, **2008**, *4*, 145-150.
- (a) M. S. Ellid, Y. S. Murayed, M. S. Zoto, S. Musić and S. Popović, *J. Radioanal. Nucl. Chem.*, **2003**, *258*, 299-305; (b) P. Raveendran, J. Fu, and S. L. Wallen, *J. Am. Chem. Soc.*, **2003**, *125*, 13940-13941.
- (a) S. T. Aruna and K. S. Rajam, *Mater. Res. Bull.*, **2004**, *39*, 157-167; (b) K. Tahmasebi and M. H. Paydar, *Mat. Sci. Phys.*, **2008**, *109*, 156-163.

