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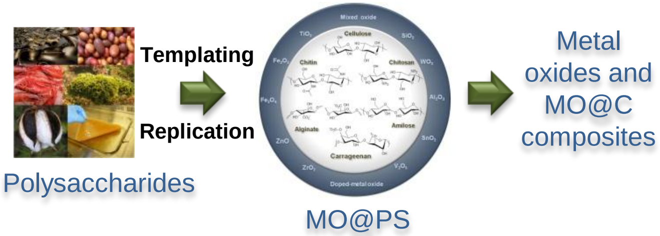

Polysaccharides are ideal templates for greening the synthesis of metal oxides by biotemplating and bio-replication

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Metal Oxides and Polysaccharides
An efficient hybrid association for material chemistry

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B. Boury , S. Plumejeau

Summary

Metal oxides and polysaccharides in nature and in laboratories; limits and aims of the review
PART 1 : Different ways to associate metal oxide and polysaccharides
PART 2 : Controlled growth of metal oxide nanoparticles throughout polysaccharide fibers
PART 3 : Biotemplating and bio-replication at the micro- to nanoscale
PART 4 : Chemical transformation of polysaccharide fibers through mineralisation
Perspectives and concluding remarks

Biopolymers and inorganic minerals are often associated in nature, and living organisms benefit from these materials with a sophisticated and hierarchical architecture. Inspired by nature, chemists try to extend these combinations by associating natural polymers with inorganic materials that do not occur naturally in living organisms.

In this review, we propose to focus only on research conducted on the association between polysaccharides and metal oxides. Over the last 10-15 years, substantial research has been focused on finding ways to combine these two types of material, with the goal of mastering the morphology, porosity, composition and structure of the hybrid materials (metal oxide@polysaccharide) or pure metal oxides obtained after polysaccharide elimination. There are many possibilities for interactions between metal cations and the chemical functionality of the carbohydrate, thus allowing different approaches, as the structure and functionality of the polysaccharide are of major importance.

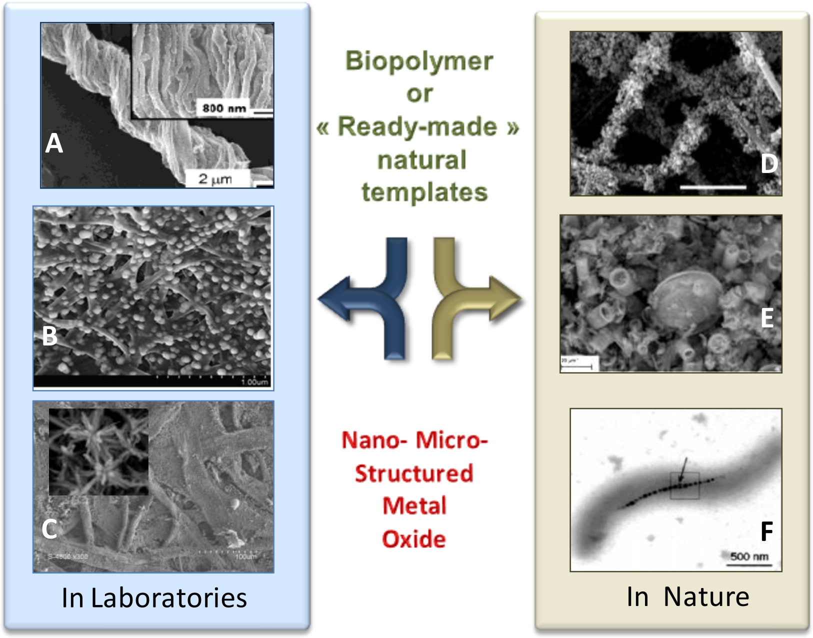
Because of the sophisticated architecture that can be achieved on one hand, and the potential sustainable use of these biopolymers (a green approach) on the other, these material elaboration processes offer a unique way for chemists to prepare functional hybrid materials and metal oxides (e.g. luminescent materials, catalysts, absorbent materials, magnetic composites, anode and photocatalyst materials).

To be as comprehensive as possible, this review is limited to some natural polysaccharides. After contextualisation, we successively consider metal oxide growth control through biotemplating, the replication of raw and refined polysaccharide templates, and ending with a discussion of the most recent approaches like mineralisation.

Glossary

PS: polysaccharide; MO: metal oxide; MMO: mixed metal oxide; NP: nanoparticle; TTIP: $Ti(O^iPr)_4$; TTB :$Ti(OBu)_4$; MM&SC : mastering morphology and size control; SSA: specific surface area; PVD : plasma vapour deposition; ALD : atomic layer deposition. For mixed material like composite or core shell materials, the A@B is used and mean that A is quantitatively the minor phase and B the major phase, example TiO_2@C is mostly carbon covered or mixed with TiO_2

Fig 1. Exemple of PS@MOsynthesied in laboratories (A, B, C) and found in nature (D, E, F).



A : Titania replica of a natural cotton fibers by sol-gel impregnation (from J. Huang et al.[1])

B : Dispersion of ZnO particles along a bacterial cellulose fibers (from S. Chen et al.[2])

C : TiO_2 replica by mineralisation of filter paper with $TiCl_4$ in anhydrous conditions (from Nair et al.[3])

D : Uranium oxide nanoparticles on fungal hyphae (from Fomina et al.[4])

E : Natural diatomite from a Borownica deposit in Poland (from Sprynskyy et al.[5])

F : Magnetite nanoparticles in Magnetospirillum magnetotacticum (from R. E. Dunin-Borkowski et al.[6])

Introduction

Biopolymers and metal oxides. Living organisms depend on abiotic factors such as the composition of inorganic solids with which they are in contact, and in turn they contribute to transformation.[7] At the same time, very early in evolution, inorganic materials were incorporated into structures of living beings such as exoskeletons of diatomaceous organisms, shells or coral,[8] endoskeletons of sponges, fishes and animals,[9] macro- or nanoparticles (otoliths of fish and mammary, magnetosomes of magnetotactic bacteria).[4,6,10] However, besides what we learn from nature, chemists can now consider new types of mineral/biomaterial associations with objectives that differ completely from those found in living organisms**.**

A limited number of minerals are used by living organism (mainly silicon oxide, carbonate, and some phosphates, oxalates and sulfides), whereas the chemist takes advantage of every opportunity offered by the elements of the periodic table. Contemporary chemists also strive to use all sources of renewable materials and the ultimate goals of chemists when using materials may differ completely from the natural functions of the same materials. Therefore, besides the substantial amount of research focused on the natural interaction between mineral and living processes (upper part of Figure 2),[8,9,11-14] field of researches with the aim of producing new materials required for energy, health and environmental applications are growing (Figure 1). In nature, metal oxides are generally not closely associated with polysaccharides but more with proteins, with the latter currently being studied for their involvement in the nucleation and growth of inorganic materials in living organisms.[11,15-18] MO@PS therefore represents a new field of research.

Context and objectives of the review. Plant fossilisation studies and the characterisation of cellulose structures were probably the first investigations related to this field, followed quickly after by the use of soluble polysaccharides in the sol-gel process and the templating of natural fibers and crystals. The interest in MO@PS is the result of knowledge and processes concerning polysaccharides and also the demand for metal oxides, mixed- or doped- metal oxides and even MO@C composites.

MO are highly demanded for industrial and high-tech applications, their properties being substantially altered by the porosity, crystallinity, morphology, doping, particle size and, last but not least, their arrangement in hierarchical structures from the macro- to the nano- and micro-scale (for example in the case of TiO_2,[19,20] and other oxides in electrochemical devices[21] or sensors[22]).

On the other hand, polysaccharides are hugely diversified in terms of structure and functionality, and those not requiring purification are among the "greenest" possible material. Their shaping at the nanoscale has also definitively opened a new area with the production of nanocrystals, nano-rods, nano-platelet~~s~~ nano-fibers or aerogels of various biopolymers.[23-28] Recently, a new type of polysaccharide was introduced in this field, i.e. exopolysaccharides (EPS) produced by microalgae and cyanobacteria for their phototaxi, has been used for photo-patterning and mineral replica.[29,30]

Therefore, at the crossroads between these two material science domains (MO and PSs) there are different fields of research: enhancing the conversion of PS into renewable fuels and chemicals, transforming PS into functional carbons, using them as modifiers of the MO surface, combining them into nanocomposites, etc.

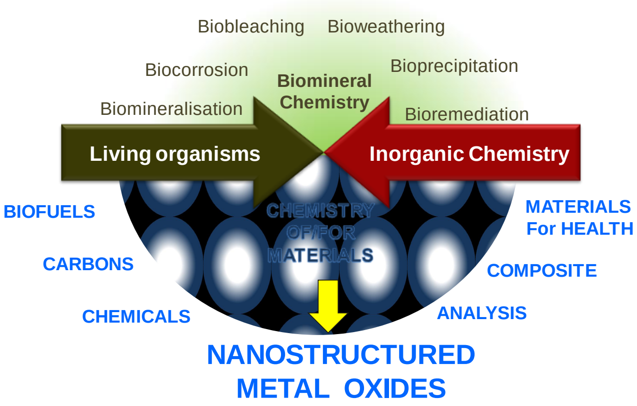


Fig. 2 Fields of researches involving combinations of different PS and many different metal oxides

Here we assess the usefulness of PS in the MO preparation process to control MO synthesis, in terms of size, morphology, porosity, composition, etc. The interplay between MO and PS is at a different level: in controlling the chemistry leading to MO formation, in MO molding (morphology, size, porosity, etc.), but also in the chemistry that is involved upon PS elimination or transformation.

Limits of the review. We will not consider the following issues, for which the reader is directed to possible references (among others) and that are closely connected to the topic of this review: micro- and nano-casting of wood[31-37] or textiles[38] by metal oxide powders, impregnation of wood as precursors of SiC or SiOC,[39] PS-to-carbon synthesis,[40-45] PS-to-biofuel and chemicals synthesis,[46] preparations of catalysts,[47] PS in electro-conductive composites,[48] MO@PS as material for biotechnology for enzyme support,[49] bacteria encapsulation [50-53]) coating of MO nanoparticles by PS or modified-PS (for diagnosis, therapy, catalysis and remediation).[54-56] Interested readers are also referred to the literature on magnetic nanoparticles,[57,58] or metal and metal hydroxides.[27,59-61]

To be comprehensive as much as possible, we limited this minireview to a few natural polysaccharides like cellulose, chitosan, chitin, amylose (starch), alginate, carrageenan. Related publications with a broader scope are also recommended.[24,62-68]

Part 1: The different ways to associate metal oxides and polysaccharides

In nature, microorganisms can form deposits of nanoparticles of different inorganic compounds, and in some cases of metal oxides or hydroxides of metals such as iron, manganese or uranium, these processes are important for biogeochemical cycles of metals throughout the environment.[4] Mineralisation processes generally involve proteins, but some of them are glycosylated.[69,70]

In laboratories, among the earliest work dealing with associations of cellulose and inorganic materials, one can mention, back in the 1940th, the infiltration of cellulose with inorganic salts to produce a "metallic shadow casting" to improve the contrast of the cellulose in the early age of microscopy.[71,72] The formation of inorganic phases was not pursued at that time. Later, different researchers, focusing on assessing the fossilisation process of wood and algae, performed infiltration and impregnation of these materials to produce their silification.[73] Amongst early work on the formation of metal oxides with polysaccharide one can mention the patent of Union Carbide[74,75] by Eliot and Huggins on $NaAlO_2$-Al_2O_3.[76]

Otherwise, progress in the sol-gel "Chimie douce" and periodic mesoporous silica fields[77,78] have also probably generated ideas. Before the use of glucose as a template in the synthesis of mesoporous silica,[79,80] polysaccharides were first considered as a template that can control the growth of functional MO particles at the nanoscale, as an alternative to the Pechini method: photocatalyst TiO_2[81,82] and magnetic Fe_2O_3 nanoparticles prepared with cellulose or alginate,[83] superconduteur YBaCuO prepared with cellulose[84,85] or luminescent $LaMnO_3$ prepared with starch.[60] Sol-gel remains the most suited process to take advantage of PS, but alternative approaches (PVD, ALD, mineralisation) recently paved the way for alternative formation of MO@PS hybrids and templated metal oxides (see Part C).

Sol-gel is indeed well suited for coating complex shapes, but the use of PSs in sol-gel processes goes far beyond this application. It quickly became evident that PSs has several advantages during the sol-gel process: (a) they are compatible with many green chemistry principles, (b) PS provide flexible scaffolds/porogens for monolithic nanocomposites and can be easily removed, (c) their hydroxyl groups are reactive in promoting/accelerating polycondensation, or in sequestering cations $[M^{n+}]$ or hydroxylated cations $[M(OH)^{m+}]$ that can undergo nucleation/growth processes, somewhat similarly to citric acid in Pechini's process, (d) entanglement of PS fibers defines a macro- to nano-cavity that can stabilize nascent MOs and control their growth, (e) many simple PS characteristics

(MW, solubility, functionality, concentration, etc.) can induce different MO structures and properties.

Four main different approaches can be tentatively classified as follows:

1/ the use of dissolved PS in homogeneous solution or as hydrogels into which a metal oxide precursor is introduced. Therefore, the polysaccharide is expected to control the chemistry and growth of the nanoparticles (situation A in Figure 3)

2/ PSs are used as an insoluble template onto which a more or less dense layer of metal oxides is formed/deposited. Here the PS fibres are considered as a mold for the preparation of hollow or porous oxide structures (situation B in Figure 3)

3/ the reaction and therefore the chemical transformation of the fibres with a metal-containing reagent. Contrary to the two previous approaches, here the polysaccharide is a template and an O-source for oxide formation (situation C in Figure 3)

4/ the impregnation of polysaccharide fibers by ready-made MO nanoparticles as a filler (situation D in Figure 3). This is frequently carried out for the treatment of textiles, packaging, papers, etc. This is a whole world in itself and is beyond the scope of this review (see, for exemple, pre-formed silicalite nanoparticles mixed in starch gel,[86,87] or preformed luminescent particles $LaVO_4$: Ln^{3+} nanorods in cellulose gels,[88] or preformed silica nanoparticles for the preparation of chitosan-silica for separation membranes,[89] or chitin/TiO_2 needles for tissue engineering scaffolds.[90]

This classification does not account for all situations, thus there is no clear limit between a deposit of some nanoparticles distributed along the fibres and complete coverage of these fibers by these nanoparticles. In addition, it is sometimes difficult to distinguish between PS "truly dissolved", fibres that form a gel (more or less solvated and concentrated) and "totally insoluble" fibers. This question is becoming even more complicated because of two advances: new nano-sized polysaccharides (nanocrystals, nanofibers, aerogels) and new media in which fibers are "dissolved", e.g. (NaOH/urea),[91] DMSO/TBAF,[92] or ionic liquids.[93,94] Regarding this, there is growing interest in the preparation of hybrid PS/MO through electro-spinning of blends, e.g. ZnO-SnO_2@cellulose acetate[95] and SiO_2@chitine.[96]

The last step of the process is calcination to remove the PS template at generally 500-600 °C. Combustion of their organic scaffold likely forms dispersed oxides in conditions in which sintering is not favored. To remove the PS other means have been explored: dissolution in complexe media, or by enzyme treatment like in the case of dextran removed by dextranase.[97] Liquid ionic could be an alternative that remain to be explore with this purpose.[93] This makes possible the recycling of the PSs, but so far, this hasn't been reported yet, probably due to no economical interest in regards to the cheapness of PS and the cost of such recycling.

Thermal oxidation of PS is considered as globally benign or with low impact by itself on MO. However, all PS do not behave equally, for example thermal decomposition of alginate is sensitive to cations with the formation of metal oxalate,[98] and differs from chitosan, chitin,[99,100] or cellulose.[101] This situation could be affected by at least two factors, i.e. MO (as a crust, nanoparticles or free ions) and PS-induced nano-sizing. More attention should be paid to this step and could lead to "element-doping" via PS.

Consequently, the next section (Part 2) is devoted to a range of combinations dealing with *soluble and jellified* polysaccharides. Data clearly identifying replication of *insoluble* natural or refined polysaccharide fibers are presented in Part 3, while Part 4 concerns mineralisation through chemical reactions of PS.

PART 2: Controlled growth of metal oxide nanoparticles throughout polysaccharide fibers

This approach, schematically depicted in Figure 4, takes advantage of the functionality of polysaccharides to control hydrolysis/polycondensation and nucleation growth processes- it is sometimes called "*in situ* precipitation". It benefits from the fact that polysaccharides are able to absorb metal cations.[102-105] This absorption may occur through different modes: complexation, solvation, M-OH….HO-PS H-bonding and also depend on the PS functionality, and the experimental procedure (pH and concentration) (illustration in Figure 5).

It has long been recognized that "a distinguishing feature of polysaccharides is that they sharply accelerate the kinetics of sol-gel processes.… Such acceleration is attributed to a catalytic effect of polysaccharides on the silica synthesis."[106] Various studies have shown the formation of metal-cellulose complexes, e.g. Fe(III)-cellulose,[107] Cu(II)-cellulose,[108] Zn(II)-cellulose,[109] Pb(II) and Cd(II),[110] or Cr(III) and Al(III).[111] This could improve or introduce properties of the cellulose (mechanical, absorbent, anti-microbial and -fungal, UV self cleanings, dissolution), but could also be detrimental to its stability.[112] These authors highlighted the important role of both the pH and the residual carboxylic group of the cellulose.

In this context, the effect of the type of PS on MO nanoparticles is an important question. For example, in pioneer works on the preparation of maghemite with polysaccharides, it was observed that "starch and gulunoric-rich alginate retains large amounts of iron … compared to chitosan".[113]

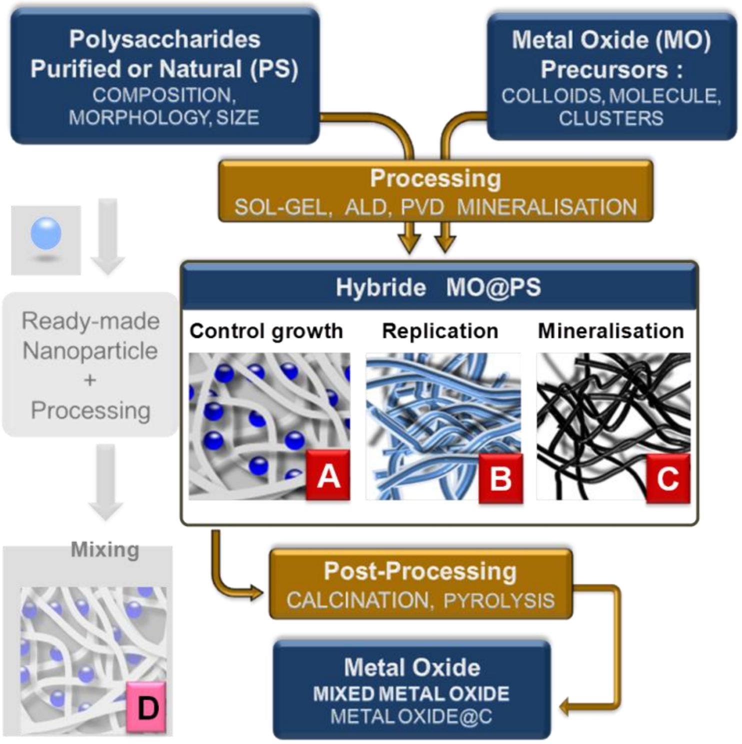


Fig.3 A general overview of the different approaches in which PSs are introduced as biotemplate for the preparation of MO@PS, the latter being an intermediate leading, after PS removal, to MO. Alternatively pyrolysis in inert atmosphere lead to MO@C composite

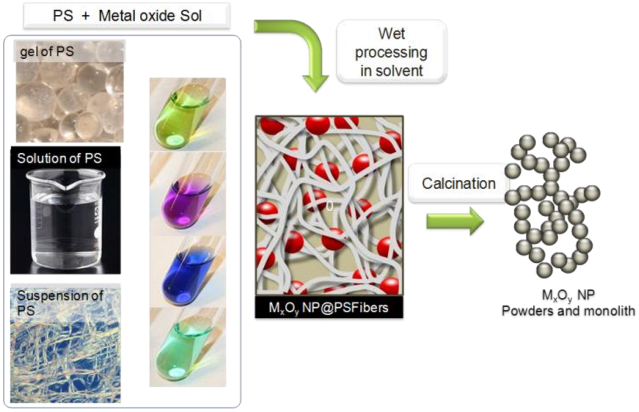


Fig. 4 The general pathway for the control of the growth of MO nanoparticles by the presence of PS

More recently, the structure and functionality of the polysaccharide was found to not only modify the microstructure and morphology of TiO_2, but it also induced a different phase, with rutile being obtained when using β-cyclodextrin and chitosan, anatase being obtained with starch.[114] Comparisons of this type are unfortunately still rare. The possibility of combining two PS is also limited to very few examples (see the case of improved chemical and mechanical stability of Fe_3O_4 particles[55]). Other processes like ALD are less commonly used. In that case, the PS's reactivity seems to be less involved since the metal oxide nanoparticles are formed before their contact with PS, but their anchoring depends on the functionality of the surface.[115,116]

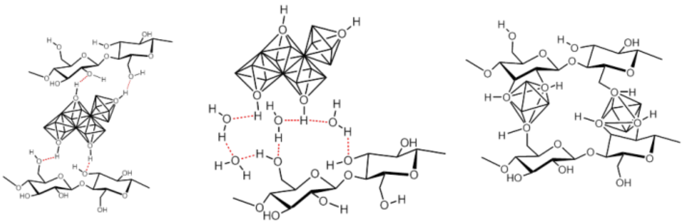


Fig. 5 Schematic representation of the possible interaction between functions of polysaccharide units and metal-containing species

The resulting MO@cellulose composite is sometimes the targeted material, but generally the metal oxide is targeted and recovered after calcination, unfortunately more seldomly a MO@C is sought through a pyrolytic treatment such as $LiFePO_4/C$,[117] or TiO_2@C (shown in Figure 6).[118]

Otherwise, a diverse range of metal oxides and supports have been explored for application or fundamental purposes. In the best cases, metal oxide nanoparticles with a ∅<50 nm are homogeneously dispersed along the fibers inside the micro- or nanofibers entanglement. Although the metal oxide structure has an effect, the most common morphology is round-shaped, which is not the most attractive, but in some rare cases PS like cellulose allows the formation of unusual morphologies such as TiO_2 cubes[119] or flowers.[120] Recently, cellulose in ionic liquid was used as a new media for metal oxide formation, showing a pronounced effect on the morphology and size when compared to aqueous processes (See e.g. $Na_{0.5}K_{0.5}NbO_3$[121]) The solvent effect on sol-gel chemistry is well-known, this is the first example of a PS-ILs media that combines the properties of PS and that of ILs.

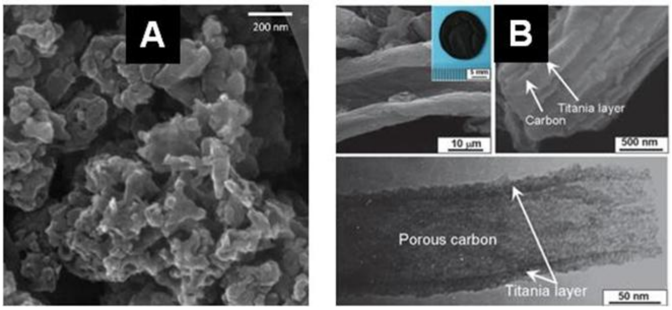


Fig. 6 SEM (A) and TEM (B) images of example of an MO@C composite obtained by pyrolytic treatment of the corresponding hybrid MO@PS **A** : $LiFePO_4$@C from filter paper after impregnation with ($LiNO_3$/$FeSO_4$) and pyrolysis under Ar+H_2[117] **B** : TiO_2@C from ashless filter paper impregnated with TTB and pyrolysis under N_2.[118]

MONP@Cellulose. (See Table 1 : MO@cellulose devoted to metal oxides and Table 2 : Mixed-MO@cellulose devoted to mixed metal oxides in SI)) Cellulose is the most popular polysaccharide. It is found in organisms ranging from bacteria to animals, forming a polymeric chain made of β(1→4) linked D-glucose units. The preparation of Fe_2O_3/Fe_3O_4,[125,126] or YBaCuO[84,85] with cellulose are among the first studies on this topic and examples of MONP@cellulose before calcination are presented in Figure 7. No benchmark has been established in this area concerning the type of cellulose, but cellulose pulp (or purified) is frequently used and bacterial cellulose is now increasingly popular as a nano-sized PS.

The use of cellulose~~,~~ avoids having to rely on a catalyst in many cases. Besides this common observation and the effectiveness of using cellulose in conjunction with sol-gel, there are two other issues that have been less discussed and need more studies. The first concerns the effect of cellulose degradation on calcination, which is an important point for some applications. For example, in the case of phosphor, some residual carbon can be present depending on the type of cellulose and the temperature, with an impact on the luminescence.[127,128]

The second point is the potentially reducing behavior of cellulose, depending on the temperature and atmosphere. Indeed, cellulose is clearly recognized as being a reducing agent in the formation of metal nanoparticles like Pt[129] Au,[61] or Ag[130] and when metal cations with high oxidation potential are involved in the effective reducing ability of hydroxyl groups, e.g. see the case of Mn(VII),[131,132] leading possibly to aldehyde and carboxylic function, or C-C bond cleavage.

MONP@Alginate. (See Table 3: MO@Alginate in SI) Alginate is extracted from brown seaweed and consists of mannuronic and guluronic acid residues randomly sequenced along the polysaccharide chain; also used in many ways for different materials.[133,134] Examples of MO prepared with alginates are shown in Figure 8. It is generally recognized that the buckled polyguluronate segments of alginate strongly bind [M^{n+}] multivalent metal cations, preferentially to Na^+, to form microcrystalline arrays through a mechanism known as the 'egg-box' model.[135]

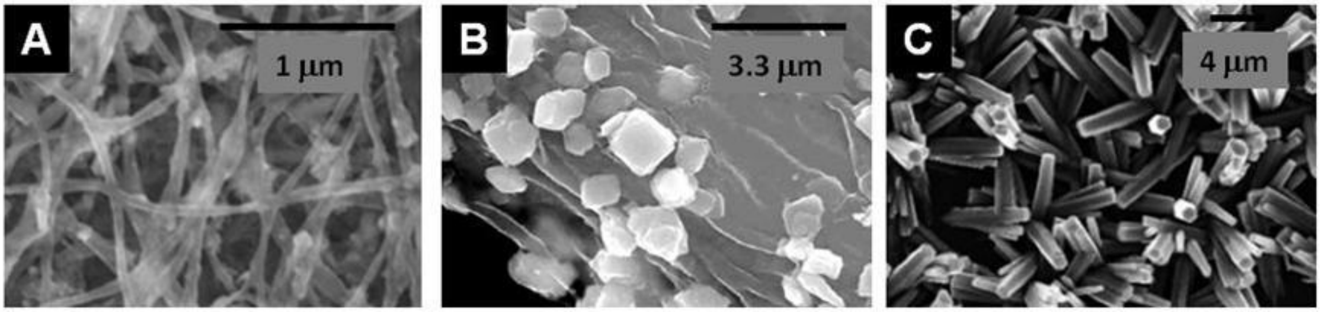


Fig. 7 SEM images of examples of different metal oxide nanoparticles assembled with or produced from cellulose-type PS A : Fe_3O_4@BNC (from *Acetobacter xylinum*);[122] B : $BiVO_4$@Cellulose (from *Eucalyptus globulus* wood cellulose fibres);[123] C : ZnO@Cellulose layer (from filter paper)[124]

Prior works targeted the formation of paramagnetic beads of alginate by reaction with iron salt for the potential preparation of biotechnology materials,[113,136,137] extended now to many other oxides. Basically alginates like chitosan are frequently processed as true solutions or after jellification by the addition of multi-valent cations. An important novelty in the process concerns the use of supercritical CO_2 drying of the gel after metal oxide formation. These conditions preserve the shape and high specific surface area of the material before calcination.

In some cases, "no memory of the fibrillar structure of the polysaccharide can be observed in the morphology and organization of oxide crystals",[138] but in the preparation of $YBa_2Cu_4O_8$ "there is more evidence of the effect of either the polyguluronate/polymannuronate ratio or the counter cation (ammonium/sodium) on metal oxide formation.";[139,140] Again, the nature of the oxide is critical on the ability to control its morphology from the PS. Interestingly, the chemical reactivity of alginate seems to be involved at two levels: first the carboxylate would act as a reducing agent, as proposed in the well-known citrate method (Pechini's method); and secondly the decomposition polymer products help prevent significant mass transport and sintering to leave sponge-like material[27,141]

MONP@Chitosan and chitin. (see Table 4: MO@Chitosan or chitin in SI) Chitosan is an abundant polysaccharide obtained through deacetylation of chitin, a naturally occurring polysaccharide found in fungi and the exoskeletons of insects and crustaceans; already used for many applications (food, cosmetics, biomedical and pharmaceutical applications[142]).

In early works, chitosan was mixed with ready-made Fe_3O_4 nanoparticles to produce a polyelectrolytic support for cell separation processes.[143] Early, SiO_2@Chitosan synthesis were targeted as artificial skin due to the high oxygen permeability of such "membrane",[144,145] but recent works focuses on TiO_2 as MO (example shown in figure 9A) Alternatively, and more frequently, chitosan is engaged as alcogel beads in which a precursor of the metal oxide diffuses from an alcoholic solution to give rise to MO coated chitosan hybrid microspheres. Similarly to alginate, before calcination and biotemplate elimination, a key step of the process is the supercritical drying with CO_2, which can prevent the collapse of the opened structure of the alcogel.[146] Alternatively, chitosan can be associated with a solvothermal process.[147]

The NH_2 group of the chitosan structure, a distinctive feature of this polysaccharide, is important for understanding its reactivity and chemistry. This group has been identified as one of the key components in the formation of the fibrous structure of oxides.[146,148] Based on IR-data of SiO_2@Chitosan, the $Si\text{-}O^{-}\text{---}{}^{+}H_2N\text{-}$ interaction is evidenced,[149]along with high hydrogen bonding.[150] The presence of the $–NH_2$ group suggests that it could be possible to N-dope some oxides prepared with chitosan and after calcination - a situation that has not yet been reported, suggesting the loss of this element upon calcination.[147]

In a limited number of cases, the presence of chitosan was postulated to orient the morphology of the recovered metal oxide, e.g. in the case of $YBa_2Cu_4O_8$ nanowires,[151] contrary to round-shaped nanoparticles obtained in the absence of chitosan. A key result showing the effect of PS and promoting their uses.

Chitin, has been less used for MONP formation than for replication (see next section). However, colloidal solution of chitin crystals can be combined with the sol-gel process, thus giving rise to nanocomposites and porous oxides like SiO_2 and TiO_2.[96,152]

MONP@Starch. (see Table 5 : MO@Starch, MO@Dextran, MO@Carrageenan, MO@Agarose in SI) Starch is produced by green plants, D-glucose sequences of D-glucose units lead to a spiral structure in linear amylose and in a highly branched structure in amylopectin. Easy to dissolve in water it is routinely combined with cellulose in the preparation of paper and nanocomposites.[153]

Due to this solubility, starch was tested as a "structure directing agent" or a "porogen", offering the advantages to be easily

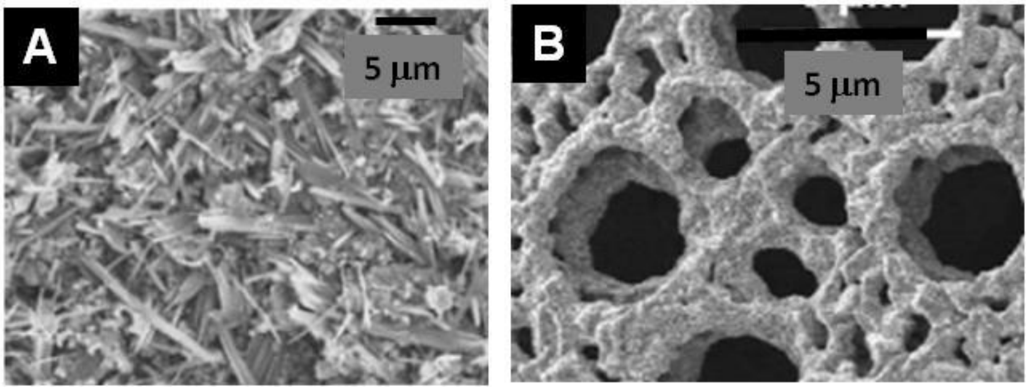


Fig. 8 SEM images of examples of different metal oxide nanoparticles assembled with or produced from alginate-type PS. A : $La_{0.67}Sr_{0.33}MnO_3$ with sodium alginate;[140] B : CuO after calcinationt of Cu-alginate aerogel from sodium alginate.[138]

removed with water, see for example for the preparation of Ni-$BaCe_{0.9}Y_{0.1}O_{2.95}$ cermet fuel cell electrodes.[154] Early studies used starch for the preparation of oxide Sr-doped $LaMnO_3$ and Sr-doped $La(Fe,Co)O_3$. The purpose is clearly to use starch as an alternative to citric acids in the Pechini method.[60 1211] It was found that starch plays an important role in the formation of homogeneously dispersed nanoparticles, while also having a marked impact on the crystal phase."[114] Indeed, aqueous Ti^{3+} solutions lead to anatase with starch, while rutile is obtained with cyclodextrin or chitosan. Although very attractive, the interpretation of such data needs investigations to promote the use of PSs

In the case of ZnO, starch layers were found to be efficient for growing uniformly oriented nano-rods, which is evidence of the strong interaction of the initial cluster oxide with the surface of such PS.[124] Other studies support the assumption that nucleation and initial crystal growth occur through starch/[Metal] species, but show it is possible to control the morphology and avoid nano-rod formation.[155]

Starch was also combined with readymade nanoparticles silicalite for macroporous sponge-like monoliths with meso-/macroporosity[86]) specially as coating to ensure their biocompatibility (SPION superparamagnetic iron oxide nanoparticles[156]).

MONP@Carrageenan Carrageenan are linear sulphated polysaccharides that are extracted from red edible seaweeds, and this family has at least 10 different chemical structures depending on the number and position of the $–OSO_3^-$ group (α,β,γ,ι,κ,λ,μ,δ,θ, etc.). The number of studies was limited but, interestingly, it was reported that the presence of carrageenan limits the growth of metal oxide particles in the case of Fe_2O_3 and that the type of carrageenan plays an important role, "with *ι*-carrageenan nanoparticles showing higher average sizes, compared to *κ*- and *λ*-carrageenan."[160] These different behaviours are probably related to the number of charges ($–OSO_3^-$) per monomer unit, a key parameter for understanding the $[Fe^{3+}]$/carrageenan interaction by charge neutralization between sulphate groups and hydrolyzed oxyhydroxide iron species.[161] Overall, carrageenan chains crosslink via metal cations, and in turn create a protective layer around iron oxide particles, thus producing a self-assembled nano-reactor for hydrolysis and condensation of oxyhydroxide iron species.

MONP@Agarose. Agarose is generally extracted from cell walls of certain algae species with essentially galactose subunits. The alcoholic gel is used as reaction medium for the formation of metal oxides though hydrolysis/polycondensation of metal alkoxides absorbed in the gel, but also as a soluble porogen (see exemple in Figure 9B). As in the case of the other gel, the impregnation process parameters (mineral/organic ratio, number of cycles, temperature, etc.) are crucial in the diffusion of titanium precursors into templates and the maintenance of a porous structure in the resulting titania beads. This could explain the differences observed with respect to previously published findings. Interestingly, the reducing ability of agarose towards Au salt was combined with its porogen properties to generate $Au@TiO_2$ catalyst,[162] an approach that should be generalized to other PS for the preparation of new composite MONP@C@M'O

MONP@Dextran is a branched polymer of dextrose (glucose) of very high molecular weight excreted by lactic-acid bacteria, with the best-known being *Leuconostoc mesenteroides* and *Streptococcus mutans*. The use of this polymer for metal oxide preparation is limited but, interestingly, in the case $YBa_2Cu_3O_7$, the use of dextran is reported to lead to a uniform crystal size and morphology and a macroporous structure (Figure 9C). With the same PS, calcination of a freeze-dried metal oxide–dextrans aqueous mixture leads to foamy porous open structures that are easy to calcine with less sintering.

PART 3: Templating of polysaccharides fibers

Bioreplication, which differs from biomorphism,[163] is the direct replication of a structure found in an organism. This is a very general approach to the synthesis of materials that is implemented to take advantage of hierarchical micro- and nano-structures produced by living organisms (Schematically depicted in Figure 10).[12,39,64,164-169] The initial aim was to demonstrate the possibility of precisely molding "raw" natural structures with MO. This is still relevant when taking advantage of cheap raw materials via the shortest possible loop, and when

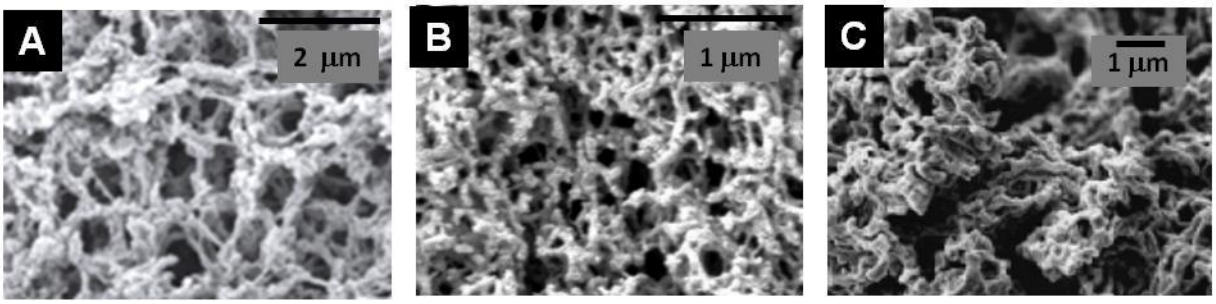


Fig. 9 SEM images of different metal oxide nanoparticles assembled with different PS A : TiO_2@Chitosan (20% acetylation);[157] B: TiO_2 after calcination of TiO_2@Agarose composite;[158] C : $YBa_2Cu_3O_7$@Dextran;[159]

preparing metal oxides with complex morphologies and hierarchical architectures (sees different examples in figure 11). Several examples have been reported from the coarse- to the nano-scale: eggshell membranes,[170] human hairs,[171,172] silk fibers,[173] pollen,[174,175] diatoms,[176] bacteria,[87,177,178] viruses,[179] protein cages,[180,181] and collagen.[182]

In such replication processes, only the outermost part of the surface of the PS is supposed to be involved in the chemical processes. This can be assumed to occur in the same manner as the process involved in the controlled growth of MONP, see above: through complexation/solvatation of cation or hydroxycation species through the organic function of the biotemplate (carboxylate, hydroxyls, amines and amides groups, etc.). In the case of ZnO, for example, it was found that "cellulosic fibers act as hydrophilic substrates for the heterogeneous nucleation of ZnO";[183] and this surface can be pre-seeded with metal salt.[184,185]

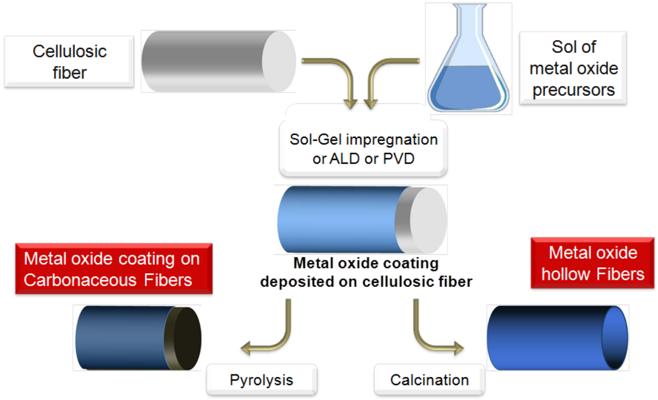


Fig. 10 General pathway for metal oxide preparation by impregnation/deposition with PS, leading to hybrids M_xO_y@PS and then M_xO_y or M_xO_y@C material upon thermal treatment.

The inner part of the fibers is probably not involved in these nucleation and seeding processes. Calcination is generally used to isolate the inorganic replica but pyrolysis could be of interest in the preparation of MO@C composites. "Biotemplating" or "bioreplicas" are therefore appropriate, contrary to "mineralisation", "petrifaction" or "fossilization", which should be limited to effective chemical transformations of the template in its massive part.

PS fibers are replicated through a Sol-Gel process, but a few exceptions are reported with other techniques, leading to a thick MO deposit of 20 to several nm, covering the template, and made of round shaped and aggregated nanoparticles of ∅<50 nm. Besides the many different supports highlighted in the Table, different "modified cellulose" supports have also been used, e.g. cellulose acetate.[186-188]

TiO_2-Cellulose. (see Table 6 Biotemplating of cellulosic fibers for TiO_2@Cellulose for TiO_2 formation in SI) Cellulose fibers are the most popular biotemplates here because of their insolubility, which render them more appropriate for bioreplication than for nanoparticle growth control. Otherwise, the most frequently targeted oxide is TiO_2 due to the numerous potential applications of this oxide: sensors for hydrogen, oxygen, humidity, glucose and hydrogen peroxide, anodes for electrochemical devices, photocatalysts for oxidation and reduction. In pioneer studies, TiO_2 micro- or nano-tubes were already targeted with cotton fibers as template.[189,190]

MO replication is achieved mainly by the impregnation or suction/filtration technique using a sol of TiO_2-precursors, the experimental details being one of the knowhow of the authors and including. An alternative to this process is to produce hydrolysis/condensation of the MO precursor by exposure to air or moisture once it has been absorbed by the cellulose fibres.[191,192] The third possibility involves the ALD process, which can be combined with multi-oxide formation and for which the presence of the hydroxyl group at the cellulose surface seems to "simplify nucleation of water-based ALD processes".[193]

Calcination (generally at 500°C) is used to remove the template but the possibility of removing the cellulose by a urea/NaOH treatment has also been reported.[194] Generally, anatase is the common phase but rutile has been reported in one case, using flame calcination after impregnation, although it was recognized that "the cellulose template plays key roles not only in obtaining the nanotubular structures, but also in achieving smaller particle sizes".[195] Exceptionally, cellulose is also considered as a source of carbon that could lead to a C@TiO_2 nanocomposite (anatase+rutile),[196] this could be further developed if considering the new materials required for energy and catalysis.

Besides relatively refined cellulosic materials, raw materials directly collected from nature, essentially plant parts, were biotemplated. In these cases, besides the cellulose-rich part of the body (skin, leave seeds, pith, etc.), other biopolymers or salts can be present and interfere in the process. Despite or because of this, some interesting and effective properties have been reported, giving rise to a direct and greener process, mainly for the potential preparation of photocatalysts (see Table 7 Biotemplating of plants for TiO_2@Plant and TiO_2 formation in SI).

M_xO_y-Cellulose. (see Table 8 Biotemplating of Cellulose for MO@Cellulose and MO formation in SI) Sol-Gel processing is the most commonly used, note that chemical modification of cellulose can be performed to enhance the formation of, for example, SiO_2 around fibers.[197] The ALD technique is attractive, it provides a possibility to adjust the thickness of the metal oxide layer by increasing or decreasing the number of cycles, more precise than Sol-Gel processing.

M_xO_y@PS and M_xO_y@modified-PS or M_xO_y@raw material. Cellulose is a kind of benchmark to test Bioreplication, therefore other polysaccharides are less reported also because some are soluble in water.

Chitin, more than chitosan, is often used due to its abundance in chitinized exoskeletons. Butterfly wings have been templated by different oxides: SiO_2 (CVD)[205] Al_2O_3 (ALD),[204] TiO_2 (impregnation),[206] TiO_2 (ALD),[207] Sn-TiO_2 (sol-gel),[208]SnO_2 (sol-gel),[209] ZnO (sol-gel),[210,211] $BaTiO_3$ (LbL),[212] TiO_2 and SiO_2(sol-gel).[213] Other chitin biotemplates have also been tested, like beetle cuticles in weevil and longhorn families, and used for the production of inorganic photonic structures by a sol–gel biotemplating method.[214] Besides arthropods, chitin is also found in marine organisms and biotemplating of a macroporous β-chitin sponge-like monolith of cuttlebone was obtained by acidic demineralisation after impregnation with sodium silicate, which provided good replication control.[215] The objective in all cases is to take advantage of the unique hierarchical structure of the biotemplate; especially for photonic materials, but not only this since hierarchical porosity is beneficial for catalysis or electrodes. ALD process was used to deposit Al_2O_3 on spines of sea mouse (*Aphrodita aculeata*) made of chitin and protein.[216]

Chitosan flakes have recently been reported as an insoluble biotemplate for the preparation of bulk and mesoporous silica. Here again, the role of the amino group is a key for understanding the role of the biotemplate.[217]

At that point, the wood structure replication can be mentioned, but because the template is a raw mixture of non-purified biopolymers, it will not be detailed. Since the early work of Drum *et al.* on the silicification of betula wood by an aqueous solution of silicate[218], many other wood/MO couples have been investigated, leading to the preparation of MO with complex and hierarchical structures: pine wood (templating Al_2O_3, TiO_2 and ZrO_2;[219] NiO;[220] $SrAl_2O_4$:Eu^{2+};[221] Fe_2O_3;[222] SiO_2;[223] Y-ZrO_2;[224] to SiOC;[225]); fir wood (templating ZnO;[226] TiO_2;[227]

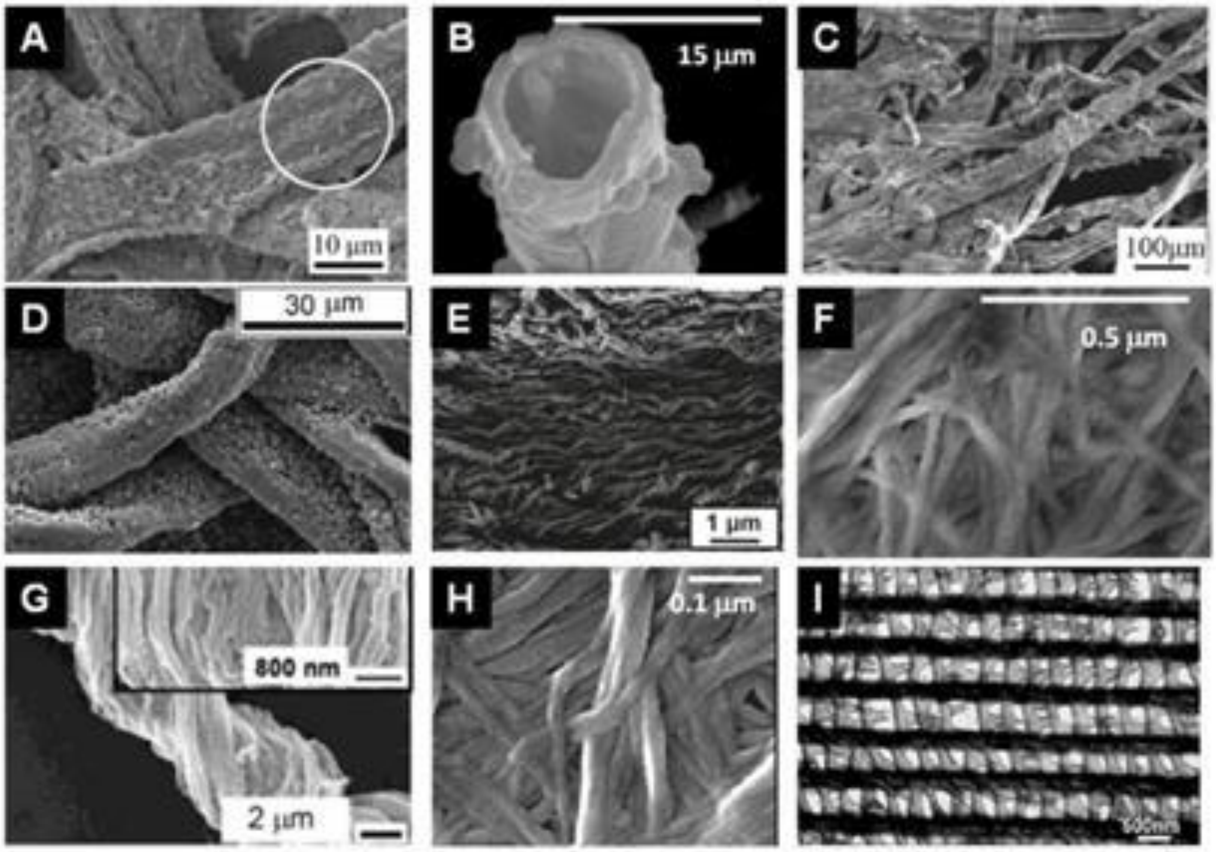


Fig. 11 SEM images the replication of polysaccharide fibers with metal oxides deposited by Sol-Gel or ALD techniques. A : MoO_3@cellulose (commercial paper) after calcination at 500°C;[198] B: TiO_2 hollow fibers after calcination of TiO_2@cellulose (woven cotton);[189] C : MnO_2@Cellulose from lens paper before calcination;[199] D : ZnO@cellulose from filter paper before calcination;[200] E : SiO_2 nanotube after calcination of SiO_2@cellulose from filter paper;[201] F : Fe_3O_4@cellulose from bacterial cellulose of *G. xylinum*;[202] G : TiO_2 after calcination of TiO_2@cellulose from natural cotton;[1] H : V_2O_5@cellulose from bacterial *G xylinum* before calcination;[203] I : Al_2O_3 replicas after calcination of Al_2O_3@butterfly wing by ALD.[204]

Mn_3O_4 and Mn_2O_3;[228] Fe_2O_3;[222,229] and Cr_2O_3[230]); cedar, cypress and judus wood (to TiO_2[227]); paulownia (templating Fe_2O_3;[222,229] Cr_2O_3;[230] Mn_3O_4 and Mn_2O_3;[228]) and lauan wood (templating Fe_2O_3[222]), poplar wood (templating SiO_2[223]); cedar wood (templating TiO_2[231] and Zeolite[232]); spruce wood (templating SiO_2;[233,234] to $Ce_{0.5}Zr_{0.5}O_2$[31]); and bamboo (templating zeolite[232]).

M_xO_y-PS through hard templates. Another approach related to the MO@PS topic is the use of micrometer size granules of PS for nanocasting. Microspheres of starch infiltrated with TiO_2 sol in supercritical CO_2 lead to the formation of mesoporous-macroporous anatase (2 nm to 5 µm).[235] In a different approach, starch granules were first converted into carbonaceous material by a solvothermal process,[236] and then used as sacrificial templates for the preparation of ZnO microspheres after impregnation with Zin(II) acetate.[237,238] This approach was initially pioneered with glucose as precursors for carbonaceous dots used, for example, for the production of metal and mixed metal oxides.[239-245] With the development of carbon dots, this approach could be fruitfully further enhanced to associate these dots with MO.

PART 4: Chemical reaction of biopolymers with metal oxide precursors

In the studies mentioned above, cellulose was exclusively considered as a template and its reactivity was generally not considered, except for the outermost layer. But in other domains, biotemplates have often been considered as a C-provider for the production of carbides, such as SiC[246-249] or [250] B_4C,[251,252] TiC, [253,254] C-doped TiO_2,[147,255] C-doped SiO_2,[256] or as a reducing agent for the preparation of metal particles,[129] and recently metal fibers.[257] However, biotemplates are very seldom considered as an O-source functioning both as a template and reagent, e.g. gas/solid metathesis between TiF_4 and SiO_2-based diatoms.[258]

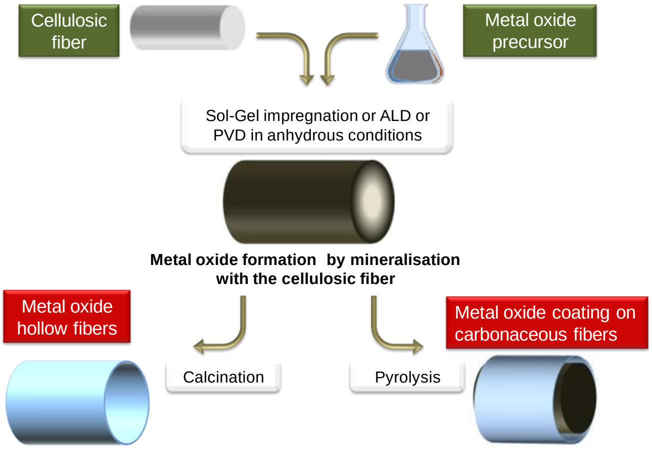


Fig.12 General scheme of the polysaccharide mineralisation process leading to hybrid M_xO_y@PS and then to either M_xO_y or M_xO_y@C materials

Polysaccharides are indeed highly reactive materials with a high oxygen content, thus making them promising O-providers. In the past, alcohol and ether have been used in the preparation of metal oxides by the so-called non-hydrolytic sol-gel process.[259,260] Figure 12 schematically illustrates such general route where polysaccharides are considered as both templates and reagents.

An ALD-type process has been developed and is based, in the case of the formation of TiO_2, on the reaction for TTIP with-and-on dried nanofibers of nanocellulose aerogels (Figure 13). Considering the temperature used in the process, i.e. 190°C at pressures of 1–5 kPa for 2 h, different reactions can occur: with cellulose hydroxyl groups to produce alcohol of the MO precursor, thermal decomposition of titanium isopropoxide, and reactions with traces of water,.[261-263]

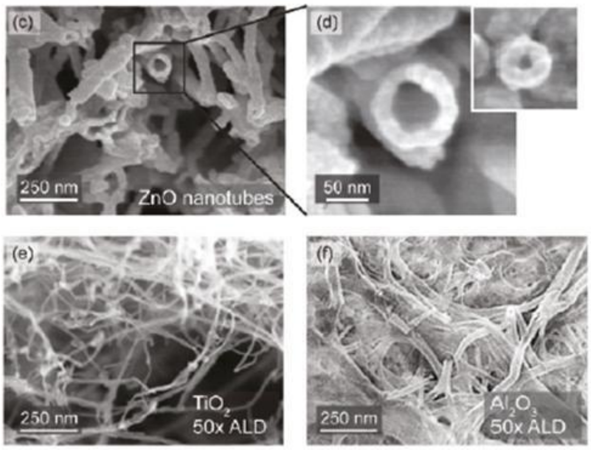


Fig. 13 SEM images of ZnO@NCA (c,d); TiO_2@NCA (e) d Al_2O_3@NCA (f) obtained reactive ALD with nanocellulose aerogel.[262]

Recently, we have reported a mineralisation, in strictly anhydrous conditions similar to non-hydrolytic sol-gel processes. TiO_2 can be obtained by reaction between $TiCl_4$ as titanium-source and a cellulosic material like *Ferrula communis* piths or cotton wool acting as oxygen source.[264] This is a one-pot metathetic liquid/solid reaction.

The most important difference with other approaches is that, under mild conditions (<80°C), mineralisation leads to the formation of nanoparticles with a non-rounded shape, i.e. nanorod-like structures assembled in needle[3] (Figure 14) or lacework formations,[265] a situation that has never been reported in sol-gel biotemplating processes. In addition, this approach can be combined with pre-impregnation of the cellulose and is efficient on aerogel of nanocellulose.

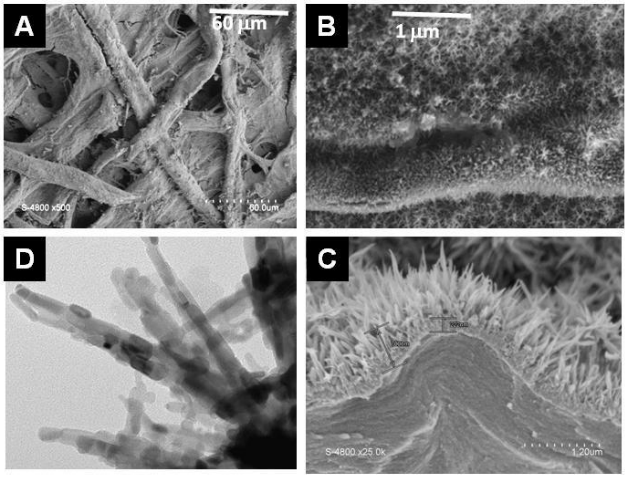


Fig. 14 SEM (A, B, C) and TEM (D) picture of TiO_2@ filter paper obtained by mineralization of filter paper by $TiCl_4$ in anhydrous condition at 80°C.[3]

Perspectives and concluding remarks

Green, dark green, pale green… How is this Green Chemistry? Answers to this question can be given in relation to the basic principles of "green chemistry", and by comparison with other methods that aim to control the synthesis of metal oxides.

In terms of maximizing the amount of raw material with no (or limited) environmental impact and toxicity, PSs and water are certainly appropriate chemicals, the use of MO precursors cannot be avoided by any process. PSs are ideal sustainable substances, although some of them require purification or extraction like for nanocrystal and nanofibers. Anyway, the use of PSs is certainly "greener" than that of surfactants and additives issued from petrochemical industry, and generally used for the same purpose.

In terms of by products, the chemicals produced by the process are usually alcohol (produced by the hydrolysis of the MO precursor) and CO_2 during calcination (plus traces of S and N containing chemicals in some cases), the latter two compounds exhibiting no particular toxicity and being easily mastered by the chemist. However, to limit contamination by metal and maximize the incorporation of all materials used in the process, a special attention must be paid to the presence of clusters and metal oxide nanoparticles in the final solution after the filtration step.

In terms of energy, one may argue of the necessity to remove the PS by thermal treatment (although elimination could be done with enzyme or ILs extraction in some case). But firstly, the syntheses of MO require generally a thermal treatment to improve the crystallinity of MO, the temperatures are generally equivalent or even higher than the one required for the elimination of the PS. Secondly, when the thermal treatment is made under inert atmosphere it leads to carbon phase issued from the PS, a situation that cannot be attained when using surfactants or additives, and that allows, in one step, the formation of MO@C composites. Finally, most of the oxides thus synthesized are required by green chemistry, especially in the catalytic and photocatalysis processes. Therefore, it is among the greenest approach to the synthesis of materials expected as Green Chemistry.

Over the last two decades, there has been a significant increase in the development of approaches and in research on the use of PS for MO preparation. This is certainly only the beginning of the story considering the importance of polysaccharides as potential materials and reagents, and of metal oxides as functional materials for chemical applications and devices. Of course, the development of the chemistry around the nano-sizing and chemical modification of PS is a major issue for the development of this domain, as mentioned above. At the end of this review, we propose to keep in mind five important issues.

First, a precise rationalisation of the effect of the polysaccharide on the formation of the oxide is not possible at the present because of the tremendous diversity of processing parameters and the complexity of PS structures. This is further hampered by the lack of a precise description and analyses of what happens *during* nanoparticles growth or replication. The descriptions of the experimental procedures should always be accurate and detailed. Comparison of different PSs engaged in the same conditions would greatly help to understand and rationalise their specificity and interest in these processes.

Secondly, the decomposition/elimination of biopolymers leading to the oxide is an important step requiring greater consideration: for instance, nano-sizing of PS and MO coatings may modify the thermal behaviour of PS, which is an important point with respect to the formation of C-doped MO or C@MO composites.

Thirdly, the reactivity of PS, beyond its role as template, opens new avenues in terms of the transfer of elements to the targeted MO and of redox reaction before or during thermal treatment for the formation of other composites (M@C, M@MO@C, etc.). Examples of the synthesis of metal nanoparticles,[130,266-269]or metal oxides (magnetite,[270] hausmannite[131]) are useful tools in such perspective.

The use of PSs is usually a control MO properties including porosity. With the exception of some water-soluble PSs (alginates), the results in this area are not very remarkable, especially compared to the results obtained with surfactants. However, the availability of new forms of PSs (nanocrystals, nanofibers) offers hope for progress in this area.

Finally, in addition to other advances in PS processing, the latter could be modified by chemical reaction or simply by adsorption of chemicals inside fibers. This offers numerous combinations for the potential preparation of complex MO@PS multifunctional composites.

From a general point of view, the sum of these results shows the diversity and richness of this synthetic pathway to MOs, using abundant natural polymers, and which can also lead to the formation of composite and nanocomposite MO@C. If today lacks a fine and precise understanding of the specific character of each PSs, it is already possible today to take advantage of them to access to materials highly demanded in new technologies and devices

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Notes and references

[a] CMOS-Institut Charles Gerhardt, Université Montpellier 2 CC1701.
Pl E. Bataillon 34090 Montpellier France

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