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Composites of Cellulose and Metal Nanoparticles

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1. Introduction

Research on inorganic/organic nanocomposite materials is a fast growing interdisciplinary area in materials science and engineering. In particular, extensive work has been undertaken in the development of sustainable and environmentally friendly resources and methods. A key idea has been the production of nanocomposites comprising biopolymers that in specific contexts can replace conventional materials such as synthetic polymers. It is well known that the properties of nanocomposite materials depend not only on the properties of their individual components but also on morphological and interfacial characteristics arising from the combination of distinct materials [1]. Therefore the use of polymers such as cellulose, starch, alginate, dextran, carrageenan, and chitosan among others, gain great relevance not only due to their renewable nature and biodegradability, but also because a variety of formulations can be exploited depending on the envisaged functionality [2, 3].

This chapter has focus on the use of cellulose as the matrix in the production of nanocomposites. Cellulose has critical importance namely because is the most abundant and widespread biopolymer on Earth. Owing to its abundance and specific properties, it is important noted for the development of environmental friendly, biocompatible, and functional composites, quite apart from its traditional and massive use in papermaking and cotton textiles [4]. Additionally different types of cellulose are available for the preparation of nanocomposites, namely vegetable cellulose (VC), bacterial cellulose (BC) and nanofibrillated cellulose (NFC). Although sharing similar chemistry and molecular structure, the different kinds of cellulose show important differences in terms of morphology and mechanical behavior. For example, BC and NFC are composed of fibers with nanosized dimensions as compared to VC, which might impart new properties, and in some cases improvements to the ensuing nanocomposite materials [5].

The association of cellulose with different fillers can bring benefits like improvement of properties (optical, mechanical, ...) and delivering unique functions by their use [6]. Cellulose has been used as a soft matrix to accommodate inorganic fillers to produce composites that bring together the intrinsic functionalities of the fillers and the biointerfaces offered by cellulose fibers [2]. Among the wide range of available inorganic fillers, in this review metal nanoparticles (Au, Ag, and Cu, among others) will be considered. Metal NPs exhibit properties that differ from the bulk analogues due to size and surface effects, thus the properties of the final materials can be adjusted as a function of the size, shape, particle size distribution of the nanofillers as well as by interactions occurring with the cellulose fibers' surfaces. Preparative strategies play a determinant role in the performance and properties of the nanocomposites, hence chemical approaches for the synthesis of these materials are reviewed namely for *in situ* and *ex situ* methods. Examples will be given for applications of cellulose nanocomposites by taking in consideration the type of nanoparticles used. As a concluding note, the development of new multifunctional cellulose nanocomposites will be put in perspective.

2. General aspects on the chemistry and properties of cellulose

The last years have seen great interest in research and application of cellulose nanocomposites namely due to the technological interest in renewable materials and environmentally friendly and sustainable resources [7]. In fact, within the polymers obtained from renewable sources, cellulose is the most abundant natural polymer in Nature as well as the most important component of the plants' "skeleton". This biopolymer formed by repeated connection of glucose building blocks is the structural basis of cell walls of virtually all plants and is usually considered an almost inexhaustible source of raw materials [8, 9]. Cellulose has particular significance owing its unique structure and distinct tendency to form intra- and intermolecular bonding. These characteristics influence the cellulose supramolecular arrangement that together with other practical aspects such as the product origin and processing treatment, have important consequences on the final properties of cellulose. This polymer is the main constituent of softwood and hardwood, representing about 40-45% of dry wood, with wood pulp remaining the most important source for cellulose processing namely in paper fabrication [8, 10, 11]. Wood pulp is also the main industrial feedstock for the production of cellulose regenerate fibers and films. This biopolymer is also used in the synthesis of different cellulose derivatives such as esters and ethers. These derivatives are well-known active components in applications which include coatings, pharmaceuticals and cosmetics, among others [11] and also used in numerous hybrids containing metal and metal oxides NPs.

Besides extraction from plants, cellulose can be produced by alternative methods, namely by using different types of microorganisms (certain bacteria, algae or fungi). Among the cellulose-forming bacteria, *Acetobacter* strains have been widely used because they are not pathogenic. In fact, these Gram-negative bacteria are usually found in fruits and can be used in laboratorial conditions in order to obtain significant amounts of cellulose [8, 11-13]. Nowa-

days, it is observed a growing interest in the use of BC, not only within applications in nanocomposites but also in other fields including food industry (e.g. calorie-free dessert) and medical field (e.g. wound dressing). Apart their three-dimensional (3D) network of nanofibers, BC has high purity (do not have lignin, hemicelluloses, pectin and other compounds associated to VC), high degree of polymerization (DP up to 8000), high crystallinity (60 to 90%), high water content and high elasticity and mechanical stability (particularly in wet form) [8, 11-15].

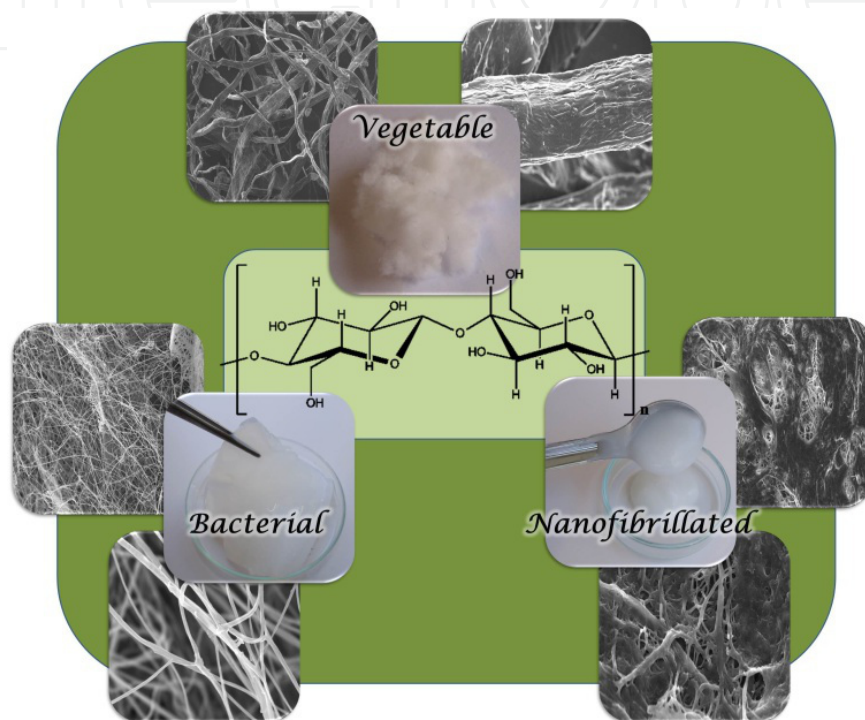


Figure 1. Chemical structure and morphological characteristics of different forms of cellulose.

Due to the complex and expensive process to produce BC, there has been interest to find other ways to obtain cellulose fibers of nanometric dimensions, namely at an industrial scale [11]. NFC can be obtained from VC fibers by distinct methods including chemical treatment and mechanical disintegration procedures, in the form of aqueous suspensions of nanoscale fibers, leading to high aspect ratio materials (5-30 nm diameter and lengths in micrometer range) with remarkable strength and flexibility [16, 17]. The mechanical properties of NFC make this polymer a good candidate for reinforcement materials in nanocomposites. However, besides their interesting mechanical properties, NFC shows other properties of practical interest. For example, NFC has a large surface area which makes it a promising candidate for filtering membranes. Appropriate chemical modifications performed on NFC result in a versatile additive for paints, lacquers or latex. Due to its biocompatibility, NFC might also be used in food and medical applications [11, 17]. As will be clear in the next section, the properties of the cellulose nanocomposites depend not only on the NPs employed as fillers but also on the type of cellulose matrix used.

From all the cellulose derivatives commonly use on the chemistry market, esters and ethers are the predominant. Although produced since the middle of the eighteen century the actually research is related with their manufacture technological improvement. The mail goal is related with the development of greener processes being investigated the use of ionic liquids (IL), microwaves irradiation and solvent-free systems in the synthesis of this cellulose derivatives. This strategy has been followed for the cellulose derivatives used in specifics applications, such as biomedical and optoelectronic and produced in small amounts. The industries responsible for the production of high amounts of these derivatives (as cellulose acetate) have neglected this mandatory necessity [18].

3. Cellulose/metal nanocomposites

3.1. Preparative strategies of cellulose/metal nanocomposites

A key aspect to consider in combining metal NPs with cellulose fibers is the methodology to be employed namely by taking in consideration the envisaged applications. In order to exploit the properties of nanocomposites, the NPs should be well dispersed over the matrix without the formation of large aggregates that may compromise the final properties and should as much as possible exhibit a small narrow size distribution. There is critical need to find effective techniques that allow the large-scale production that at the same time maintain control of the NPs dispersion in the cellulose matrix. A number of approaches have been developed to attach metal NPs onto cellulose fibers. Table 1 gives examples of methods employed in the preparation of cellulose/metal nanocomposites.

3.1.1. Blending of components

The blending of inorganic NPs and polymers by promoting their homogeneous mixture to form nanocomposites materials has been widely employed [19]. Although this method offers the advantage of simplicity, the use of cellulose as matrix commonly lead to NPs aggregates that decrease the benefits associated to the presence of nanosized fillers. This process often leads to poor laundering durability of the materials and, for example when Ag NPs have been used, the antibacterial efficiency are lower than expected and discontinuous in time [20]. The direct deposition of Ag and Au NPs, by dropwise addition of the respective colloids onto filter papers, has been reported [21, 22]. Usually, this methodology does not lead to an homogeneous distribution of NPs on the paper substrates and the formation of aggregates at the edge of the droplets during the drying process is common [23].

3.1.2. *In situ* reduction of metal salts

The preparation of cellulose/metal nanocomposites by the *in situ* reduction of metal salts in cellulose aqueous suspensions has been extensively investigated. Typically this involves the use of a soluble metal salt as precursor, a reducing agent and a co-stabilizer to avoid agglomeration. However, the *in situ* method can be employed without addition of an external

reducing agent, because adsorption of metal ions on the cellulose surfaces may be subsequently reduced to metal NPs by organic moieties such as terminal aldehyde or carboxylic groups, whose presence depend on pulp bleaching. In this case, the unique structure and the presence of ether and hydroxyl groups in cellulose fibers constitute an effective nano-reactor for *in situ* synthesis of the NPs. The ether and hydroxyl functions not only anchor the metal ions tightly onto the fibers via ion–dipole interactions, but also after reduction stabilizes the as prepared NPs via surface interactions [27, 57]. This process presents some advantages compared to the simple mixture of the composite components. The template role of the host macromolecular chains for the synthesis of NPs helps to improve their distribution inside the cellulose matrix and also prevents formation of aggregates. At the same time the polymer chains play an important role leading to a narrow size distribution and well defined shape for the metal NPs [69].

Cellulose matrix	Preparative method	Metal NPs	
Vegetable	Blending of components	Ag [20, 21], Au [22]	
	<i>In situ</i> reduction	Cellulose reducing groups	Ag [24-29], Au [29, 30], Cu [31, 32], Pt [33, 34]
		External reducing agents	Ag [20, 27, 28, 35-38], Au [27, 36, 39, 40], Cu [31, 41, 42], Pt [27, 36, 43, 44], Co [45], Pd [27, 36]
		UV reduction	Ag [28, 46, 47]
	Electrostatic assembly	Ag [28, 36], Au [36, 39], Cu [48], Pt [36], Pd [36]	
	Microwave-assisted preparation	Ag [49-51]	
	Surface pre-modification	Ag [52], Au [52-54]	
Bacterial	<i>In situ</i>	Cellulose reducing groups	Ag [55]
		Reducing agents	Ag [19, 28, 37, 43, 56-60], Au [39, 43, 61-63], Cu [64], Pt [43, 65], Co [66]
	Electrostatic assembly	Au [39]	
	UV reduction	Ag [28]	
	Surface pre-modification	Ag [67]	
Nanofibrillated	Diffusion	Ag [28]	
	Blending of components	Ag [68]	
	Electrostatic assembly	Ag [16]	

Table 1. Preparative methods of cellulose/metal nanocomposites.

3.1.2.1. Addition of reducing agents

The most commonly used *in situ* approach to prepare a dispersion of NPs in cellulose matrices involves the entrapment of metal cations in the fibers followed by their reduction with an external reducing agent. In this procedure the reducing agent also act as a co-stabilizer (together with the cellulose fibers) for the metal NPs. Sodium borohydride has been exten-

sively used to reduce metal ions in cellulose matrices. The particle size distribution is adjusted by varying the NaBH_4 : metal salt molar ratio. The use of tri-sodium citrate has also been reported as reducing and stabilizing agent. Some reports have described the loading of Ag NPs into grafted filter paper [35], in BC and VC matrices [37].

The use of hydrazine, hydroxylamine and ascorbic acid together with gelatin or polyvinylpyrrolidone (PVP) as colloidal stabilizers has been investigated [58]. Ascorbic acid acted as an efficient reductant for Ag^+ and gelatin a good colloidal stabilizer to avoid NPs coalescence and to control particle size. *In situ* Ag ions reduction by the chelating-reducing agent triethanolamine (TEA) has been reported to produce small spherical particles with 8.5 nm average size, appearing well dispersed in the BC bulk ultrafine reticulated structure [59].

Reduction of gold salts by flowing H_2 over the cellulose matrix has been reported [40]. This methodology allows the preparation of NPs about 2 nm mean diameter. A facile one-step method, in aqueous medium, makes use of poly (ethyleneimine) (PEI) as reducing and macromolecular linker [61]. In this case the thickness of the Au coating surrounding the cellulose fibers can be adjusted by adding different halides (Fig. 2).

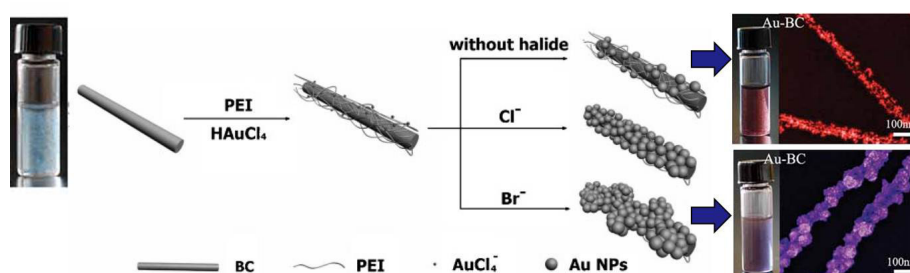


Figure 2. Scheme illustrating the formation of Au-BC nanocomposites using the polyelectrolyte PEI (Adapted by permission from ref [61] (Copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

3.1.2.2. Reduction of metals salts by cellulose reducing groups

An alternative route for the *in situ* preparation of cellulose based nanocomposites involves the reducing groups of cellulose that simultaneously can entrap NPs within the fibers net. This process shows the advantage that external chemicals are not added to the reacting mixture, thus avoiding adventitious contaminations that may interfere in some applications such as catalysis [36].

This methodology constitutes a green approach to the synthesis of a variety of metal NPs in cellulose matrices in which no additional reducing agents or colloidal stabilizers are used. Kunitake et al. [27] have reported pioneer research using VC fibers with following work reporting the use of BC fibers for the production of silver and gold nanostructures [28, 39]. This strategy has been reported for other types of biomaterials, hence Ag NPs have been prepared by using the *in situ* reduction of a silver(I) salt in the presence of cotton fibers. The washing durability of these nanocomposites and the small amounts of silver NPs required, make this an alternative path to produce cellulose based functional textiles. BC and porous

cellulose have also been used as reducing and stabilizer for several metal NPs using a hydrothermal method [43, 55].

In the context of composite science, ionic liquids have attracted substantial interest because of their ability to dissolve biopolymers like cellulose. This has been illustrated in the formation of cellulose/Au nanocomposites [30]. The combined use of cellulose and IL allowed the NPs morphology control in a process in which the IL was retrieved after metal reduction. The use of unbleached kraft fibers have the advantage of limiting metal leaching due chemical affinity between the NPs and the substrate. In this case NPs are formed directly on the VC fiber surfaces by a redox reaction with the associated lignin. This has not been observed for fibers that do not contain lignin [29].

3.1.2.3. Photo-induced metal growth using irradiation

The *in situ* reduction using UV irradiation is a simple method to produce metal NPs on the surface of cellulose fibers. The preparation of the nanocomposites is based on the photo-activation of cellulose surface by photons, followed by chemical reduction of metal salts. A possible mechanism is based on the number of reducing sites at the surface of cellulose fibers that are activated by UV photons [46]. The active role of reducing ends of cellulose chains in this mechanism has been demonstrated by employing cellulose fibers (VC and BC) in which such groups had been removed to show that metal NPs are not formed [28]. For cellulose/Ag nanocomposites [28, 46, 47] it was demonstrated the relevance of UV light intensity and time of irradiation as important parameters to control the amount of silver and their dispersion in the final composites. The metal NPs formed by this method tend to coat the cellulose fibers, with tendency to aggregate over prolonged times of UV irradiation, eventually leading to NPs with variable morphologies.

3.1.3. Electrostatic assembly

The electrostatic assembly of NPs is based on the sequential adsorption of oppositely charged species on a solid substrate which very often is mediated by ionizable polymers [70]. This assembly technique offers some advantages over other methodologies due to the possibility of a better control of inorganic content in the final nanocomposites, full control of NPs size and morphology, and normally leads to less agglomeration of previously prepared NPs.

Cellulose fibers dispersed in water are negatively charged over a wide pH range (2-10), due to the presence of ionizable moieties such as carboxyl and hydroxyl groups, resulting from chemical processing or from minor polysaccharides such as glucuronoxylans [71]. The deposition of Au NPs [39, 72] onto cellulosic fibers was achieved by previous treatment of fibers using multi-layers of poly (diallyldimethylammonium chloride) (polyDADMAC), poly (sodium 4-styrenesulfonate) (PSS), and again polyDADMAC. The use of a positively charged polyelectrolyte as the outer layer favored electrostatic interactions of the fibers with negatively surface charged Au NPs. This methodology has been also applied to the fabrication of Ag/NFC composites using distinct polyelectrolytes as macromo-

lecular linkers [16]. Another example of an electrostatic assembly procedure was based on the chemical modification of cellulose with (2,3-epoxypropyl) trimethylammonium chloride (EPTAC) [36, 73]. This methodology allowed the grafting of the cellulose substrates with positive ammonium ions which is particularly useful for attachment of metal NPs with surface negative charge.

3.1.4. Other methodologies

Chemical modification of cellulose can be performed to produce distinct types of cellulose/metal nanocomposites. In this context, common cellulose derivatives such as carboxymethyl-cellulose, cellulose acetate and hydroxypropyl cellulose have been used [74-76]. 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) has been used to oxidize selectively the C6 primary hydroxyl groups of cellulose resulting in the corresponding polyuronic acids [67]. In this context, BC acts as an efficient template with the surface carboxylate groups used to quantitatively anchor metal ions via an ion-exchange reaction. The subsequent reduction of the cations at the nanofibers' surfaces originated metal NPs with a narrow size distribution. Chemical surface modification of hydroxyl groups into aminic groups, which act as selective coordination sites [52] and the use of thiol labeled cellulose through spontaneous chemisorption [53] has been demonstrated. In the latter, chemical attachment of the NPs onto the fibers' surface limits particle desorption, hence extending the lifetime of the resulting hybrid materials.

The fabrication of size-controlled metal nanowires using cellulose nanocrystals as biomolecular templates has been reported [54]. This method allowed designing Au nanowires of variable sizes that exhibit unique optical properties by controlling the thicknesses of gold shells. In another approach microwave irradiation was used as an efficient method to prepare cellulose/metal nanocomposites [49]. In this study cellulose was treated in a lithium chloride (LiCl)/ N,N-dimethylacetamide (DMAc) and ascorbic acid mixture to produce a homogeneous distribution of Ag NPs within the cellulose matrix. More recently the same group has reported the use of ethylene glycol as solvent, reducing reagent, and microwave absorber, thus excluding an additional reducing agent [50]. This one-step simultaneous formation of Ag NPs and precipitation of the cellulose is a suitable method due to its characteristics of rapid volumetric heating, high reaction rate, short reaction time, enhanced reaction selectivity, and energy saving [49, 77]. A similar methodology was applied in a one-pot process to produce Ag-cellulose nanocomposites, however in this case the cellulose matrix was used as the reducing and stabilizer agent in water suspensions [51].

3.2. Metal nanoparticles as cellulosic composite fillers and their applications

There are a variety of metal NPs that can be used as dispersed phases in bionanocomposites with cellulose. In the last decades there has been great progress in the colloidal synthesis of inorganic NPs. Colloidal metal NPs have received great attention due to their unique optical, electronic, magnetic, antimicrobial properties. Their small size, large specific surface area and tunable physico-chemical properties that differ significantly from the bulk analogues led to intense research on their use in composite materials [78]. This section gives ex-

amples of research on metal NPs used as fillers in cellulose nanocomposites. The applications of these materials are related with the type of NPs present though new properties arise due to the combined use of the metal NPs and cellulose. Table 2 summarizes important applications of cellulose/metal nanocomposites and a brief description will follow in this section.

3.2.1. Silver

Nowadays a renewed interest in Ag antimicrobial materials has reappeared mainly due to the increase of multi-drug resistance of microbial strains to conventional antibiotics. The design of protective medical clothing or antibacterial packaging materials are examples of this current trend [35]. Ag NPs are well known by their strong cytotoxicity towards a broad range of microorganisms, such as bacteria and fungi [79].

Similarly to other applications, well dispersed Ag NPs in the cellulose matrix are required otherwise the antimicrobial effect decreases. However, important parameters such as particle size distribution, metal content, cationic silver release and interaction with the surface of cellulose are also relevant parameters that influence the antimicrobial activity of these nanocomposites [23, 69]. Due to the high water holding capacity and biocompatibility, BC wound dressing materials with improved antimicrobial activity have been prepared using Ag [57, 60]. Other examples include the development of antibacterial food-packaging materials [35, 80], bactericidal paper for water treatment [20] and the study of laundering properties of nanocomposites [24, 81].

The cellulose fibers can be chemically functionalized creating reactive sites in order to control the *in situ* synthesis of Ag NPs. Few examples are known of composites of NFC and metal NPs [16, 68]. Thus NFC functionalization with fluorescent Ag nanoclusters has been performed by dipping nanocellulose films into a colloid of Ag protected with poly(methacrylic acid) (PMAA) [64]. The electrostatic assembly of commercial Ag NPs onto NFC mediated by polyelectrolyte linkers have been described as a possible route to scale up the preparation of Ag/NFC composites [16].

Nanostructured metals such Ag and Au are well known substrates for surface enhanced Raman scattering (SERS). Strong enhancement of the Raman signals is observed for certain molecules chemisorbed to the surface of these metals. Therefore the combined use of these metal NPs and cellulose is of great interest to develop molecular detection and biosensing platforms [37]. In this context, the use of cellulose nanocomposites might bring several advantages such as the fabrication of handy and low cost substrates in the form of paper products. A study on the use of distinct cellulosic matrices containing Ag NPs has shown that the BC/Ag nanocomposites were more sensitive as compared to the vegetable analogues, namely in biodetection of amino acids [37]. The use of filter paper with Ag NPs or Au NPs demonstrate the potential of these materials as SERS platforms to study diverse analytes such as *p*-hydroxybenzoic [21], single-walled carbon nanotubes [82] and binary mixtures of 9-aminoacridine-acridine and acridine-quinacrine separated by paper chromatography [83].

A simple and low-cost approach to the fabrication of fuel cells has been described based on a nanostructured Ag electrocatalyst and cellulose. Heat removal of the template and combination with graphite improved oxygen reduction in basic medium [38].

Metal NPs	Application	Metal NPs	Application
Ag	Anti-counterfeiting	Au	Biosensors
	Artificial skin		Catalytic
	Food-packaging		Conducting
	Antimicrobial		Electronic devices
	Water treatment		Medical (Drug and protein delivery)
	Wound dressing		SERS
	Biosensors		Smart papers and textiles
	Catalytic		Antimicrobial
	Paper industry		Catalytic
	SERS		Catalytic
Pt	Textiles	Pd	Catalytic
	Catalytic	Co	Electronic actuators
	Electrocatalytic		Magnetic
	Photocatalytic		Microfluidics devices
Fuel cells			

Table 2. Common applications of cellulose/metal nanocomposites.

3.2.2. Gold

The noble metal gold has long been a cornerstone precious metal occupying a premier position in the world economy, representing wealth and high value. Traditionally it has been used in its yellow lustrous bulk metallic form for monetary and jewelry applications and over recent decades as an electrical conductor and chemically inert contact material in the electronics industry [29]. Au NPs are among the most studied particles in modern materials science namely due to the number of available methods to produce colloids with uniform-particle sizes and well-defined morphologies. Stable Au NPs colloids have been prepared whose particles surfaces are efficiently stabilized by citrate anions in hydrosols or by alkanethiols when organic solvents are used [84].

Cellulose/Au nanocomposites have been used as catalysts in glucose oxidation [40]. It has been reported that good dispersion of Au NPs in cellulose allowed effective contact with reactants making these materials good catalysts for the reduction of 4-nitrophenol. [85] Furthermore, cellulose can be used in several solvents having potential applicability in a variety of reactions. Another interesting possibility is the transformation of renewable biomass resources into valuable chemicals. Selective conversion of cellulose or cellobiose into gluconic acid catalyzed by polyoxometalate- [86] or CNT-supported by Au NPs [87] has been demon-

strated. Agglomeration of the Au NPs in the cellulose nanocomposites has been described as a major limitation decreasing the catalytic activity of the composite materials.

Cellulose based sensors have great interest in several applications including in fields as diverse as medical diagnosis, environmental control and food safety. It is important to develop materials that show good electron transfer capability, biocompatibility, stability and easy accessibility towards the analyte. Additionally large surface area for immobilization of the analytes, rapid response, high sensitivity, good reproducibility and anti-interference are also required characteristics. As expected, it is a great challenge to develop a single material that include all these important characteristics [63].

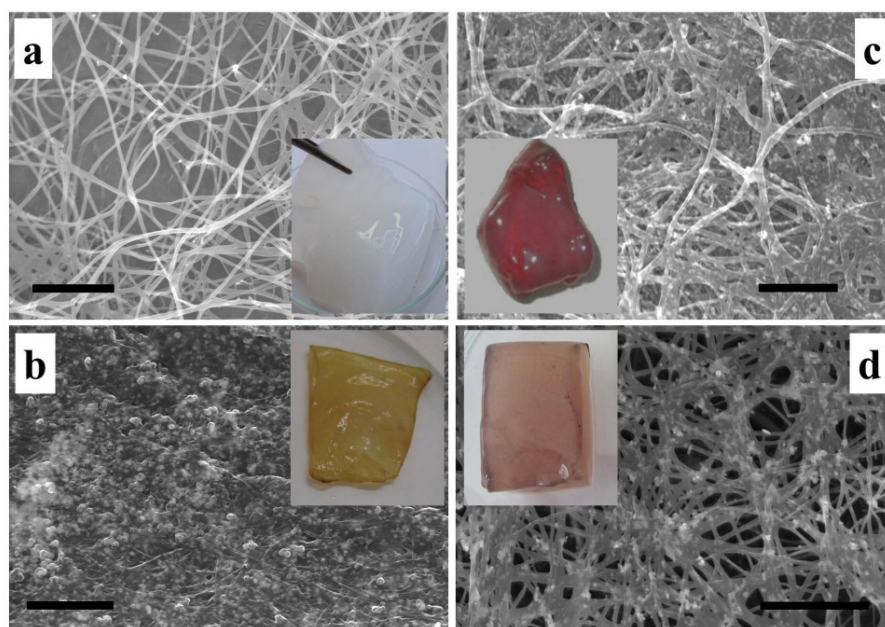


Figure 3. SEM images and micrographs (inset) of bacterial cellulose (BC) and derived composites: a) BC; b) BC/Ag; BC/Au and d) BC/Cu (bar: 1.5 μm).

Cellulose based sensors are inexpensive, disposable, and environmentally friendly. These materials transport liquids via capillary action with no need of external power [88]. BC/Au nanocomposites have been reported to exhibit good sensitivity, low detection limit and fast response toward hydrogen peroxide making these materials suitable matrices for enzyme immobilization [61-63]. The practical application of these nanocomposites for glucose biosensors in human blood samples has been reported. The values obtained showed good agreement with corresponding values obtained in hospital trials. The entrapment of Au NPs and enzymes in a paper coating material of sol-gel derived silica has been reported as a versatile material to be used as an entrapment medium and hydrophobic agent. This characteristic allowed more reproducible enzyme loading on rough and non-uniform paper surfaces [88].

Conductive or semi-conductive nanocomposites containing Au NPs are very attractive for electronic applications. Although uniform NPs dispersions are required for many applica-

tions, for some cases controlled aggregation is used as an advantage. Electrical conductive cellulose films containing Au NPs have been prepared by self-assembly showing electrically conducting above a gold loading of 20 wt % [84]. The mechanism of electronic conduction in Au NPs-cellulose films is strongly dependent on the resistivity of the film [89].

3.2.3. Copper

Copper NPs were found to be good candidates as efficient catalysts in hydrogen production [90]. An important use for Cu NPs include the fabrication of low electrical resistance materials due to their remarkable conductive properties [91]. In addition Cu NPs and their oxides show broad spectrum biocide effects and the antimicrobial activity has been reported in studies of growth inhibition of bacteria, fungus, and algae [48].

Antimicrobial nanocoatings of Cu NPs on cellulose have been fabricated via electrostatic assembly [48]. In this process, a chemical pre-treatment step was performed in order to impart surface charge on the cotton substrate that promoted binding of cupric ions, followed by chemical reduction to yield metal nanostructured coatings. The resulting composites showed high effectiveness killing to multi-drug resistant pathogen *A. baumannii*. Compared to the Ag analogous there was no particle leaching for the copper nanocomposites.

The use of microcrystalline cellulose as a porous natural material supporting copper ions has been demonstrated [31, 42]. Reducing agent and respective amount have critical importance to achieve Cu NPs (or the metal oxides) with controlled particle size. Conversion of CuO into Cu using cellulose as a reducing agent under alkaline hydrothermal conditions was described as a green process for the production of Cu at power low cost [32]. This process gives rise to the conversion of cellulose into value-added chemicals, such as lactic acid and acetic acid. The possibility of modifying the surface of cellulosic fibers and using chitosan has also been reported [41]. In this case, chitosan-attached cellulose fibers were used in the immobilization of Cu ions followed by a reduction step in the presence of borohydride to obtain Cu NPs. Unlike Au e Ag, non-coated Cu NPs oxidize extensively under ambient atmosphere. Although this detrimental effect is limited by incorporating the Cu NPs in bacterial cellulose, stable Cu/cellulose composites have been prepared by using Cu nanowires as inorganic fillers [64]. These nanocomposites are attractive for the emerging technologies based on electronic paper.

3.2.4. Platinum

Platinum is an useful material for numerous industrial catalytic applications and several reports have described the synthesis of Pt NPs using a variety of methods [33]. This metal is also considered the best electrocatalyst for the four-electron reduction of oxygen to water in acidic environments as it provides the lowest overpotential and the highest stability [65]. The preparation of Pt/cellulose nanocomposites generally involves the reduction of ionic Pt by addition of a reducing agent (NaBH_4 , HCHO, ...) in the presence of cellulose, which might act as a structural-directing agent [43].

Nanocomposites of Pt and amorphous carbon films were obtained by the catalyzed carbonization of cellulose fibers [44]. This type of NPs has been synthesized using NaBH_4 as reducing agent in hydrothermal conditions in the presence of nanoporous cellulose [43]. The Pt NPs were well dispersed and stabilized in the cellulose network thus avoiding particle aggregation. Cationic cellulose bearing ammonium ions at the surface has also been used to produce this type of nanocomposites [36]. In this method, the attachment of negatively charged Pt NPs onto cationic cellulose substrates was promoted via electrostatic interactions, which result into high surface coverage of the fibers.

Thermally stable proton-conducting membranes have been prepared by the *in situ* deposition of Pt NPs on BC membranes, via liquid phase chemical deoxidation method in the presence of the reducing agents NaBH_4 or HCHO [65]. The obtained black nanocomposite have been reported to display high electrocatalytic activity, with good prospects to be explored as membranes in fuel cell field [63]. However in case of Pt/cellulose nanocomposites, the reducing groups of cellulose are less effective in the reduction of metal precursors. A supercritical CO_2 / water system for reducing H_2PtCl_6 precursor to PtNPs using suspended crystalline cellulose nanofibrils of cotton has been described [33]. In this methodology VC was employed in a direct reduction route to form cellulose/Pt nanocomposites using a renewable reducing agent. The same authors have reported the use of cellulose nanocrystals (large surface area per unit weight in relation to normal cellulose fibers) for the same purpose. In this alternative the reaction temperature can be lowered to achieve Pt NPs with an average diameter of approximately 2 nm and with narrow particle size distribution [34].

The incorporation of irregularly shaped Pt NPs dispersed in IL and cellulose acetate lead to a nanocomposite that exhibits synergistic effects in the activity and durability enhancement of the catalyst [92]. The authors have suggested that the presence of IL caused higher separation of the cellulose macromolecules which result in a higher flexible and lower viscous material. The ensuing nanocomposites displayed higher catalytic activity and stability when compared to the Pt NPs dispersed in the IL. Potential uses of cellulose/Pt nanocomposites in catalysis comprise the hydrogenation of cyclohexene [92] and hydrogen production [93].

3.2.5. Cobalt

Co NPs in cellulose matrices has been a topic of interest due to the potential application as magnetic nanocomposites. However, due to easy oxidation their use has been associated to the formation of metal alloys such as FeCo, as will be described in section 3.2.6. The properties of magnetic Co NPs are determined in large extent by surface atoms. In addition, crystallinity, size distribution, particles shape and neighboring particles, affect the response of the material when submitted to a magnetic field. Therefore the matrix in which the NPs are embedded, in this case cellulose, has strong influence on the magnetic properties of the NPs as well as the distance between them [45].

The structure and morphology of Co NPs synthesized in cellulose matrix and resulting magnetic properties have been reported [45]. The authors have used two distinct chemical routes

to investigate the effect on the structural properties of the NPs. In the borohydride reduction amorphous Co–B or Co oxide composites were obtained in which a detrimental effect on the magnetic properties was observed as compared to bulk Co. In contrast, using a NaH_2PO_2 reduction method, well-ordered ferromagnetic cobalt nanocrystals were obtained in which the magnetic properties of the samples resemble those of bulk cobalt.

3.2.6. Metal alloys

The properties of metallic systems can be significantly varied by blending the metal components into intermetallic compounds and alloys. The diversity of compositions, structures, and properties of metallic alloys not only can originate new properties but might also improve certain properties of the metal components due to synergistic effects [94]. The association of metal alloys (typically bimetallic) to cellulose yields interesting materials with well-defined, controllable properties and structures on the nanometer scale coupled with easier processing capability of the matrix. A tubular FeCo bimetallic nanostructure was obtained by using a cellulose/cobalt hexacyanoferrate (Fe–CN–Co) composite material as precursor [95]. The metal was then deposited onto a cellulose template via H_2 gas-phase reduction that converted the precursor in FeCo bimetallic NPs. The FeCo NPs formed hollow tubular structures that mimic the original precursor composite morphology via a template-direct assisted method.

Lightweight porous magnetic aerogels made of nanofibrils of VC and BC have been compressed into a stiff magnetic nanopaper [66]. The thick cellulose fibrils act as templates for the growth of discrete ferromagnetic cobalt ferrite NPs forming a dry, lightweight, porous and flexible magnetic aerogel with potential application in microfluidics devices and as electronic actuators. PdCu/BC nanocomposites showing high catalytic activity have been obtained, in which the PdCu NPs were homogeneously and densely precipitated at the surface [96]. Although the cost of these materials need to be considered, these composites are of potential interest in water remediation processes because the Pd Cu alloy is considered the best catalyst for the denitrification of polluted water.

3.3. Multifunctional cellulose/metal nanocomposites

The combination of cellulose with distinct metal NPs to design multifunctional nanocomposites is an interesting approach to extend the scope of these materials to several areas of applications. A fluorescent nanocomposite exhibiting antibacterial activity has been achieved through the functionalization of NFC with luminescent silver metal nanoclusters [68]. A novel type of supramolecular native cellulose nanofiber/nanocluster adduct was obtained by using poly(methacrylic acid) (PMMA) as the mediator between Ag nanocluster and cellulose. The PMMA not only stabilized the Ag nanoclusters but also allowed hydrogen bonding between the particles and cellulose. Another example reports Au and Ag NPs as colorfast colorants in cellulose materials for textiles with antimicrobial and catalytic properties [29].

Also the combination of metal NPs with metal oxides is an emerging strategy to produce a range of multifunctional cellulose nanocomposites. The linkage of Ag NPs on magnetite containing BC substrates has been reported to produce magnetic and antimicrobial composites [97]. The possibility of bringing together diverse types of inorganics NPs and distinct cellulose matrices opens a new field for future applications, where the design of natural based multifunctional materials will be privileged.

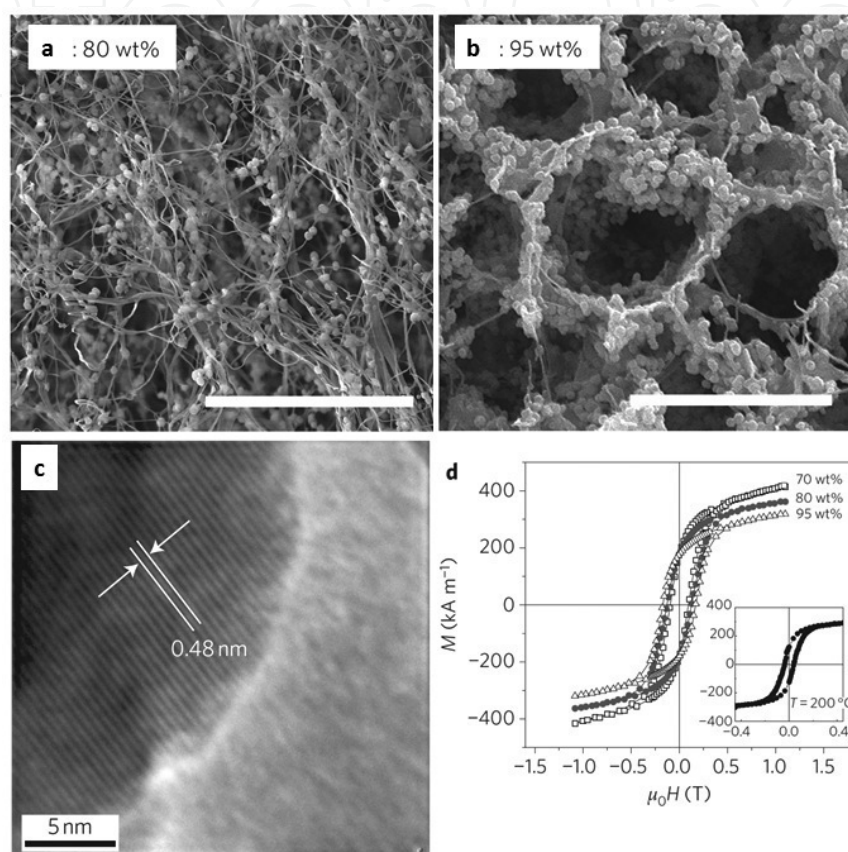


Figure 4. Magnetic aerogels at different loadings of cobalt ferrite nanoparticles. SEM images of sample (a) 80 wt% of particles and sample (b) 95 wt% of particles (Scale bars, 4 μm). (c) HRTEM image of a single particle from sample (b) showing the lattice fringes corresponding to the {111} reflections of the spinel structure, and the corresponding distance. The image was fast Fourier transform (FFT) filtered for clarity. (d) Magnetic hysteresis loops of cobalt-ferrite-based aerogels. Inset: hysteresis loop of cobalt ferrite-based of sample (a) at $T = 200\text{ }^\circ\text{C}$. (Adapted by permission from Macmillan Publishers Ltd: Nature Nanotechnology([66]) (Copyright 2010).

4. Concluding remarks and future trends

The combination of metal nanoparticles and distinct types of cellulose matrices takes benefit of the properties of both components and simultaneously might result in properties due to synergistic effects. Besides the nature of the components in the final nanocomposite, the performance of the final material depends on the preparative methodologies employed in their production. This review has shown the relevance on the nanocomposite performance not

only of the type of metal NPs used as fillers but also the origin of the cellulose matrix. In this context, methods that allow the chemical modification of both components, metal NPs and cellulose matrices, appear a very promising field of research to develop new functional materials. The combination of diverse metal NPs in cellulosic matrices is an important but less exploited strategy to prepare multifunctional composites. Fundamental studies concerning physico-chemical interactions that occur between the composite components have been scarce despite their obvious relevance in the optimization of the materials properties. Finally, the impact of these nanocomposites on health and environment is an issue in the agenda of the scientific community but whose importance will increase due to the commercialization of products based on these materials.

5. List of abbreviations

BC	Bacterial cellulose
CNT	Carbon nanotubes
DMAC	N,N-dimethylacetamide
DP	Degree of polymerization
EPTAC	(2,3-epoxypropyl)trimethylammonium chloride
FFT	Fast Fourier transform
HRTEM	High resolution transmission electron microscopy
IL	Ionic liquids
NFC	Nanofibrillated cellulose
NPs	Nanoparticles
PEI	poly(ethyleneimine)
PMMA	poly(methacrylic acid)
polyDADMAC	poly(diallyldimethylammonium chloride)
PSS	poly(sodium 4-styrenesulfonate)
PVP	polyvinylpyrrolidone
SEM	Scanning electron microscopy
SERS	Surface enhanced Raman scattering
TEA	Triethanolamine
TEMPO	2,2,6,6-tetramethylpyperidine-1-oxy radical
UV	Ultraviolet
VC	Vegetable cellulose

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