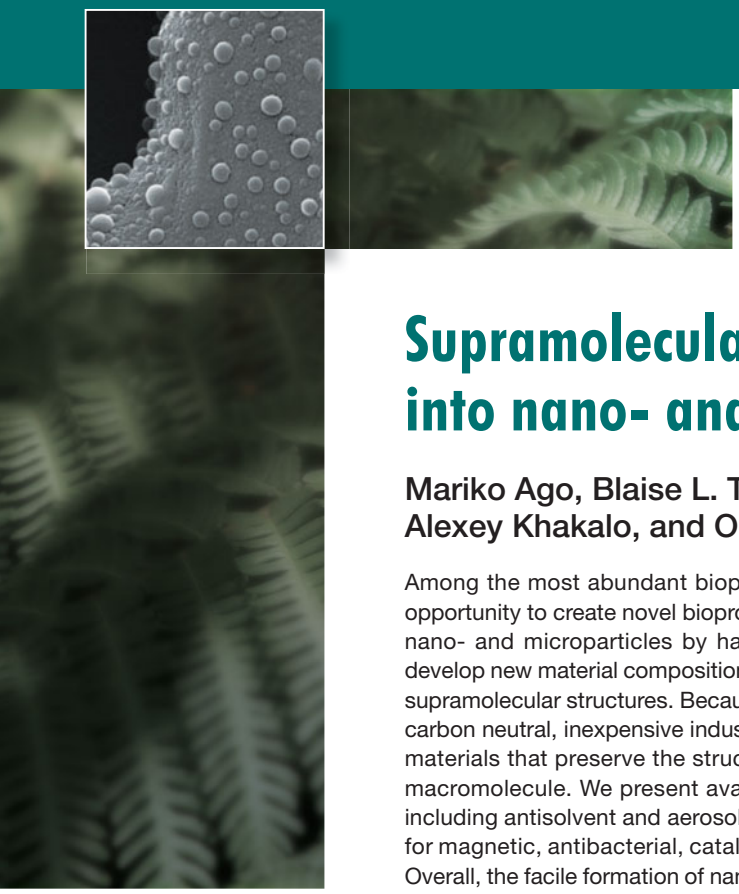


Supramolecular assemblies of lignin into nano- and microparticles

Mariko Ago, Blaise L. Tardy, Ling Wang, Jiaqi Guo, Alexey Khakalo, and Orlando J. Rojas

Among the most abundant biopolymers in the biosphere, lignin represents an untapped opportunity to create novel bioproducts. In this article, we discuss possibilities to synthesize nano- and microparticles by harnessing lignin's inherent tendency to associate and to develop new material compositions and functions by controlling its capacity to assemble into supramolecular structures. Because lignin is biodegradable, antimicrobial, antioxidative, and carbon neutral, inexpensive industrial lignin streams could generate value-added particulate materials that preserve the structure, composition, and colloidal features inherent to this macromolecule. We present available routes for synthesis or isolation of lignin particles, including antisolvent and aerosol processing. Metallic and polymeric lignin particle hybrids for magnetic, antibacterial, catalytic, photonic, and other applications are also discussed. Overall, the facile formation of nano- and microparticles from lignins is expected to open new pathways toward future material development.

Lignins and their untapped potential

Wood fibers are widely utilized in mature industries that take advantage of unique chemical and structural features of cellulose. However, the same cannot be said about lignin, another important component in wood. Lignin is a highly branched and amorphous biomacromolecule that displays different interunit linkages and is derived from complex phenylpropanoid pathways. In plants, lignin provides protection against various biotic/abiotic stresses and support to sap-conducting elements. The existence of lignin has contributed to the capacity of land-based plants to dominate terrestrial environments.[1,2]

The main source of lignin, readily available for use on a large scale, comprises so-called "black liquors" produced as side streams during fractionation of wood fibers for use in pulp and paper industries.[3,4] Lignin extracted from the most typical process, so-called kraft pulping (a method that uses alkaline liquors for lignin solubilization), has a low degree of polymerization, with a weight-averaged molecular weight of 1–5 kDa (1–5 Kg/mol), lower than other commercially available lignins such as lignosulfonates (5–400 kDa [5–400 kg/mol]). Other lignins, such as those extracted with organic solvents (organosolv lignins) are in the range of 0.5–3 kDa ([0.5–3 kDa]; note that the polydispersity of lignosulfonate and kraft lignins is high compared to organosolv lignins). These technical lignins comprise low quantities of oxygen-containing functional groups (such as phenolic hydroxyl, carboxyl, and sulfonate groups, depending on the type), making them a viable feedstock for biomaterials production.[5] Water-soluble lignosulfonates are, by far, the most used technical lignin today.[5] Lignin represents a suitable source of bioenergy, considering its density and calorific value (similar to that of ethanol, 27 KJ/g).[6,7] For this and other practical reasons, most industrial lignins are burned, on-site, for energy cogeneration; only a small fraction are used for materials.

Assessments performed on extracted kraft lignin have determined that it may be a preferable precursor compared to synthetic organic counterparts of similar molecular complexity. This is due to the energy efficiency of lignin extraction over organic synthesis. Recent environmental life cycle cradle-to-gate analyses of the impact of integrating a commercial-scale lignin extraction process and lignin co-product to an existing kraft pulp mill indicated a considerable reduction in global warming.[8] Thus, lignin isolated from pulp mills represents an emerging opportunity to create new co-products and

Mariko Ago, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; mariko.ago@aalto.fi
Blaise L. Tardy, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; blaise.tardy@aalto.fi
Ling Wang, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; ling.wang@aalto.fi
Jiaqi Guo, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; jiaqi.guo@aalto.fi
Alexey Khakalo, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; alexey.khakalo@aalto.fi
Orlando J. Rojas, Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Finland; orlando.rojas@aalto.fi
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novel biomaterials. Lignin is biodegradable, antimicrobial, antioxidative, and CO_2 neutral.[4,9–11] In this article, we discuss the use of lignin for its colloidal or supramolecular assembly (e.g., in particles), one of its many promising possibilities.

Micro- and nanoparticles from lignins

In materials science, nano- and colloidal particles (herein, referred to as microparticles) are used to achieve properties that are otherwise difficult to realize (i.e., to impart color, thermal and light stability, or to improve material strength).[12] Typically, nanoparticle isolation is less energy demanding than chemical-synthesis routes. This is a direct result of nanoparticles possessing surface energies that are comparatively smaller than typical reaction enthalpies (e.g., dissolution, reduction).[12] In particular, polymer nanoparticles are playing a pivotal role in a wide spectrum of areas.[13] Compared to other biomolecules,[14] lignin superstructures are not an exception since they can also be converted into functional nanoparticles. Industrial or technical lignins have been proposed for the development of value-added particulate materials that preserve the structure, composition, and colloidal features of the macromolecule. They are of high interest for controlled release, encapsulation, and protection.[15] Some of the functions are already bestowed to lignin by nature, to fight against (bio)degradation (microbial, UV, heat), oxidation, and dehydration.

Lignin assemblies extruded or coalesced from fibers and self-assembly

The tendency of lignin to form particles is exemplified by the coagulation process that occurs, *in situ,* in the cell walls of stems of plants subjected to heating or mild hydrolytic treatments. This was observed, accidentally, in efforts aimed at enhancing the access of cellulose to enzymes.[16–18] The temperature onset for particle formation was identified to be above 175°C after a 30-min hydrothermal treatment, with a large number of particles already formed at 205°C.[19,20] The lignin particles were revealed on or inside the fibers, presumably after cleavage of the carbohydrate–lignin bonds and formation of a continuous lignin phase above its glass-transition temperature.

Particles ranging in size between 5 nm and 10 μm have been reported, depending on the thermochemical treatment type at 150–220°C.[21] The particles were noted to be smooth (by scanning electron microscopy [SEM]),[22] while a significant increase in roughness occurred for pseudo-lignins or lignin–carbohydrate complexes.[21,23] The particle size was reduced when the fibers were treated with ionic liquids.[24] Fourier transform infrared analysis highlighted strong absorption from the aromatic character of lignin; however, no bands were observed for the alcohol C-O stretching, typical of carbohydrates attached to lignin.[21,22] This was further confirmed by nuclear magnetic resonance analysis and cytochemical staining. When alkali-extracted lignin was heat treated, it formed highly porous grains.[25] The lignin particles showed a strong affinity to cellulose (Avicel[26] or filter paper[21]).

The suggested mechanism for the formation of lignin particles (**Figure 1**) involves lignin coalescence into a fluid phase at high temperature and migration toward the cell surface, leading to collapse of the underlying fiber and particle formation by extrusion. This migration occurred mostly toward the cell wall rather than cell corners.[27] Similar phenomena may occur upon acid pretreatment at relatively lower temperatures (130°C).[28]

While the *in situ* formation of lignin particles is a fascinating observation, their isolation in such a state is a challenging task. In fact, scalable production of lignin particles is more likely to rely on lignin that has been extracted and processed in the dissolved state, as in the "black liquors." Such particle formation strategies may take advantage of the self-assembling and self-polymerizing abilities already noted for lignin, combined with solvent exchange, heat, or enzymatic treatment, as well as acid hydrolysis or condensation in alkali.[29–33]

The kinetics of assembly or aggregation of lignin into particles can be controlled by tuning salinity, temperature, pH,[29] or solvency.[34] When the particles form by precipitation, small aggregates initially form, clustering into larger entities.[32] Alternatively, fractal networks of lignin that display a high surface area can be obtained via sol-gel processing.[24,29]

Within each lignin precursor there is usually a large diversity of structures, chemical functionalities, and molecular masses. Despite this, it is remarkable that the formation of such networks closely follows the aggregation behavior observed for systems that use only a few, well-defined components.[5,29] This suggests supramolecular aggregation of lignin into clusters and then into particles of known composition and properties. In addition to factors previously discussed that affect particle homogeneity upon self-aggregation, the interactions between functional groups with the solvent are expected to control clustering, especially in the initial stages of particle formation.

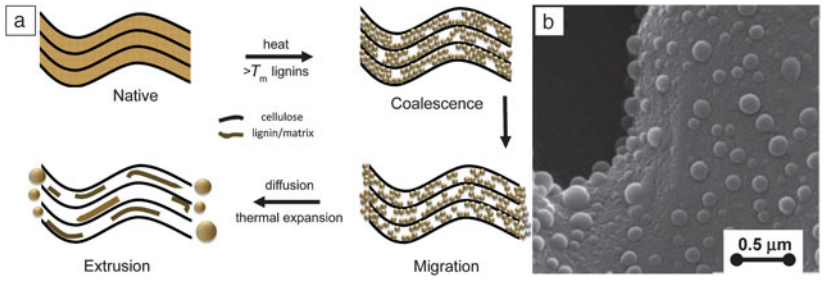


Figure 1. (a) Schematic illustration of the process of lignin particle formation in the fiber upon heat or mild hydrolytic treatments. The fibers coalesce at or above the melting temperature of lignin (T_m), followed by cleavage of the carbohydrate-lignin bond, resulting in free-flowing lignin that migrates to the cell wall with phase separates forming the particles on the surface. (b) Appearance of lignin particles as observed on the fibers. Adapted with permission from Reference 21. © 2008 Wiley.

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The nonhomogeneous charge distribution as well as the molecular stiffness of the aromatic groups suggest π-π stacking of lignin molecules, which plays an important role in their self-assembly into clusters and particles.[35] It has been shown that such stacking can be favored when the particles are formed in a solvent exchange process, in the absence of alkali groups. In such cases, better particle stability has been noted compared to that observed for particles formed (e.g., by precipitation).[33]

Routes for the synthesis of lignin nano- and microparticles

The large interest in fabricating polymeric particles has triggered recent efforts to use lignin in this context. The fabrication methods reported to date (summarized in **Table I**[22,32,35–61]) include precipitation with acid[33,36–38] or gas saturated with CO_2,[39] ultrasonic irradiation,[40] mechanical homogenization,[41] chemical modification,[42–45] antisolvent exchange, emulsion inversion, a combination of methods,[32,46–49] as well as procedures involving enzymes[22,50] or simply by drying.[51–53] Among these, acid precipitation, antisolvent exchange, and their combination have been the most popular. In the acid-precipitation process, lignin is initially dissolved in alkaline aqueous media (pH > 11), which favors electrostatic stabilization by deprotonation of carboxylic groups and phenolic OH. Upon reduction of pH (~3), the carboxylic and hydroxyl groups partially protonate, decreasing the surface charge density, resulting in destabilization of the lignin colloids. This triggers association and favors particle formation.

Only two generic methods from Table I will be discussed here, the antisolvent and the aerosol drying methods (for a complete list, please refer to **Table SI**, available online). In the antisolvent precipitation method, lignin is first dissolved in an appropriate solvent such as tetrahydrofuran (THF). Then spherical colloidal particles are formed by the addition of an antisolvent (e.g., water[32]) or by slow solvent exchange to water via dialysis.[34] A simple mechanism for colloidal formation has been proposed (**Figure 2**a).[32]

First, it is hypothesized that local lignin clusters form via hydrophobic interactions in the homogeneous solution, which then grow into colloidal spheres.[32] A nucleation-growth mechanism has been used to explain lignin particle formation when THF solvent is replaced with water during dialysis,[32] somewhat related to what has been proposed for other systems (see Table I).[33,34,36–38,61] In the nucleation-growth mechanism, acid precipitation occurs from an ethylene glycol solution, whereby planar phenol groups present in lignin stack in layers and afford densely packed nanoparticles (Figure 2b). In contrast, acidic precipitation of lignin from alkaline solution does not favor formation of stable stacks due to electrostatic repulsion via the negative charges in the aromatic groups, which are partially ionized under these conditions (Figure 2b).[33] Besides changes in pH, aggregation in aqueous solution can be influenced by ionic strength and temperature,[29] as well as factors inherent to the lignin such as concentration[35] and polydispersity.[62]

Contrary to previous cases where lignin particles were obtained in colloidal dispersions, we recently reported the facile fabrication of dry spherical lignin particles by using the aerosol flow method. This resulted in particle sizes ranging from the nano- to the micrometer scale (**Figure 3**). Additionally, *in situ* separation in fractions of different size ranges was possible. In this process, particle formation is speculated to occur by a sequential process that first involves evaporation of solvent

Table I. Methods reported to synthesize lignin nano- and microparticles.

Lignin Source	Preparation	Morphology	Application	References
Wheat straw, wood chips	*In situ* via ethanolic pulping and simultaneous saccharification and fermentation	Precipitate in fiber walls (1 μm). *In situ* particle formation (5–10 μm).	Antioxidant and UV protectant. Dispersion stability and solubility enhancer. Hydrophilicity/hydrophobicity. Pickering emulsions. pH responsiveness. Free-radical scavenging. Filler in composites. Wood resistance to biodegradation. Antibacterial activity.	22, 54
Kraft, sulfate, and organosolv lignins	Antisolvent and acid precipitation; acetylation; self-assembly; freeze drying; inverse suspension polymerization; aggregation; polymer grafting; mechanical homogenization; flash precipitation; aerosol flow	Beads, spherical, and quasi-spherical nanoparticles; mesopore and sheet-like structures		32, 34, 36, 44, 45, 52, 53, 55, 59–61
Black liquors	Enzymatic saccharification and physical comminution; acid and CO_2 gas-induced precipitation	Spherical, loosely bound, and irregular shapes		37–39, 41, 49, 50
Other	Nanoprecipitation by addition of water to acetone and water co-solution; supernatant phase generated from the epoxidation reaction; precipitation; hydroxymethylation; ultrasonic irradiation	Spherical and clustered structures		40, 42, 43, 46–48, 51, 56, 58

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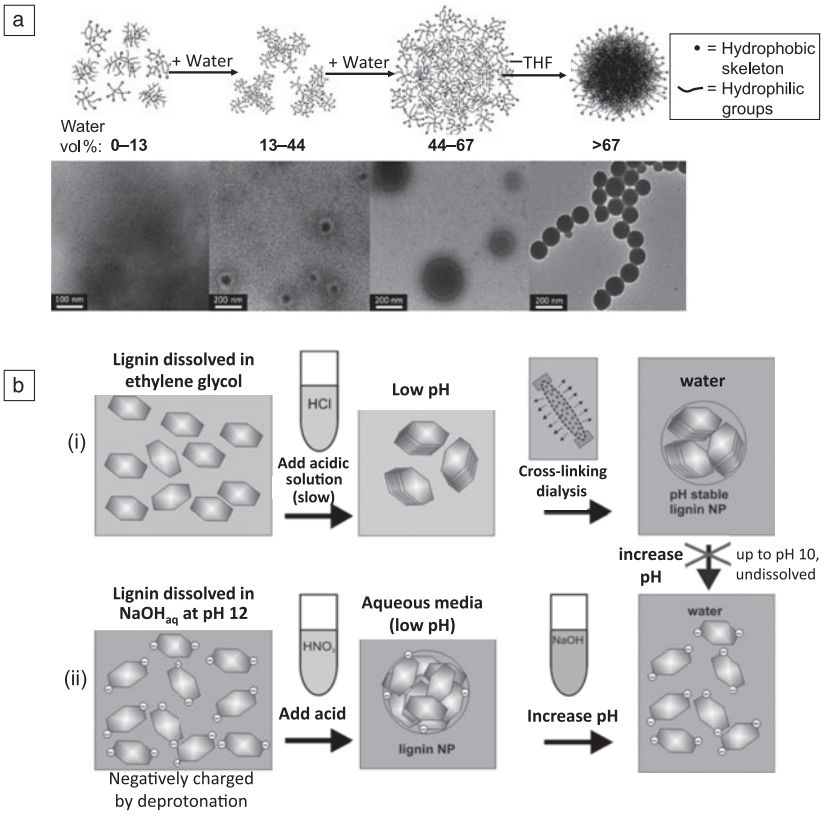


Figure 2. (a) Schematic representation of the formation process of lignin colloids after solvent exchange (tetrahydrofuran [THF]–H_2O) and respective transmission electron microscope images from the dispersions at different water content, as indicated. Adapted with permission from Reference 32. © 2014 Royal Society of Chemistry. (b[i]) Proposed mechanism for particle formation by precipitation with HCl (aq.) from lignin dispersions in ethylene glycol and subsequent cross-linking with glutaraldehyde upon dialysis. (ii) Alternatively, precipitation in the form of lignin nanoparticles can occur after lowering the pH of an aqueous solution with high pH. The lignin particles produced in this route can dissolve at a pH > 5, while those produced in (i) are stable up to a pH of 10. Adapted with permission from Reference 33. © 2012 Wiley. Note: NP, nanoparticle.

from the droplet surface. Simultaneously, a macromolecular shell forms on the droplet, while solvent remaining in the droplet interior gradually diffuses radially. Consequently, the solute condenses as the droplets evolve into dried, solid particles.[52] Although the number of reports that use drying is quite limited, this method is promising because of the high yield that can be achieved; in addition, it is a scalable nanomanufacturing approach that affords size control and high production capacity.[52]

Use of lignin particles in organic–inorganic hybrids and multiple component systems

The complexation of lignin with organic or inorganic compounds provides powerful control over the structure and properties of the formed particles. For example, silver ions infused in lignin nanoparticles coated with cationic polyelectrolytes (for increased adhesiveness onto negatively charged bacteria) resulted in excellent antimicrobial effects (**Figure 4**).[63] The Ag-lignin hybrid particles were capable of neutralizing both gram-negative (e.g., *Escherichia coli*) and gram-positive (*Staphylococcus epidermidis*) human pathogens as well as strong strains, for example, *Ralstonia-solanacearum*. This was achieved while using 10× less silver than that used in conventional aqueous solutions. In addition, Ag-lignin hybrids with antimicrobial capacity afforded filters with high activity against multidrug resistant strains.[64,65]

Hybrids of lignin with other metals such as iron have been reported as well.[66–68] In the latter case, morphology control was achieved, from hollow or solid nanospheres (**Figure 5**a).[69] Such metal-lignin hybrids can be used as magnetic, antibacterial, catalytic, photonic, and gas- and moisture-barrier materials, depending on the components.

Silica composites, in particular, are of high interest since this mineral enhances thermal and chemical stability, bioactivity, and biocompatibility. Reported procedures for preparing hybrid silica-lignin particles typically involve a sol-gel process. Tetraethoxysilane has been used as a silica precursor to prepare silica-lignin hybrid particles in the presence of sulfuric acid as a catalyst,[70] and mesoporous hybrids have been synthesized by using the same process.[71] Some features of the hybrid particles, such as pore size and surface area, were found to strongly depend on the pH and the mass ratio of lignin to silica. The resultant spherical, hybrid particles (ca. 60-nm dia.) were reported to have surface areas of ~472 m^2/g when prepared in optimized conditions (2:3 lignin:silica ratio at 90°C and pH 3 for 6 h). Coprecipitation processes were also introduced in the preparation of hybrid silica-lignin particles.[72] The obtained hybrid particles (300–400-nm dia.) underwent an undesired reduction in surface area, 386–55 m^2/g with increasing lignin loading. In this aspect, black liquors obtained from rice straw pulping are of interest since they contain sodium silicates. A facile and "green" approach was proposed to coprecipitate lignin-silica particles (50–100-nm dia.) by adjusting the pH via CO_2 bubbling.[73] The use of hybrid lignin particles with silica is expected to impact diagnostic and therapeutic efforts as well as the development of energy-storage materials, among others.

In the case of organic composites, functional lignin particles have been obtained via covalent conjugation. Lignin is composed of a large number of hydroxyl functional groups that can be covalently modified to develop new functionalities. For example, azo-modified (azo-lignin) particles have been synthesized with this concept in mind.[45,74] Azo-lignin with photoprocessing capability was achieved by coupling alkali lignin with diazonium salts of 4-aminobenzoic acid. The nanoparticles showed self-assembly and photo-induced

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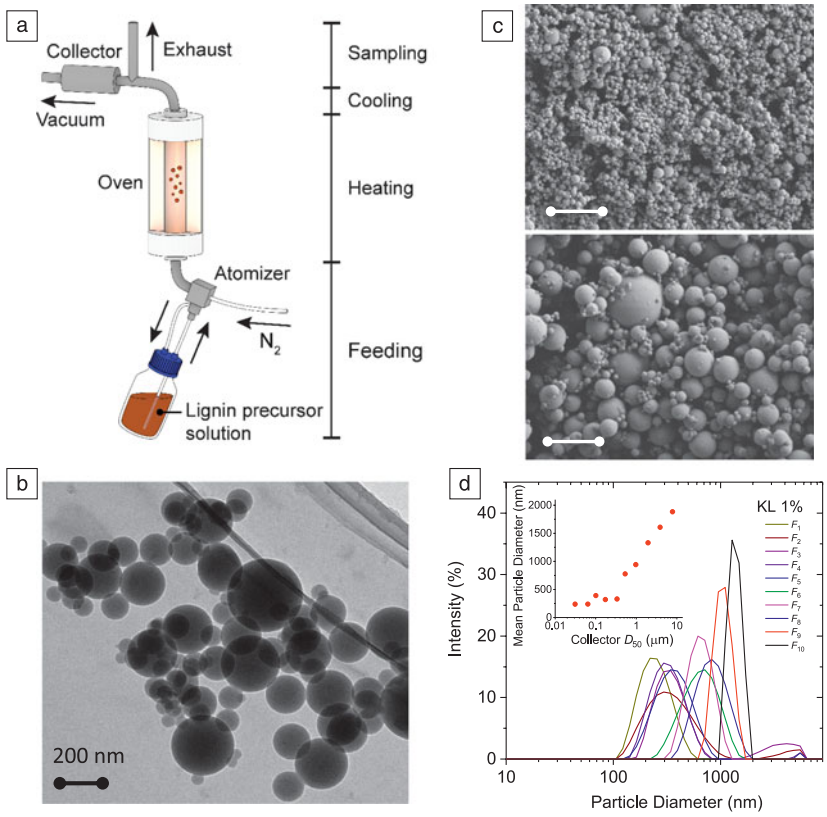


Figure 3. (a) Simplified schematic of an aerosol flow reactor used for the synthesis of lignin particles. (b) Transmission electron micrograph of kraft lignin (KL) solid particles from fraction F5, which corresponds to particle sizes <200 nm. The image indicates a homogeneous interior structure after isotropic shrinking from drying and perfectly spherical shapes. Scale bar = 200 nm. (c) Scanning electron micrographs are compared for solid lignin spheres obtained from two different particle fractions synthesized from organosolv lignin: top, F_5 (<200 nm) and bottom, F_8 (average size: 1 μm). Scale bar = 2 μm.[52] (d) Distribution and mean diameter (inset) of particles obtained from 1% KL precursor solution and separated *in situ* into different fractions by using a collector (see [a]) with different orifices (F_n or collector number). The size distribution for the different populations are displayed together with a plot of the relationship between collector orifice size (cutoff diameter, D_{50}) and mean particle diameter. The mean diameter of the lignin particles ranged from ~200 to ~1900 nm with increasing collector orifice size (fraction number). The particle size distribution became broader as the mean particle size decreased.[52]

morphological response. After 15-min exposure under a linearly polarized laser beam (488 nm), the colloidal spheres were deformed along the polarization direction of the light. More recently, an azo-lignin polymer was obtained by modification of lignin with aniline ($C_6H_5NH_2$). Hollow lignin colloidal spheres were found to be capable of self-assembling and encapsulating photosensitive avermectins (naturally occurring macrocyclic lactone derivatives with anthelmintic and insecticidal properties).[75] Lignin facilitated the controlled-release behavior of the drug and also acted as a photoprotectant to avoid the photodegradation of photosensitive pesticides.

One of the important challenges underlying the formation of composite materials with lignin is the compatibility of lignin with polymers that engage in hydrophilic–hydrophobic interactions at the interface. Composite polymer-lignin particles formed thus far mainly use biopolymers such as pectin, cellulose (Figure 5b), alginate (polysaccharide), and silk sericin (protein).[76–79] For example, macroporous Ca-alginate-lignin (MCAL) beads (4.1 ± 0.4 mm) were obtained with an immobilized white rot fungus, *Phanerochaete chrysosporium* (*P. chrysosporium*), endowing the system with a capacity to degrade aromatic hydrocarbon (phenanthrene).[80] The presence of lignin in the beads led to a ~29-fold increase in the phenanthrene adsorption capacity, and its four-day degradation was increased to ~42% compared to that of macroporous Ca-alginate beads. The enhanced growth and degradation indicated the role of lignin in MCAL-immobilized *P. chrysosporium* as an effective microbial model for intensified biodegradation of phenanthrene. Other examples of porous composite particles include those obtained after cross-linking lignin with sodium alginate via epichlorohydrin (epoxy resin with a high reactivity to phenols), which exhibited excellent adsorption efficiency for Pb ions and were used for their removal from aqueous media.[81]

The formation of structured assemblies such as nano- and microparticles from lignin opens the pathway to many applications traditionally dominated by synthetic, petrochemically derived, or inorganic particles, but with the added benefits inherent to lignin such as low toxicity, biodegradability, low cost, carbon footprint reduction, and abundance.

The presence of aromatic, phenolic, and amphiphilic groups in lignin makes it an ideal candidate for the formation of material for the adsorption of metal ions and chemicals. Lignin contains high amounts of methoxy, aldehyde, keto, hydroxyl, and phenolic functional groups, providing a large range of interactions that can be exploited for specific adsorption of small molecules or for metal chelation.[82–84] Compared to commercially available amorphous lignin powders, porous lignin particles have a larger surface area, bear more active sites, and display better efficiency for metal-ion sorption. Lignin spheres used in packed-bed columns efficiently extracted metal ions from solution and were identified as candidates for wastewater treatment or ore extraction;[69,76,81,85,86] mesoporous TiO_2-containing nanoparticles prepared via calcination of Ti-lignin systems showed excellent photocatalytic activity, which can be useful in similar applications.[67]

Overall, the prospects of lignin particles stem not only from their inexpensive, renewable sourcing and the structure they form, but also from the inherent macromolecular properties of lignin. This includes antioxidant behavior and high UV stability, both of which are of interest in fields such as

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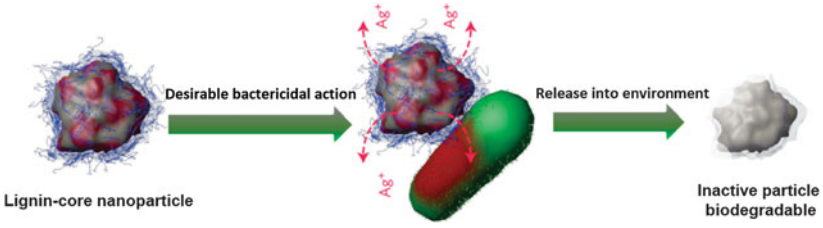


Figure 4. Schematic illustration showing the antimicrobial mechanism of silver ion-infused lignin-core nanoparticles. The cationic polyelectrolyte coating promotes the attachment of the nanoparticle onto negatively charged cell walls (green). Adapted with permission from Reference 63. © 2015 Macmillan Publishers Ltd.

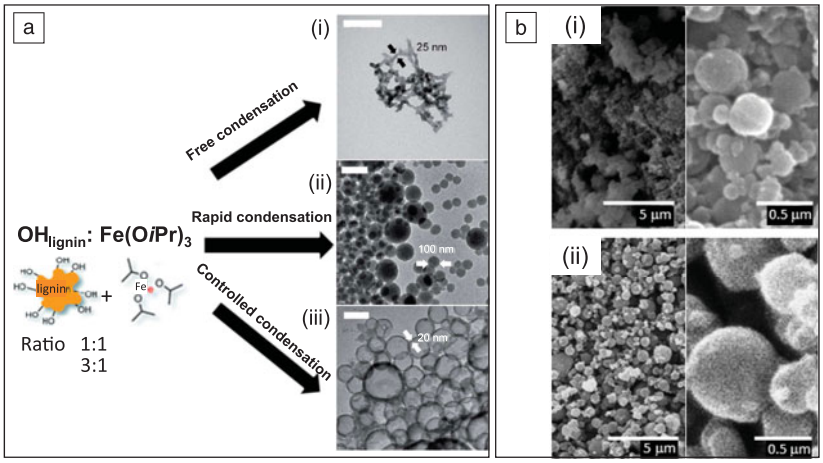


Figure 5. (a) Schematic illustration of the synthesis of different nanoparticle morphologies with iron and respective transmission electron microscope (TEM) images of the various structures obtained: (i) When a $Fe(OiPr)_3$ solution was added to a lignin solution at OH_{lignin}-to-$Fe(OiPr)_3$ ratio of 1:1, a precipitate formed immediately and hydrolysis yielded $Fe(OiPr)$-coated lignin nanoparticles forming fishnet-type open network structures. (ii) When less $Fe(OiPr)_3$ is used, for OH_{lignin}-to-$Fe(OiPr)_3$ ratio of 3:1, full condensation of OH groups with $Fe(OiPr)$ yielded large structures, and the lignin clusters were partially covered with $Fe(OiPr)$. The partially covered clusters fused together to form larger (ca. 200 nm) particles. (iii) Under conditions of controlled condensation (slow solution addition), the fusing of Fe:lignin nanoparticles created hollow spheres. Scale bars in all TEM images = 200 nm. Adapted with permission from Reference 69. © 2016 Royal Society of Chemistry. (b) Scanning electron microscope images for aggregates obtained with (i) alkaline lignin, hydroxyethyl cellulose, and sodium dodecylbenzenesulfonate as well as (ii) alkaline lignin, hydroxyethyl cellulose, NaOH, and sodium dodecylbenzenesulfonate, at (left) low and (right) high magnifications. The solvent was a mixture of water and $CHCl_3$. Reproduced with permission from Reference 78. © 2015 American Chemical Society.

nutritional and pharmaceutical formulations, and cosmetics.[45,55,58,59] Addition of lignin in cellulose hydrogel beads improved the activity and stability of immobilized enzymes (lipase), suggesting potential applications for biocatalysis, as well as in biomedical and bioelectronic applications.[11] Finally, other applications for lignin particles have been introduced, including templates for catalysts and supercapacitors,[67,68,78] bioprotective coatings,[43] and flame retardants.[50]

Outlook

The global market for inorganic and polymeric micro- and nanoparticles is considerable and, within this sector, lignin could play an important role because of its many advantages compared to synthetic polymers. In comparison to other polymers, lignin utilization is in its infancy. Developments that take advantage of the aromatic structure of lignin, its use along the biomass cycle as a whole, may have positive effects in the carbon dioxide targets of the global bioeconomy. Lignins are produced in biorefineries and bioproduct mills, and its properties (including surface energy and reactivity) can be tuned depending on the source of the fiber material and processing conditions. Beyond its current use in energy cogeneration as well as its potential to synthesize (carbon) fibers, lignin can be a platform for developing micro- and nanoparticles. The next generation of applications will require development of isolation processes to realize lignin streams that yield sufficient levels of purity and reactivity. Other aspects to be explored include the precise control over particle size and morphology as well as the possibility to endow new functional properties, by physicochemical transformation or by combination with other active substances.

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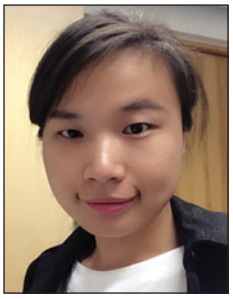


Mariko Ago is a research fellow in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. Previously, she was with the Department of Nanomaterials and Bio-Engineering, Tokushima Bunri University, Japan. Her research focuses on new functional materials from lignocellulose. She received the 2015 Young Investigator Award from the Cellulose Society of Japan. Ago can be reached by phone at +358 50 3841759 or by email at mariko.ago@aalto.fi.



Blaise L. Tardy is a postdoctoral researcher in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. He obtained his MSc degree in bioengineering from the Swiss Federal Institute of Science and Technology, Switzerland, in 2009, and his PhD degree in chemical and biomolecular engineering from The University of Melbourne, Australia, in 2015. His current research interests include the formation of structured materials from fiber-cell-wall components. Tardy can be reached by phone at +358 50 5979156 or by email at blaise.tardy@aalto.fi.

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Ling Wang is a doctoral candidate in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. She received her MS degree in bioproduct technology from Aalto University. Her research interests include cellulose-based filaments, lignin-based composites, and advanced biomaterials. Wang can be reached by phone at +358 50 5907467 or by email at ling.wang@aalto.fi.



Alexey Khakalo is a doctoral candidate in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. He is a renewable materials engineer with interest in sustainable product development with advanced functions. His research interests include biomaterials, bio(nano)composites, surface chemistry and interactions, paper technology, packaging, and advanced materials. Khakalo can be reached by phone at +358 50 4018149 or by email at alexey.khakalo@aalto.fi.



Jiaqi Guo is a doctoral candidate in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. He received his BE degree from Qilu University of Technology, China, in 2010, and his MS degree in chemical engineering from Åbo Akademi University, Finland. His current research interests focus on nanoparticle synthesis, novel chemical modification of nanocellulose and wood-derived structures, and design and synthesis of hybrid nanomaterials. Guo can be reached by phone at +358 50 3440872 or by email at jiaqi.guo@aalto.fi.



Orlando J. Rojas is professor of bio-based materials in the Department of Bioproducts and Biosystems, School of Chemical Engineering, at Aalto University, Finland. He is an elected Fellow of the American Chemical Society (2013) and a Finland Distinguished Professor (2009–2014). He chaired the Division of Cellulose and Renewable Materials of the American Chemical Society from 2009 to 2011, and is the recipient of the 2015 Nanotechnology Division Technical Award for outstanding contributions to the nanotechnologies of renewable materials. His research focuses on the development of nanostructures from the fiber cell wall and cellulose derivatives, dynamics of enzymatic reactions, and design of stimuli-responsive materials and multiphase systems. Rojas can be reached by phone at +358 50 5124227 or by email at orlando.rojas@aalto.fi.

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