



Role of a waste-derived polymeric biosurfactant in the sol–gel synthesis of nanocrystalline titanium dioxide

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Received 18 February 2014; received in revised form 26 March 2014; accepted 10 April 2014

Abstract

An inexpensive polymeric biosurfactant isolated from urban bio-wastes is shown to be a useful chemical aid in the synthesis of nanostructured materials with tunable pore size and surface hydrophilicity. Photocatalytic active TiO₂ powders were prepared by sol–gel reaction in the presence of variable amounts of a waste-derived polymeric biosurfactant. The products were characterized for morphology, crystal structures and surface hydrophilicity. The porosity data indicate that an increase of the biosurfactant amount in the reaction medium causes a decrease of pore size, pore volume and specific surface area in the synthesized oxide, whereas TEM and XRD data indicate that particle size decreases by increasing biosurfactant amount. These results suggest that biosurfactant molecules play a role in the nucleation step, during the formation of the titanium dioxide particles. The biosurfactant amount in the synthesis mixture affects also the hydrophilicity of the titanium dioxide surface, as demonstrated by water-adsorption microcalorimetry measurements, but the results suggest that this aspect is also connected to crystal nucleation and growth during the oxide formation. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Biosurfactants; Structure-directing effect; Titanium dioxide; Urban waste; Green sol–gel synthesis

1. Introduction

Within the current trend to develop inexpensive and sustainable procedures for the fabrication of functional nanomaterials, various biological substances have been applied as tailoring agents for the preparation of nanostructured inorganic particles, monoliths and films [1–11]. The utilization of natural substances as structure directing agents is indeed attractive from several reasons: (i) they show specific reactivity; (ii) their anisotropy allows the fabrication of complex inorganic structure by facile synthetic procedures; and (iii) they are renewable and often inexpensive ready-available materials.

Specific reviews [1,2] report various examples of bio-materials used as structure directing agents in the sol–gel synthesis of ceramic materials. For instance, silicon carbide cellular structures [3] have been obtained by infiltration of fused silicon or of tetraethyl orthosilicate (TEOS) in a large variety of woods (oak, maple, beech, ebony, pine, poplar, etc.) and other lignocellulosic supports [3–5]. Metal oxide fibers have been obtained via sol–gel process also in the presence of cotton [6] or pure cellulose [7]. Starch has been applied in the preparation of titanium dioxide and silica monoliths having hierarchical porous structure [8,9]. Recently, yeast cells have been utilized as templating agents for the preparation of photoactive titanium oxide [10] and mesoporous zirconium phosphate [11] powders.

In this context, waste-derived biosurfactants (BSs) are interesting structure directing agents for the preparation of nanostructured materials, because of their green origin, inexpensiveness, and their ability to organize themselves in different supramolecular structures depending on composition, concentration and pH [12]. The origin,

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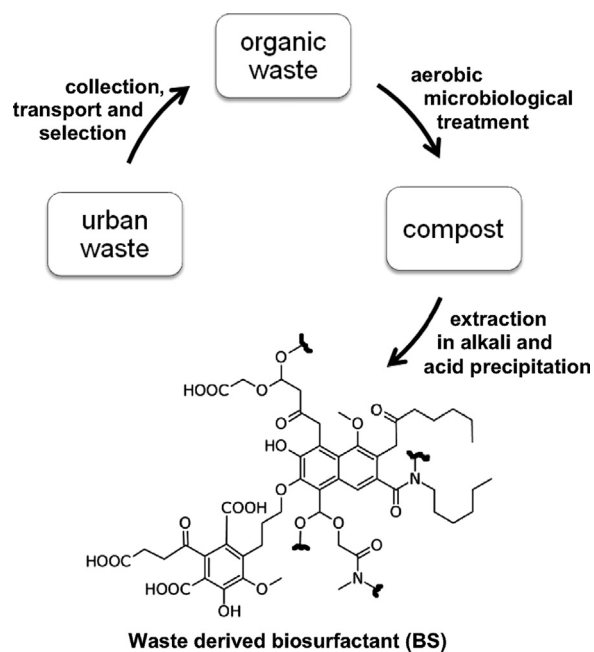


Fig. 1. Source and process steps for the extraction of a waste derived biosurfactant (BS). The chemical structure represents a hypothetical BS fragment.

the extraction process, and the general structure of these biosurfactants are depicted in Fig. 1. Modern cities create vast quantities of waste, which is collected and transported to dedicated treatment plants. In these facilities the organic fraction of the urban waste is typically stabilized by composting, i.e. an aerobic biodegradation process. The so obtained compost can be disposed in landfill areas or used as soil amendment, i.e. to improve soil physical properties, such as aeration and water retention. On the other hand, compost has been shown to contain large concentrations (up to 12 w%) of BSs, which can be easily isolated by extraction in alkali and precipitation at $\text{pH} < 1.5$. These BSs bear chemical similarity with soil organic matter [12,13] and might be exploited as valuable specialty chemicals. They are complex mixtures of polymeric molecules with average molecular weight ranging from 10^4 to 10^6 g mol^{-1} and polydispersity index in between 6 and 60. These macromolecules contain several functional groups and C atoms of different polarities. They appear to be formed by flexible aliphatic chains substituted by aromatic rings and several functional groups as carboxylic acid (COOH), amide (CON), keto (C=O), phenol (PhOH), alkoxy (O-alkyl), anomeric carbon (O-C-O), and amines (NRR', with R and R' being alkyl or H) groups. At basic and neutral pH, negatively charged carboxylic acid groups guarantee biosurfactant solubility in water; whereas at low pH, carboxylic acids are in their protonated form and these waste-derived biosurfactants show scarce solubility. Simultaneous the presence of hydrophobic aliphatic chains and acid moieties, as carboxylic acids and phenols, confers anionic surfactant-like behavior. Thus, BSs have been proposed as chemical auxiliaries for a broad spectrum of industrial and environmental applications, in substitution of the more expensive commercial synthetic surfactants, which are typically produced from oil-derived chemicals. BSs application spectrum encompasses detergency [14], textile dyeing [15,16], soil

washing [16], photodegradation of organic pollutants in waste effluents [17,18]. The regional differences and the seasonal fluctuations in the composition of organic waste might raise concern about BS reproducibility. However, it has been shown that BS structure, hydrophilicity and surfactant properties tends to level if the organic waste is treated for several days under aerobic conditions [19]. During the composting process, the organic components of the refuse are indeed metabolized by microorganisms, and BS structure becomes similar to the one of the humic substances present in the surface water and soil.

The polyelectrolytic structure and the surfactant properties of BSs make them attractive chemical auxiliaries for the fabrication of nanostructure materials. Over the last three decades synthetic surfactants have been indeed largely applied as soft templates for the fabrication of inorganic materials with defined pore structure [20–22] or to stabilize (micro)emulsions for the synthesis of inorganic nanoparticles with well-defined size and shape [22,23]. A BS has been recently applied for the first time as sacrificial tailoring agents for the preparation of mesoporous silica powders [24] by the sol–gel method. Fig. 2 shows the TEM picture of the silica particles prepared at a BS concentration of 3 g L^{-1} . This powder consisted of hollow spheres with $\sim 4 \text{ nm}$ large cavities. In the sample prepared at a BS concentration of 10 g L^{-1} these particles were organized in large aggregates showing also interparticle pores with average size of about 30 nm. The advantages related to the use of BS as synthesis assisting agent, are twofold: to exclude expensive oil-based products from synthesis, and to add practical and economic meaning to the collection and recycling of wastes. Hence, the application of BSs to the synthesis of nanostructured materials is here extended to the preparation of TiO_2 powders, whose production has a highly practical relevance, in reason of the photocatalytic properties of this type of materials, e.g. in the remediation of aqueous effluents

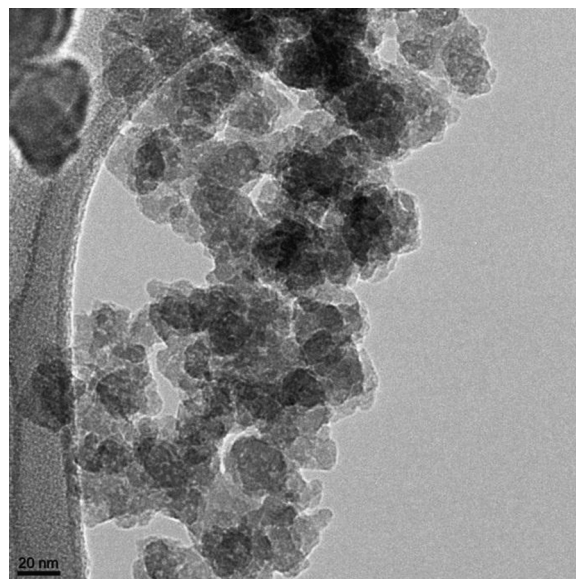


Fig. 2. Silica nanoparticles prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the presence of a waste-derived biosurfactant (3 g L^{-1}).

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