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Research Article

Precipitation of Hemicelluloses from DMSO/Water Mixtures Using Carbon Dioxide as an Antisolvent

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Supercritical antisolvent precipitation is a relatively recent technology which can be used for controlled preparation of polymer particles from solutions. This is done by the addition of an antisolvent to a polymer solution causing supersaturation of the polymer, especially under supercritical conditions. The particle size of the precipitates can be adjusted mainly by the rate of supersaturation. Spherical xylan or mannan particles having a narrow particle size distribution were precipitated from hemicellulose solutions in dimethyl-sulfoxide (DMSO) or DMSO/water mixtures by carbon dioxide as an antisolvent. By depending on the type of hemicellulose, the DMSO/H_2O ratio, and the precipitation conditions such as pressure and temperature, the resulting particle size can be adjusted within a wide range from less than 0.1 to more than 5 μm. Nano- and microstructured native xylans and mannans as obtained can be used in many applications such as encapsulation of active compounds, slow release agents, or chromatographic separation materials.

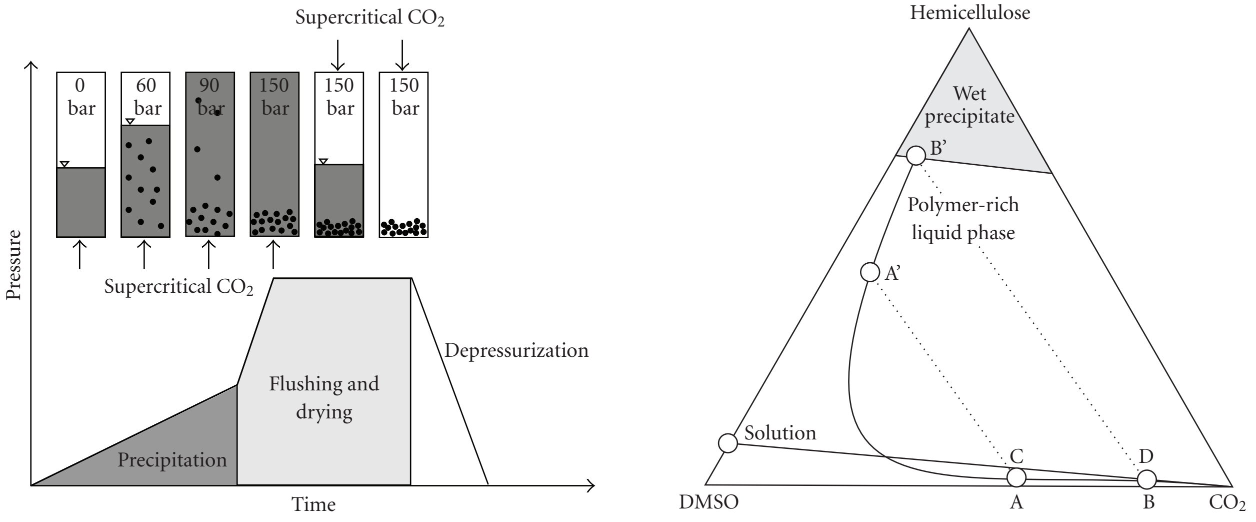
1. INTRODUCTION

Biopolymers as renewable raw materials are currently attracting enormous interest. Hemicelluloses represent an important percentage amongst these classes of natural compounds. About 15–35% of the dry biomass of woody tissues and up to 50% of cereal grains consist of such polysaccharides. The most abundant hemicelluloses are xylans and mannans. Whereas hemicellulose in hardwood mainly consists of pentosans (mostly xylans), the majority of softwood hemicelluloses are hexosans with mannan as the dominating polysaccharide [1].

Apart from using hemicelluloses as feedstock for the production of chemicals, their utilization for designing novel materials increasingly attracts interest and is realizable but challenging as well. Applications which take advantage of the unique properties of hemicelluloses are still more or less restricted to utilization as natural adhesives in board and paper manufacturing. However, increasing attention is paid to the bioside of these polymers. Xylans, for instance, are able to regulate blood pressure, bind hydrophobic mutagens, inhibit mutagenicity, and contribute to the effects of dietary fibers [2]. However, purification of hemicelluloses is a crucial prerequisite to applications, in particular on larger industrial scale.

Several concepts of xylan purification have been proposed [3, 4]. Ebringerova et al. [5] found that DMSO and DMSO/water mixtures are efficient solvents for low-branched heteroxylans. An interesting feature of DMSO is its good miscibility with CO_2 at high pressure [6, 7]. Water can additionally be used to modify the CO_2/DMSO system for supercritical antisolvent precipitation [8–10].

For antisolvent precipitation, CO_2 is mixed with a solution of the respective solid in an organic solvent. The mixing process is indicated as a straight line in the diagram of the ternary system DMSO/CO_2/hemicellulose (cf. Figure 1(b)). With increasing CO_2 content and after crossing the binodial, the homogeneous solution splits into a solvent/CO_2 phase (point A) and a liquid phase which is rich in DMSO and hemicellulose (point A'). Continued addition of CO_2 to point D leads to supersaturation in the polymer-rich liquid phase (point B') and finally precipitation of hemicellulose particles.



(a) (b)

FIGURE 1: (a) Scheme of antisolvent precipitation and (b) diagram of the ternary system DMSO/CO_2/hemicellulose.

A scheme of the antisolvent precipitation process is given in Figure 1(a). After precipitation, the solvent/CO_2 phase can be flushed out, and remaining traces of the solvent are finally removed from the precipitate by a continuous flow of supercritical carbon dioxide (scCO_2; supercritical drying).

Temperature and pressure can be varied to influence the precipitation rate and, thus, particle size and shape. Particle formation below the critical point of the mixture is strongly influenced by the solvent-transfer resistance between the liquid and gas phases. Increasing pressure and temperature beyond the critical values of the solvent/antisolvent mixture causes complete miscibility of the solvent with CO_2. Precipitation under these conditions is no longer influenced by any mass transfer resistance.

In the present paper, we would like to communicate the first results of antisolvent precipitation of hemicelluloses from solutions containing DMSO as the principal solvent. The controlled preparation of xylan and mannan particles was successful for both batch mode and semicontinuous mode.

2. EXPERIMENTAL

All precipitation experiments were performed at 40°C. DMSO (>99.5%) was purchased from Carl Roth GmbH & Co. KG, Karlsruhe, Germany and carbon dioxide (>99.8%) was purchased from Linde (Austria).

The studied xylan was extracted from beech sulfite pulp (Lenzing AG, Austria), and spruce mannan was kindly provided by S. Willför (Abo Academy, Turku, Finland).

Pressure-dependent solubility of the hemicellulose samples was determined by measuring the optical density of the solutions (OD 250 nm) at 10 different pressure levels covering the range from 1 to 150 bar. A logistic dose response model was fitted to the data in order to relate the reduced concentration c/c_0 to the applied pressure (Table Curve 2D 5.0, Cranes Software Inc, Troy, MI, USA).

Batch experiments were performed using high-pressure equipment consisting of an HPLC pump (TSP minipump, Thermal Separation Products, Toms River, NJ, USA) with cooled dual pistons and an empty 40 mL semipreparative HPLC column (Alltech Grom GmbH, Rottenburg-Hailfingen, Germany) with a stainless steel frit at the bottom as batch cell. 20 mL of the saturated hemicellulose solutions (pure DMSO or DMSO/water mixtures) were placed in the batch cell and heated up to the respective temperature. After temperature equilibration, the column was pressurized with CO_2 at a flow rate of $5\,\mathrm{g\,min^{-1}}$. After 15 minutes of equilibration time, the supernatant liquor was flushed out with scCO_2. The precipitate was dried with scCO_2 for 60 minutes.

Semicontinuous experiments were performed in a 0.2 l atomisation vessel (Separex, Champigneulles, France). After pressurizing with CO_2 and equilibrating (5 minutes) the atomization vessel at 150 bar and 40°C, the saturated polymer solution was sprayed into the vessel at a flow rate of $1\,\mathrm{mL\,min^{-1}}$. Hemicellulose particles were collected on a stainless steel frit at the bottom of the vessel. Removal of the supernatant liquor and drying of the precipitate were carried out as described above. DMSO can be recovered by depressurizing the supernatant.

Scanning electron microscopy was performed on a Phillips XL 30 ESEM instrument. All samples were sputtered with gold and mapped at an acceleration voltage of 10 kV.

3. RESULTS AND DISCUSSION

The principle of antisolvent mediated precipitation of xylans and mannans from DMSO solutions is based on a CO_2-induced phase separation into a liquid phase rich in DMSO and hemicelluloses and a solvent/antisolvent phase. With increasing CO_2 content, hemicellulose becomes augmented in the liquid phase (solvent is transferred to the solvent/antisolvent phase) which eventually causes

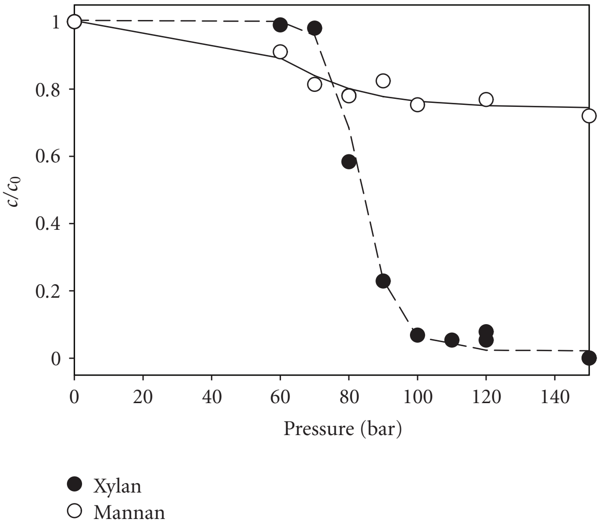


Figure 2: Pressure dependence of the solubility of xylan and mannan in DMSO/CO_2 at 40°C.

supersaturation and precipitation of the hemicellulose. As solubility of the solute plays a decisive role for precipitation, the pressure-dependent solubility of xylan and mannan samples in the binary mixture DMSO/CO_2 was studied starting from saturated (1010 mbar, 25°C) solutions of the hemicelluloses in pure DMSO.

The solubility of xylan and mannan in DMSO becomes quite different when approaching the critical pressure of the binary mixture DMSO/CO_2 at 40°C (see Figure 2).

Beyond the critical pressure of 87 bar, DMSO is fully miscible with $scCO_2$ and supersaturation occurs very fast. However, even under subcritical conditions a certain amount of the solute can be precipitated. Thus, two different pathways exist to obtain hemicellulose particles from solutions: supersaturation (a) below or (b) beyond full miscibility of the antisolvent with the solvent. Below full miscibility, the precipitation process is limited by the mass transfer of CO_2 into DMSO, and supersaturation of the solute is reached only slowly, which results in the formation of comparatively large hemicellulose particles. In case of supercritical conditions, precipitation occurs very fast, and much smaller particles can be obtained.

In batch mode, where a solution of the particular hemicellulose in DMSO is slowly pressurized with CO_2, supersaturation at subcritical conditions and hence size of the precipitating particles can be easily controlled by CO_2 flow rate and final pressure. At a low flow rate of 5 g min^{-1} and at a pressure of 90 bar, particles with an average diameter of 2–5 μm were obtained. An important factor affecting the particle size is the type of hemicellulose. Whereas spherical xylan particles having a diameter of 2-3 μm were obtained from DMSO in batch mode, distinctly bigger particles (5-6 μm) were obtained for mannan under the same conditions (cf. Figure 3).

The SEM pictures also reveal the presence of very small particles which might be formed due to impurities, fragmentation of initially formed bigger particles, or partially fast precipitation of a smaller hemicellulose fraction. The latter is most likely as supercritical conditions were achieved at the end of the precipitation process in order to initiate $scCO_2$ drying.

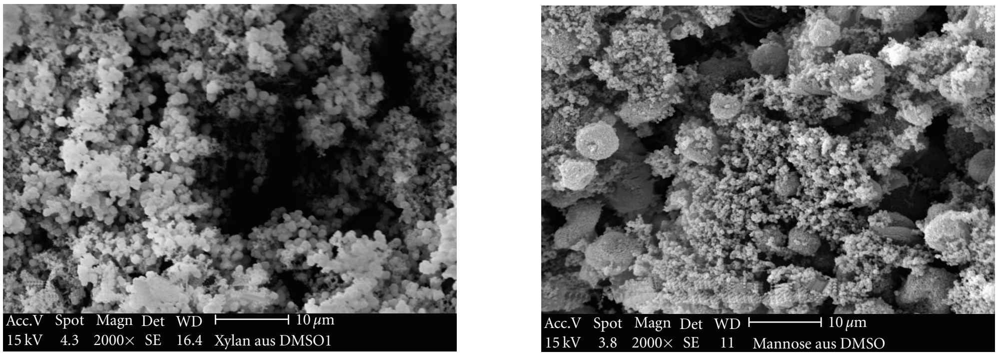
It is evident from the SEM pictures that all hemicellulose precipitates are low porous. This can be explained by a liquid-liquid phase separation occurring during subcritical precipitation after having overcome the mass transfer resistance of the binary solvent/antisolvent system [11]. During this process, agglomeration of solute molecules and eventually precipitation of polymer particles occur. Under subcritical conditions, the agglomerates usually form droplets which can be stable or unstable upon drying with $scCO_2$. Precipitation of xylan under subcritical conditions, for example, yields stable droplets. In contrast, mannan forms droplets that are only partly stable. As the particle size of the mannan precipitate is distinctly larger, it might be better suited for applications like coating.

The addition of small amounts of water shifts the critical point of the binary system DMSO/CO_2, and hence the coexistence of the two phases, to higher pressure values [7, 8]. Upon addition of a sufficient amount of water, a liquid-liquid phase split occurs in the ternary system as it is well known from other ternary systems consisting of H_2O, CO_2, and any polar organic solvent [12]. The formation of this additional phase increases the above-mentioned mass transfer resistance, causes slower precipitation, larger particle sizes, and enhanced agglomeration compared to water-free DMSO/CO_2 mixtures.

Increasing water contents also extend the subcritical range of the ternary system DMSO/H_2O/CO_2. This effect is quite advantageous since it facilitates tuning of the particle size and morphology as the amount of added water can be freely chosen due to the insolubility of hemicelluloses in water. SEM pictures of hemicellulose particles precipitated from aqueous DMSO (10% H_2O, v/v) are shown in Figures 4(a) and 4(b).

The size of the individual xylan particles—no matter whether obtained by precipitation from pure or aqueous DMSO—was very similar. Spheres of about 1 μm were initially formed which agglomerated to stable, grape-like clusters with an average diameter of about 10 μm. Mannan tends to form even bigger clusters under the same precipitation conditions, and also sponge-like structures can be obtained (cf. Figure 4(b)).

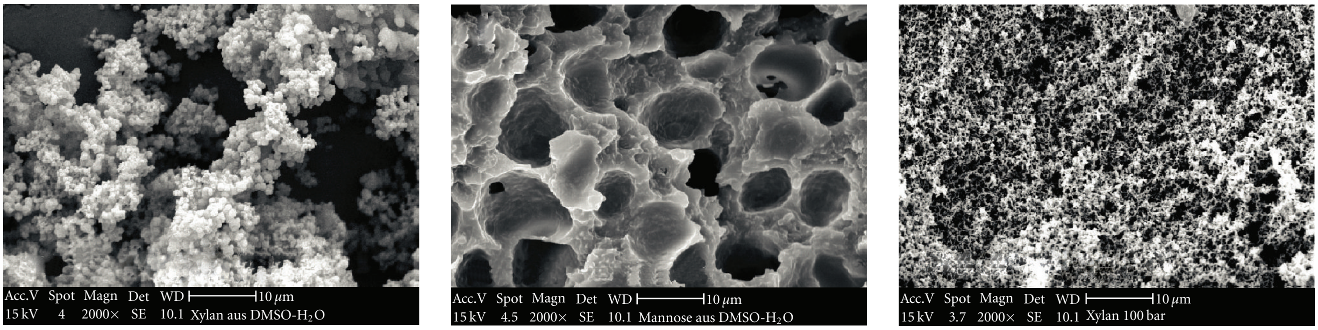
In contrast to the two batch methods where the principle of subcritical precipitation is applied to obtain large hemicellulose particles from DMSO or DMSO/H_2O mixtures, very small particles are formed when xylan or mannan is precipitated beyond the critical pressure of the binary system DMSO/CO_2 at 40°C (cf. Figure 4(c)). This can be achieved by semicontinuously spraying a nearly saturated hemicellulose solution in DMSO into $scCO_2$ (e.g., 150 bar, 40°C). As DMSO and CO_2 are fully miscible under supercritical conditions, mass transfer resistance becomes very low; supersaturation develops fast and hence very small particles precipitate. For the studied xylans, particle diameters in the 10 nm range were obtained.



(a)

(b)

Figure 3: (a) SEM pictures of xylan and (b) mannan particles obtained in batch mode by precipitation from DMSO solutions using carbon dioxide as antisolvent.



(a)

(b)

(c)

Figure 4: (a) SEM pictures of subcritically precipitated xylan and (b) mannan obtained in batch mode from aqueous DMSO (10% H_2O, v/v). (c) SEM picture of xylan precipitates obtained in semicontinuous mode by spraying a solution of xylan in DMSO into $scCO_2$ at 40°C and 150 bar.

The results obtained so far confirm the proposed mechanism of antisolvent precipitation. As solvent and antisolvent are fully miscible under supercritical conditions, supersaturation, solidification, and liquid-liquid phase separation occur at the same time. Thus, no droplets are formed and the resulting particles do not agglomerate.

4. CONCLUSION

Common chemical precipitation methods and thermal drying methods are often harmful to thermolabile substances, as many biopolymers are. Antisolvent precipitation in combination with supercritical drying is a valuable alternative for controlled precipitation, adjusting of largely uniform particle sizes and retention of the fragile particle structures.

Antisolvent precipitation can be performed in both batch and semicontinuous modes. In batch mode, low isothermal pressurization rates afford precipitation under subcritical conditions. Semicontinuous precipitation can be performed subcritically as well as supercritically.

In batch mode, pressurizing rate and type of hemicellulose largely affect the size and agglomeration tendency of the precipitates. Low CO_2 pressurizing rates were found to yield large particles. The studied mannan had a higher agglomeration tendency than the xylan.

The addition of small quantities of water extends the subcritical range of the ternary system DMSO/H_2O/CO_2. This effect can be used to tune the particle size and morphology as the amount of added water can be freely chosen due to the insolubility of hemicelluloses in water. Batch precipitation in presence of water can be used to prepare large xylan aggregates or sponge-like mannan structures. Small particles with a very narrow particle size distribution can be obtained in semicontinuous mode.

Antisolvent precipitation facilitates controlled preparation of hemicellulose particles at comparatively moderate conditions (40°C, <100 bar) and enables a recovery of DMSO and CO_2. The described technology has a great potential for increasing the number of hemicellulose applications.

REFERENCES

[1] D. Fengel and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, Walter de Gruyter, Berlin, Germany, 1989.

[2] M. B. Roberfroid, “Health benefits of non-digestible oligosaccharides,” *Advances in Experimental Medicine and Biology*, vol. 427, pp. 211–219, 1997.

[3] A. Ebringerová and T. Heinze, “Xylan and xylan derivatives—biopolymers with valuable properties, 1: naturally occurring xylans structures, isolation procedures and properties,”

Macromolecular Rapid Communications, vol. 21, no. 9, pp. 542–556, 2000.

[4] D. Nabarlatz, C. Torras, R. Garcia-Valls, and D. Montané, "Purification of xylo-oligosaccharides from almond shells by ultrafiltration," *Separation and Purification Technology*, vol. 53, no. 3, pp. 235–243, 2007.

[5] A. Ebringerova, Z. Hromadkova, W. Burchard, R. Dolega, and W. Vorwerg, "Solution properties of water-insoluble rye-bran arabinoxylan," *Carbohydrate Polymers*, vol. 24, no. 3, pp. 161–169, 1994.

[6] A. Kordikowski, A. P. Schenk, R. M. van Nielen, and C. J. Peters, "Volume expansions and vapor-liquid equilibria of binary mixtures of a variety of polar solvents and certain near-critical solvents," *The Journal of Supercritical Fluids*, vol. 8, no. 3, pp. 205–216, 1995.

[7] A. E. Andreatta, L. J. Florusse, S. B. Bottini, and C. J. Peters, "Phase equilibria of dimethyl sulfoxide (DMSO) + carbon dioxide, and DMSO + carbon dioxide + water mixtures," *The Journal of Supercritical Fluids*, vol. 42, no. 1, pp. 60–68, 2007.

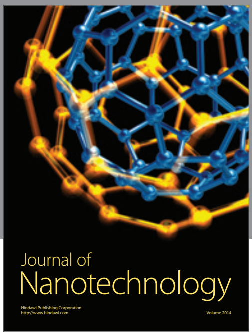
[8] Y. Pérez de Diego, H. C. Pellikaan, F. E. Wubbolts, G. Borchard, G. J. Witkamp, and P. J. Jansens, "Opening new operating windows for polymer and protein micronisation using the PCA process," *The Journal of Supercritical Fluids*, vol. 36, no. 3, pp. 216–224, 2006.

[9] A. R. C. Duarte, M. D. Gordillo, M. M. Cardoso, A. L. Simplício, and C. M. M. Duarte, "Preparation of ethyl cellulose/methyl cellulose blends by supercritical antisolvent precipitation," *International Journal of Pharmaceutics*, vol. 311, no. 1-2, pp. 50–54, 2006.

[10] S. Moshashaée, M. Bisrat, R. T. Forbes, H. Nyqvist, and P. York, "Supercritical fluid processing of proteins. I: lysozyme precipitation from organic solution," *European Journal of Pharmaceutical Sciences*, vol. 11, no. 3, pp. 239–245, 2000.

[11] Y. Pérez de Diego, H. C. Pellikaan, F. E. Wubbolts, G. J. Witkamp, and P. J. Jansens, "Operating regimes and mechanism of particle formation during the precipitation of polymers using the PCA process," *The Journal of Supercritical Fluids*, vol. 35, no. 2, pp. 147–156, 2005.

[12] T. Adrian, M. Wendland, H. Hasse, and G. Maurer, "High-pressure multiphase behaviour of ternary systems carbon dioxide-water-polar solvent: review and modeling with the Peng-Robinson equation of state," *The Journal of Supercritical Fluids*, vol. 12, no. 3, p. 221, 1998.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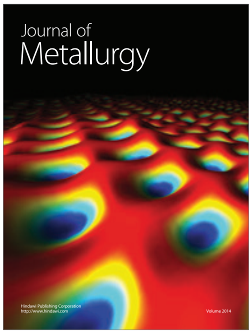
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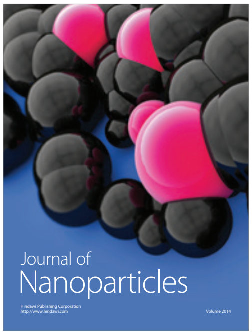
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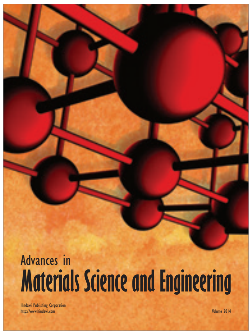
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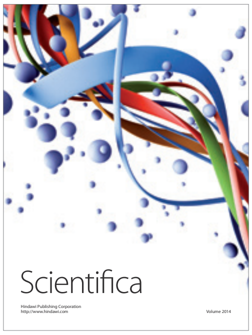
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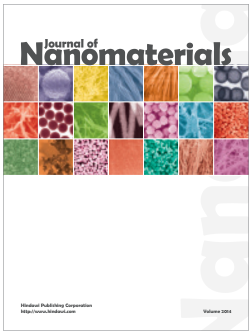
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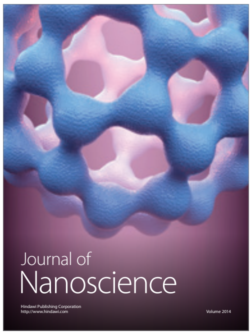
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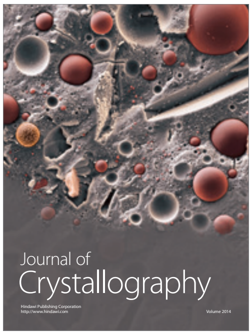
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