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Conference Paper

Spanish Broom (*Spartium junceum* L.) as New Fiber for Biocomposites: The Effect of Crop Age and Microbial Retting on Fiber Quality

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Recently, there has been a revival of interest in Spanish broom (*Spartium junceum* L.) as a possible source of fibers to be used in biocomposite materials. The aim of this work was to evaluate the role of two selected strains of *Clostridium felsineum* (NCIMB 10690 and NCIMB 9539) in the retting of Spanish broom vermenes. Chemical composition and physical, mechanical, and morphological properties of fibers were investigated. The obtained results indicate that the process provides an ecofriendly method for Spanish broom retting and support the hypothesis that these fibers can be successfully used in composite materials.

1. Introduction

Since the last years, polymer composites reinforced with natural fibers are gaining ever more interest especially for industrial applications. Their low cost, high specific mechanical properties, and biodegradability represent the main advantages in their utilization as renewable alternatives instead of the majority of synthetic reinforcement, such as glass fibers [1]. The sources of raw material used in composites as reinforcement or fillers are mainly represented by flax, cotton, hemp, jute, kenaf, sisal, and coconut fiber.

Spanish broom (*Spartium junceum* L.), a member of the Leguminosae family, has been considered a potential interesting source of natural, sustainable, and renewable fiber for textile and technical applications [2, 3]. These fibers derived from the plant branchlets (known as vermenes) show extraordinary tensile resistance and flexibility and are able to produce materials in combination with biodegradable and plastic matrices [1, 4]. Spanish broom (*Spartium junceum* L.) is a perennial shrub growing in hot and dry climate throughout the Mediterranean area, where it naturally occurs in hilly soils, contributing to lower erosion and risks of nutrient leaching. This plant is somewhat adapted to alkaline and salty soils. The name *Spartium* is from the Greek word denoting "cardage," in allusion to the use of the plant. The stem fibers have been used since ancient time as hemp substitute, being used mainly for coarse fabrics and cordage. Spanish broom cortical fibers are multiple elementary fibers (ultimates) arranged in bundles. The elementary fibers are bound together by lignin. A thick secondary cell wall indicates a high cellulose content. The diameter of ultimates varies from 5 to 10 μm while the diameter of the whole bundle is about 50 μm [4].

The retting process is the major limitation to efficient and high-quality fiber production. In the last years, pectinolytic enzymes produced by microorganisms have gained most attention. These enzymes degrade the pectin of the middle lamella and primary cell wall, leading to separation of the cellulose fibers [5]. Microorganisms of the genus *Clostridium* are primarily involved in retting under anaerobic conditions. The aim of this work was to evaluate the role of two selected strains of *Clostridium felsineum* (NCIMB 10690 and

NCIMB 9539) in the retting of Spanish broom fibers obtained from 2- and 7-year-old crops (establishment year excluded). Morphology and the chemical, physical, and mechanical properties of the derived fibers were examined in order to evaluate the feasibility to use them in biocomposites.

2. Materials and Methods

2.1. Field Experiment. The vermenes were obtained from cultivation trials carried out at the Department of Agriculture, Food and Environment of University of Pisa (Italy, 43°40′ N; 10°19′ E; 5 m elevation) on a deep silt loam soil (sand 15.5%; silt 65.5%; clay 18.0%; organic matter 1.62%; pH 8.1; total nitrogen 0.12%; available P_2O_5 29.2 mg kg^{-1}; exchangeable K_2O 137 mg kg^{-1}). The soil was characterised by a water table rather superficial with a depth of 120 cm during the driest season. The soil displayed the following hydrological characteristics: field capacity 27.3% dw, wilting point 9.4% dw. A selected clone (PI DAGA92) of *Spartium junceum* from local population was used in this evaluation. Stump sprouts were transplanted at the end of April 2002. A plant density of 20.000 plants ha^{-1} with an interrow spacing of 1 m and an intrarow spacing of 0.5 m was adopted. Plot size was 48 m^2 (8×6 m). During the establishment year, plants were cut at the end of the growing season to allow the vegetative regrowth in the second year. Thereafter it was possible to harvest *Spartium junceum* one time in each year during autumn. In order to evaluate maximum crop yield, plants were maintained in optimum water supply conditions. All plots received the same amount (100 kg ha^{-1}) of preplanting fertilization of N, P, and K. The nitrogen dose was split into two equal preplanting and late-spring applications. From the second growing season, plots received only 50 kg ha^{-1} of N at the end of winter. Plots were kept weed-free by harrowing in the interrow and hand hoeing in the intrarow. The experiment was laid out in a randomised block design with four replicates. Productive determinations were performed on a minimal area of 6 m^2 in the inner part of each plot. After harvest, all plants in the plots were cut 15 cm above ground for allowing uniform vegetative regrowth. Dry vermenes were decorticated by hand, in order to remove the outer bark/epidermis and the bast from the woody core of the stems.

2.2. Retting Process. 100 g of bark, obtained from manually decorticated vermenes, was placed in 9 L of water tanks constantly heated at 30°C for 7 days. Tanks were inoculated with anaerobic bacteria *Clostridium felsineum* strains NCIMB 10690 and NCIMB 9539 selected for high pectinolytic activity, using a 1 : 8 ratio between broth culture and water. Finally, fiber bundles were washed with water under pressure and oven-dried at 60°C until constant weight.

2.3. Chemical and Mechanical Characterization. In accordance with the TAPPI OM 250 method, the lignin content was determined as the sum of insoluble and soluble lignin, the latter being determined spectrophotometrically at 205 nm. Pentosan content was determined according to the TAPPI T 223 hm 84 and ash content according to the TAPPI 15 OS 58 method. The TAPPI 284 OM 82 method was used to assess the extractives content and the UNI 8282 method to determine the degree of cellulose polymerization in cupriethylenediamine (CED) after delignifying the material with sodium chlorite. The index of crystallinity is given by the ratio to the area of the (002) peak to the intensity of the amorphous background [6]. Fibre bundles were confined in small plastic sleeves and then cross-sectioned. Scanning microscopy (SEM) was carried out on gold coated cross-sections. The tensile properties of selected filaments were determined with an Instron 1185 (load cell 10 N) at the cross-head speed of 1 mm min^{-1} at room temperature (20 ± 2°C) and 70 ± 5% relative humidity. Since the diameter of filaments was not uniform, selection of suitable samples was made with the help of a low magnification microscope; the diameter for each filament was taken at different places with the help of a precision gauge meter and the average value was used. To measure the strength and the elongation of fibers, different gauge lengths were used, in the range 10–50 mm; a minimum of 50 filaments was taken for each gauge length to give data statistical meaning. The elastic modulus (E) was measured by the slope of the conventional stress-strain curves taking the distance between grips as the gauge length.

2.4. Statistical Analysis. All the variables were subjected to the analysis of variance (ANOVA) using the statistical software CO-STAT Cohort V6.201-2002. A factorial design with crop age and microbial strain as main treatments was used. Means were separated on the basis of least significance difference (LSD) test only when the ANOVA *F*-test per treatment was significant at the 0.05 or 0.01 probability level [7].

3. Results and Conclusions

The agronomic characteristics of Spanish broom were investigated for seven years in the pedoclimatic conditions of Central Italy. The dry yield components, evaluated after 2 and 7 years of cultivation, were reported in Table 1. The dry yield was composed of 53% new branches, representing the economic yield. The average yield per annum of dry vermenes was 10.5 and 7.8 t ha^{-1} after 2 and 7 years of cultivation, respectively. The moisture content of branchlets averaged 60% and it is important for the necessity to store raw material with low moisture content and to maximise the marketable products. The cultivation trials, carried out for 7 years, showed that this species was drought tolerant; moreover, being a nitrogen fixing plant, it could be cultivated on marginal lands due to its low input requirements.

The vermenes were manually decorticated and the obtained bast was processed using *Clostridium felsineum* strains NCIMB 10690 and NCIMB 9539 for microbial retting. The fiber yield was significantly affected by the crop age, microbial strains, and their interaction. The highest yield was obtained in the vermenes from the younger crop degummed with NCIMB 10690 while the ones derived from older plants degummed using NCIMB 9539 have given about 20%

Table 1: Effect of crop age on dry yield components (t ha^{-1} year^{-1}) and bast/vermenes ratio in Spanish broom crops.

Crop age	Total above-ground dry yield (t ha^{-1} year^{-1})	Vermenes dry yield (t ha^{-1} year^{-1})	Bast dry yield (t ha^{-1} year^{-1})	Bast/vermenes ratio
1-2 years†	20.0 ± 2.7^{a}	10.5 ± 2.5^{a}	4.2 ± 1.1^{a}	0.40 ± 0.05^{a}
1–7 years†	14.9 ± 5.5^{a}	7.8 ± 3.0^{a}	3.5 ± 1.2^{a}	0.47 ± 0.08^{a}

Mean values followed by the same letters are not significantly different for $P \leq 0.05$ following a one-way ANOVA test with crop age as variability factor. †Establishment year excluded.

Table 2: Effect of crop age and microbial strain on chemical composition and crystallinity of broom fibers.

	Humidity (%)	Extractives (%)	Lignin (%)	Ash (%)	Pentosans (%)	Cellulose†† (%)	X-ray index of crystallinity (%)
2-year-old NCIMB10690	5.47^{a}	6.34^{a}	15.15^{bc}	0.37^{a}	4.55^{a}	73.94^{ab}	77.2^{a}
2-year-old NCIMB9539	5.10^{a}	6.47^{a}	13.01^{c}	0.30^{a}	4.04^{a}	76.48^{a}	73.7^{b}
7-year-old NCIMB10690	5.26^{a}	7.02^{a}	17.11^{b}	0.32^{a}	4.75^{a}	71.12^{b}	73.4^{b}
7-year-old NCIMB9539	5.05^{a}	7.32^{a}	21.71^{a}	0.23^{a}	4.42^{a}	66.55^{c}	70.3^{c}
			Analysis of variance				
Crop age (A)	n.s.	n.s.	**	n.s.	n.s.	*	*
Strain (S)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
A × S	n.s.	n.s.	*	n.s.	n.s.	*	*

Mean values followed by the same letters are not significantly different for $P \leq 0.05$ following a two-way ANOVA test with crop age and microbial strain as variability factors. $^{*}P \leq 0.05$; $^{**}P \leq 0.01$; n.s.: not significant ($P \geq 0.05$). ††Determined as difference.

Table 3: Effect of crop age and microbial strain on fiber diameter: mean, minimum, and maximum values.

	Mean diameter†† (μm)	Min (μm)	Max (μm)
2-year-old NCIMB10690	63.1 ± 18.2^{a}	30	140
2-year-old NCIMB9539	53.0 ± 9.3^{b}	25	70
7-year-old NCIMB10690	48.8 ± 8.6^{c}	30	80
7-year-old NCIMB9539	48.6 ± 8.7^{c}	20	70

Mean values followed by the same letters are not significantly different for $P \leq 0.05$ following a two-way ANOVA test with crop age and microbial strain as variability factors. ††Mean value for $n = 133$–148.

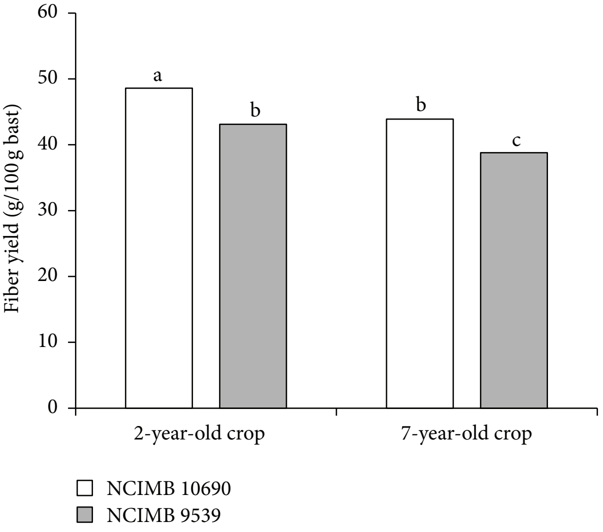


Figure 1: Influence of crop age and microbial strain on fiber yield. Mean values followed by the same letters are not significantly different for $P \leq 0.05$ following a two-way ANOVA test with crop age and microbial strain as variability factors.

less fibers (Figure 1). The chemical composition and the crystallinity index of the derived fibers were shown in Table 2. The results outlined a high content of cellulose (67–76%), while lignin (13–22%), pentosans (4-5%), and extractives (6-7%) were low (Table 2). The microorganisms used for the retting carried out a selective attack against pectins and cellulose, with the lowest percentage of lignin and the highest value of cellulose in the 2-year-old fibers after retting with NCIMB 9539 (Table 2). The fibers obtained from younger plants generally provided a fiber characterized by a higher tensile strength (Figure 2(a)), a lower lignin content (Table 2), and a greater diameter (Table 3). In these plants the retting with NCIMB 10690 presented a lesser percentage of cellulose compared to retting with NCIMB 9539, which would suggest a greater strength of the fiber. In spite of this, the use of strain NCIMB 10690 provided a greater crystallinity index that gives a higher resistance (tensile strength) to the fiber compared to ones obtained with strain NCIMB 9539 which are characterized by an intermediate crystalline/amorphous ratio (Figure 2(a)). By definition, the elastic modulus, shown in Figure 2(b), is a quantity independent of the length of the fiber, as it represents the initial slope of the stress-strain curve. The elastic modulus of Spanish broom processed with microbial retting is 13.2 GPa (as overall mean) and it is yet greater than that of most rigid nonoriented polymers (1–3 GPa) making it possible to stiffen commodity plastics such as, polyolefins [4]. It is interesting to note that the value of the Spanish broom fibers obtained by mechanical retting in a study conducted in the same field by Angelini et al. [4]

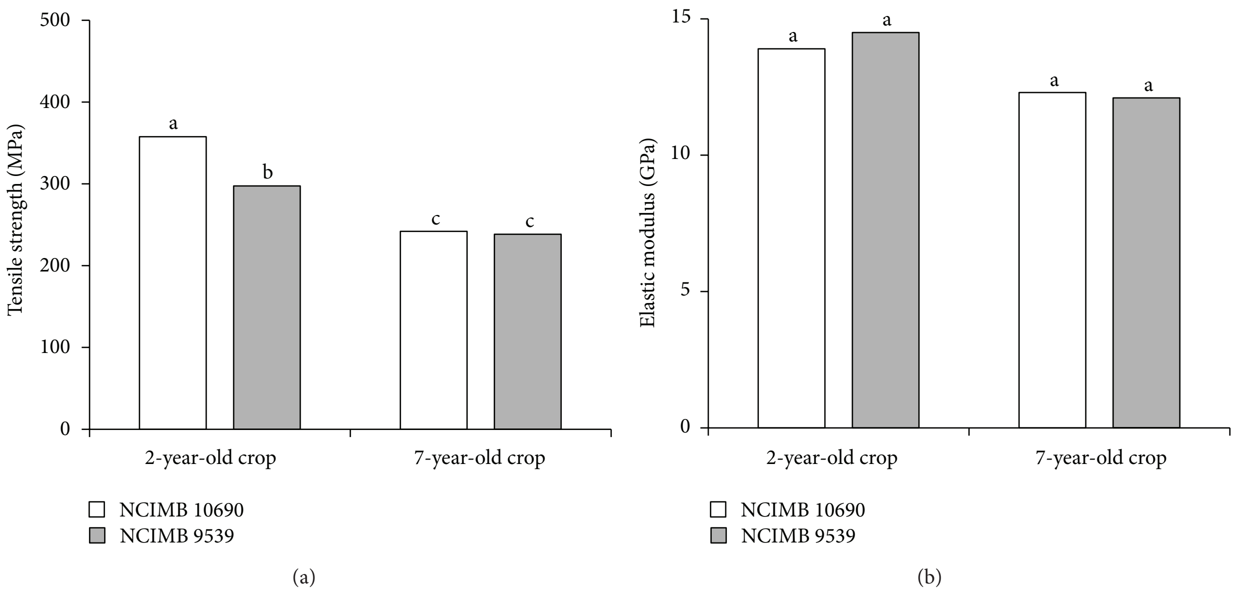


Figure 2: Influence of crop age and microbial strain on tensile strength (a) and elastic modulus (b). Mean values followed by the same letters are not significantly different for $P \leq 0.05$ following a two-way ANOVA test with crop age and microbial strain as variability factors.

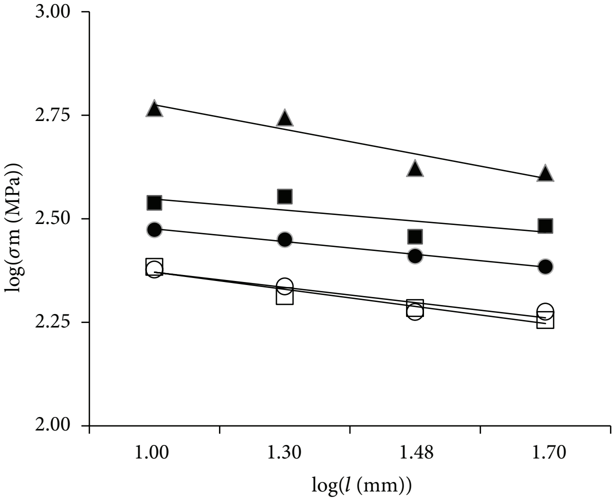


Figure 3: Comparison of the influence of gauge length on strength of Spanish broom fibers obtained from two different crop ages and two different rettings (mechanical and microbial). ■: retting of 2-year-old broom with NCIMB 10690; •: retting of 2-year-old broom with NCIMB 9539; □: retting of 7-year-old broom with NCIMB 10690; ○: retting of 7-year-old broom with NCIMB 9539; ▲: mechanical retting [4].

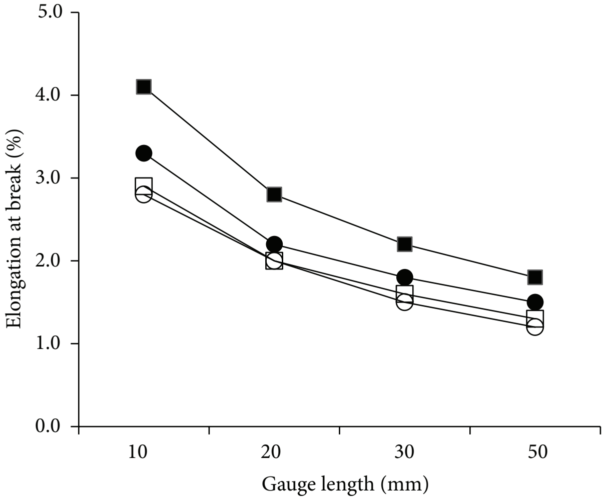
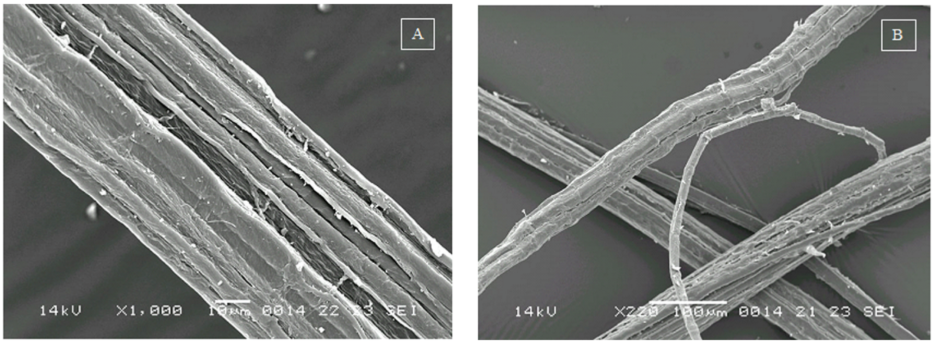


Figure 4: Influence of gauge length on elongation at break of broom fibers. ■: retting of 2-year-old broom with NCIMB 10690; •: retting of 2-year-old broom with NCIMB 9539; □: retting of 7-year-old broom with NCIMB 10690; ○: retting of 7-year-old broom with NCIMB 9539.

was 21.5 GPa, greater than those obtained in the present study and thus would present a greater tensile strength. This result is confirmed also by the analysis reported in Figure 3 where the plots of log (mean stress) versus log (gauge length) for Spanish broom fibers are shown (the solid line represents the regression line). It is observed that for all treatments, the fiber strength increased with the decrease of gauge length. Consequently, the strength of fibers obtained from vermenes of 2-year-old crop degummed with NCIMB 10690 was the highest. The comparison of regression lines confirms that the strength of fibers obtained by mechanical retting was higher than those observed in this study. This could be due to the cellulose degradation operated by the microbes that confers a greater weakness to fibers. However, we can point out that the slope of the line obtained in this work was lower than that reported in the literature [4]. This highlights a higher reliability of these fibers as the slope of the regression line deals with the speed with which the tensile strength



(a)

(b)

Figure 5: Longitudinal view of Spanish broom fibers obtained by SEM. (a) retting of 2-year-old broom with NCIMB 10690; (b) retting of 2-year-old broom with NCIMB 9539.

decreases. Furthermore these results confirm that the natural fibers can reach a good reliability in the mechanical behaviour comparable with the artificial ones, although the natural fibers are characterized by greater surface irregularities. In Figure 4 the influence of gauge length on elongation at break is shown. The range of variation in the average elongation at break (strain) was comprised between 1.2% and 4.1%, for fibers of 5 and 1 cm long, respectively. According to the theory of Weibull [8], the shorter fibers exhibited a higher value of elongation at break due to a lower number of defects. As the length increases, the probability that the fiber section contains a defect is higher and, therefore, the mean value of elongation decreases. The longitudinal SEM view of the Spanish broom bundles (Figures 5(a) and 5(b)) clearly showed these irregularities and defects.

In conclusion, the obtained results showed the good agronomic characteristics of Spanish broom with low environmental impact of its cultivation and a good fiber productivity during the years. The microbial retting here tested provided fibers characterised by a good reliability in the mechanical behaviour.

The two microorganisms used in the retting showed a different activity depending on crop age and the considered parameter, such as lignin and cellulose content or crystallinity index. As general trend, the NCIMB 10690 strain provided a greater index of crystallinity in fibers from both crops, even if a higher tensile strength was observed only in the vermenes from the younger crop. The chemical and mechanical properties of the obtained fibers are promising and support the hypothesis that these fibers can be a potential replacement for man-made fibers in composite materials. The importance of the microbial retting in the degumming of Spanish broom as well as the choice of the most suitable microbial strain awaits elucidation on the basis of these preliminary results.

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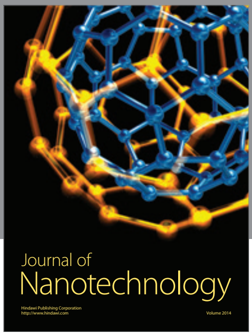
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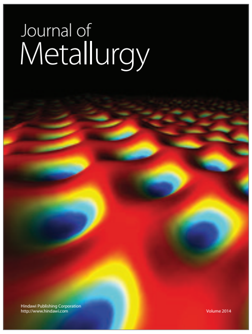
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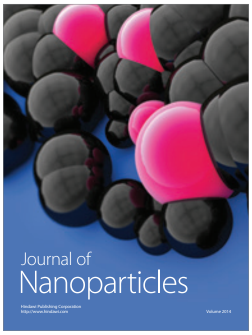
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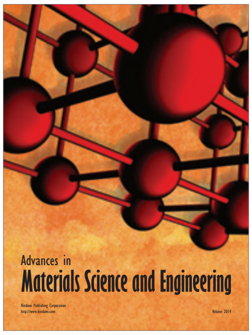
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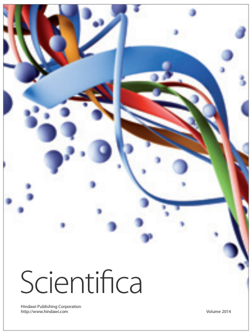
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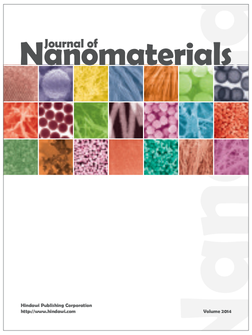
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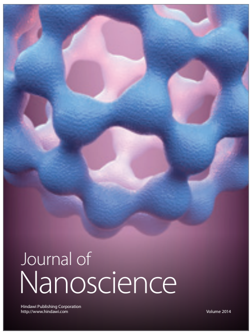
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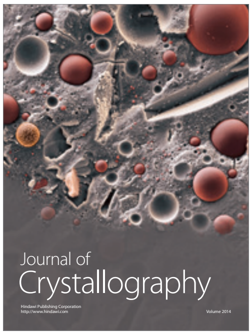
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