

Research Article

The Synthesis of a Novel Cellulose Physical Gel

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Cellulose possessing β -cyclodextrin (β -CD) was used as a host molecule and cellulose possessing ferrocene (Fc) as a guest polymer. Infrared spectra, differential scanning calorimetry (DSC), ultraviolet spectroscopy (UV), and contact angle analysis were used to characterise the material structure and the inclusion behaviour. The results showed that the β -CD-cellulose and the Fc-cellulose can form inclusion complexes. Moreover, ferrocene oxidation, and reduction of state can be adjusted by sodium hypochlorite (NaClO) as an oxidant and glutathione (GSH) as a reductant. In this study, a physical gel based on β -CD-cellulose/Fc-cellulose was formed under mild conditions in which autonomous healing between cut surfaces occurred after 24 hours. The physical gel can be controlled in the sol-gel transition. The compressive strength of the Fc-cellulose/ β -CD-cellulose gel increased with increased cellulose concentration. The host-guest interaction between the side chains of cellulose could strengthen the gel. The cellulose physical gel may eventually be used as a stimulus-responsive, healing material in biomedical applications.

1. Introduction

In light of heightened environmental and energy concerns, cellulose based on nature biomass has been receiving increasing attention in recent years. Cellulose is the most abundant naturally occurring polymer of glucose, found as the main constituent of plants and natural fibres such as cotton and linen and is considered a renewable and sustainable resource of raw material to satisfy the increasing demand for environmentally friendly [1] and energy-generating products [2, 3]. Cellulose-based hydrogels are biocompatible and biodegradable materials which show promise for a number of industrial uses, especially in cases where environmental issues are important. Such natural polysaccharides have been widely used for the preparation of gels in various fields [4–7], for example: wastewater treatment, the food industry, cosmetics, biomedical, pharmaceutical, and tissue engineering applications, due to their unique properties such as high swelling capacity, biocompatibility, biodegradability, and biological functions.

Cellulose, the cellulose, the most abundant renewable polysaccharide on earth, is a strong candidate for the fabrication of gels and cellulose-based gels have been reported including cellulose-polymer composite gels and cellulose-inorganic hybrid gels. The design and use of cellulose-based hydrogels, which usually couple their biodegradability with a smart stimuli-sensitive behaviour, together with the large availability of cellulose in nature and the low cost of cellulose derivatives, make cellulose-based hydrogels particularly attractive.

Cellulose-based gels [8, 9] can be obtained by either physical or chemical stabilisation of aqueous solutions of celluloses [10–14]. Cellulose-based gels, either reversible or stable, can be formed by properly cross-linking aqueous solutions of cellulose ethers [12, 15, 16], such as methylcellulose, hydroxypropyl methylcellulose, ethyl cellulose (EC), hydroxyethyl cellulose (HEC), and sodium carboxymethylcellulose (NaCMC), which are among the most widely used cellulose derivatives. Depending on the cellulose derivative used, a number of cross-linking agents and catalysts can be used

to form gels. Epichlorohydrin, aldehydes, aldehyde-based reagents, urea derivatives, carbodiimides, and multifunctional carboxylic acids are the most widely used cross-linking agents for cellulose [17–21]. In light of material application concerns, cellulose gels have received increasing attention in recent years [22, 23]. Cellulose supramolecular materials linked by noncovalent bondshave attracted much more attention and have been widely studied [24]; their responsiveness to the external environment [25], such as temperature [26], pH [27], and medicine (drug release carriers) [28] have been of particular interest.

However, there are few reports on the application of cellulose gel used in healing. In this study, a novel cellulose physical gel was synthesised by β -CD-cellulose and Fc-cellulose. The host-guest interaction between the β -CD-cellulose and the Fc-cellulose, the sol-gel transition, and the redox stimuli properties of the supramolecular material were also studied.

2. Experimental

2.1. Material and Methods. Cellulose, β -cyclodextrin, epichlorohydrin, sodium hydroxide, lithium chloride, N,N-dimethyl acetamide, methylene chloride, ferrocene carboxylic acid, oxalyl chloride, sodium hypochlorite and glutathione were commercially available and used as received.

IR spectra were recorded by FTIR (Nicolet iN10 Thermo Fisher Scientific China) in the region of 400–4000 cm^{-1} . DSC measurements were carried out using a Diamond DSC apparatus (NETZSCHDSC 204). The dried samples were placed in pressure tight aluminum DSC cells from 20 to 150 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Surface contact angles were measured using a dynamic contact angle analyzer (HARKE-SPCA, error value of $\pm 0.1^{\circ}$, Beijing HARKE Experimental Instrument Factory). The cellulose powder samples were compressed using an infrared tablet. Surface contact angles were measured during liquid exposure to the test materials for 1 s in order to avoid material penetration factors as far as possible. The morphological characterization of gel was performed with scanning electron microscopy (S-3400N, HIACHI, Japan).

The gravimetric method was employed to measure the swelling ratios of the gels in distilled water at 25 $^{\circ}\text{C}$. After immersion in distilled water for about 48 hr to reach swelling equilibrium, the gel samples were taken out and weighed after removing the excess water on the surfaces. Each data was measured three samples, and the average value of three measurements was taken. The equilibrium swelling ratio (SR) was calculated as $\text{SR} = W_s/W_d$, where W_s is the weight of the swollen gel and W_d is the weight of the gel at the dry state.

Reswelling ratios of the gels were measured as follows: the dry gel was placed in deionized water of 25 $^{\circ}\text{C}$. At predetermined time, the gel samples were taken out from the aqueous solution and weighed the quality W_t , until it reached swelling equilibrium. Reswelling rate (r_{SR}): $r_{\text{SR}} = 100 * (W_t - W_d)/m_d$.

2.2. Preparation of Cellulose Inclusion Complexes

2.2.1. Preparation of Cellulose-CDs. Cellulose was dissolved in sodium hydroxide/urea. To this solution, cyclodextrin and epichlorohydrin were added. After stirring for 2 h, β -CD was added and the solution was stirred for another 12 h at room temperature. The polymer product was reprecipitated from distilled water and washed with distilled water. The degree of substitution is 0.32 wt%, which was detected by the phenolphthalein probe method [29].

In NaOH aqueous solution, cellulose and epichlorohydrin generate the epoxy cellulose, which connected hydroxy of β -cyclodextrin by the epoxy group as a cross-linking bridge.

2.2.2. Synthesis of Fc-COCl. Ferrocenecarboxylic acid was suspended in dichloromethane (DCM). Then oxalyl chloride was added dropwise, and the suspension was stirred for 3 h at room temperature. The orange suspension turned into a red solution. After evaporating the solvent, the solid product was collected.

2.2.3. Synthesis of Cellulose-Fc. Cellulose was dissolved in lithium chloride/dimethylacetamide (LiCl/DMAc). The ferrocenecarboxylic chloride solution was added dropwise. After stirring overnight at room temperature, the solution was washed with distilled water. The orange solid was washed with lithium chloride; the solid product was collected via a centrifuge and dried for 4 days at 50 $^{\circ}\text{C}$ to obtain cellulose-Fc as a yellow powder. The ferrocene grafting rate is 0.57~5.7 wt%, which was detected by weighing before and after the cellulose reaction.

2.2.4. Preparation of Redox Inclusion Complex. The oxidized state (or educed state) products were prepared by shaking appropriate amounts of NaClO aq. (14 mM) (or GSH) and Fc-CD-cellulose inclusion complexes (or oxidized state products) at room temperature for 24 h. The solution was washed with distilled water and then the solid product was collected via a centrifuge and freeze-dried. A complex mixture was prepared by grinding powders for 20 min.

2.2.5. Synthesis of Cellulose Gel. The ferrocene-cellulose and cyclodextrin-cellulose were dissolved in N,N-Dimethylformamide (DMF) lithium chloride solution. We poured the solution into a glass mould in a humid box until the gel was stabilized.

3. Results and Discussion

3.1. Characterization. Figure 1 (curve (a)) and Figure 1 (curve (b)) show the infrared spectra of the cellulose and β -CD-cellulose. According to Figure 1 (curves (a) and (b)), absorption was observed at 3380 cm^{-1} (hydroxyl stretch influenced by hydrogen bonding), 1646 cm^{-1} and 1354 cm^{-1} (carbonyl stretch), 1043 cm^{-1} (carboxyl in ethers), and 2920 cm^{-1} (methylene), which were characteristic absorptions in cellulose and β -CD-cellulose structures. As seen from Figure 1

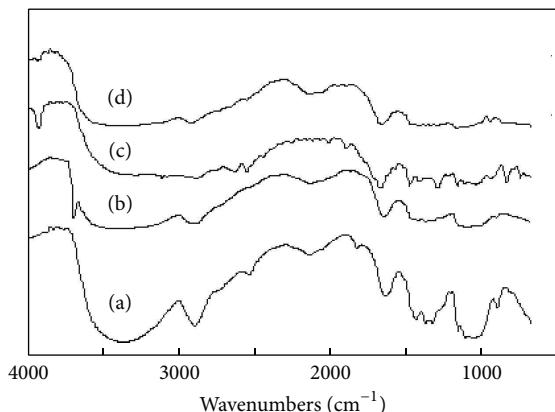


FIGURE 1: Infrared spectra of cellulose ((a) cellulose, (b) cellulose-CD, (c) cellulose-Fc, and (d) cellulose-CD-Fc inclusion).

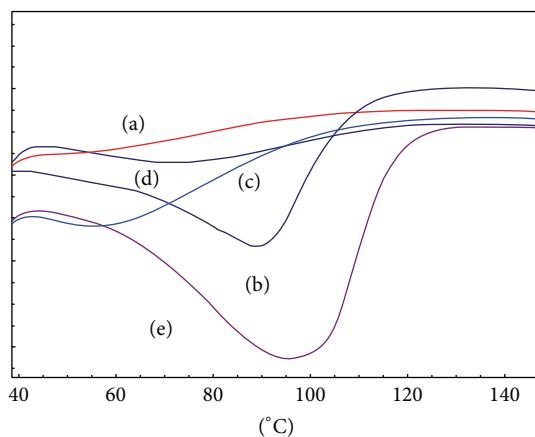


FIGURE 2: DSC curves of the series of cellulose ((a) cellulose, (b) cellulose-CD, (c) cellulose-ferrocene, (d) cellulose-CD-ferrocene inclusion, (e) simple mixing of cellulose-ferrocene, and cellulose-CD).

(curve (c)) the characteristic peaks of ferrocene-cellulose were 1402 cm^{-1} , 1100 cm^{-1} VC-C (cyclopentadienyl ring), and 816 cm^{-1} DC-H (cyclopentadienyl ring). The characteristic peaks of ferrocene disappeared from the infrared spectra of the envelope of the inclusion compound (curve (d)). This indicated that the ferrocene-cellulose and cyclodextrin cellulose have been formed in the inclusion complex. Similar findings were reported in the literature [30, 31].

3.2. Thermal Analysis. The thermal analysis curves of the cellulosic inclusion complexes are shown in Figure 2 where it can be seen that the curve (a) of cellulose is almost a straight line, but the curves (b) (CD-cellulose) and (e) (simple physical mixing of CD-cellulose and Fc-cellulose) had a strong exothermic peak (cyclodextrin dehydration absorption peaks [32] at 88.9°C and 95.9°C , resp.), corresponding to the loss of water from the CD cavity to atmosphere, indicating that CD was free from guest complexation in the physical mixture [32]. Otherwise, the curve (d) (the inclusion complex) showed a lack of endothermic peaks,

which suggested that a different molecule was present in the CD cavity, instead of the water molecules and a lack of pure CD in the complex sample. Similar results were reported in the literature for interactions between other drugs and CDs [30, 31, 33, 34].

3.3. The Redox Properties.

The redox regulation process of inclusion complexes containing ferrocene has been studied extensively.

The host-guest interaction between the metal ferrocene with β -CD can also be a reversible regulation by oxidation and reduction of the ferrocene. More than 20 years ago, it was reported that the reduced ferrocene effectively forms an inclusion compound with the β -CD, while the oxidation of the ferrocene was impossible [35, 36]. The nature of ferrocene is hydrophobic in its reduced state and hydrophilic in its oxidized state. The reversible regulation of the inclusion complexes forming a binary complex can be achieved by changing the redox state of the ferrocene. Therefore, the cellulose materials were expected to have a redox response performance by grafting ferrocene onto the cellulose.

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The redox behaviour of ferrocene was studied by measuring the surface contact angle with water. The cyclodextrin-cellulose contact angle was 59.6° (Figure 3(a)) and the ferrocene-cellulose contact angle was 82.1° (Figure 3(b)). The contact angle changed from 82.1° to 61.2° (Figure 3(c)) when the ferrocene-cellulose and cyclodextrin-cellulose formed inclusion complexes. This demonstrated that the ferrocene was an inclusion in the cyclodextrin cavity.

Aqueous NaClO was chosen as an oxidant and GSH as a reductant. Adding aqueous NaClO to the cellulose- β CD/cellulose-Fc inclusion complexes increased the contact angle from 61.2° to 71.7° (Figure 3(d)). In contrast, continuous addition of GSH to the inclusion complexes recovered the Fc group, causing the contact angle to revert to its former value (Figure 3(e)). Cellulose- β -CD showed a high affinity for the reduced state of the Fc group due to its hydrophobic nature, whereas the oxidized state of the Fc group (Fc^+) exhibited a low affinity for cellulose- β -CD due to the cationic Fc^+ group [35–37]. Moreover, the cellulose inclusion complexes exhibited excellent lock and unlock properties controlled by the redox of ferrocene.

3.4. The Compressive Strength of Fc-Cellulose/ β -CD-Cellulose Gel.

Gels are composed of a three-dimensional hydrophilic

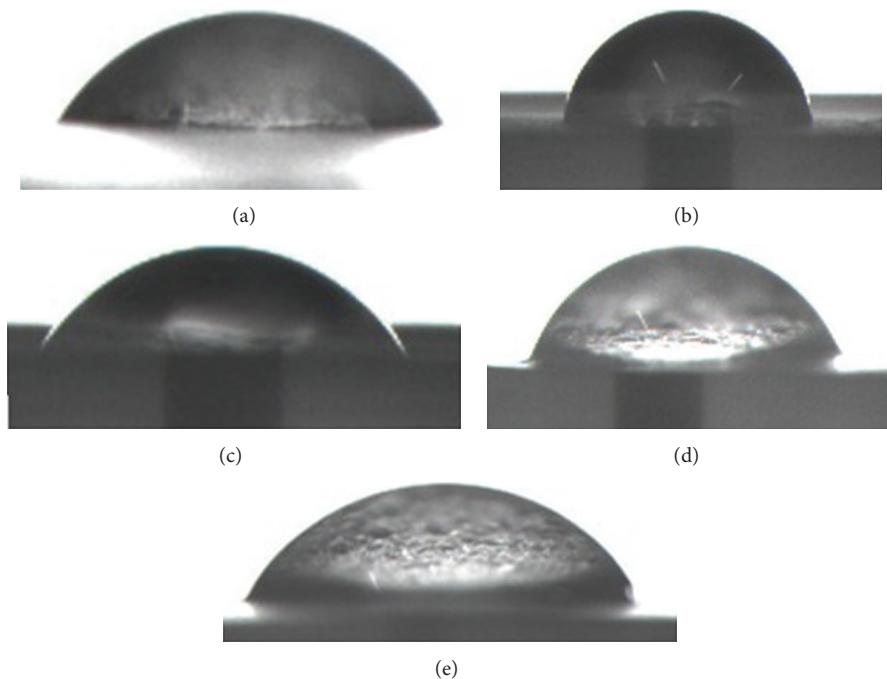


FIGURE 3: Contact angle images of the series of cellulose ((a) cellulose-CD, (b) cellulose-ferrocene, (c) cellulose-CD-ferrocene inclusion, (d) NaClO treated sample, and (e) GSH treated sample).

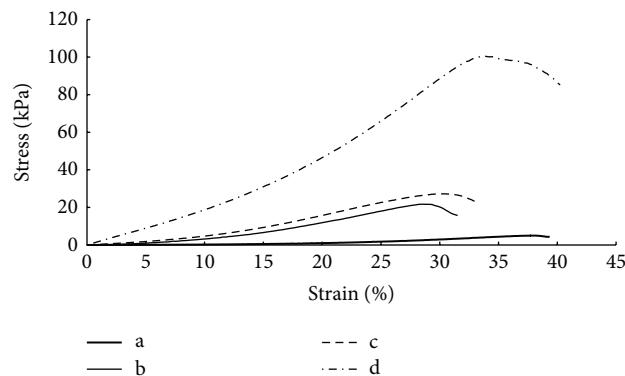


FIGURE 4: The compressive strength of different cellulose content ((a) 1 wt%, (b) 3 wt%, (c) 4 wt%, and (d) 5 wt%).

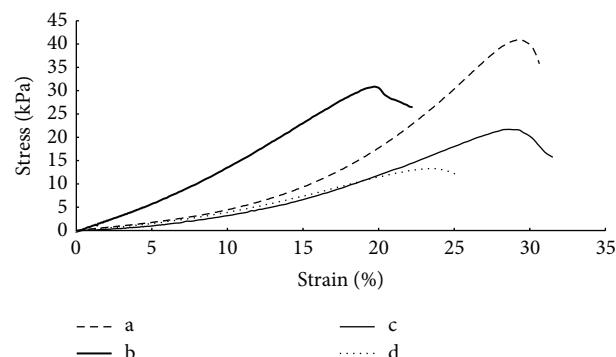


FIGURE 5: The compressive strength of different grafting ratio of ferrocene ((a) 5.66 wt%, (b) 2.83 wt%, (c) 1.41 wt%, (d) 0.57 wt%).

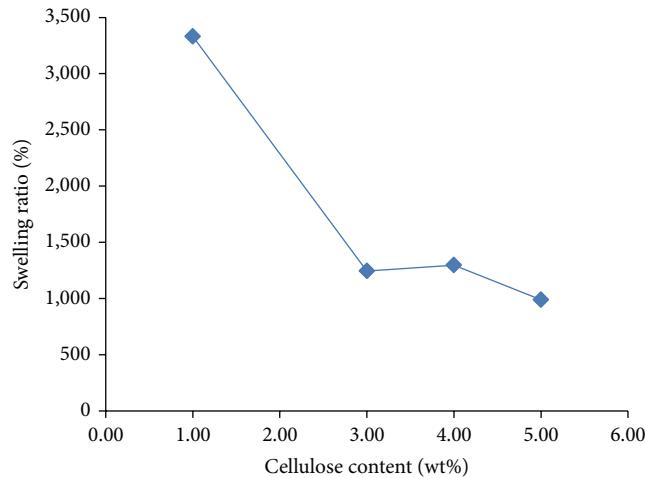


FIGURE 6: The swelling ratio of the Fc-cellulose/β-CD-cellulose hydrogel.

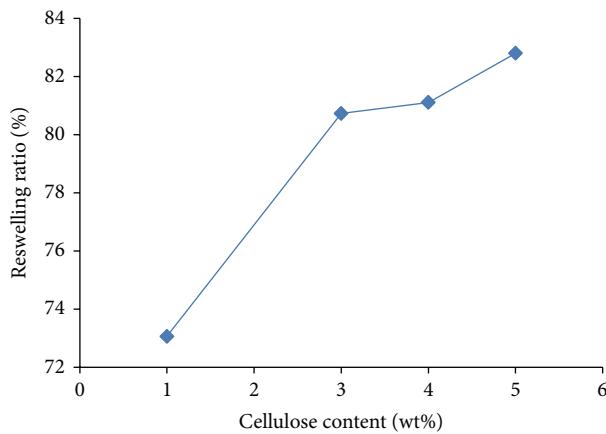


FIGURE 7: The reswelling ratio of the Fc-cellulose/β-CD-cellulose hydrogel.

polymer network in which a large amount of water is interposed. The cross-linking ratio of the network is important to the mechanical properties. As the concentration of cellulose increased from 1% (w/w) to 5% (w/w) the gel strength increased from 5 kPa to 100.5 kPa (Figure 4). This was because the number of cross-linking sites *per unit volume* of the network increased with an increased number of functional groups on the molecular chain which was caused by the increased concentration of cellulose [38]. Similar improvements in the mechanical strength were also observed when increasing the cross-linking degree by changing the grafting ratio of Fc. The compressive strength of Fc-cellulose/β-CD-cellulose gel changed from 13.32 kPa to 40.97 kPa as the grafting ratio of Fc changed from 0.57% (w/w) to 5.66% (w/w) (Figure 5), indicating that the host-guest interaction between the side chains of cellulose participated in the formation of the three-dimensional network structure of the gel and also affected its strength.

3.5. The Water Absorption of Fc-Cellulose/β-CD-Cellulose Gel.

The swelling ratio of the gel was the most important

variable to be evaluated for given environmental conditions, as it affected the diffusive, mechanical, optical, acoustic, and surface properties of the gel itself. The swelling ratio of the Fc-cellulose/β-CD-cellulose gel decreased as the concentration of cellulose increased (Figure 6). This was because the amount of water retained by the mesh of the hydrogel network depended on the structure of the polymer network itself [39]. The Fc-cellulose/β-CD-cellulose gel was formed by properly cross-linking the cellulose chains. The number of cross-linking sites *per unit volume* of the polymer network increased with increasing cellulose concentration. The larger degree of cross-linking was not conducive to the diffusion of water molecules.

The reswelling ratio of the Fc-cellulose/β-CD-cellulose gel decreased from 3330% (w/w) (Figure 6) to 73.06% (w/w) (Figure 7), when the dry gel was placed in deionised water again. The pore sizes of the super-absorbent gel showed that it was the water retention capacity that engendered the efficiency of absorption. It can be observed that the larger number of pores can retain more water. Figure 8 shows the freeze-drying morphology of the cellulose gel and Fc-cellulose/β-CD-cellulose gel; compared with the cellulose gel,

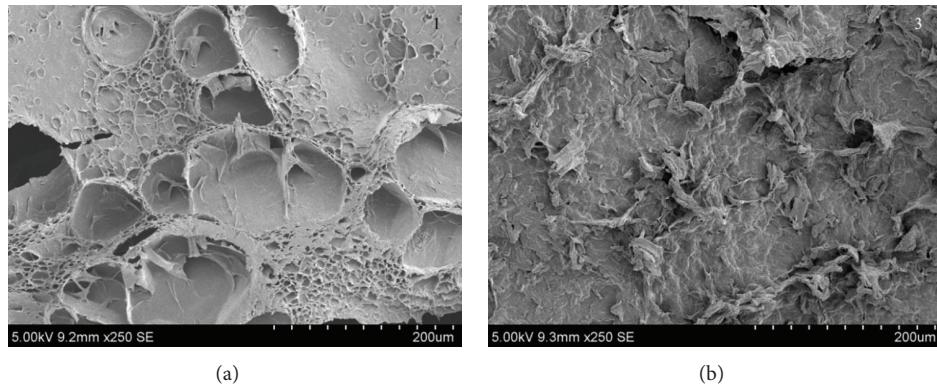


FIGURE 8: The SEM images of gel ((a) cellulose hydrogel and (b) Fc-cellulose/β-CD-cellulose hydrogel).

the Fc-cellulose/β-CD-cellulose gel had a more dense pore structure. After drying the gel, the dense pore structure was easily collapsed and confined; therefore, the reswelling ratio of the Fc-cellulose/β-CD-cellulose gel was poor.

3.6. The Surface Morphology of the Gel. The surface morphology of the gel is also shown in Figure 8. Cellulose and Fc-cellulose/β-CD-cellulose inclusion complexes gels were prepared by the same method. Cellulose gel (Figure 8(a)) had a relatively large, porous structure; as well as the Fc-cellulose/β-CD-cellulose inclusion complexes, the gel had a relatively dense surface structure. This may have been caused by the different intermolecular forces arising from the alteration of the cellulose molecular chain structure.

4. Conclusions

Ferrocene and cyclodextrin were grafted onto the cellulose surface, respectively. The cellulose physical gel was prepared by Fc-cellulose and β-CD-cellulose at room temperature. The β-CD-cellulose and the Fc-cellulose can form inclusion complexes. Moreover, ferrocene oxidation and reduction of state can be adjusted by sodium hypochlorite (NaClO) as an oxidant and glutathione (GSH) as a reductant. The sol-gel transition can be controlled. The compressive strength of Fc-cellulose/β-CD-cellulose gel increased with increasing cellulose concentration. The host-guest interaction between the side chains of cellulose can strengthen the gel. Thus, it was believed that these stimulus-responsive, healing properties may eventually be used in various biomedical applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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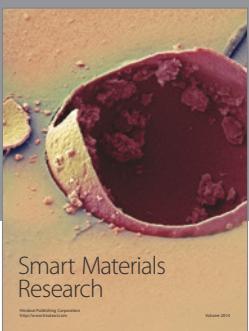
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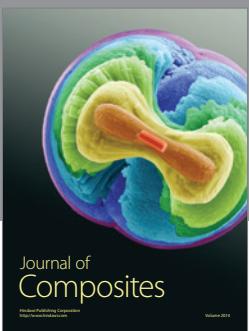
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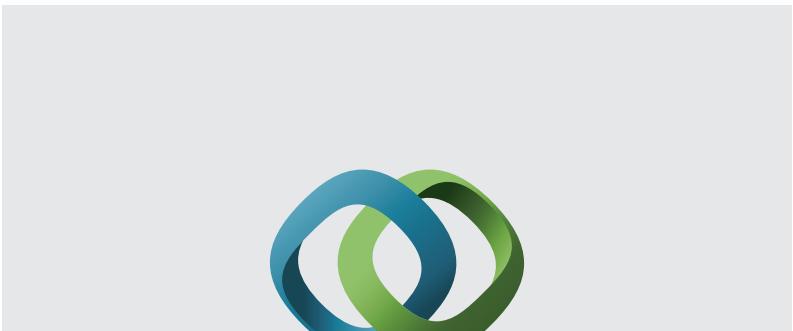
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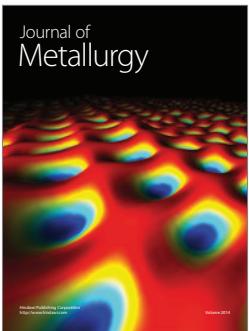


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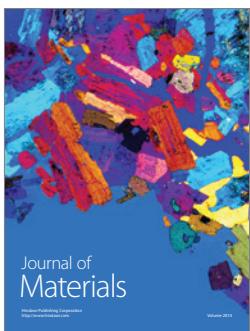
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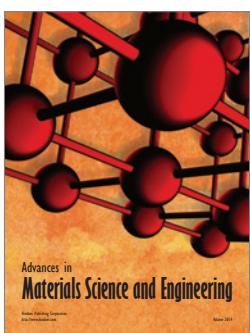
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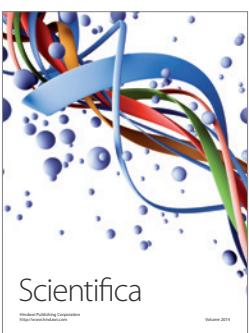
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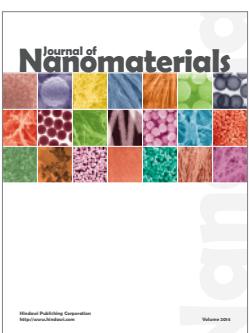
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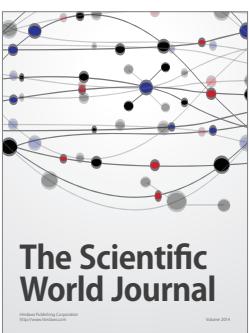
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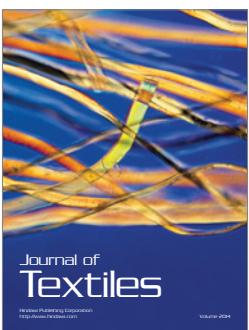
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