

Research Article

Novel Composite Materials for Chiral Separation from Cellulose and Barium Sulfate

Wei Chen,^{1,2} Zhaoqun Wang,² Xiaolin Xie,¹ Xingping Zhou,¹ and Zheng-Wu Bai²

¹ Key Lab for Large-Format Battery Materials and Systems, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

² Key Laboratory of Green Chemical Process of the Ministry of Education, Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology, Wuhan Institute of Technology, Wuhan 430073, China

Correspondence should be addressed to Xingping Zhou; xpzhou@mail.hust.edu.cn and Zheng-Wu Bai; zhengwubai@163.com

Received 17 August 2013; Revised 3 October 2013; Accepted 6 November 2013

Academic Editor: Yingkui Yang

Copyright © 2013 Wei Chen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Cellulose was dissolved in an aqueous solution of sodium hydroxide (NaOH) and urea followed by the addition of barium sulfate (BaSO_4) to yield the BaSO_4 /cellulose composite particles. The morphology, particle size, and BaSO_4 content of the composite particles were adjusted by controlling the feed ratio of cellulose and BaSO_4 . The cellulose within the composite particles then reacted with 3,5-dimethylphenyl isocyanate. The resulting materials were utilized as the chiral stationary phases (CSPs) whose enantioseparation capabilities were evaluated by various chiral analytes. Due to the mechanical enhancement effect of BaSO_4 , the composite particles could be applied to the chromatographic packing materials.

1. Introduction

Cellulose is one of the most abundant polysaccharides in nature and consists of glucose units linked with 1, 4- β -glucans [1, 2]. Because of strong intra- and intermolecular interactions between hydroxyl groups, cellulose is insoluble in water and common organic solvents [3]. However, Zhang et al. [4] reported that cellulose could be dissolved in a precooled sodium hydroxide (NaOH)/urea solution rapidly. Moreover, the chiral complexation between organic molecules and the substituents attached to the skeleton of the cellulose derivatives can take place due to the helical cavity of cellulose. Till now, the cellulose derivatives have been employed as the adsorbents for chromatographic separation of organic compounds, in particular, for the enantioseparation of chiral compounds [5–8]. In general, cellulose has been first functionalized by aryl carbamoylation or acylation, and the as-synthesized derivatives have been then coated or covalently immobilized on the silica gel to obtain the chiral separation materials [9, 10]. However, chromatographic-grade porous silica gel is very expensive. Luo and Zhang [11] prepared the cellulose microspheres in a pre-cooled NaOH/urea solution and then employed them

as the packing materials to fractionate polyethylene oxide. It was usually necessary for the cellulose microspheres to be cross-linked in order to enhance the mechanical and structural stability before use [12]. However, the cross-linking of the cellulose derivatives affects their enantioseparation capabilities because the superstructure of cellulose is altered [13]. Therefore, it is highly desirable to prepare a cellulosic material showing both sufficient mechanical strength and satisfactory chromatographic separation ability.

Organic/inorganic composites generally combine the functions of two components with the mechanical enhancement effect of inorganic counterparts [14–16]. In this work, BaSO_4 and cellulose were used as the inorganic and the organic components, respectively, and their composite particles were prepared by the emulsification-solidification method. In the BaSO_4 /cellulose composites, oxygen (O) atoms in the sulfate (SO_4^{2-}) ions can interact with the hydroxyl (–OH) groups present in cellulose to form the hydrogen bonding, and hence resulting in the improved mechanical and structural stability for the as-prepared composite materials. Furthermore, the resulting composite particles were modified with 3,5-dimethylphenyl isocyanate for

the use of the chiral stationary phases (CSPs), and their chromatographic separation capabilities were studied.

2. Experimental

2.1. Materials. Cotton linter pulp (α -cellulose) with a viscosity average molecular weight (M_{η}) of 8.3×10^4 g/mol was obtained from Hubei Chemical Fiber Group Ltd. (China). BaSO_4 powder with an average particle size of 80 nm was obtained from Foshan Onmillion Nano Materials Co., Ltd. (China). 3,5-Dimethylphenyl isocyanate was obtained from Puyang Hongda Shengdao New Materials Co., Ltd. (China). Pyridine was successively dried over potassium hydroxide (KOH) and calcium hydride (CaH_2) under reflux and redistilled before use. Toluene was refluxed over sodium and redistilled. Triethylamine (TEA) was dried over P_2O_5 before distillation. Other chemicals were of analytical grade and used as received without further purification.

2.2. Characterization. The infrared (IR) spectra of the composite particles and CSPs were recorded on a Nicolet Fourier transform-IR (FT-IR) instrument (USA) with KBr pellets. The thermogravimetric analysis (TGA) of the samples was conducted using a thermogravimetric analyzer (TGA Q50 V20.10 Build 36, USA). The particles (approximately 10 mg) were placed in an Al_2O_3 crucible and heated from 25 to 800°C at a rate of $10^\circ\text{C}/\text{min}$. The particles and CSPs were coated with gold in the usual manner, and their morphologies were observed by scanning electron microscopy (SEM) (JSM-5510LV, Japan) with an accelerating voltage of 20 kV. The surface areas and pore diameters were measured using a specific surface area analyzer (JW-BK, USA) through the nitrogen adsorption method. The dispersion of the nanoscale BaSO_4 in the particles was observed using a JEM-2100F TEM (Jeol, Japan) operated at 200 kV. For this purpose, the particles were embedded in an epoxy resin and cut into 70 nm thickness using an ultramicrotome instrument (Leica Ultracut UCT, Leica, Austria) equipped with a diamond knife. The cut resins were placed on a 100 mesh copper grid for TEM measurement. The volume-average diameter of the composite particles was determined using a laser particle size analyzer (Microtrac S3500, USA) with deionized water as the fluid.

2.3. Preparation of Composite Particles. According to the reported method [4, 17], the cellulose solution (3%, wt/wt) was prepared in a NaOH/urea solution as the solvent. BaSO_4 (1.3 g) was added to the cellulose solution (42 g). The mass ratio of cellulose to BaSO_4 was 1:1. The resulting mixture was stirred vigorously for 5 min followed by centrifugation at a speed of 4000 rpm for 10 min. The supernatant cellulose- BaSO_4 solution (30 g) was added dropwise to a mixture of paraffin (200 g) and Span 80 (24 g). The resulting mixture was stirred at a speed of 1000 rpm at 20°C for 5 h, then at 40°C for 2 h. After neutralizing with dilute hydrochloric (HCl) acid, the mixture was separated into two layers. The crude particles were collected by centrifugation of the aqueous layer and washed with water, acetone/water, and acetone in turn. The

particles were dried in vacuum for 12 h, dispersed in water by sonication, and washed again with water, acetone/water, and acetone. The suspension of the particles in water was filtered through a stainless steel sieve (270 meshes) to remove any residual cotton linter pulp. A white powder (3.42 g, named as CP 1) was finally obtained after drying in vacuum. CP 2 and CP 3 samples were prepared by varying the feed ratios of BaSO_4 and cellulose to 2:1 and 3:1, respectively, using the same manner as described previously.

2.4. Modification of the Composite Particles. Before modification, the composite particles were azeotropically dried with benzene. CP 1 (3.36 g) was mixed with a solution of TEA (3 mL) and pyridine (10 mL) in toluene (25 mL), and the resulting mixture was heated to 85°C . To the previous solution was added 5 mL of 3,5-dimethylphenyl isocyanate and stirred for 10 h under nitrogen atmosphere. The modified particles were washed with toluene (10 mL) and extracted with dimethyl formamide (DMF)/ethyl acetate (3:4, v/v) using a Soxhlet apparatus. After the removal of the volatiles, the remaining product of CSP 1 (3.59 g) was obtained. IR (KBr, cm^{-1}) *v*: 1720 (C=O), 1655 (NHC=O), 1563 (NH). CSP 2 was prepared by the same method using CP 2 instead of CP 1. IR (KBr, cm^{-1}) *v*: 1719 (C=O), 1652 (NHC=O), 1557 (NH).

2.5. CSP Packing and Enantioseparation. The CSPs were treated with a mixture of isopropanol and *n*-hexane (10:90, v/v) to form slurries which were then pressed into empty stainless steel columns (150 \times 4.6 mm) under a pressure of 4000 psi with *n*-hexane as the displacer solvent. The dead time of the columns was determined with 1,3,5-tri-*tert*-butylbenzene. The sample solutions (1 mg/mL) were prepared by dissolving the chiral compounds in ethanol and filtering through a 0.2- μm membrane. The enantioseparation was performed using a Waters chromatograph (USA) equipped with a 996 photodiode array detector, 600E Quat Pump, Empower I system controller, and 717 plus autosampler. The flow rate was set at 0.5 mL/min, and the column temperature was set at 25°C for all the detections.

3. Results and Discussion

3.1. Characterization and Properties of Composite Particles. The preparation schemes of the particles and CSPs are shown in Figure 1. A small amount of gel formed when the cellulose solutions were mixed with nanoscale particles of BaSO_4 , particularly in the case when BaSO_4 was fed at a high ratio. The resulting gels were removed by centrifugation affording clear supernatants that were subsequently used to prepare the particles.

The BaSO_4 contents in the particles were determined by TGA measurement, as shown in Figure 2. CP 1, CP 2, and CP 3 were found to show similar TGA profiles in the temperature range tested. As the feed ratio of BaSO_4 to cellulose increases from 1:1, 2:1 to 3:1, the weight content of BaSO_4 in the composite particles increases from 34.1, 52.6 to 57.4%, respectively. CSP 2 accordingly shows a higher

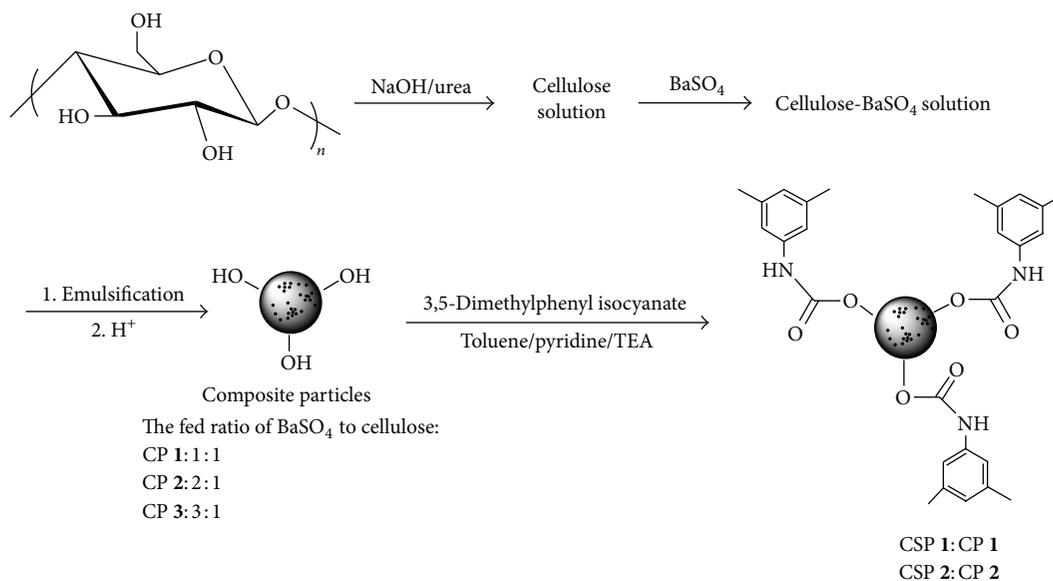


FIGURE 1: The preparation scheme of the composite particles and the CSPs.

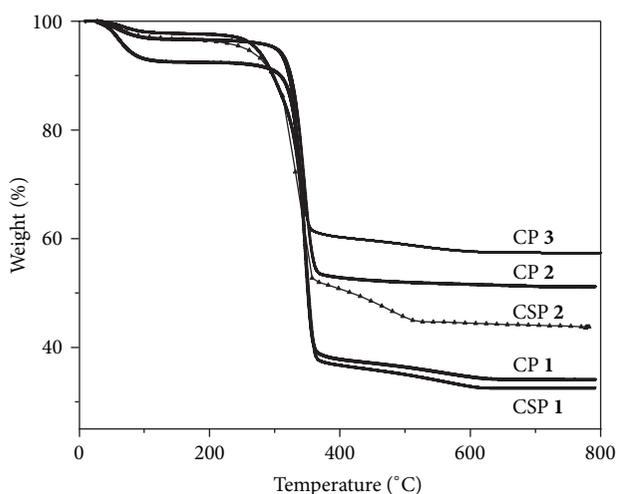


FIGURE 2: TGA curves of the composite particles and the CSPs.

remaining amount after thermolysis than CSP 1 due to the higher BaSO₄ loading of the former.

The morphology of the composite particles was examined by TEM in conjunction with SEM technology. CP 1 was here selected as a representative sample. As shown in both Figures 3 and 4, the structure of CP 1 is approximately spherical shape with an average diameter of 12.2 μm. It can be rationally deduced that BaSO₄ nanoparticles are mainly embedded inside the composite particles and some of them may be attached to their surfaces due to the hydrogen bonding between cellulose and BaSO₄. Furthermore, the specific surface areas of CP 1, CP 2, and CP 3 were found to be 197, 100.9 and 110.4 m²/g, respectively, according to the BET (Brunauer-Emmett-Teller) method. According to the BJH (Barrett-Joyner-Halenda) mode, the pore diameters of CP 1, CP 2 and CP 3 were measured to be 1.61, 9.66, and

9.32 nm, respectively. It is expected that such high specific surface areas and small pore sizes will be useful for the use of the chromatographic packing materials.

3.2. Preparation of CSPs. The hydroxyl groups of cellulose within CP 1 and CP 2 could partially react with 3,5-dimethylphenyl isocyanate, and the resulting CSP 1 and CSP 2 contain new urethane groups as revealed by their IR spectra. Because there are no small molecule produced during carbamylation, the increment in the weight for the composite particles should be attributable to the introduction of 3,5-dimethylphenyl isocyanate after reaction. Therefore, the degree of substitution (DS) of the hydroxyl groups can be calculated by the following equation (1):

$$DS (\%) = \frac{(w_{b1}/w_{b2}) \times w_{c2} - w_{c1}}{(w_{c1} - w_{b1}) ((147 \times 3)/162)} \times 100\%, \quad (1)$$

where 162 and 147 are the molecular weights of the repeating unit (C₆H₁₀O₅) in the cellulose and 3,5-dimethylphenyl isocyanate, respectively. w_{b1} and w_{b2} are the mass percentage of BaSO₄ in the premodified CPs and CSPs, respectively. w_{c1} and w_{c2} are the mass percentages of the dried substances in the premodified CPs and the CSPs, respectively. The values of w_{b1} , w_{b2} , w_{c1} , and w_{c2} were determined by TGA. The DS values of CSP 1 and CSP 2 were calculated to be 6.6 and 13.3%, respectively.

3.3. Enantioseparation of CSPs. CSP 1 and CSP 2 were packed into two empty columns, respectively. The packed columns were then used to separate the enantiomers of various chiral compounds whose chemical structures are shown in Figure 5. The enantioseparation capabilities of the columns based on CSP 1 and CSP 2 were evaluated by using the same mobile phase conditions and the results are summarized in Table 1. It was found that both CSP 1 and CSP 2 could separate most

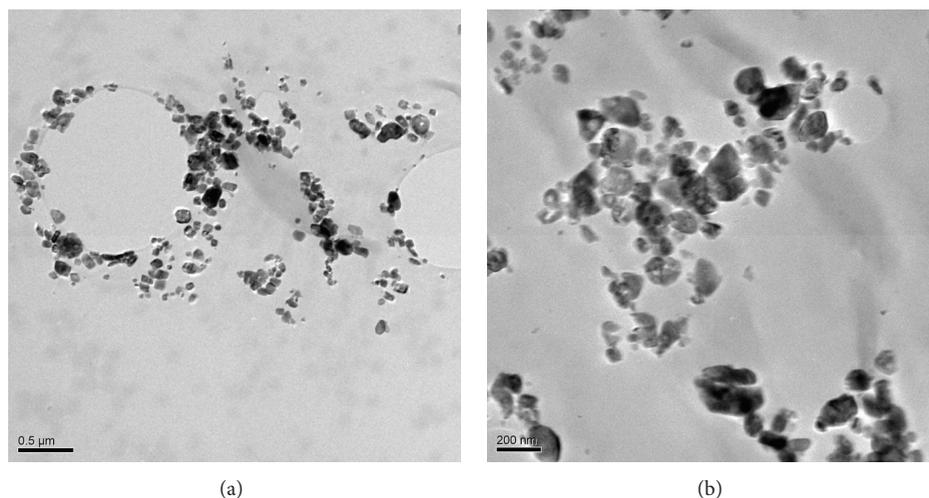


FIGURE 3: TEM images of CP 1 taken at low (a) and high (b) magnifications.

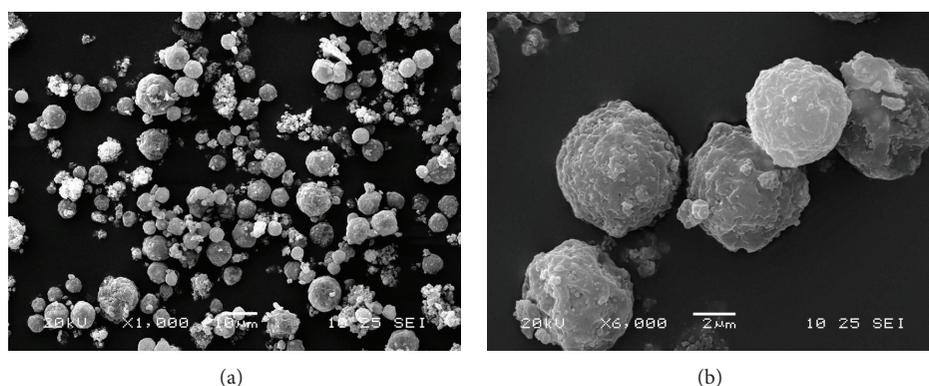


FIGURE 4: SEM images of CP 1 taken at low (a) and high (b) magnifications.

enantiomers. CSP 1 and CSP 2 provided the enantioseparations of 18 and 14 compounds, respectively. Thus, the chiral recognition ability of CSP 1 was slightly better than that of CSP 2. However, five baseline separations ($R_s \geq 1.5$) were observed on CSP 2 but only three baseline separations for CSP 1. Moreover, the general chromatographic resolutions (Table 1) on CSP 2 were higher than those on CSP 1. The chromatograms of typical enantioseparation on CSP 2 are shown in Figures 6(a) and 6(b).

Another important aspect is the stability of the columns during working. For this purpose, the columns filled with CSP 1 and CSP 2 were subjected to the chromatographic separation, and the collected eluent was distilled to dryness. However, no solid was observed in the distillate, confirming that the BaSO_4 nanoparticles did not escape from the composite particles. This is probably ascribed to the hydrogen bonding interaction between the residual hydroxyl groups of cellulose and sulfate ions of BaSO_4 . Although the composite particles were not chemically cross-linked, they seemed to be structurally stable due to the physical cross-linking of hydrogen bonding in combination with the mechanical enhancement effect of BaSO_4 . For the comparison purposes,

the graphite/cellulose composite particles were prepared and then modified by 3,5-dimethylphenyl isocyanate using the same method as the BaSO_4 -based CSPs. However, when the column packed with the graphite/cellulose CSP was employed for the chromatography, the black solid corresponding to the graphite particles was dialyzed out due to the lack of interaction between graphite and cellulose.

Meanwhile, after the CSPs continuously worked for a long time or worked at a higher pressure such as 3200 psi, the CSPs inside the columns were partially compressed, and a slight vacancy was created at the entrance of the columns. However, after the vacancy was refilled with the same CSPs, the chiral separation capability of the columns recovered. For instance, compound 14 was initially separated by CSP 2 with a resolution value of 1.45 (Figure 6(c)). After the column of CSP 2 was run for 150 injections, it was found that there was a slight vacancy at the entrance of the column. Then the vacancy was refilled with CSP 2, and compound 14 was separated again. The latter resolution value was 1.40 (Figure 6(d)). The resolution values of two separations were almost the same, indicating that the enantioseparation capability of the column was recovered.

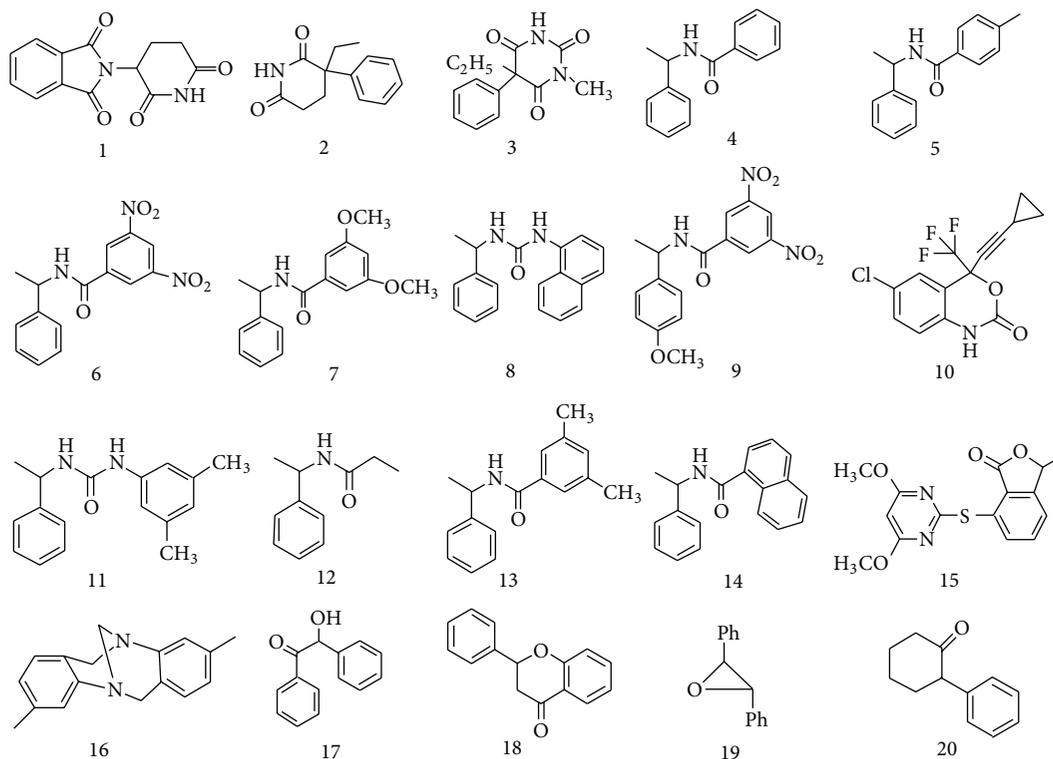


FIGURE 5: Chemical structures of chiral analytes resolved by CSP 1 and CSP 2.

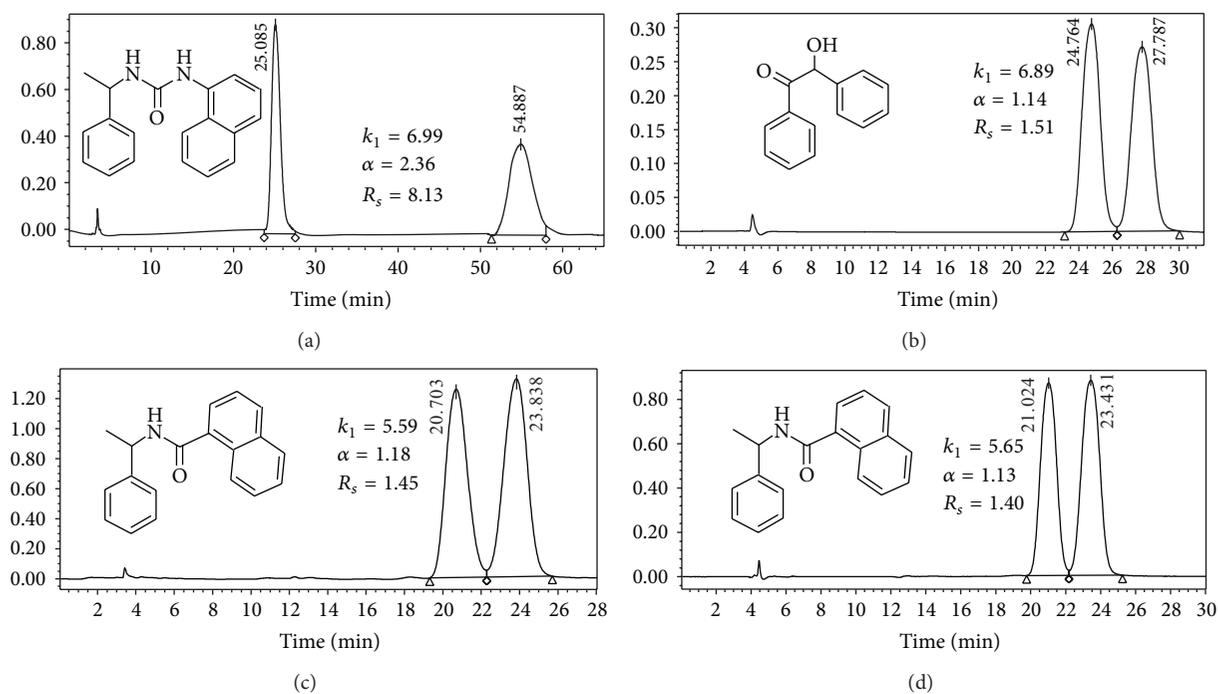
FIGURE 6: The typical chromatograms of the chiral compounds separated by CSP 2. (a) compound 8; (b) compound 17; (c) compound 14; (d) the second time separation of compound 14 while the vacancy in the column input had been refilled. Mobile phase: *n*-hexane/ethanol/methanol (90/5/5, v/v/v); flow rate: 0.5 mL/min.

TABLE 1: The enantioseparation evaluation of CSP 1 and CSP 2.

Chiral analytes	CSP 1				CSP 2			
	k_1	α	R_s	Eluent	k_1	α	R_s	Eluent
1	6.59	1.21	0.18	B	No separation			
2	4.93	1.36	0.24	B	No separation			
3	4.20	1.25	0.95	A	No separation			
4	6.59	1.14	0.42	A	3.61	1.09	0.21	B
5	No separation				3.35	1.07	0.44	C
6	3.41	1.08	0.18	B	No separation			
7	2.47	2.06	2.52	E	5.97	1.21	1.81	C
8	1.22	2.57	3.25	F	6.99	2.36	8.18	C
9	9.63	1.19	0.57	E	No separation			
10	1.87	1.35	0.64	A	No separation			
11	No separation				12.33	1.10	0.99	D
12	0.86	1.27	0.10	B	2.07	1.19	0.77	C
13	0.78	1.37	0.34	B	2.78	1.15	1.26	C
14	2.01	1.10	0.08	B	6.56	1.15	1.53	C
15	3.37	1.09	0.12	E	8.74	1.08	0.15	B
16	1.35	1.45	1.54	A	1.26	1.32	1.56	C
17	4.10	1.20	0.99	A	6.89	1.14	1.51	C
18	2.45	1.14	0.41	A	2.21	1.11	0.22	C
19	0.78	1.44	0.37	A	1.01	1.15	1.00	A
20	1.36	1.10	0.12	E	2.02	1.14	1.00	D

The retention factors (k_1 and k_2) were calculated from the formulas of $(t_1 - t_0)/t_0$ and $(t_2 - t_0)/t_0$, where t_1 and t_2 are, respectively, the retention time of the first- and the second-eluted enantiomers, and t_0 is the dead time determined by using 1,3,5-tri-*t*-butylbenzene. The separation factor (α) was calculated from the formula of k_2/k_1 . The resolution (R_s) was calculated from the formula of $2(t_2 - t_1)/(w_1 + w_2)$, where w_1 and w_2 are the bandwidth of the first- and the second-eluted enantiomers, respectively.

A: *n*-hexane/isopropanol (90/10, v/v); B: *n*-hexane/ethanol (90/10, v/v); C: *n*-hexane/ethanol/methanol (90/5/5, v/v/v); D: *n*-hexane/ethanol (95/5, v/v); E: *n*-hexane/isopropanol (70/30, v/v); F: *n*-hexane/ethanol (70/30, v/v).

4. Conclusions

The BaSO₄/cellulose composites were successfully prepared by employing a pre-cooled NaOH/urea solution to dissolve the cellulose before the addition of BaSO₄ nanoparticles. The presence of BaSO₄ improved the mechanical and structural stability of the composite particles due to the hydrogen bonding interaction between two components. The composites were then modified by the isocyanate reactant and appeared as the microsized spherical particles when the feed ratio of BaSO₄ to cellulose was 1:1 in weight. The as-functionalized composite particles were further used as the chromatographic packing materials for the separation of chiral compounds. Of note, the composites as the CSPs were found to possess different enantioseparation capabilities toward chiral compounds depending on the loading level of BaSO₄. This implies that the enantioseparation ability of the BaSO₄/cellulose-based CSPs can be readily adjusted by controlling the feed ratio of BaSO₄ to cellulose and may provide a new way to develop the packing materials for liquid chromatography.

Acknowledgments

The financial supports from the National Natural Science Foundation of China (50973086 and 51273073) and Hubei Provincial Department of Education of China (Z 20081501) are gratefully acknowledged.

References

- [1] S. van de Vyver, J. Geboers, P. A. Jacobs, and B. F. Sels, "Recent advances in the catalytic conversion of cellulose," *ChemCatChem*, vol. 3, no. 1, pp. 82–94, 2011.
- [2] Y. Nishiyama, J. Sugiyama, H. Chanzy, and P. Langan, "Crystal structure and hydrogen bonding system in cellulose I_α from synchrotron X-ray and neutron fiber diffraction," *Journal of the American Chemical Society*, vol. 125, no. 47, pp. 14300–14306, 2003.
- [3] R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, "Dissolution of cellose with ionic liquids," *Journal of the American Chemical Society*, vol. 124, no. 18, pp. 4974–4975, 2002.
- [4] J. Cai and L. Zhang, "Rapid dissolution of cellulose in LiOH/urea and NaOH/urea aqueous solutions," *Macromolecular Bioscience*, vol. 5, no. 6, pp. 539–548, 2005.
- [5] Y. Okamoto and E. Yashima, "Polysaccharide derivatives for chromatographic separation of enantiomers," *Angewandte Chemie International Edition*, vol. 37, no. 8, pp. 1021–1043, 1998.
- [6] J. Trygg, P. Fardim, M. Gericke, E. Mäkilä, and J. Salonen, "Physicochemical design of the morphology and ultrastructure of cellulose beads," *Carbohydrate Polymers*, vol. 93, no. 1, pp. 291–299, 2013.
- [7] W. de Oliveira and W. G. Glasser, "Hydrogels from polysaccharides. I. Cellulose beads for chromatographic support," *Journal of Applied Polymer Science*, vol. 60, no. 1, pp. 63–73, 1996.
- [8] K.-F. Du, M. Yan, Q.-Y. Wang, and H. Song, "Preparation and characterization of novel macroporous cellulose beads regenerated from ionic liquid for fast chromatography," *Journal of Chromatography A*, vol. 1217, no. 8, pp. 1298–1304, 2010.
- [9] Y. Okamoto, M. Kawashima, and K. Hatada, "Chromatographic resolution. XI. Controlled chiral recognition of cellulose triphenylcarbamate derivatives supported on silica gel," *Journal of Chromatography A*, vol. 363, no. 2, pp. 173–186, 1986.
- [10] T. Kubota, C. Yamamoto, and Y. Okamoto, "Phenylcarbamate derivatives of cellulose and amylose immobilized onto silica gel as chiral stationary phases for high-performance liquid chromatography," *Journal of Polymer Science A*, vol. 42, no. 18, pp. 4704–4710, 2004.
- [11] X. G. Luo and L. N. Zhang, "Creation of regenerated cellulose microspheres with diameter ranging from micron to millimeter for chromatography applications," *Journal of Chromatography A*, vol. 1217, no. 38, pp. 5922–5929, 2010.
- [12] T. Ikai, C. Yamamoto, M. Kamigaito, and Y. Okamoto, "Preparation and chiral recognition ability of crosslinked beads of polysaccharide derivatives," *Journal of Separation Science*, vol. 30, no. 7, pp. 971–978, 2007.
- [13] T. Ikai, R. Muraki, C. Yamamoto, M. Kamigaito, and Y. Okamoto, "Cellulose derivative-based beads as chiral stationary phase for HPLC," *Chemistry Letters*, vol. 33, no. 9, pp. 1188–1189, 2004.
- [14] Y. Chujo, "Organic-inorganic hybrid materials," *Current Opinion in Solid State and Materials Science*, vol. 1, no. 6, pp. 806–811, 1996.

- [15] B. M. Novak and C. Davies, "Inverse' organic-inorganic composite materials. 2. Free-radical routes into nonshrinking sol-gel composites," *Macromolecules*, vol. 24, no. 19, pp. 5481-5483, 1991.
- [16] M. W. Ellsworth and B. M. Novak, "Inverse' organic-inorganic composite materials. 3. High glass content "nonshrinking" sol-gel composites via poly (silicic acid esters)," *Chemistry of Materials*, vol. 5, no. 6, pp. 839-844, 1993.
- [17] D. Ruan, L. Zhang, A. Lue et al., "A rapid process for producing cellulose multi-filament fibers from a NaOH/thiourea solvent system," *Macromolecular Rapid Communications*, vol. 27, no. 17, pp. 1495-1500, 2006.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

