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# Preparation and physical properties of superhydrophobic papers

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## 1. Introduction

Wood fibers are typical hydrophilic natural materials. With biodegradability, renewability, and low cost, wood fibers have been widely used as package materials. One of the problems of using wood fiber material in packaging containers is its hydrophilicity that results in high water and moisture absorptions. The simple approaches for increasing the hydrophobicity of cellulose paper containers include internal and surface sizing or surface barrier coating. Although paper hydrophobicity can be significantly improved, paper sizing alone cannot meet the high water repellent requirement when paper products are used as food and drink packages. For such applications, barrier coating is the most important technique manufacturing high water resistance paper containers. With regard to the barrier coating layer formation, a wide range of candidates are available, such as organic polymers [1,2], inorganic ceramic and metals [3,4], and sol-gel coating layers [5-8], etc. Polymers are the most common coating materials used for improving water resistance of paper packages. However, thick coating layers, usually  $>50 \mu m$ , must be applied to achieve desired water resistant levels. This does not only result in a high coating cost but also poor paper recyclability. In order to reduce the coating cost, the industry widely uses wax as the barrier coating material. However, because of the low melting temperature, the melted wax forms deposition on paper machine and wood fibers when temperature reduces below its melting temperature. Therefore, waxed papers are unrecyclable.

The common way for increasing hydrophobicity is lowering the surface energy. However, even materials with the lowest surface

#### ABSTRACT

In this study, we developed a facile method for preparing a superhydrophobic paper surface using a multi-layer deposition of polydiallyldimethylammonium chloride (polyDADMAC) and silica particles, followed by a fluorination surface treatment with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS,  $CF_3(CF_2)_5CH_2CH_2Si(OC_2H_5)_3$ ). The superhydrophobic wood fiber products prepared in this study have contact angles of water greater than 150° and sliding angles less than 5°. Besides their high water repelling property, the superhydrophobic paper products kept a high tensile strength at high relative humidity condition. The superhydrophobic paper products also showed high resistance to bacterial contamination.

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energy (6.7 mJ/m<sup>2</sup> for a surface with regularly aligned closesthexagonal-packed –CF<sub>3</sub> groups) only around 120° of water contact angle can be achieved for a smooth substrate. There have been numerous recent reports regarding successful generation of superhydrophobic surfaces (water contact angle  $>150^{\circ}$ ) by developing a roughness on a substrate surface utilizing lithographic patterning [9,10], laser/plasma etching [11-13], vertical alignment of nanotubes/nanofibers [14-17], sol-gel method [18-20], phase separation [21,22], binary colloidal assembly [23], glancing angle deposition [24], and so forth [25-28]. However, to the best of our knowledge, superhydrophobic paper products have not yet been reported. It is well known that wood fibers are hollow and highly hydrophilic materials. The porous substrate of paper provides multi micro- and macro-channels for water penetration. Therefore, it is very interesting to know if such porous materials can be converted to superhydrophobicity. Undoubtedly, low-coast, superhydrophobic, water-repellant, and self-cleaning fibers can bring a large number of benefits to the paper industry, food package industry, medical supplying industry, and military applications. For example, the biodegradable paper can be extremely interesting materials using for self-cleaning paper packages.

Multi-layer assembly technology has been proven to be a simple and inexpensive way to fabricate various kinds of surfaces with tailored chemical deposition and architecture in micro- and nano-scales [29-32]. The assembly technology also enables the deposition of multilayer films on rough surfaces [33-36]. The character of multi-layer deposition technology holds great promise in fabricating superhydrophobic surfaces on large areas in a simple and inexpensive way. This study focuses on developing a simple and inexpensive way to prepare superhydrophobic paper products using multi-layer deposition method, followed by a fluorination treatment. Three types of paper specimens are prepared for the

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comparative study: untreated paper (UP), hydrophobic paper (HP) that was treated by POTS, and superhydrophobic paper (SHP) that was prepared by silica particles deposition, followed by POTS treatment. The resistance to both liquid water and moisture was investigated. The resistance of the superhydrophobic paper specimens against bacterial contamination was also studied.

#### 2. Experimental

#### 2.1. Materials

The silica particles with diameters of about 220 nm, 420 nm, 800 nm, and 1 µm were synthesized according to literature reported method [37]. The reagents used for silica particle synthesis, including tetraethyl orthosilicate (TEOS) (98%), ammonium hydroxide (NH<sub>4</sub>OH) (28%), and ethanol (99.5%), were all purchased from Sigma-Aldrich. The top layer of commercial linerboard made from unbleached kraft softwood fiber was used as wood-fiberbased substrate. The aqueous solution of poly(diallyldimethylammoniūm chloride) (polyDADMAC, 20 wt% in water), with molecular weight of 100,000-200,000, was purchased from Sigma-Aldrich. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS, 97%) used for surface hydrophobic modification was purchased from Alfa Aesar. Deionized water purified in an ultrapure water system (NANOpure) was used in all the experiments. Escherichia coli-Ampicillin<sup>R</sup> was used as model bacteria for antibacterial contamination test. Luria-Bertani (LB) medium used for growing and maintaining bacteria cultures was purchased from Sigma-Aldrich. All chemicals were used as received.

#### 2.2. Synthesis of silica particles

Silica particles were synthesized according to the process described by Stober et al. In the present work, TEOS was hydrolyzed to form silica particles in ethanol with catalyst, NH<sub>4</sub>OH at room temperature over a period of two days. Spherical silica particles with a smooth surface were obtained. Silica particles were then dried at room temperature.

#### 2.3. Preparation of silica-coated substrate

Cationic polyDADMAC and anionic silica particles were used for multi-layer self-assembly deposition. PolyDADMAC aqueous solution was prepared by dissolving 1 g of polyDADMAC in 19 g of deionized water, and silica particle suspension was prepared by dispersing 0.2 g of silica particles in 19.8 g of deionized water. The silica suspension was sonicated by ultrasonicator (W-385) for 10 min before use. The negative charged paper substrate was first immersed in polyDADMAC solution for 20 min to render the substrate positively charged, followed by rinsing with deionized water for 1 min. The substrate was then immersed in silica suspension for 10 min, followed by rinsed with deionized water for 1 min. By repeating above steps, a thin film of multilayer polyDADMAC/silica particles was fabricated on the paper surface.

#### 2.4. Surface modification of silica-coated substrate

The surface modification carried out by chemical vapor deposition of POTS was shown in Scheme 1. The silica-coated paper substrate was placed in a sealed vessel, on the bottom of which was dispensed a smaller unsealed vessel within a small amount of POTS. The sealed vessel was then put in an oven at 125 °C to enable the silane groups of POTS vapor to react with the hydroxide groups on the silica surface. After 2.5 h, the paper substrate was removed to another clean sealed vessel and heated to 150 °C for another 2.5 h to volatilize the unreacted POTS molecules on the paper substrate.



Scheme 1. Schematic illustration of the surface modification on silica-coated paper surface.



Fig. 1. SEM image of synthesized silica particles with average size of 220 nm.

#### 2.5. Characterization

The surface morphology of the samples was examined with LEO 1530VP field emission scanning electron microscope and Hitachi 800 field emission scanning electron microscope. The specimens were pressed slightly sputter-coated with gold. The water contact angles of the samples were measured by First Ten Angstroms dynamic contact angle analyzer (FTA 200) at ambient temperature with a droplet volume of 0.013 ml. Humidity environment was prepared by a vacuumed oven (VWR 1400E). Lab Master tensile tester (84-91 LTL, Test Machine Inc.) was employed to measure the tensile strength of the samples under different humidity conditions. All the samples were cut into specimens with a dimension of  $15 \times 7.25 \times 0.4$  mm<sup>3</sup> before the tension strength measurements.

#### 3. Results and discussion

#### 3.1. SEM Morphology

Fig. 1 showed the SEM micrograph of synthesized silica particles, which had an average diameter of about 220 nm. The silica particles dispersed very well in deionized water after applying ultrasonication. The superhydrophobic surface was fabricated by multi-layer deposition of polyDADMAC and silica particles on linerboard substrate, followed by a fluorination treatment. Fig. 2



**Fig. 2.** SEM images of (a) and (b) are paper surface coated by silica particles using multi-layer technique. Image of (b) is the magnification of (a).

depicted the SEM micrograph silica-coated paper after POTS treatment which exhibited the surface was irregularly packed with multilayer of silica particles and only with a few interstices. Fig. 2 also showed that although the surface of the wood fibers was coated by silica particles, the large pores of the paper sheet, ranged from a few micrometers to millimeters, were not blocked by the silica particles.

#### 3.2. Contact angle of superhydrophobic surface

Because of the fast wetting of water on untreated paper surface, the water contact angles were measured right after water droplets contacted the sample surfaces. However, for HP specimens and SHP specimens, the contact angles were rechecked after 10 min of contact time. As shown in Fig. 3, the water contact angle of untreated paper surface was 51°, which changed to 110° on HP surface, and 155° on SHP surface, indicating a superhydrophobic surface was obtained. The water contact angle results showed, to a noticeable extent, how the surface energy and surface roughness affected the hydrophobicity of paper surface, and thus the water contact angle. The sliding angle (the angle that water droplet rolls off the surface) was lower than 5° for the SHP prepared in this study, indicating the water droplet on the SHP surface could roll off easily.

Cassie's equation,  $\cos \theta_A = f_1 \cos \theta - f_2$ , could be used to explain the hydrophobicity of the linerboards treated by different methods.  $\theta_A$  was the apparent contact angle measured on the interested substrate surface;  $\theta$  (100°) was the water contact angle on fluoridated smooth surface [38];  $f_1$  and  $f_2$  were the fractions of solid surface and air in contact with water droplet and  $f_1 + f_2 = 1$ . For the HP paper with apparent contact angle  $\theta_A$  of 110°, the  $f_1$  calculated using Cassie's equation is 0.80, which indicated that 20% of the surface was occupied by air. However, for superhydrophobic linerboard surface ( $\theta_A = 155^\circ$ ), the  $f_1$  calculated using the same equation is 0.11, which indicated that 89% of the surface was occupied by air. The surface allowed air to be trapped more easily



**Fig. 3.** Shapes of water droplet on (a) UP (untreated paper) surface, (b) HP (hydrophobic paper treated by POTS only) surface, and (C) SHP (superhydrophobic paper) surface.

underneath the water droplets, so the droplets essentially rested on a layer of air. Therefore the water contact angle on the superhydrophobic linerboard surface increased significantly.

#### 3.3. Moisture resistance analysis

Properties of wood-fiber-based material were greatly dependent on its moisture content. The moisture content of specimen was calculated by the following equation:



Fig. 4. Relative moisture content vs relative humidity of UP (untreated linerboard), HP (hydrophobic paper treated by POTS only), and SHP (superhydrophobic paper) specimens.

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moisture content (%)
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$$= \frac{\text{weight of specimen} - \text{weight of dry specimen}}{\text{weight of dry specimen}},$$

where the weight of dry specimen was obtained by drying paper specimen at 105 °C until a constant weight was obtained. In this analysis, specimens were placed in a sealed oven at ambient temperature under different relative humidity which was controlled by the amount of total water in the sealed oven for 24 h before measuring the moisture content. Fig. 4 showed the relative moisture content as a function of relative humidity (%) for UP, HP, and SHP, respectively. The relative moisture content of specimen was calculated by the following equation:

$$=$$
  $\frac{\text{moisture content of specimen}}{\text{moisture content of specimen under 15% relative humidity}}$ 

It was found that the relative moisture content of UP increased to about 650% when the relative humidity increased from 15 to 90%. Contrary to UP, the HP and SHP had much higher moisture resistance for which the relative moisture content of HP specimens and SHP specimens only increased by around 100%. Nevertheless, as expected, the superhydrophobic linerboard had almost the same moisture resistance as the hydrophobic linerboard.

#### 3.4. Tensile strength at different relative humidity

In this analysis, the tensile strength of specimen was measured after the specimens being conditioned at ambient temperature under different relative humidity for 12 h. Fig. 5 showed the relative tensile strength  $(kN/m^2)$  against relative humidity (%) for UP, HP, and SHP specimens, respectively. The relative tensile strength of specimen was calculated by the following equation:

relative tensile strength (%)

tensile strength of specimen under 15% relative humidity

It was found that the relative tensile strength of UP specimens decreased significantly under high relative humidity condition. As compared with UP specimen, the HP and SHP specimens presented higher moisture resistance, and thus the tensile strength although a slight decrease in the relative tensile strength was observed as the relative humidity increased from 15% to about 90%. The high



**Fig. 5.** Relative tensile strength vs relative humidity of UP (untreated linerboard), HP (hydrophobic paper treated by POTS only), and SHP (superhydrophobic paper) specimens.



Fig. 6. Moisture content (solid-square) and water contact angle (open-cycle) vs immersing time of SHP (superhydrophobic paper).

relative tensile strength of both HP and SHP specimens under high humidity condition suggested that the fiber–fiber bonds were well protected in these surface modified linerboard specimens by TEOS treatment. However, no significant difference between HP and SHP samples were found, suggesting that the anti-humidity effects are mainly from TEOS surface treatment.

#### 3.5. Water resistance after immersing in water

With hydroxyl groups covering the surface, wood-fiber-based materials were very hydrophilic and could absorb water or disperse in water easily. However, in many package applications, high water resistance fibers or paper products were required. In this study, the water resistance of SHP was investigated. The experiments were carried out by immersing SHP specimens in water up to three days, followed by measuring the moisture content (%) and the water contact angle (degree) of the specimens. As shown in Fig. 6, it was found that the moisture content increased to 6% after the specimen was fully immersing in water to 1 h, and the figure shows that the moisture content was still around 6% after the specimen was fully immersing in water to 72 h. It was also found that the water contact angle was kept above 150° in the whole



**Fig. 7.** Bacteria culture on UP (untreated paper), HP (hydrophobic paper treated by POTS only), and SHP (superhydrophobic paper) specimens after offering an inclining angle of  $5^{\circ}$  for 5 s and with fully immersing in water for 1 s.

process, which demonstrated the extremely high water resistance of SHP was developed.

#### 3.6. Bacteria resistance analysis

The bacteria resistances of UP, HP, and SHP were evaluated by measuring the contamination of the bacteria after the paper specimens contacted with Escherichia coli-Ampicillin<sup>R</sup> solution. During the experiment, the paper specimens with different hydrophobicities were cut into  $15 \times 7.25 \times 0.4$  cm<sup>3</sup>, and placed on a plastic film. About 0.01 ml of Escherichia coli-Ampicillin<sup>R</sup> solution with 10<sup>5</sup> colony forming units per milliliter was uniformly sprayed on the surface of paper specimens. In this study, the paper samples were divided in to two groups. Each group has UP, HP, and SHP specimens. The first group of the specimens was offered an inclining angle of 5° for 5 s right after the Escherichia coli-Ampicillin<sup>R</sup> was sprayed, and then the specimens were submerged in Luria-Bertani (LB) medium, respectively. The second group of the specimens was submerged in water for 1 s right after the Escherichia coli-Ampicillin<sup>R</sup> was sprayed, and then the specimens were submerged in LB broth medium, respectively. The specimens were fully immersed in LB broth medium and cultured at 37 °C for 24 h before measuring the equivalent colony forming units (CFU). All the experiments were performed in dark. The CFU of Escherichia coli-Ampicillin<sup>R</sup> incubated in LB broth medium presented the Escherichia coli-Ampicillin<sup>R</sup> units on the specimens before incubation.

Fig. 7 displayed the CFU of Escherichia coli-Ampicillin<sup>R</sup> on UP, HP, and SHP specimens for 2 groups of the samples. For the first group, it was found that the CFU of Escherichia coli-Ampicillin<sup>R</sup> on the specimens decreased as the hydrophobicity of specimen increased. Compared with UP specimens, approximate 70% of bacteria were left on the HP specimens and approximate 7% of bacteria were left on the SHP specimens. The significant lower of the bacterial contamination on the SHP specimens than HP specimens is due to the factor that the E-coli solution rolled off from the surface of SHP specimens, but adhered on the surface of HP specimens when a sliding angle of 5° was applied to the specimens. For the second group, the CFU of Escherichia coli-Ampicillin<sup>R</sup> on the specimens decreased intensely as the hydrophobicity of specimen increased. As compared with the UP specimens, there were only about 30% of bacteria remained on the HP specimens and less than 1% of bacteria remained on the SHP specimens. It was noted that the bacteria on the SHP specimens



Fig. 8. Bacteria culture on SHP (superhydrophobic paper) surface after offering an inclining angle for 5 s.

was much easier to be wash out by immersing contaminated paper in water. As discussed before, the water resistance increased as the hydrophobicity of the linerboard surface increased. With higher anti-wetting property, the bacteria could be washed easier. The results shown in Fig. 7 clearly demonstrated that superhydrophobicity of a substrate plays an important role in fabricating a surface with anti-contamination of biological materials property.

The sliding angle on the superhydrophobic paper was lower than 5°, which meant the bacteria droplets on the SHP surface could be rolled off after the surface was offered an inclining angle of 5°. However, it was found that some bacteria were remained after offering a sliding angle of 5°. The reason could be the microporous linerboard surface trapped some of the bacteria droplets, although the surface was superhydrophobic. To demonstrate that, sliding angle effect on SHP surface was studied. The SHP specimens were offered with different sliding angles for 5 s respectively right after the Escherichia coli-Ampicillin<sup>R</sup> was sprayed, and then the specimens were submerged in LB broth medium. The culturing process was the same as before. Fig. 8 displayed the CFU of bacteria against different sliding angles. The CFU on the SHP surface decreased significantly after the specimen was offered a small inclining angle, and the CFU decreased gradually with the inclining angle increasing. After offering an inclining angle of 90°, no bacterium was remained on the superhydrophobic surface. The results reflected the bacteria cannot contaminate the superhydrophobic surface at this condition even though the superhydrophobic paper has large porous on its surface.

#### 3.7. Particle size effect

It was well known that the nano-scaled surface roughness is one of the critical factors for creating a superhydrophobic surface. In the study, silica spherical particles with different particle sizes were used respectively for the surface roughness treatment. After fluorination treatment, the hydrophobicity of surface was then characterized by contact angle analyzer. As shown in Fig. 9, the water contact angle changed from 110° on HP specimen surface, to 155°, 152°, 150°, and 145° on the SHP specimen surface coated with 220 nm, 420 nm, 680 nm and 1000 nm of silica particles, respectively. It was found that the water contact angle increased significantly from HP surface to SHP surface and the water contact angle decreased slightly on the superhydrophobic linerboard surface as the silica particle size increased.



Fig. 9. Water contact angles of surface modified silica-coated paper surface with different silica particle sizes.

#### 4. Conclusions

In this work, we demonstrated that the superhydrophobic paper could be made by multi-layer deposition, followed by a fluorination treatment although the paper is a porous material. It was shown that the moisture resistance of SHP sample is identical from that of HP sample. However, water resistance and bacteria resistance were significantly different between these HP and SHP samples. The superhydrophobic paper remained high tensile strength at high relative humidity condition. The present method for preparing a superhydrophobic surface is simple with a low cost. In principle, the method developed in this study using a linerboard paper can be applied to different types of paper, textiles, and other porous materials.

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#### References

- [1] R.D. Hagenmaier, R.A. Baker, J. Agric. Food Chem. 45 (1997) 349.
- [2] E. Bosquez-Molina, I. Guerrero-Legarreta, E.J. Vernon-Carter, Food Res. Int. 36 (2003) 885.
- [3] A.G. Erlat, B.M. Henry, J.J. Ingram, D.B. Mountain, A. McGuigan, R.P. Howson, C.R.M. Grovenor, G.A.D. Briggs, Y. Tsukahara, Thin Solid Films 388 (2001) 78.
- [4] G. Garcia-Ayuso, R. Salvarezza, J.M. Martinez-Duart, O. Sanchez, L. Vazquez, Adv. Mater. 9 (1997) 654.
- [5] M.W. Ellsworth, B.M. Novak, Chem. Mater. 5 (1993) 839.
- [6] B.M. Novak, Adv. Mater. 5 (1993) 422.
- [7] P. Schwarz, M. Mahlke, in: Proc. 2003 TAPPI Eur. PLACE Conf., vol. 2, 2003, p. 1451.
- [8] M. Krook, M. Gallstedt, M.S. Hedenqvist, Packag. Technol. Sci. 18 (2005) 11.
- [9] D. Oner, T.J. McCarthy, Langmuir 16 (2000) 7777.
- [10] R. Furstner, W. Barthlott, C. Neinhuius, P. Walzel, Langmuir 21 (2005) 956.
- [11] T. Baldacchini, J.E. Carey, M. Zhou, E. Mazur, Langmuir 22 (2006) 4917.
- [12] M.H. Jin, X.J. Feng, J.M. Xi, J. Zhai, K. Cho, L. Feng, L. Jiang, Macromol. Rapid Commun. 26 (2005) 1805.
- [13] K. Tsujii, T. Yamamoto, T. Onda, S. Shibuchi, Angew. Chem. Int. Ed. 36 (1997) 1011.
- [14] H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang, D.B. Zhu, Angew. Chem. Int. Ed. 40 (2001) 1743.
- [15] L. Huang, S.P. Lau, H. Yang, E.S. Leong, S.F. Yu, J. Phys. Chem. B 109 (2005) 7746.
- [16] M.H. Jin, X.J. Feng, L. Feng, T.L. Sun, J. Zhai, T.J. Li, L. Jiang, Adv. Mater. 17 (2005) 1997.
- [17] L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, Angew. Chem. Int. Ed. 41 (2002) 1221.
- [18] H.Y. Ebril, A.L. Demirel, Y. Avci, O. Mert, Science 299 (2003) 1377.
- [19] N.J. Shirtcliffe, G. McHale, M.I. Newton, C.C. Perry, P. Roach, Chem. Commun. (2005) 3135.
- [20] K. Tadanaga, J. Morinaga, A. Matsuda, T. Minami, Chem. Mater. 12 (2000) 590.
- [21] A. Nakajima, K. Abe, K. Hashimoto, T. Watanabe, Thin Solid Films 376 (2000) 140.
- [22] N. Zhao, J. Xu, Q.D. Xie, L.H. Weng, X.L. Guo, X.L. Zhang, L.H. Shi, Macromol. Rapid Commun. 26 (2005) 1075.
- [23] G. Zhang, D. Wang, Z.Z. Gu, H. Mohwald, Langmuir 21 (2005) 1075.
- [24] S. Tsoi, E. Fok, J.C. Sit, J.G.C. Veinot, Langmuir 20 (2004) 10771.
- [25] M.H. Sun, C.X. Luo, L.P. Xu, H. Ji, Q. Ouyang, D.P. Yu, Y. Chen, Langmuir 21 (2005) 8978.
- [26] H. Tavana, A. Amirfazli, A.W. Neumann, Langmuir 22 (2006) 5556.
- [27] Z.G. Guo, F. Zhou, J.C. Hao, W.M. Liu, J. Am. Chem. Soc. 127 (2005) 15670.
- [28] W. Ming, D. Wu, R. van Benthem, G. de With, Nano Lett, 5 (2005) 2298.
- [29] G. Decher, Science 277 (1997) 1332.
- [30] X. Zhang, J.C. Shen, Adv. Mater. 11 (1999) 1139.
- [31] P.T. Hammond, Adv. Mater. 16 (2004) 1271.
- [32] P. Bertrand, A. Jonas, A. Laschewsky, R. Legras, Macromol. Rapid Commun. 21 (2000) 319.
- [33] F. Caruso, Chem. Eur. J. 6 (2000) 413.
- [34] F. Caruso, R.A. Caruso, H. Mohwald, Science 282 (1998) 1111.
- [35] E. Donath, G.B. Sukhorukov, F. Caruso, S.A. Davis, H. Mohwald, Angew. Chem.
- [35] E. Donarti, G.D. Suthorukov, F. Cardso, S.A. Davis, H. Mohwald, Angew. Chem. Int. Ed. 37 (1998) 2202.
  [36] W. Kong, X. Zhang, M.L. Gao, H. Zhou, W. Li, J.C. Shen, Macromol. Rapid Com-
- mun. 15 (1994) 405.
- [37] W. Stober, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
- [38] S. Pilotek, H.K. Schmidt, J. Sol-Gel Sci. Technol. 26 (2003) 789.