Preparation and characterization of tricomponent SiO$_2$/SnO$_2$/TiO$_2$ composite nanofibers by electrospinning

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[C$_2$H$_5$O)$_4$Si+PVP]/[SnCl$_4$+PVP]/[Ti(OC$_4$H$_9$)$_4$+CH$_3$COOH+PVP] precursor composite fibers have been fabricated through self-made electrospinning equipment via electrospinning technique. SiO$_2$/SnO$_2$/TiO$_2$ composite nanofibers were obtained by calcination of the relevant precursor composite fibers. The samples were characterized by thermogravimetric-differential thermal analysis (TG-DTA), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM). Results showed that the precursor composite fibers are amorphous in structure, and pure phase SiO$_2$/SnO$_2$/TiO$_2$ composite nanofibers are obtained by calcination of the precursor composite fibers at 800～900 ℃ for 8 h. The surface of precursor composite fibers is smooth, and solvents, organic compounds and inorganic in the precursor composite fibers are decomposed and volatilized totally, and the mass of the sample kept constant when sintering temperature was above 800 ºC, and the total mass loss percentage is 80%.

1. Introduction

One-dimensional nanomaterials, such as nanofibers, nanowires, nanobelts, nanoribbons, and nanorods, are a new class of nanomaterials that have been attracting a great research interest in the last few years. These materials have been demonstrated to exhibit superior optical, acoustic, electrical, magnetic, thermal, and mechanical properties, and thus, can be used as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices.

Electrospinning technique as a simple, convenient, and versatile method has been utilized in the preparation of many one-dimensional nanostructural materials such as long fibers with diameters ranging from tens of nanometers up to micrometers [1]. Recently, this technique was used as an approach to fabricate composite nanofibers. For example, Zhang, et al [2] synthesized SnO$_2$/TiO$_2$ composite nanofibers through electrospinning technique. Synthesis of composite nanofibers materials with unique optical, electronic, magnetic, and catalytic properties, which are fundamentally important and technologically useful. To the best of our knowledge, there have been no reports on the preparation of SiO$_2$/SnO$_2$/TiO$_2$ composite nanofibers by electrospinning technique.

In this paper, SiO$_2$/SnO$_2$/TiO$_2$ composite nanofibers were fabricated by calcination of the electrospun precursor composite fibers of [C$_2$H$_5$O)$_4$Si+PVP]/[SnCl$_4$+PVP]/[Ti(OC$_4$H$_9$)$_4$+CH$_3$COOH +PVP] composite fibers, and some new results were obtained and this preparation technique can be applied to prepare other composite nanofibers.

2. Experimental section

2.1 Chemicals

Polyvinyl pyrrolidone (PVP) (Mw=1300000,AR), Ethanol (CH$_3$CH$_2$OH), Butyl titanate (Ti(OC$_4$H$_9$)$_4$), Stannic chloride (SnCl$_4$·5H$_2$O), Tetraethyl orthosilicate (TEOS, (C$_2$H$_5$O)$_4$Si), Acetic acid (CH$_3$COOH) and N,N-dimethylformamide (DMF, AR) were bought from Tiantai Chemical Co. Ltd., All chemicals were analytically pure and directly used as received without further purification.

2.2 Preparation of precursor composite sol

2.5 g of PVP powders and 5 ml of (C$_2$H$_5$O)$_4$Si were dissolved in10 ml of CH$_3$CH$_2$OH, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [(C$_2$H$_5$O)$_4$Si+CH$_3$CH$_2$OH+PVP] was obtained; 2.5 g of PVP powders and 1.8 g of SnCl$_4$·5H$_2$O were dissolved in 20 ml of DMF, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [SnCl$_4$+DMF+PVP] was obtained; 2.0405g of PVP powders and 17 ml of CH$_3$CH$_2$OH and 3ml of CH$_3$COOH were dissolved in 5 ml of Ti(OC$_4$H$_9$)$_4$, and stirred at room temperature for 10 h. The above sol was placed in an airtight container for about 5 h, and then, transparent viscous sol of [Ti(OC$_4$H$_9$)$_4$+CH$_3$CH$_2$OH+CH$_3$COOH+PVP] was obtained.

2.3 Characterization methods

XRD analysis was performed on a Holland Philip Analytical PW1710 BASED X-ray diffractometer using Cu Kα_1 radiation, with the working current and voltage at 30 mA and 40 kV, respectively. Scans were made from 10 ° to 90 ° at the speed of 4 (°)/min, and the step was 0.02 °. The morphology and size of the samples were observed with an S-4200 scanning electron microscope made by Japanese Hitachi Company. TG-DTA analysis was carried out on an SDT-2960 thermal analyzer made by American TA instrument company in atmosphere, and the temperature rising rate was 10 °C/min. FTIR spectra of the samples were recorded on BRUKER Vertex 70 Fourier transform infrared spectrophotometer made by Germany Bruker company, and the specimen for the measurement was prepared by mixing the samples with KBr powders and then the mixture was pressed into pellets, the spectrum was acquired in a wave number range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4 Preparation of SiO_2/SnO_2/TiO_2 composite nanofibers

Schematic diagram of electrospinning setup was shown in Fig. 1. The above precursor sol were placed in three focusing syringes and delivered at a constant flow rate using plastic capillaries. The anodes were placed in the sol, and a grounded aluminum foil served as counter electrode and collector. When a high voltage (26 kV in this work) was applied, and the distance between the capillary tip and the collector was fixed to 18 cm, a dense web of [C$_2$H$_5$O)$_4$Si+PVP]/ [SnCl$_4$+PVP]/[Ti(OC$_4$H$_9$)$_4$+CH$_3$COOH+PVP] precursor composite fibers were collected on the aluminum foil. These fibers were calcinated at a rate of 1 °C/min and remained for 8 h at 800 and 900 °C, respectively. Thus, SiO_2/SnO_2/TiO_2 composite nanofibers were obtained.
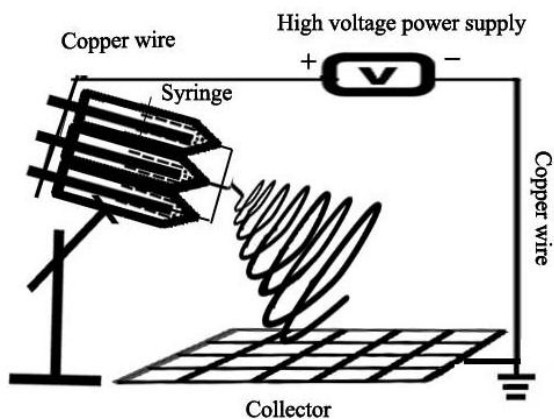

Fig.1 Schematic diagram of electrospinning setup for preparation of precursor composite fibers.

3. Results and discussion

3.1 TG-DTA analysis

Fig. 2 shows the thermal behavior of precursor composite fibers. The weight loss was involved in four stages in TG curve. The first weight loss is 24% in the range of 40 to 300 ℃ accompanied by a small endothermic peak near 72 ℃ in the DTA curve, which is caused by the loss of the surface absorbed water or the residual water molecules in the precursor composite fibers. The second weight loss step (24%) is between 300 and 352 ℃ accompanied by an exothermic peak near 349 ℃ in the DTA curve because of the decomposition of the Ti(OC$_4$H$_9$)$_4$, CH$_3$COOH and side-chain of PVP. The third weight loss (28%) in the TG curve (352-535 ℃) was possibly corresponded to the decomposition of SnCl$_4$·5H$_2$O, (C$_2$H$_5$O)$_4$Si [3] and main-chain of PVP. In the DTA curve, an exothermic peak was located at 477℃. The last weight loss is 4% in the temperature change from 535 to 800 ℃. In the DTA curve a small endothermic peak is located at 568 ℃. This is likely to be the totally oxidation combustion of the inorganic salts. And above 800 ℃, the TG and DTA curves were all unvaried, indicating that water, organic compounds and inorganic salts in the precursor composite fibers were completely volatilized and pure SiO_2/SnO_2/TiO_2 composite nanofibers could be obtained above 800 ℃. The total weight loss was 80%.
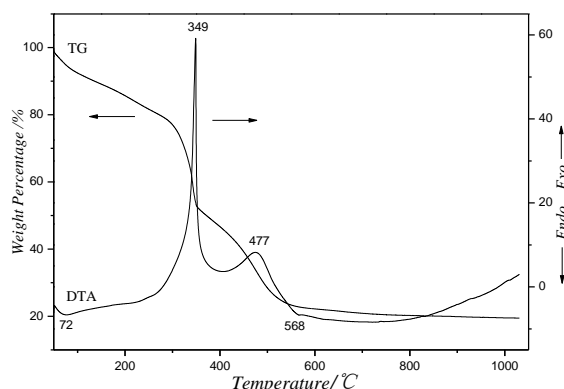
Fig. 2. TG–DTA curves of precursor composite fibers.

3.2 XRD analysis

[C$_2$H$_5$O)$_4$Si+PVP]/[SnCl$_4$+PVP]/[Ti(OC$_4$H$_9$)$_4$+CH$_3$CO OH+PVP] precursor composite fibers and samples obtained after being calcined at 800 and 900 ℃ were characterized by XRD, as indicated in Fig. 3. Precursor composite fibers (Fig.3a) only have a broad peak around 20°, which is the typical peak of the polymer [4]. This revealed that precursor composite fibers were amorphous in structure. In order to investigate the variety of phase, the From Fig.3b, XRD patterns displayed some new

diffraction peaks when calcined at 800 ℃, and meanwhile, the diffraction peak of precursor composite material disappeared, indicating that PVP was decomposed and removed out from precursor composite nanofibers, observed reflections were indexed to (110), (101), (200), (220) and (301) of TiO_2, and the d values and relative intensity of the peaks are consistent with those of JCPDS standard card (21-1276), indicating that the prepared TiO_2 is tetragonal in structure with space group $P4_2/mnm$; and observed reflections can be indexed to (110), (101), (200), (211), (220) and (311) of SnO_2, and the d values and relative intensity of the peaks are consistent with those of JCPDS standard card (41–1445) [5–9]; As can be seen from Fig.3b have a broad peak around 22°, which is the typical peak of the SiO_2 amorphous in structure. Therefore, $SiO_2/SnO_2/TiO_2$ composite nanofibers with stable phase can be prepared at 800 ℃. It can be seen from Fig. 3c (900 ℃), The results s were in good agreement with calcined at 800 ℃, but significant increase in intensity of diffraction peaks, indicating the calcination temperature reaches 900 ℃, can be more well-developed nanocrystalline composite nanofibers. Therefore, the best preparation temperature is 900 ℃.
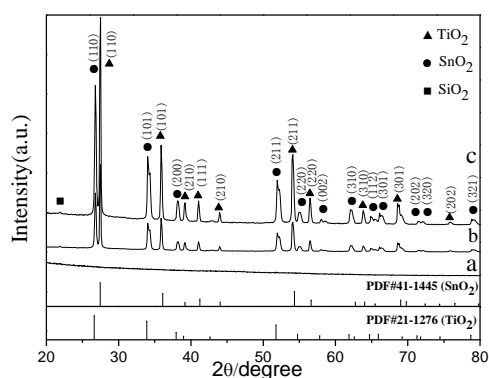

Fig. 3. XRD patterns of the precursor composite fibers (a) and samples calcined at 800 ℃ (b) and 900 ℃ (c) for 8 h.
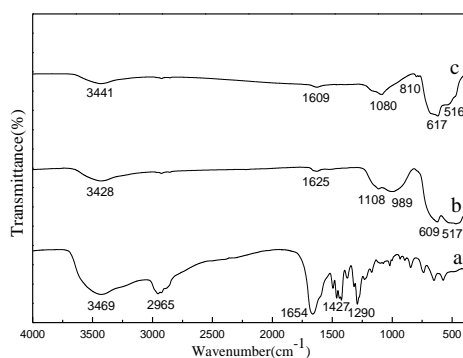
3.3 FTIR spectra analysis

Fig. 4. FTIR spectra of the precursor composite fibers (a) and samplescalcined at 800 ℃ (b) and 900 ℃(c)for 8 h.

The formation of the [C₂H₅O)₄Si+PVP]/[SnCl₄+PVP]/[Ti(OC₄H₉)₄+CH₃COOH +PVP] precursor composite fibers and samples calcined at 800 and 900℃ for 8 h is further supported by the FTIR spectra in Fig. 4. As seen form Fig. 4a, the FTIR spectrum of precursor composite fibers indicated that the wide absorption peak at 3469 cm⁻¹ attributes to the stretching vibrations of O-H of the surface absorbed water [10]. The absorption peaks at 2965 cm⁻¹, 1654 cm⁻¹, 1427 cm⁻¹ and 1290 cm⁻¹ corresponding to the stretching vibrations of C-H, C=O, C-N and C-C bond in PVP [11]. It can be seen from Fig. 4b(800 ℃) that the wide absorption peak at 3428 cm⁻¹ and 1625 cm⁻¹ of the surface absorbed water became weaker and all peaks of PVP disappeared. At the same time, four new absorption peaks at low wavenumber are appeared, the wide absorption peak at 1108 cm⁻¹, which ascribe to the vibration of Si-O-Si bonds[12], the wide absorption peak at 989 cm⁻¹, which ascribe to the vibration of Si-OH bond, the wide absorption peak at 517 cm⁻¹ and 609 cm⁻¹ which ascribe to the vibration of Ti-O-Ti bonds and Sn-O-Sn bonds[13], indicating that the formation of $SiO_2/SnO_2/TiO_2$ composite nanofibers. It can be seen from Fig. 4c, the calcination temperature reaches 900 ℃, can be more well-developed nanocrystalline composite nanofibers. The results of FTIR analysis were in good agreement with XRD results.

3.4 SEM and distribution histograms analysis

The morphology of the precursor composite fibers and $SiO_2/SnO_2/TiO_2$ composite nanofibers were investigated by SEM and distribution histograms analysis. As seen from Fig. 5a~5b, the surface of the precursor composite fibers is very smooth. The width of the precursor composite fibers is ca. 1.160±0.461 μm (Fig. 6a), The diameter of one of the precursor composite fibers is ca. 0.387±0.154 μm. The $SiO_2/SnO_2/TiO_2$ composite nanofibers became coarser and narrower (Fig. 5c~5d) with the increase of calcination temperatures, caused by the decomposition of PVP, organic compounds and inorganic salts. The width of composite nanofibers calcined at 800 ℃ is *ca.* 472.202±131.220 nm (Fig. 6b), The width of composite nanofibers calcined at 900 ℃ is *ca.* 734.726±45.390 nm (Fig. 6c), The diameter of one of the composite nanofibers is ca. 244.909±15.130 nm.
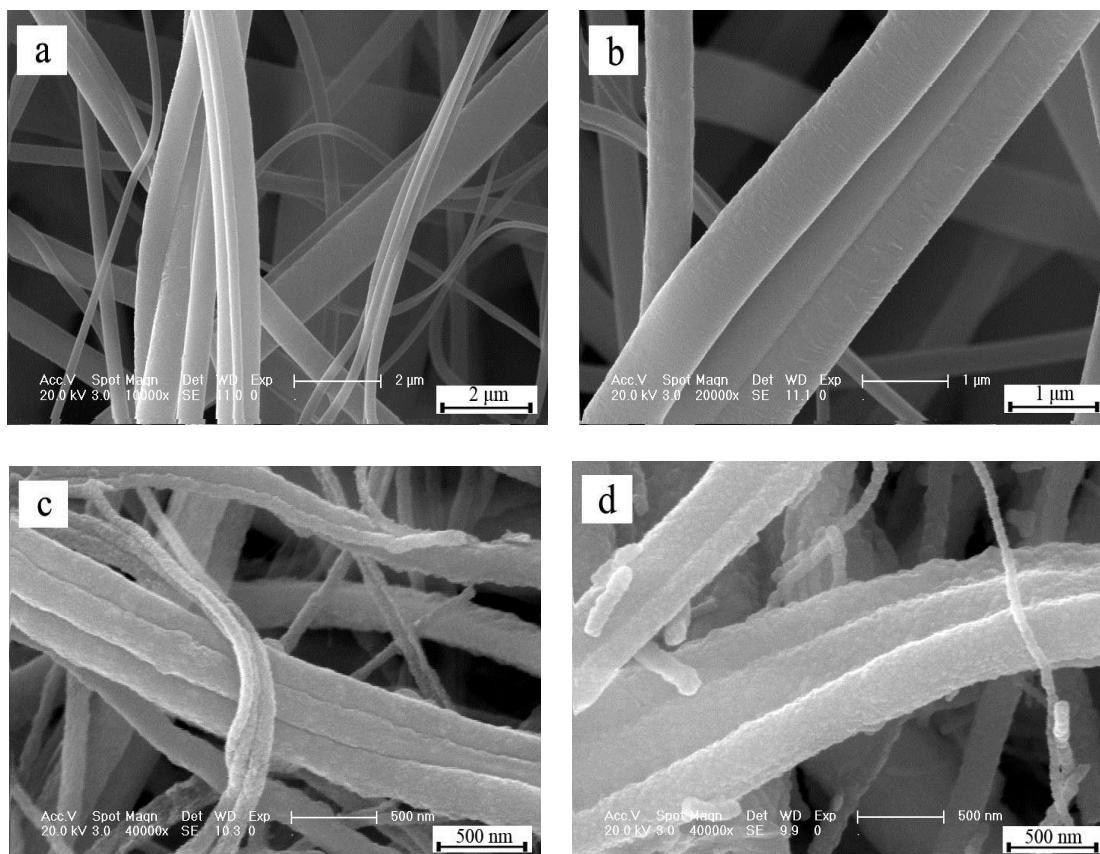
Fig. 5. SEM images of the precursor composite fibers (a and b) and samples
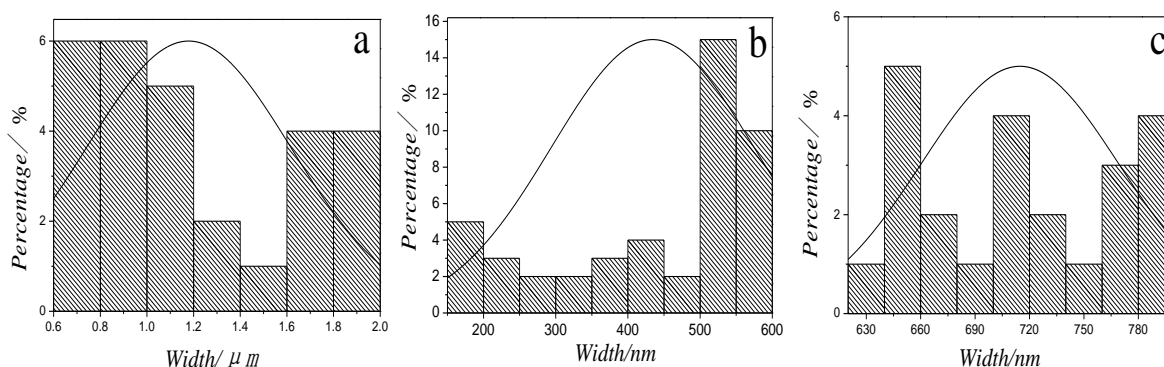*calcined at 800 ℃ (c) and 900 ℃ (d) for 8 h.*

Fig. 6. Width distribution histograms of the precursor composite fibers (a) and samples
calcined at 800 ℃(b) and 900 ℃(c) for 8 h.

3.5 EDS analysis

To determine the composite nanofibers component further, energy dispersive spectroscopy (EDS) of the samples was performed. The EDS analysis results revealed that by calcining the precursor composite fibers (Fig. 7a) at 800 ℃ (Fig. 7b) and 900 ℃ (Fig. 7c) for 8 h the $SiO_2/SnO_2/TiO_2$ composite nanofibers are only composed of Ti, Sn, Si and O elements. The results of EDS analysis were in good agreement with the above results.
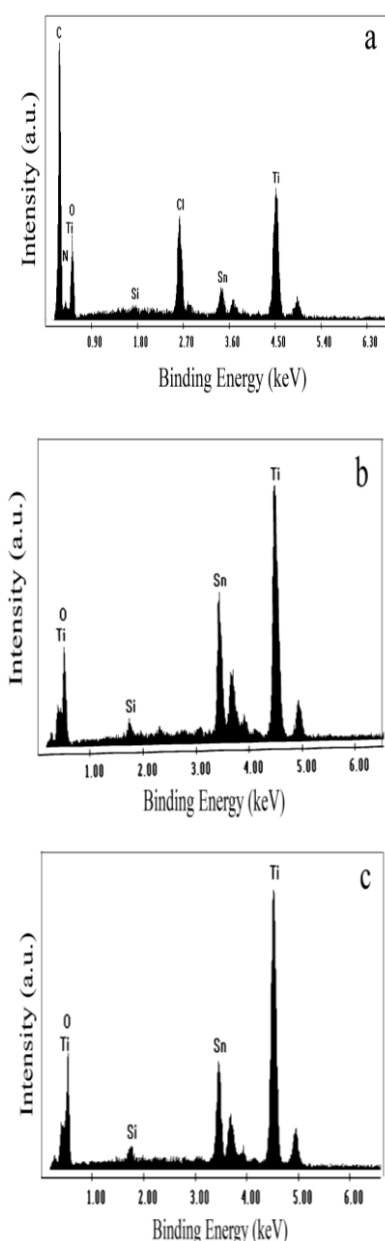
Fig. 7. EDS images of the precursor composite fibers (a)
and samples
calcined at 800 ℃(b) and 900 ℃(c) for 8 h.

4. Conclusions

$[(C_2H_5O)_4Si+PVP]/[SnCl_4+PVP]/[Ti(OC_4H_9)_4+CH_3COOH+PVP]$ precursor composite fibers were successfully fabricated using an electrospinning technique, and $SiO_2/SnO_2/TiO_2$ composite nanofibers were synthesized by calcining the precursor composite fibers at 800 and 900 °C for 8 h. TG-DTA and FTIR revealed that the formation of $SiO_2/SnO_2/TiO_2$ composite nanofibers was largely influenced by the calcination temperatures. SEM micrographs indicated that the surface of the precursor composite fibers was smooth and became coarse with the increase of calcination temperatures. EDS analysis results revealed that $SiO_2/SnO_2/TiO_2$ composite nanofibers were only composed of Ti, Sn, Si and O elements.

References

[1] Formhals A. Process and Apparatus for Preparing Artificial Threads [P]. US Patent, 1975504.1934.
[2] Zhaoyang Liu, Darren Delai Sun, Peng Guo, and James O. Leckie. Nano Letters, **7**(4), 1081 (2007).
[3] Yuan Ren, Min Chen, Yang Zhang, LiminWu. Langmuir., **26**(13), 11391 (2010).
[4] JiunYu Chen, HungCheng Chen, JiunNan Lin, Changshu Kuo. Materials Chemistry and physics., **107**, 480 (2008).
[5] Cheng Sun, Nripan Mathews, Minrui Zheng, Chorng Haur Sow, Lydia Helena Wong, Subodh G. Mhaisalkar., J. Phys. Chem. C., **114**, 1331 (2010).
[6] Jie Liu, Feng Gu,Yanjie Hu, Chunzhong Li, J. Phys. Chem. C., **114**, 5867 (2010).
[7] Yu-Jin Chen, Peng Gao, Rui-Xuan Wang, Chun-Ling Zhu, Li-Jiao Wang, Mao-Sheng Cao, Hai-Bo Jin, J. Phys. Chem. C., **113**, 10061 (2009).
[8] Changhua Wang, Changlu Shao, Xintong Zhang, and Yichun Liu, Inorg. Chem., **48**, 7261 (2009).
[9] V. Senthilkumar. P. Vickraman, J Mater Sci, Mater Electron., **21**, 578 (2010).
[10] Remant Bahadur K. C., Chul Ki Kim, Myung Seob Khil, Hak Yong Kim, Ick Soo Kim Mater. Sci. Eng. C., **28**, 70 (2008).
[11] B. Ding, H. Kim, C. Kim, M. Khil, S. Park Nanotechnology., **14**, 532 (2003).
[12] Kyoung G. Lee, Rinbok Wi, Muhammad Imran, Tae Jung Park, Jaebeom Lee, Sang Yup Lee, Do Hyun Kim, Nano, **4**(7), 3933 (2010).
[13] D. N. Srivastava, S. Chappel, O. Palchik, A. Zaban, A. Gedanken, Langmuir., **18**, 4160 (2002).

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