Supplementary Material

Preparation of Organosilica Cellulose 3,5-Dimethylphenylcarbamate Particles of pH-Sensitive Morphology and Porosity for Chromatographic Application

Xilun Weng, Zongbi Bao*, Zhiguo Zhang, Baogen Su, Huabin Xing, Qiwei Yang, Yiwen Yang, Qilong Ren

Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

* To whom correspondence should be addressed

Tel: 86-571-8795-2773; Fax: 86-571-8795-2773.

Email: baozb@zju.edu.cn (Z. Bao)
Supplementary discussion:

Figure S1. $^1$H NMR spectrum of the cellulose derivative

The peaks at 7.9-8.4 ppm and 6-7.5 ppm belong to the amide groups and benzene ring, respectively. The peak at 2.8-5 belongs to the hydrogen of cellulose ring and methylene at position 6, and 2-2.3 indicates H presence of CH$_3$-aryl groups. Since the characteristic peak of acetone-d$_6$ appears at 2.05 ppm, 0-overlaid by the peak of CH$_3$-aryl groups, the peak appears at 1 ppm belongs to the methyl group of SiOCH$_3$CH$_3$. 
Figure S2. IR spectrum of the cellulose, CDMPC and hybrid material (H-15-7)

The IR spectroscopy was used to check an effective derivatization on the hydroxyl groups of cellulose. The overlaid FTIR spectra of the cellulose, CDMPC and hybrid material are shown in Figure S3. Line (a) shows a characteristic spectrum of cellulose with -OH group at 3500-3200 cm\(^{-1}\), and methylene and methyl group at 3000-2800 cm\(^{-1}\). While line (b) with lessen –OH group at 3500-3200 cm\(^{-1}\) shows a comparatively weak secondary amine adsorption at almost the same wave number, indicating a disappearance of hydroxyl group and appearance of amino group. The new peak at about 1750 cm\(^{-1}\), certificated as carbonyl group and frame vibration of benzene at 1600-1450 cm\(^{-1}\), could indirectly confirm a successful synthesis of 3,5-dimethylphenyl isocyanate. Line c with a wide and weak –OH group of residual product of hydrolysis, the characteristic 1750 cm\(^{-1}\) for carbonyl group indicates the hybrid material preserves the functional group of organic component. Particularly, the peak at 470 cm\(^{-1}\) is due to the bending mode of Si-O-Si and Si-OH group, which is the key intermediate, being instrumental to the whole process, where the silanol groups of the CDMPC are highly capable of hydrolysis and condensed with the silanol groups.
of TEOS. The wide peak in 1200-1000 cm$^{-1}$ is ascribed to asymmetric stretching vibrations of the Si-O-Si bonds of the silica component, which is produced by in situ complete condensation between SiOR and/or SiOH groups. Compared to line b, the peak intensity in 1750 cm$^{-1}$ in line c is weaker in contrast to 1200-1000 cm$^{-1}$ peak, which demonstrates an effective composite of CDMPC and silica.

**Figure S3.** Solid $^{13}$C NMR spectrum of sample HH-15-7

The peak at 152 ppm belongs to the carbamate carbon. The peaks at 116-138 ppm belong to the benzene ring, respectively. The peaks at 65-102 ppm belong to the cellulose ring. Peak at 21 ppm is from methyl carbon and peak at 1.2 is from TMSCl. Solid $^{13}$C NMR spectrum indicates CDMPC preserve its structure in hybridization.
**Figure S4.** SEM micrographs of dimethylphenyl carbamate/3-(triethoxysilyl)propyl ratio 98:2 particles (HI-15-7) prepared under aging pH=7