Supporting information

Intelligent cellulose nanofibers with excellent biocompatibility enable sustained antibacterial and drug release via a pH-responsive mechanism

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Physical and chemical characterization

FT-IR characterization: The change of functional groups before and after modification was determined by FT-IR. The test conditions are as follows: the mass ratio of potassium bromide to sample is 100:1, and the test range is 4000 cm\(^{-1}\) - 400 cm\(^{-1}\).

XPS characterization: XPS mainly to determine the kinds and contents of elements on the surface of samples, and fine scanning of C, O and N elements to judge the changes of surface functional groups before and after modification. The test conditions are as follows: firstly, the sample was dried and pressed it into a smooth sheet with a tablet press. Using 12 (or 15) kV voltage and monochromatic Al K radiation to determine the element content and valence state, the current is 16-25 mA.

\textsuperscript{13}C NMR characterization: The changes of functional groups before and after modification were characterized by solid \textsuperscript{13}C NMR. First, dry the sample and then the

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sample was powder to test it directly. The test conditions are: field strength 7.05 T, rotating speed 5 kHz, 7 mm magic angle probe, cross polarization time 4 μs, pulse width 90 °, contact time 800 μs, sampling interval time 2.5 s, scanning time 10 h.

AFM characterization: The original roughness before and after modification and the roughness of each sample after acid-base pretreatment were characterized by AFM. The sample is made into a film, which is cut into small pieces, pasted on the round iron sheet, placed on the AFM stage, modulated the scanning area by 5 μm, started scanning, and recorded the roughness.

The method of sample pH change is as follows: immersed CNF-COOH and CNF-PEI in the solution with pH = 1 to 9 for 30 min respectively, and then dried in a vacuum oven at 60 °C for 12 h to obtain the sample after acid-base pretreatment.

**Morphology and Chemical Characterization**

**Table S1** Amino contents determined by EA, EDS and XPS analysis

<table>
<thead>
<tr>
<th>Determination method</th>
<th>EA analysis</th>
<th>XPS analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amino content (mmol·g⁻¹)</td>
<td>Amide content (%)</td>
</tr>
<tr>
<td></td>
<td>Alkyl amino content (%)</td>
<td>1° amino content (%)</td>
</tr>
<tr>
<td>CF</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DACF</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-COOH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-PEI</td>
<td>10.57</td>
<td>11.59</td>
</tr>
</tbody>
</table>

From Table S1, attachments appeared on the surface of CNF-PEI, and new elemental N (20.64%) appeared in the EDS analysis. This can be explained by the fact that PEI was encapsulated on the surface of the fibers by condensation reaction with the carboxyl group on the surface of CNF-COOH. The new element N content (10.57%) in CNF-PEI measured by EA analysis was lower than that in the surface
energy spectrum detection (20.64%). The main reason was that the surface steric hindrance of the CNF-COOH surface was relatively small relative to the interior, and PEI was more likely to be grafted onto the surface of CNF-COOH, resulting in a surface N content of CNF-PEI much higher than its overall content.

![Figure S1](image1.png) ![Figure S2](image2.png)

**Figure S1.** Diameter distribution map of CNF-COOH (a) and CNF-PEI (b)

**Figure S2.** Antibacterial properties of CNF-COOH toward *E. coli* under pH = 1, 7 and 9

From Figure S2, it can be found that the antibacterial rate of CNF-COOH was 97.4% under pH = 1, the reason could be that hydrochloric acid remained on the surface of the CNF-COOH after the pretreatment of acid solution (pH = 1), microorganisms could not be exposed to the highly acidic environment, which inhibited the growth of bacteria. While the CNF-COOH has no antibacterial effect under pH = 7 and 9, compared with CNF-COOH, the antibacterial rates of CNF-PEI against *E. coli* (93.9%) and *L. monocytogenes* (94.0%) under pH = 7 were significantly increased, thus the CNF-PEI
showed the good antibacterial property.

Figure S3. The $^1$H NMR (a) and $^{13}$C NMR (b) spectra of CF at pH = 1, 7 and 9

The NMR spectra of CF at pH=1, 7 and 9 are shown in Figure S3. As shown in Figure S3(a), the $^1$H NMR spectra of CF had only a sharp characteristic peak, the width of the characteristic peaks gradually widened with the pH increased from 1 to 7 to 9, the signal of the chemical shifts moved towards a higher field and the chemical shift decreased.

The intensity of the chemical shifts gradually decreased from pH 7 to 1 and then to 9 (Figure S3(b)), the intensity of chemical shifts of CF at pH=9 was the weakest because the hydroxyl groups on cellulose was easily formed oxyanions under alkaline conditions.
**Figure S4.** The standard deviation diagram of the surface roughness of CNF-COOH and CNF-PEI

The surface roughness of CNF-COOH and CNF-PEI was determined by using AFM, the surface roughness was an average roughness by calculated from three parallel tests for each sample.