Supporting Information

High-Performance Hollow Microspheres for UV Protection from Cinnamate-Functionalized Cellulose Nanocrystals and Inorganic Nanoparticles

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1 FTIR Spectra for Pristine CNCs and Cin-CNCs

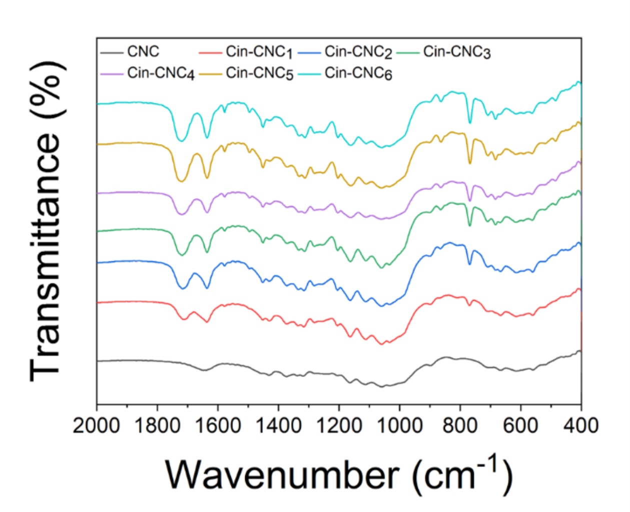

Figure S1. FTIR spectra of pristine CNCs and Cin-CNCs synthesized at varying weight ratios of CNCs to cinnamoyl chloride (1:1, 1:2, 1:3, 1:4, 1:5, and 1:6).

2. The calibration curve and UV absorbance of a blank CNC suspension and Cin-CNCs (4 × 10^{-5} g·mL^{-1})

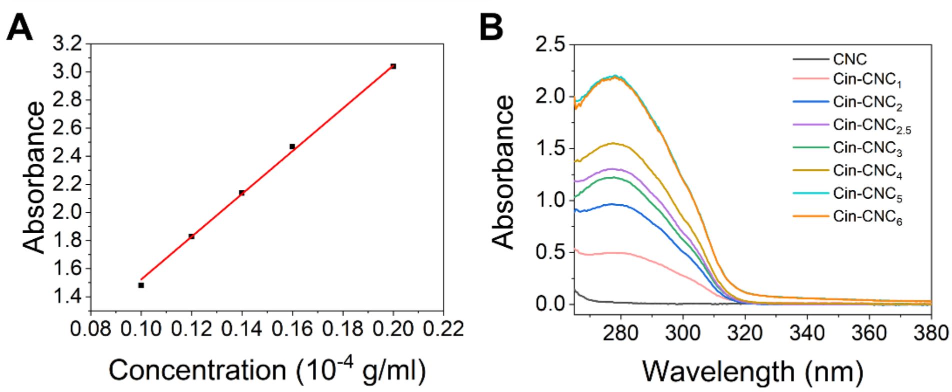

Figure S2. (A) Calibration curve plotting absorbance against cinnamoyl chloride concentration. (B) UV absorption spectra of CNCs and Cin-CNCs with varying grafting fractions.

3. Photostability of Hollow Microspheres

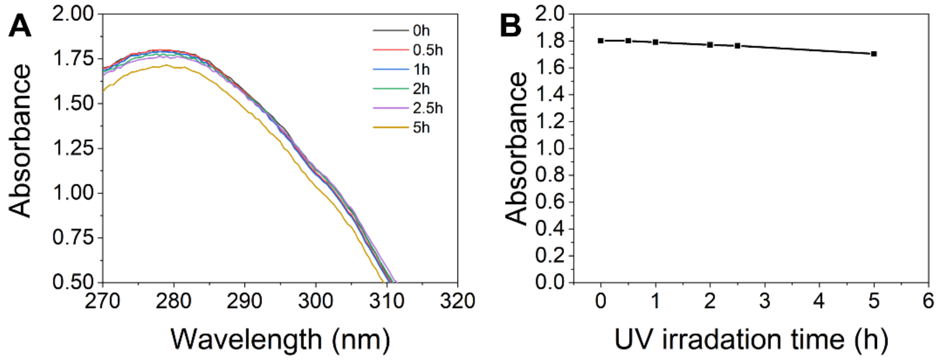

Figure S3. (A) Evolution of the UV absorption of Cin-CNCs/SiO_2 hollow microspheres irradiated at 365 nm for different durations. (B) Maximum absorbance of Cin-CNCs/SiO_2 hollow microspheres at 278 nm as a function of UV irradiation time.

4. Calculation of Grafting Fractions of Cinnamate Groups

Calibration curve derived from UV-visible spectroscopy:

$$y = 152257 \cdot x\#(1)$$

Thus，

$$A = 152257 \cdot c_{Cinnamoyl\ chloride}\#(2)$$

Where $c_{cinnamoyl\ chloride}$ is the concentration of cinnamoyl choride in DMF (solvent) in g·ml^{-1}. After the esterification reaction, the relative molecular mass of the actual cinnamate groups grafted onto CNCs is:

$$M_{Cin} = 147 - 17 = 130\ g \cdot mol^{-1}\#(3)$$

Thus，

$$A = 152257 \cdot c_{Cin} \cdot \frac{M_{Cinnamoyl\ chloride}}{M_{Cin}} = 193517c_{Cin}\#(4)$$

Assuming that1g of CNC can provide x moles of reacting sites for grafting cinnamate groups.

Thus，

$$n_{reacting\ site} = x \cdot m_{CNC}\#(5)$$

Let φ be defined as the grafting fraction, which represents the ratio of the reacting sites where grafting occurs to the total reacting sites on the CNCs. The molar mass and mass of the grafted cinnamate groups can be calculated as follows:

$$n_{Cin} = \varphi \cdot n_{reacting\ site} = \varphi \cdot x \cdot m_{CNC}\#(6)$$

$$m_{Cin} = n_{Cin} \cdot M_{Cin} = 130 \cdot \varphi \cdot x \cdot m_{CNC}\#(7)$$

Thus，the total mass of Cin-CNCs in the dispersion used for testing is:

$$m_{Cin-CNC} = m_{Cin} + m_{CNC} = m_{Cin} + \frac{m_{Cin}}{130 \cdot \varphi \cdot x} = \left(1 + \frac{1}{130 \cdot \varphi \cdot x}\right) \cdot m_{Cin}\#(8)$$

Since the concentration of Cin-CNCs is 4×10^{-5} g·ml^{-1},

$$m_{Cin-CNC} = c_{Cin-CNC} \cdot V_{sample} \#(9)$$

Thus，

$$m_{Cin} = c_{Cin} \cdot V_{sample} = \frac{A}{193517} \cdot V_{sample} \#(10)$$

Dividing both sides of equation (8) by V_{sample} and substituting equation (10):

$$0.00004 = \left(1 + \frac{1}{130 \cdot \varphi \cdot x}\right) \cdot \frac{A}{193517} \#(11)$$

Substituting $\varphi = 1$ into equation (11), where $A = A_{Cin-CNC} - A_{CNC}$, we obtain $x = 0.003\ mol \cdot g^{-1}$.

Substituting the value x = 0.003 into equation (11), we can calculate the expression for φ：

$$\varphi = \frac{100(A_{Cin-CNC} - A_{CNC})}{302 - 39(A_{Cin-CNC} - A_{CNC})} \#(12)$$

5. Sample Information

Table S1. Sample information.

<table>
<tr><th></th><th>Sample</th><th>Oil (1 ml)</th><th>Water (4 ml)</th><th>Grafting Fraction of Cin-CNCs</th></tr>
<tr><td rowspan="7">Effect of Cin-CNCs grafting fraction</td><td>A1</td><td rowspan="7">0.5 w.t % Aerosil R974</td><td rowspan="7">0.5 w.t % Cin-CNCs</td><td>0</td></tr>
<tr><td>A2</td><td>0.17</td></tr>
<tr><td>A3</td><td>0.36</td></tr>
<tr><td>A4</td><td>0.47</td></tr>
<tr><td>A5</td><td>0.51</td></tr>
<tr><td>A6</td><td>0.63</td></tr>
<tr><td>A7</td><td>1</td></tr>
<tr><td rowspan="4">Effect of SiO_2 concentration</td><td>B1</td><td></td><td rowspan="4">0.5 w.t % Cin-CNCs</td><td rowspan="4">0.47</td></tr>
<tr><td>B2</td><td>0.25 w.t % Aerosil R974</td></tr>
<tr><td>B3</td><td>0.5 w.t % Aerosil R974</td></tr>
<tr><td>B4</td><td>1 w.t % Aerosil R974</td></tr>
<tr><td rowspan="2">Effect of Cin-CNCs concentration</td><td>B5</td><td rowspan="2">0.5 w.t % Aerosil R974</td><td></td><td rowspan="2">0.47</td></tr>
<tr><td>B3</td><td>0.5 w.t % Cin-CNCs</td></tr>
</table>

	B6		1 w.t % Cin-CNCs	
Cin-CNCs/ TiO_2 hollow microspheres	C1	0.5 w.t % TX-85	0.5 w.t % Cin-CNCs	0
	C2			0.47

6. The Appearance Photos of Hollow Microspheres Dispersed in Water and Oil

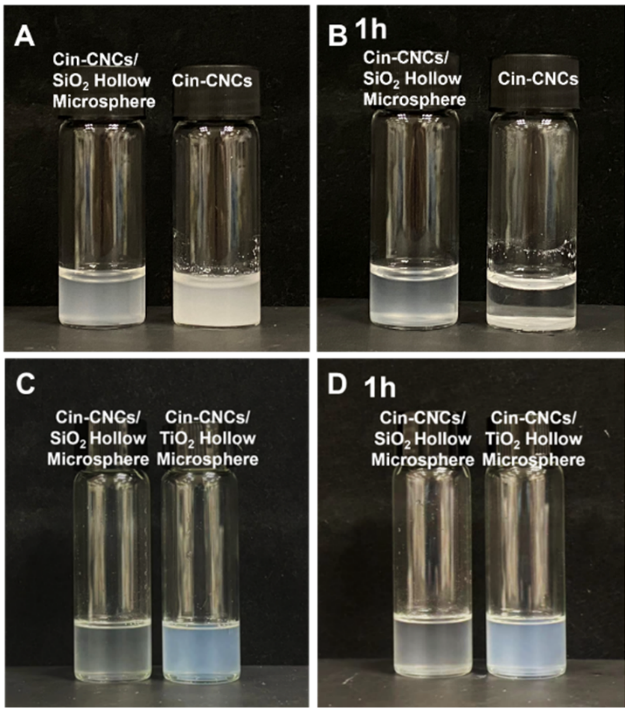

Figure S4. Appearance photographs of 1×10^{-3} g·mL^{-1} Cin-CNCs/SiO_2 hollow microspheres and Cin-CNCs in water taken immediately after preparation (A) and after 1 hour (B). The grafting fraction of Cin-CNCs used is 0.47. Appearance photographs of 1×10^{-3} g·mL^{-1} Cin-CNCs/SiO_2 hollow microspheres and Cin-CNCs/TiO_2 hollow microspheres in GTCC taken immediately after preparation (C) and after 1 hour (D). The grafting fraction of Cin-CNCs used is 0.47.

7. Sunscreen Formulations for SPF Testing

Table S2. Sunscreens formulation for SPF testing

	Ingredients	Concentration (w.t %)
Oil Phase	GTCC	37.75
	UV filter	5
	Cetiol 868	3.75
	Eutanol G	4.5

	PGPH	0.75
	Span 83	1.5
	EM 90	2.25
Water Phase	water	35
	glycerin	5
	butylene glycol	4
	phenoxyethanol	0.4
	1,2-Octanediol	0.1