

## Supporting Information

# Conductive natural rubber/carbon black nanocomposites via cellulose nanowhiskers templated assembly: Tailored hierarchical structure leading to synergistic property enhancements

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Table 1. The experimental vulcanization formula for preparation of NR based nanocomposites

Component	Zinc oxide	Stearic acid	Sulfur	CBS	OP emulsifier
Content ( phr <sup>a</sup> )	3	1.8	1.68	0.9	0.25

<sup>a</sup> parts per hundred parts of natural rubber

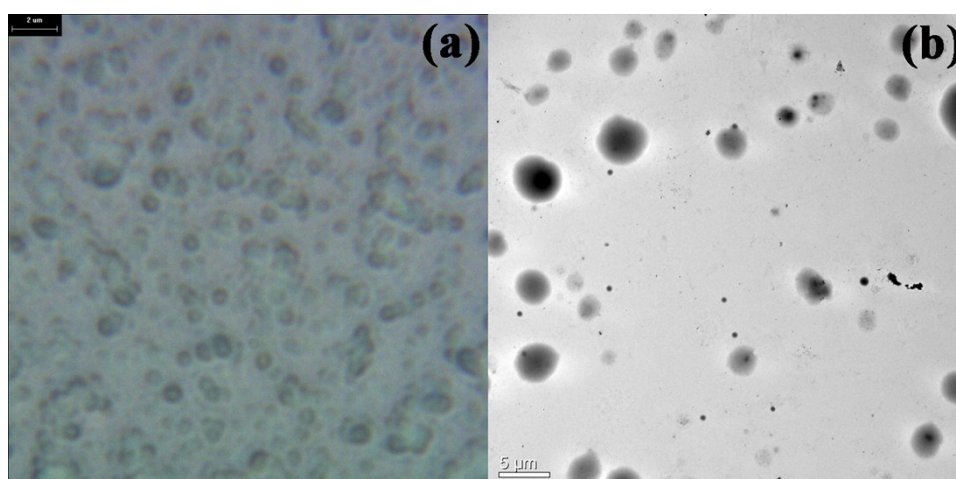


Figure S1. Optical microscope image of NR latex (scale bar at top left corner: 2  $\mu\text{m}$ ) (a); TEM image of NR latex (scale bar: 5  $\mu\text{m}$ ) (b)

Optical microscope was used to investigate the dispersion state and microstructures of NR latex using a microscope (UB 200i, Chongqing UOP Photoelectric Technology Co., Ltd., China) with a digital camera. The NR latex suspension was dropped on a glass slide and covered with a cover-slip. Then the samples were dried and observed. As shown in Figure S1a, well dispersed NR latex microspheres with a diameter of several hundred nanometers to several micrometers can be observed. However, the particle size of NR latex microspheres cannot be measured due to the low resolution of optical microscope.

Because of the low resolution of optical microscope, TEM analysis was employed to investigate the particle size of the original NR latex microspheres. As shown in Figure S1b, the

NR latex microspheres are approximately spherical in shape with a wide distributed diameter from dozens of nanometers to several micrometers. Smaller NR latex microspheres are gray, while larger microspheres are darker. This is attributed to that larger size samples exhibit higher contrast in TEM observation.

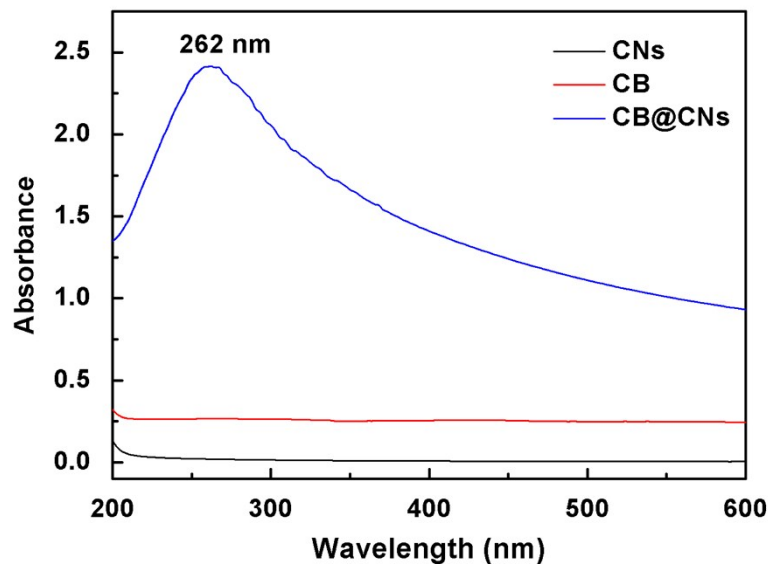


Figure S2. UV-vis spectra of CNs, CB, and CB@CNs nanohybrid

UV-Vis spectrum was applied to characterize the CNs, CB@CNs nanohybrid, and pure CB suspensions. The CNs, CB@CNs nanohybrid, and pure CB suspensions (containing same content of CNs and CB, respectively) were sonicated to disperse the aggregation. The suspensions were put into a quartz cuvette with an optical path of 1 cm. The measurement was conducted at room temperature by Shimadzu UVmini-1240 spectrophotometer.

As shown in Figure S2, at the same CB concentration (0.017 mg/mL), the absorption peak of CB suspension is very weak because that CB was poorly dispersed in water and usually precipitated out as large aggregation. For comparison, the much higher absorbance of CB@CNs nanohybrid indicates the enhanced dispersity of CB by CNs. The absorbance band around 262 nm is attributed to the  $\pi$ - $\pi^*$  transitions of CB<sup>1</sup>. Because of the nanometric and excellent dispersity of CNs, CNs suspension is translucent (Figure 3) at low concentrations. Therefore, CNs suspension exhibited low absorbance in the UV-vis spectrum. In addition, the absorbance of CB@CNs nanohybrid is much higher than the absorbance superposition of CB and CNs, indicating a synergistic effect of CB and CNs.

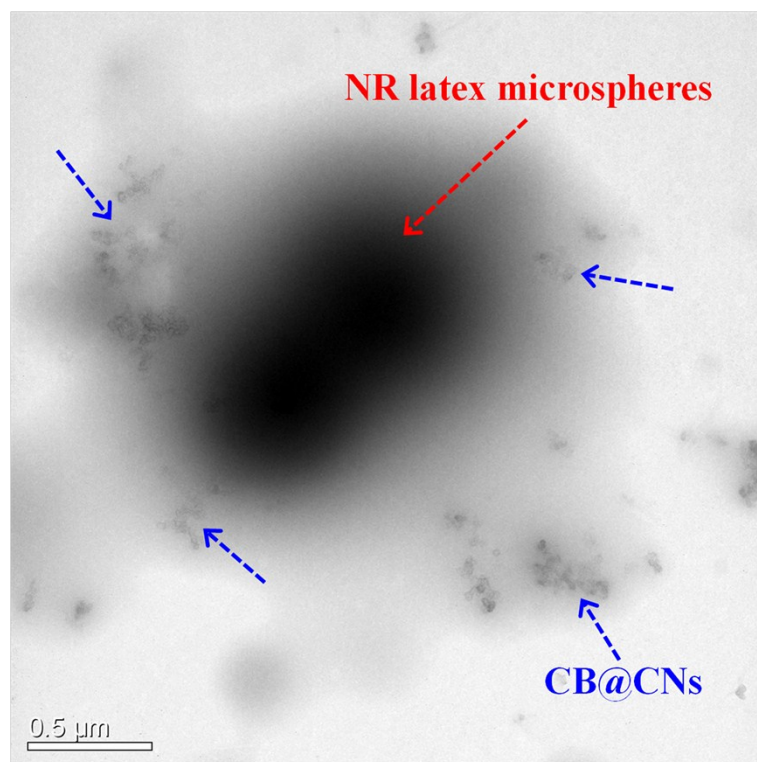


Figure S3. TEM image of the CB@CNs/NR mixture prepared by self-assembly of CB@CNs and NR latex microspheres, scale bar: 0.5 μm

To investigate the CNs templated assembly procedure and formation mechanism of the 3D hierarchical conductive structure in NR matrix, we observed the morphology of CB@CNs and NR latex mixture using TEM. CB@CNs suspensions (containing 0.05 g CB@CNs nanohybrid) and 0.574 g NR latex (58 wt%) were mixed and sonicated adequately for uniform mixing. The mixture was diluted and put on the copper grids for observation. As shown in Figure S3, NR latex microspheres, with a diameter of several hundred nanometers, were surrounded by a layer of CB@CNs nanohybrid. This CB@CNs shells around NR latex microspheres were the prototype of the continuous CB@CNs network structure. During the subsequent co-coagulation procedure, the CB@CNs nanohybrid around NR latex microspheres connected with each other and selectively located in the interstitial space between the NR latex microspheres, thus a 3D hierarchical continuous conductive structure was formed (Figure 4).

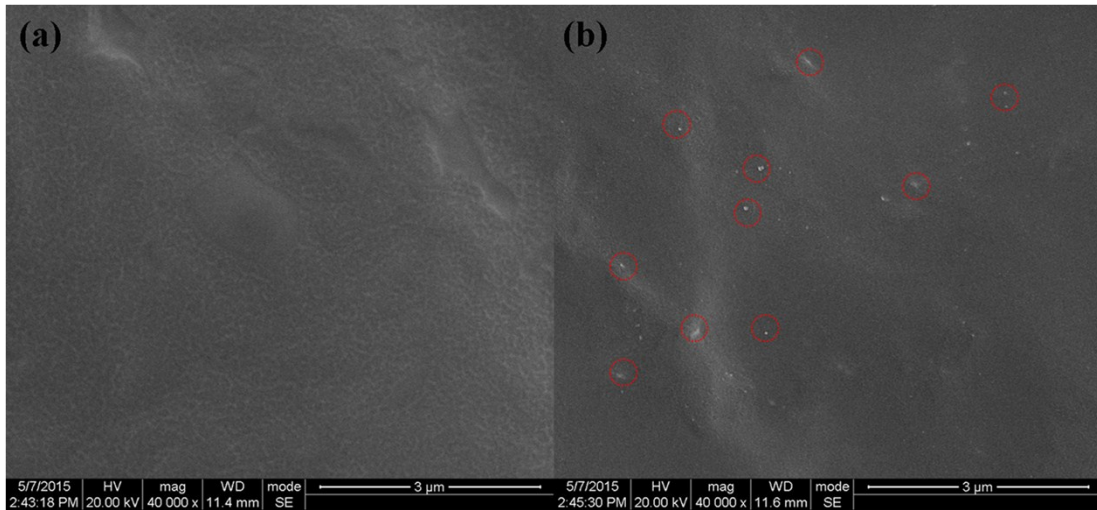


Figure S4. SEM images of the freeze-fractured cross-sections of neat NR (a) and CB/NR composite (b), scale bars: 3 μm

For comparison, the morphology of neat NR and CB/NR (20/100 wt./wt.) composites were characterized by SEM. It can be seen that neat NR shows a smooth cross-section with no fillers filled (Figure S4a). A few of randomly dispersed CB particles (as red circles show) could be observed clearly in the CB/NR composite (Figure S4b), indicating that most CB aggregates were broken into individual CB nanoparticles by the dynamic shear force during two-roll mixing.

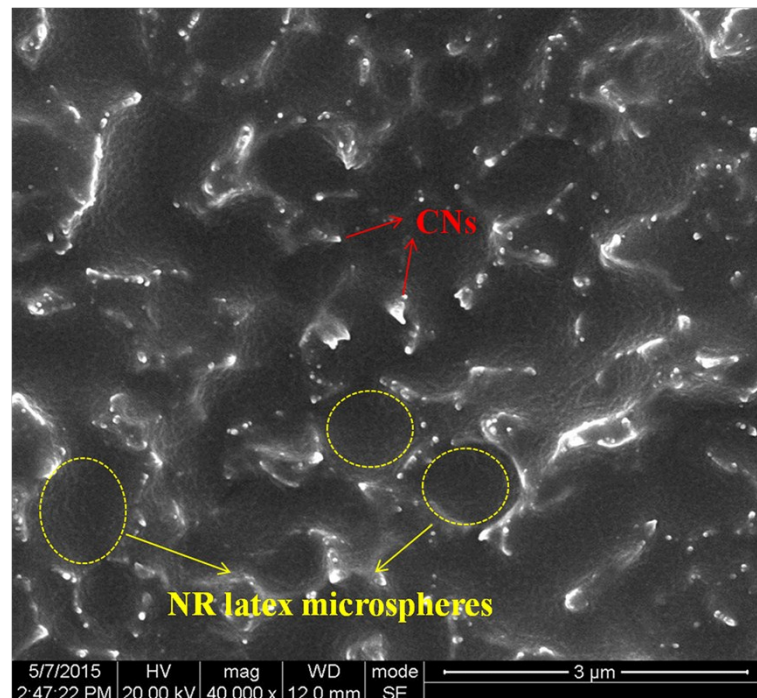


Figure S5. SEM image of the freeze-fractured cross-sections of CNs/NR composite, scale bar: 3 μm

To investigate the microstructure of the CNs/NR composite, CNs/NR (20/100 wt./wt.) composite, prepared via CNs assisted assembly, was freeze-fractured and characterized by SEM. As shown in Figure S5, little bright dots, which resulted from the fracture of CNs and the drawn CNs could be observed clearly. Furthermore, it is noticed that CNs selectively locates in the interstitial space between NR latex microspheres, which provides a direct evidence for the template effect of CNs in the fabrication of the 3D hierarchical conductive structure in NR.

#### **Reference**

1. M. Sharif Sh., F. Golestani Fard, E. Khatibi and H. Sarpoolaky, *J. Taiwan Inst. Chem. E.*, 2009, **40**, 524-527.