Antistatic Structural Color and Photoluminescent Membranes from Co-assembling Cellulose Nanocrystals and Carbon Nanomaterials for Anti-counterfeiting

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Abstract Static charges on optical anti-counterfeiting membranes may lead to materials structural changes, dust stain aggravation, and misreading of optical information. Incorporating conductive particles is a common way to transfer accumulative charges, but the key issue is how to achieve high dispersion and effective distribution of particles. According to the strategy of assembly-induced structural colors, cellulose nanocrystals (CNCs) were employed as a solid emulsifier to stabilize hydrophobic carbon nanoparticles (CNPs) in aqueous media; subsequently, by solvent-evaporation-modulated co-assembly under a condition of 30 °C and 20 RH%, the binary suspensions containing 2 wt% CNC and CNPs with the equivalent concentration relative to CNC ranged from 1:40 to 1:10 were used to prepare antistatic composite membranes. Surface chemistry regulation of CNCs was applied to optimize the dispersibility of CNPs and the orientation of assembled CNC arrays; and the hydrophilic CNCs were more favorable for dispersion and assembly of binary suspension systems. Meanwhile, one-dimension carbon nanotube (CNT) and zero-dimension carbon black (CB) were found to show better dispersibility than two-dimension graphene, which was verified by a semi-quantitative theoretical study. Moreover, the stable binary systems of CNT/CNC and CB/CNC were chosen for co-assembly as membranes, and the uniaxial orientation could be optimized as the full-width of 9.8° at half-maximum deviation angle while the surface resistivity could also drop down to 3.42 × 10³ Ω·cm·cm⁻¹. The structural color character of such paper-homology and antistatic-integrated membranes contributes to optical information hiding-and-reading, and shows great potential as optical mark recognition materials for electrostatic discharge protective packaging and anti-counterfeiting applications.

Keywords Cellulose nanocrystal; Solid-state photoluminescent; Carbon nanoparticles; Antistatic

INTRODUCTION

Materials with structural colors have been widely applied in the fields of optical anti-counterfeiting,[1,2] sensing,[3-5] and so on. Among them, the structural colors induced by assembly have a broad prospect in information encryption because they are free of photo-bleaching and have a long service life, which is different from the common photoluminescent materials based on fluorescence.[6,7] Besides, the monochromaticity of structural colors is usually an important factor for anti-counterfeiting materials.[8] Cellulose nanocrystals (CNCs), a one-dimensional nano-crystal extracted from natural bio-based resources,[8,9] were recently focused due to their self-assembling ability to obtain structural colors.[10,11] The structural colors could be further regulated by controlling self-assembly conditions and the properties of CNCs, such as length,[11] aspect ratio,[12] and surface chemistry structure.[13] Besides, uniaxial-assembled CNCs can even induce an emission based on virtual transitions of electrons, which makes CNCs an excellent candidate material for information security.

However, static charges on anti-counterfeeting CNC membranes with structural colors and uniaxial-assembly-induced emission may destroy the chemical structure of the optical materials, lead to a short service life, and adsorb dust, which affects reading optical information. Coating conductive polymers, like polyaniline, on CNCs is a feasible method for solving the static problem, whereas those polymers can also adsorb emission of CNCs and weaken the structural colors.[14] Another way to increase the conductivity is to add a small number of conductive fillers into the assembly membranes of
CNCs,\textsuperscript{15,16} Gold nanorods and silver nanowires were reported to co-assemble with CNCs,\textsuperscript{17} whereas the obtained assembly membranes owned a chiral structure, which was not suitable for assembly-induced emission of CNCs.

Carbon nanomaterials, such as carbon nanotube (CNT), carbon black (CB), and graphite, were also reported to disperse uniformly in CNC suspension.\textsuperscript{18-21} Researchers have proved that CNCs could act as solid emulsifier to make hydrophobic carbon nanoparticles (CNPs) dispersed well in aqueous solutions.\textsuperscript{22-24} However, we found that CNC might lose the assembling ability after CNPs were introduced in. The reason should be related to the complicated interactions between hydrophilic CNC and hydrophobic CNPs in the aqueous condition. Thus, we further modified CNCs to study the effect of chemical structure on its co-assembling ability with hydrophobic CNPs. The co-assembling mechanism was investigated by studying the co-assembling process of CNCs and CNPs with different dimensions. The mass ratio between CNC and CNPs was also controlled to optimize the photoluminescent and conductive properties of the co-assembling membranes. In general, the co-assembly membranes based on CNPs and CNCs combined both photoluminescent and antistatic properties, and it had potential to be used in electrostatic discharge (ESD) protective packaging materials with optical encryption.

**EXPERIMENTAL**

**Materials**

Carbon nanotube (CNT, NC7000, with the length of 1533.9 ± 231.9 nm and the diameter of 9.2 ± 2.8 nm) was purchased from Nanocyl (Belgium). Carbon black (CB, Vulcan XC-72R type, with the diameter of 23.2 ± 2.2 nm) was purchased from Cabot Corporation. Graphite was purchased from Shanghai Huayi Group Huayuan Chemical Co., Ltd. (China). Cotton (linters) was supplied by Hubei Chemical Fiber Group Co., Ltd. (China). The solution of sodium hypochlorite (NaClO, 14.5% available chlorine) was purchased from Energy Chemical. Sodium bromide (NaBr), sodium hydroxide (NaOH, 96.0%, granular), ethanol (95.0%), acetic anhydride (AA), pyridine, sodium chloride (NaCl), acetone (99.5%), and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEP0, C\textsubscript{6}H\textsubscript{12}O\textsubscript{7}N, 98%) was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China).

**Methods**

CNC that was extracted by H\textsubscript{2}SO\textsubscript{4} hydrolysis with cotton was coded as SCNC and prepared according to our previous report.\textsuperscript{25} The obtained SCNCs were 156.2 ± 40.2 nm in length and 9.0 ± 1.2 nm in diameter.\textsuperscript{25} Via replacing H\textsubscript{2}SO\textsubscript{4} solution with 4 mol·L\textsuperscript{-1} aqueous HCl, CNC powders were also obtained and coded as HCNC, according to a previous report,\textsuperscript{26} and the length and diameter were 182.6 ± 59.9 nm and 14.2 ± 4.5 nm, respectively. SCNC was further acetylated according to our previous study,\textsuperscript{26} and the modified CNC was coded as ACN with 142.3 ± 33.1 nm in length and 9.0 ± 0.9 nm in diameter. The surface-carboxylated CNC was coded as OCN and was prepared according to our previous report with some changes.\textsuperscript{28}

Briefly, 2.0 g of SCNC was dispersed in distilled water for 3 min with an ultrasonic cell breaker. TEMPO and NaBr were then added into the SCNC dispersion with magnetic stirring at 20 °C. NaClO solution (7 or 10 mL) was added dropwise into the dispersion at a pH of 10 with a 0.5 mol·L\textsuperscript{-1} aqueous NaOH solution, and these two kinds of OCNs were coded as OCN-7 and OCN-10, respectively.\textsuperscript{29,30} When the pH was not changing, the reaction was finished. Methanol (6 mL) was then added to react with the excess of NaClO and the pH was adjusted to 7 with 0.5 mol·L\textsuperscript{-1} HCl. The oxidation degree was controlled by the volumes of the NaClO solution, and the length and diameter of OCN-7 were 143.0 ± 28.9 nm and 8.8 ± 0.9 nm, respectively, while those of OCN-10 were 140.0 ± 26.3 nm and 8.9 ± 1.1 nm, respectively. All the particle sizes were statistically obtained by collecting more than 200 particles to calculate their average values and the corresponding standard deviations.

To prepare the CNP/CNC uniaxial co-assembled membranes, firstly, 0.2 g of CNC (or OCN-10) powders and a certain amount of CNPs (CBs or CNTs) were dispersed into 10 mL water and treated with ultrasound (300 W) for 10 min. Then, a hydrophilic glass plate was vertically inserted into the dispersion. Black membranes were obtained by solvent-evaporation-induced self-assembly at a condition of 30 °C and 20 RH%. The membranes were coded as CNT/SCNC(0.05), CNT/SCNC(0.1), and CNT/SCNC(0.2) when the CNT concentration in 2 wt% SCNC suspension was 0.05 wt%, 0.1 wt%, and 0.2 wt%, respectively. Similarly, via replacing CNCs or CNPs, the membranes were coded as CNT/OCN(0.05), CNT/OCN(0.1), CNT/OCN(0.2), CB/OCN(0.05), CB/OCN(0.1), and CB/OCN(0.2), respectively.

**Characterization**

Fourier-transformed infrared (FTIR) spectra of CNC, OCNs, and ACN were recorded with a Nicolet 6700 FTIR spectrometer (Nicolet Instruments) in the range of 4000–400 cm\textsuperscript{-1}, using the method of KBr platelets. Ultraviolet and visual adsorption (UV-Vis) tests were carried out on a Cary Lambda 750 S spectrophotometer. Photoluminescence (PL) spectra of CNP/CNC membranes were tested on the 5JL-004 (Hitachi High-technologies Corporation). The conductivity of CNP dispersion was measured at the concentration of 0.01 wt%, 0.05 wt%, and 0.1 wt% for CNPs after the dispersion had been ultrasonicated for 5 min. Zeta potential of CNCs and CNPs aqueous dispersion (1 mg·mL\textsuperscript{-1}) was measured by a NanoBrook Omni (Brookhaven). The atomic force microscopy (AFM) measurements were carried out on the Dimension icon from BRUKER, whose surface scans were performed in a Scanasyst mode. The full width at half-maximum (FWHM) of the included-angle of the CNC arrays was counted by collecting more than 200 particles to calculate their average values.

The measurement of the oxidation degree of OCNs was carried out by a previous method, and the calculation of oxidation degree (DO) and carboxyl content was carried out by Eq. (1) and Eq. (2), respectively:\textsuperscript{30}

\[
DO = \frac{162c(V_2 - V_1)}{\omega - 36c(V_2 - V_1)}
\]
\[ c_{\text{COOH}} = \frac{(V_2 - V_1) \cdot c}{m_{\text{OCN}}} \]  

where \( V_1 \) and \( V_2 \) are the initial and terminal volumes of NaOH (in mL) during titration, \( c \) is the concentration of NaOH (in mol\( \cdot \)L\(^{-1} \)), \( \omega \) is the mass of OCN samples (in mg), and \( m_{\text{OCN}} \) is also the mass of OCN (in g).

The contents (%) of carbon (C), hydrogen (H), and sulfur (S) in different CNCs were measured from elemental analysis (Elemental Vario EL Cube, Germany), and the degree of acetyl substitution (DS\(_{\text{surface-acetyl}}\)) for ACN was calculated according to our previous report with Eq. (3):[27,31]

\[ \text{DS}_{\text{surface-acetyl}} = \frac{n_{\text{surface-acetyl}}}{n_{\text{surface-OH}}} = \frac{\Delta C}{C_{\text{CNC}} - C_{\text{ACN}}} \]  

where DS\(_{\text{surface-acetyl}}\) is the amount of surface acetyl groups on ACN, \( n_{\text{surface-OH}} \) is the amount of surface hydroxyl groups on CNCs, and \( \Delta C \) is the increment of carbon content after surface acetylation (\( \Delta C = C_{\text{ACN}} - C_{\text{CNC}} \)).

To make quantitative measurement of the stability of CNP dispersion, the mixed dispersion of CNPs and CNCs was prepared at a mass ratio of 1:2 with ultrasonic treatment of a cell crusher (300 W, 10 min). Centrifugal sedimentation was carried out at different rotating speeds with a Bench Centrifuge (3-30 KS, Sigma). Characterization of UV-Vis spectrophotometry was obtained after the centrifugation. Samples were loaded with a 1 cm quartz dish and under the conditions of scanning interval in 800−200 nm and the scanning rate at an interval speed. All the UV-Vis data were tested twice, and the error was less than 0.1%.

According to the previous report, the absorbance values of the CNP supernatants at 500 nm were collected as a function of relative centrifugal force (RCF).[27,31] The stability constant of CNP/CNC suspension without centrifugation, \( y \) is the absorbance values at 500 nm, \( A_0 \) is the initial absorbance of CNP/CNC suspension without centrifugation, \( x \) is the RCF (kg), and \( k_s \) is the rate constant of centrifugal settling (kg\(^{-1}\)) with a large \( k_s \) indicating poor dispersion stability.[32] Eq. (4) can be written in a linear form by taking the natural logarithm of both sides of the equation as Eq. (5):

\[ \ln y = \ln A_0 - k_s x \]  

The absorbance values at 500 nm reflected the CNP concentration in aqueous solution.

**RESULTS AND DISCUSSION**

**Semi-quantitative Theoretical Calculation of Phase Separation**

The dispersion of CNPs in the assembly structure of cellulose nanocrystal (CNC) was studied thermally with the change of Gibbs free energy of phase separation.[33] In general,

\[ \Delta G_{a,b} = n (G_{a-a} + G_{b-b} - 2G_{a-b}) \]  

where \( \Delta G_{a,b} \) is the Gibbs free energy change from uniform to phase separation, \( G_{a-a} \), \( G_{b-b} \) and \( G_{a-b} \) are the Gibbs free energy of two connected dispersing nanoparticles, two connected assembly nanoparticles, and connected dispersing nanoparticle and assembly nanoparticle, respectively. \( n \) is a constant.

Here, we labelled CB, CNT, graphene, and SCNC with subscript 0, 1, 2, and 1', respectively, to discuss \( \Delta G \) of each system. Researches have proved that the interaction between graphene nanoparticles should be strong due to their \( n-n \) stacking,[34] leading to a low \( G_{2-2} \). The high lipophilicity of graphene and high hydrophilicity of SCNC should lead to a high \( G_{2-1} \). We thus believed that \( \Delta G_{2-1} \) should semi-quantitatively be a negative one and should induce spontaneous phase separation of CNCs and graphene. The AFM image of the co-assembly membrane of graphene and SCNC also confirmed such phase separation (Fig. 1c). Although CB and CNT had lower zeta potentials (ZPs) than that of graphene (seen in Table 1), the lower dimension of CB and CNT should result in a fact that the \( n-n \) stacking of CB and CNT should be much less than that of graphene. Thus, \( \Delta G_{1-1} \) and \( \Delta G_{2-1} \) should be larger than \( \Delta G_{2-2} \). However, co-assembling with SCNC, CB also aggregated severely (Fig. 1b) while CNT did not (Fig. 1a). Thus, the compatibility between CNPs and CNC should be further modified.

**Co-assembly of CNP/CNC**

**Surface modification of CNCs**

FTIR spectra of SCNCs and modified CNCs are shown in Fig. 2. For acetylated CNC (ACN), the infrared spectrum band at 1745 cm\(^{-1}\), which should be attributed to stretching vibration (\( \sim C=O \)) of ACN, indicated carbonyl groups of the acetyl ester. The stretching vibration band (\( \sim C=O \)) at 1236 cm\(^{-1}\) also proved the introduction of acetyl groups in ACN.[35] In the

![Fig. 1](https://doi.org/10.1007/s10118-020-2414-x)
spectrum of OCN, the $\mathrm{--CO}$ stretching vibration band appeared at 1616 cm$^{-1}$, indicating that carboxyl groups were introduced on the OCN surfaces. 

The band located at 1033 cm$^{-1}$ was attributed to the stretching vibration ($\mathrm{--SO_3}$) of SCNC.

Compared with SCNC, HCNC lacked $\mathrm{--SO_3}$ group derived from the H$_2$SO$_4$ hydrolysis, so the stretching vibrations of the $\mathrm{--SO_3}$ group located at 1033 cm$^{-1}$ was absent in the spectrum of HCNC. The results of elemental analysis in Table 2 also proved an increase in the content of carbon element from SCNC to ACN, which is consistent with the results of the infrared analysis above.

The contents of elements in HCNC, SCNC, and ACN samples are displayed in Table 2. Oxidation degree (DO) of OCN-7 and OCN-10 was calculated to be 3.9% and 4.7%, respectively, with Eq. (1). Also, the carboxyl content was calculated to be 0.24 and 0.3 for OCN-7 and OCN-10, respectively, with Eq. (2). Besides, DS$_\text{surface-acetyl}$ of ACN was measured and calculated to be 37.1% with Eq. (3).

Quantitative analysis towards dispersion stability of CNP/CNC suspension
By controlling the surface chemistry structure of CNCs to adjust their hydrophilicity, we could obtain appropriate CNCs for co-assembling with hydrophobic CNPs. As shown in Figs. 3(a) and 3(b), the dispersion of different CNPs could be stable in water when appropriate CNCs were introduced. However, some sediment could be observed in the systems of CNT/HCNC and CNT/ACN after 24 h. Moreover, CB aggregated completely after 24 h in water with SCNC, which could be seen in Fig. 3(d). By contrast, CNT/SCNC, CNT/OCN-7, CNT/OCN-10, and all CB/CNC (except CB/SCNC) were still stable after several weeks. The combination of CNCs and graphite showed little effect, which is in accordance with the result of semi-quantitative theoretical calculation. Thus, this work only discussed CNPs of CNTs and CBs, and the properties of graphite/CNC systems are displayed in the electronic supplementary information (ESI).

A dispersion constant, $k_s$, was used to measure the stability of CNP and CNP/CNC dispersion quantitatively. Figs. 4(a)−4(c) show that the CNT dispersion with SCNC or OCNs adding owned a lower $k_s$ value than neat one at different concentrations, which means these kinds of CNCs could improve the CNT dispersion stability in water. However, introducing ACN and HCNC even increased the $k_s$ value of CNT dispersion. These results imply that CNCs with higher surface charge...
could increase the dispersion stability of CNTs in water. In details, SCNC and OCNs could be negatively charged due to their abundant sulfonic groups and carboxyl groups, respectively, while HCNC and ACN could not. The surface charge of CNT and various CNCs could be compared through the ZP data displayed in Tables 1 and 3, and are further analyzed in the following discussion.

By contrast, the $k_s$ values of CB/HCNC and CB/OCN systems were similar to that of neat CB, as shown in Figs. 4(d) and 4(e). Although the $k_s$ value of CB/ACN sample was about twice as that of neat CB at the CB concentration of 0.05 wt%, it was not high enough compared with CNT/SCNC, which means the CB/ACN system was also stable at that concentration. Besides, according to the results of element analysis, the sulfonic acid groups and carboxyl groups could improve the dispersion of CNT (1D carbon particle), and excessive sulfonic acid groups could even prevent the dispersion of CB (0D carbon particle). However, the $k_s$ value of CB/SCNC sample was much higher than that of neat CB, which means that SCNC limited rather than improved the dispersion stability of CB in water. Since the neat CB dispersion owned a much lower $k_s$ value than that of CNT dispersion, the higher ionic strength from the negative charge of SCNC might account for the main effect on CB dispersion. We thus used NaCl to control the ionic strength of all CB/CNC (except SCNC) system at the same level of the pure CB/SCNC sample (seen in ESI). Then the $k_s$ value of CB/CNC (except SCNC) systems increased to similar values of CB/SCNC system, as shown in Fig. 4(f), which proves the effect of ionic strength on CB dispersion.

**The difference in the dispersion of CNP caused by CNC dispersity**

Since CNCs could affect the stability of CNP dispersion, they might be able to prevent CNPs from aggregation during co-assembling, and we thus used AFM to analyze CNP/CNC systems. In the drop-coating membrane of CNT/OCN dispersion, the OCNs were found to adhere on the CNTs (Fig. 5b), making CNTs separate from each other rather than entangling. By contrast, in the CNT/HCNC system, HCNCs tended to aggregate instead of adhering on the CNTs, so CNTs entangled and aggregated (Fig. 5d). Considering that the dispersion stability of HCNC itself in water was poor (the HCNC aggregated seriously, as shown in Fig. 5c), those results indicate that CNCs with a higher ZP value could well disperse in water, as seen in Table 3. It is reported that the stability of the colloid system could be evaluated by the corresponding regions of the absolute ZP values, i.e. lower than 10 mV indicates highly unstable, 10–20 mV indicates relatively stable, 20–30 mV indicates moderately stable, and higher than 30 mV indicates highly stable. Thus, the aqueous suspension of OCNs and SCNCs with the absolute ZP value of higher than 30 mV
should be very stable, while the aqueous suspensions of HCNs and ACNs were relatively stable due to their ZP values around \(-20\) mV, and tended to aggregation. Those well dispersed CNCs could adsorb on positively charged CNTs and separate them from aggregation, resulting in the potential of CNTs to be well distributed in the co-assembled membranes, as shown in Scheme 1(a).

No apparent adhesion between CB and HCNC was observed, as shown in Fig. 5(e) and schematically displayed in Scheme 1(b), which might be attributed to a much lower specific surface of CB than CNT.\(^{40,41}\) However, when SCNCs were introduced into the CB dispersion, CBs aggregated seriously (Fig. 1b), which is consistent with the result that the CB/SCNC system owned the highest \(k_s\) value among all CB/CNC systems.

**The orientation of the CNP/ CNC co-assembled membranes**

According to the quantitative analysis and AFM tests, we chose CNT/SCNC, CNT/OCN, and CB/OCN systems to co-assemble and fabricate anti-static photoluminescent membranes. The obtained membranes were characterized by the distribution of the included angle between CNC long-axis and vertical direction in the CNP/CNC co-assembly by AFM tests as shown in Fig. 6. FWHM of the included angle was used to evaluate the orientation of CNC assembly. From Fig. 7 and Table 4, we found that CNT/OCN and CB/OCN membranes had a large FWHM, while the FWHM of CNT/SCNC membranes was much smaller. OCNs had a high ZP and they could easily adhere on the surface of CNTs, which caused a random assembly of OCNs. By contrast, CNTs distributed very well in CNT/OCN membranes, so CNT/OCN membranes displayed much higher conductivity than the others but lower photoluminescence. Meanwhile, there were weak interactions between CBs and OCNs, so that CBs were separated by OCNs and finally aggregated in the CB/OCN membranes, which led to a high resistivity and bad solid-state luminescence. CNT/SCNC membranes had lower FWHM and could luminesce. Besides, a high concentration of CNTs could bring out good conductivity. These

![AFM images of drop-coating membrane prepared by 10 μL of 0.001 wt% dispersion of (a) neat CNT, (b) CNT/OCN, (c) HCNC, (d) CNT/HCNC, and (e) CB/HCNC.](https://example.com/afm_images.png)

**Scheme 1** Illustration of the interaction between (a) CNC and CNT, (b) CNC and CB.\(^{40,41}\)}
results would be further discussed in the following sections.

**Anti-static Properties of CNP/CNC Co-assembled Membranes**

The surface resistivity of CNP/CNC co-assembled membranes with different concentrations is collected in Table 5. CNT/SCNC membranes had a high resistivity at the initial concentration of 0.05 wt% and 0.1 wt%, which was $3.22 \times 10^6 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$ and $1.15 \times 10^6 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$, respectively. In contrast, CNT/SCNC(0.2) displayed a lower surface resistivity as $5.62 \times 10^4 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$.

According to “Handbook for Electrostatic Discharge Protective Packaging (GJB/Z86-97)”, the membranes with a surface resistivity between $10^5$ and $10^{12} \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$ are the static dissipative materials, while the static conductive materials have the surface resistivity of less than $10^5 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$, which are the best for electrostatic discharge (ESD) protective packaging. However, when the resistivity of the membrane is too low as less than $10^4 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$, it cannot be directly used as ESD protective packaging material because it may produce electrostatic induction and electrostatic discharge in the electrostatic field and damage the product.

Thus, CNT/SCNC(0.05) was static dissipative material, while CNT/SCNC(0.1) and CNT/SCNC(0.2) were static conductive materials. As for CNT/OCN, CNT/OCN(0.05) showed a high surface resistivity of more than $2 \times 10^7 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$. However, the resistivity rapidly decreased to $5.40 \times 10^3 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$ when the initial concentration of CNT was 0.1 wt%, while CNT/OCN(0.2) had a surface resistivity of $3.42 \times 10^2 \Omega \cdot \text{cm} \cdot \text{cm}^{-1}$. These results imply that CNTs might be separated from OCNs during the co-assembling. However, CNT/OCN(0.2) was not suitable for ESD protective packaging materials, for its surface resistivity was too low. By contrast, CNT/OCN(0.1) was a good static conductive material.

The surface resistivity of CB/OCN was very high. This is attributed to the spherical structure of CBs. CBs could be well dispersed in aqueous solution, but the introduction of OCNs

![AFM images of co-assembled membranes of (a) CNT/SCNC(0.05), (b) CNT/SCNC(0.1), (c) CNT/SCNC(0.2), (d) CNT/OCN(0.05), (e) CNT/OCN(0.1), (f) CNT/OCN(0.2), (g) CB/OCN(0.05), (h) CB/OCN(0.1), and (i) CB/OCN(0.2).](https://doi.org/10.1007/s10118-020-2414-x)
separated them in the co-assembled membranes. Thus, CBs could not contact each other, causing a low surface resistivity of the membrane.

Photoluminescent Properties of CNP/CNC Co-assemble Membranes

The results of the photoluminescent properties are shown in Fig. 8. The same kinds of CNP/CNC membranes displayed similar

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**Table 4** FWHM of the included angle of CNP/CNC samples.

| Sample          | CNT/SCNC (0.05) | CNT/SCNC (0.1) | CNT/SCNC (0.2) | CNT/OCN (0.05) | CNT/OCN (0.1) | CNT/OCN (0.2) | CB/OCN (0.05) | CB/OCN (0.1) | CB/OCN (0.2) |
|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| FWHM (°)        | 11.3            | 10.3           | 9.8            | 28.9           | 12.0           | 17.0           | 66.1           | 63.8           | 79.8           |

**Table 5** Surface resistivity of CNP/CNC co-assembled membranes with different concentrations.

| Dispersion system | Surface resistivity (Ω·cm⁻¹) |
|-------------------|-----------------------------|
|                   | 0.00 wt% | 0.05 wt% | 0.1 wt% | 0.2 wt% |
| CNT/SCNC          | >2.00 x 10⁷ | 6.22 x 10⁶ | 1.15 x 10⁶ | 5.62 x 10⁴ |
| CNT/OCN           | >2.00 x 10⁹ | >2.00 x 10⁷ | 5.40 x 10³ | 3.42 x 10² |
| CB/OCN            | >2.00 x 10⁹ | >2.00 x 10⁷ | >2.00 x 10⁷ | 1.82 x 10⁷ |

separated them in the co-assembled membranes. Thus, CBs could not contact each other, causing a low surface resistivity of the membrane.

Photoluminescent Properties of CNP/CNC Co-assemble Membranes

The results of the photoluminescent properties are shown in Fig. 8. The same kinds of CNP/CNC membranes displayed similar
extinction and photoluminescent wavelength at different concentrations, which was mainly affected by the length of CNCs. Among them, for CNT/SCNC membranes, CNT/SCNC(0.1) had the lowest intensity, while CNT/SCNC(0.2) showed the highest. Moreover, compared with CNT/SCNC, CNT/OCN and CB/OCN co-assembled membranes showed much lower intensity. The photoluminescent intensity of uniaxial assembled membranes was affected by both CNP concentration and regularity of CNC arrangement, which was coordinated with the results of AFM tests.

CONCLUSIONS

To enhance the potential of optical anti-counterfeiting application, CNPs were introduced to impart antistatic function to the uniaxial arrays of CNCs with structural color. In this case, it is crucial that hydrophilic CNCs served as a solid emulsifier to promote the dispersion stability of CNPs in blending media and hence achieved uniform distribution of CNPs with uniaxial CNC arrays in the binary-component membranes. The surface chemistry regulation of CNCs determined the hydrophilic/hydrophobic properties and thus affected the colloidal stability of binary CNP/CNC suspensions. A semi-quantitative theoretical calculation predicted the requirement in Gibbs free energy for two-phase separation of these binary colloid systems containing CNCs with various surfaces structures and CNPs with different dimensions. As expected, 1D CNTs and 0D CBs could co-exist with hydrophilic CNCs in water and showed enough dispersion stability, but 2D graphene consistently tended to aggregation due to a very low requirement of Gibbs free energy from uniform dispersion to individual component aggregation. As a result, CNT and CB together with hydrophilic SCNC and OCN were selected to combine as the CNP/CNC pairs for co-assembly as the binary-component membranes, but an unexpected factor, i.e. high ionic strength of SCNC, aggravated the aggregation of CBs and hence led to the failure in the co-assembly of the CB/SCNC pair. The solvent-evaporation-modulated co-assembly process still produced uniaxial CNC arrays with structural color in the binary CNP/CNC membranes integrated with antistatic function, which could emit blue light under ultraviolet irradiation. As usual, the surface resistivity dramatically dropped down with an increase of CNP, and 1D CNT showed a more predominant contribution to conductivity than 0D CB. Moreover, by selecting the CNO/CNC pair and controlling the CNPs loading-level, the co-assembled membranes could be suitable as static dissipative material with the surface resistivity of $1.82 \times 10^{-2}$–$1.15 \times 10^{6}$ $\Omega$·cm·cm$^{-1}$ and static productive materials with the surface resistivity of $5.62 \times 10^{-2}$ and $3.42 \times 10^{2}$ $\Omega$·cm·cm$^{-1}$, respectively. As for luminescence properties, highly uniaxial orientation favored the enhancement of luminous intensity. The CNT/SCNC co-assembled systems with a weight equivalent of CNT versus

Fig. 8 (a–c) Extinction (abbreviation as Ex) and (d–f) emission (abbreviation as Em) spectra for the co-assembled membranes of (a, b) CNT/SCNC, (c, d) CNT/OCN, and (e, f) CB/OCN.
SCNC as 1:10 showed the narrowest full-width as 9.8° at half-maximum deviation angle from assembly orientation, and showed the highest luminous intensity among all the co-assembled specimens; combined with the surface resistivity of 5.62 × 10⁶ Ω-cm·cm⁻¹, it showed a great potential as optical mark recognition materials with ESD protective function. Overall, this kind of composite membranes, which integrate conductive carbon nanoparticles into bio-based structural color arrays, take the advantages of paper homology and are free from photobleaching, and could be considered as a good antistatic anti-counterfeiting candidate by virtue of optical information hiding-and-reading function.

Electronic Supplementary Information
Electronic supplementary information (ESI) is available free of charge in the website at https://doi.org/10.1007/s10118-020-2414-x.

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