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Let It Shine: A Transparent and Photoluminescent Foldable Nanocellulose/Quantum Dot Paper

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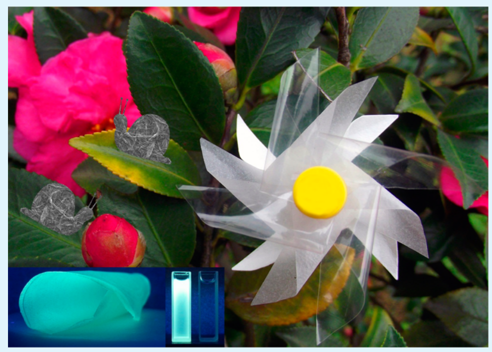
Supporting Information

ABSTRACT: Exploration of environmentally friendly light-emitting devices with extremely low weight has been a trend in recent decades for modern digital technology. Herein, we describe a simple suction filtration method to develop a transparent and photoluminescent nanocellulose (NC) paper, which contains ZnSe quantum dot (QD) with high quantum yield as a functional filler. ZnSe QD can be dispersed uniformly in NC, and a quite low coefficient of thermal expansion is determined for the resultant composite paper, suggesting its good dimensional stability. These results indicate that the meeting of NC with ZnSe QD can bring a brilliant future during the information age.



KEYWORDS: *quantum dot, nanocellulose, photoluminescence, flexibility*

Thanks to the explosion of digital technology, seeking smart, extremely light, and foldable light-emitting devices that can bring us a visual feast is urgently required to replace conventional rigid glass in recent decades.[1−5] Although many polymeric plastics with adequate toughness and optical property are excellent candidates for flexible displays, their coefficients of thermal expansion (CTE) are excessively high for the popular roll-to-roll technique as well as common applications.[1,2] Therefore, reports on such light-emitting polymer-based composite films are very limited, and most substrates referred to mainly originate from petroleum resources.[6−10] As far as we know, up to now, no work has dealt with light-emitting biobased films with features of high transparency and flexibility, which may possess a strong competitive power against conventional petroleum-based materials. Cellulose, a ubiquitous natural polymer, holds excellent biodegradability, biocompatibility, and renewability.[11−14] Moreover, nanoscale cellulose fiber (nanocellulose, NC), commonly presented in plant bodies with a diameter of about 20 nm, has attracted much attention because of its extremely good mechanical property.[12,15,16] Very recently, Yano et al. used a high speed shearing method to develop transparent NC films, whose light scattering was effectively avoided because of dense packing of nanofibers.[1] Particularly, the CTE of NC is as low as that of quartz glass[1,2] making it suitable as a substrate of foldable displays. Herein, we describe a facile way to fabricate a novel transparent and photoluminescent foldable NC paper with impressive light emitting, mechanical properties, and thermal stability. This material can bring a new thinking on future electronic displays and 3D printing papers.

Generally, plant fibers have complex original structures and are of various directions.[17,18] In order to obtain NC, the original fibers should be first disassembled in water.[15,19] In this work, wood flour was selected as the starting material, in which lignin and hemicellulose were removed by the Wise method.[20] A NC paper with thickness less than 20 μm was then prepared by a simple suction filtration approach,[21] whose morphology was investigated by microscopy analyses. NC was uniformly and closely packed together (Figure 1a). In addition, almost no pores were determined for the paper, which was favorable to the inhibition of light scattering as well as the improvement of optical performance. From a further investigation of TEM, the average diameter of NC was determined to be less than 20 nm with a high length-to-diameter ratio (Figure 1b), which was desirable for good mechanical properties. Compared with an ordinary filter paper with nearly no transparency, the NC paper showed a transmittance higher than 60% at wavelength of 600 nm (Figure 2), under which patterns of the picture could be clearly seen. Furthermore, the density of material is important in terms of development of portable devices.[11] The NC paper possessed a density as low as 0.91 g cm^{-3}, indicating its advantage of light weight.

As a semiconductor nanocrystal, quantum dot (QD) has been already used in the fields of biolabeling and integrated optical electronic devices,[22−26] because of its high quantum yield, long fluorescence lifetime and broad absorption

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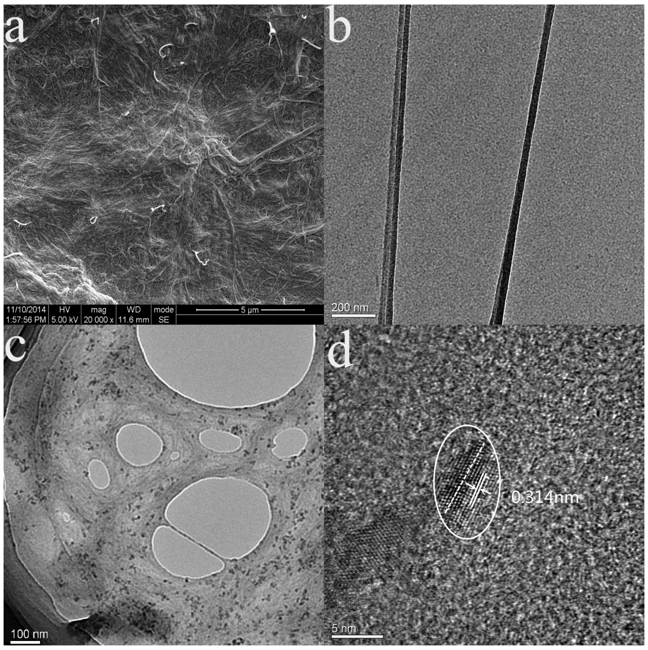

Figure 1. (a) SEM and (b) TEM images of NC. (c) TEM images of NC-QD composite. (d) HRTEM image of ZnSe QD.

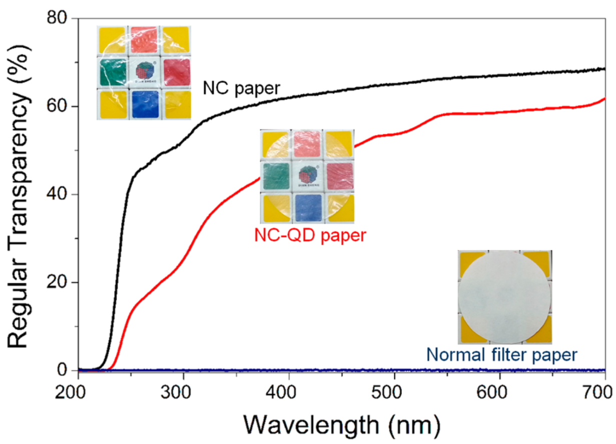

Figure 2. Light transmittance of normal filter paper, NC paper, and NC-QD paper. Inset are their photos.

spectra.[27−29] Nevertheless, high toxicity of QD is the main obstacle to its wide applications. Considering the long-term contact with human body, biocompatible QDs are more expected to be used as an optical material. In this work, ZnSe QD with a good light-emitting property as well as biocompatibility was synthesized.[27,28] Its characteristic XRD peaks were detected at (100) 28.8°, (220) 47.6°, and (311) 56.3°, suggesting the QD was of a zinc blende cubic crystal structure[27,29] (Figure S1 in the Supporting Information). To further confirm the presence of Zn and Se as well as investigate their molar ratio in QD, XPS analysis was performed. As shown in Figure S2 in the Supporting Information, molar ratio of Zn versus Se was about 5.94:1, which was caused by excessive feeding of Zn^{2+} during the synthesis of QD. Moreover, composition of the QD was further confirmed by ICP-AES measurement (5.33:1). The Raman peaks at 213 and 481 cm^{-1} were attributed to the longitudinal optical 1LO phonon mode and 2LO photon mode of ZnSe (Figure S3 in the Supporting Information). Compared with previous reports,[28] the red-shift of two peaks was caused by the QD size and different excitation line (532.17 nm in this work). During the synthesis of ZnSe QD, 3-Mercaptopropionic acid (MPA) was added as a stabilizer to maintain the QD structure and improve its solubility in water. The optimum molar ratio of Zn^{2+}:NaHSe:MPA was confirmed to be 25:1:83. ZnSe QD synthesized at the feeding ratio had a high quantum yield of 40.5% (using rhodamine B as a standard) compared with previous reports[27] (Figure S4 in the Supporting Information), which can be due to uniform size of QD.[30] Moreover, a positive correlation was determined between the concentration of ZnSe QD and its fluorescence intensity, complying with the Lambert−Beer's law. Particularly, luminescence property of the QD maintained well even after 1 month storage at room temperature (Figure S5 in the Supporting Information), presenting a good stability and a long fluorescence lifetime. In addition, its fluorescence excitation and emission spectra were not obviously changed in the aqueous solution containing NC (Figures S6 and S7 in the Supporting Information).

Because of the presence of MPA, the ZnSe QD exhibited a good solubility in water, which was convenient for the homogeneous mixing with NC. Although the suction filtration method can be still employed to prepare the NC-QD composite paper, most ZnSe QDs passed through the filtration membrane, resulting in a quite low retention rate at 21.3%, which was not desirable for development of optical materials with good luminescence properties. Polyethylenimine (PEI) is well-known and possesses abundant amino groups that can form hydrogen bonds with both carboxyl and hydroxyl groups. To confirm whether the interaction existed in the composite system, we conducted FTIR measurement on NC/PEI and ZnSe/PEI blends, respectively. Compared with native NC and PEI, their blend showed a broadened peak within 3100−3500 nm, which red-shift from 3416 to 3371 cm^{-1} (Figure S8a in the Supporting Information), indicating the presence of hydrogen bond between NC and PEI. Moreover, the peak at 1680 cm^{-1} attributed to the carbonyl group of MPA attached on ZnSe shifted to 1622 cm^{-1} after mixing with PEI (Figure S8b in the Supporting Information), which suggested hydrogen bonds were also formed between ZnSe QD and PEI. Therefore, a retention rate of ZnSe QD as high as 85.6% was achieved for the preparation of NC-QD paper in the presence of PEI by the same suction filtration method, which meant the QD content in the NC-QD paper was 29.97%.

Generally, the dispersion of filler in matrix is a very important issue for composites. As evaluated by TEM (Figure 1c), ZnSe QDs were well-dispersed in the NC matrix without aggregation, which would allow maintenance of the flexibility of composite paper. Size of the QD was observed to be about 5 nm (Figure 1d). The particles still possessed well-resolved lattice fringes, demonstrating the good preservation of their crystalline structure during preparation of the composite paper. In addition, interplanar spacing (3.14 Å) calculated from the HRTEM image is in good agreement with (3.09 Å) that from XRD.

For the sake of a higher transparency, an acrylic resin was selected as a coating layer on the NC-QD paper.[1,2] As shown in Figure S9 in the Supporting Information, the surface of NC-QD paper became smooth after being coated with the acrylic resin, and root-mean-square roughness of its surface was decreased from 768 ± 5.70 to 14.5 ± 0.50 nm. For the NC-QD paper, although a slight decrease in transmittance attributed to the absorbance of ZnSe QD was detected (Figure 2), the

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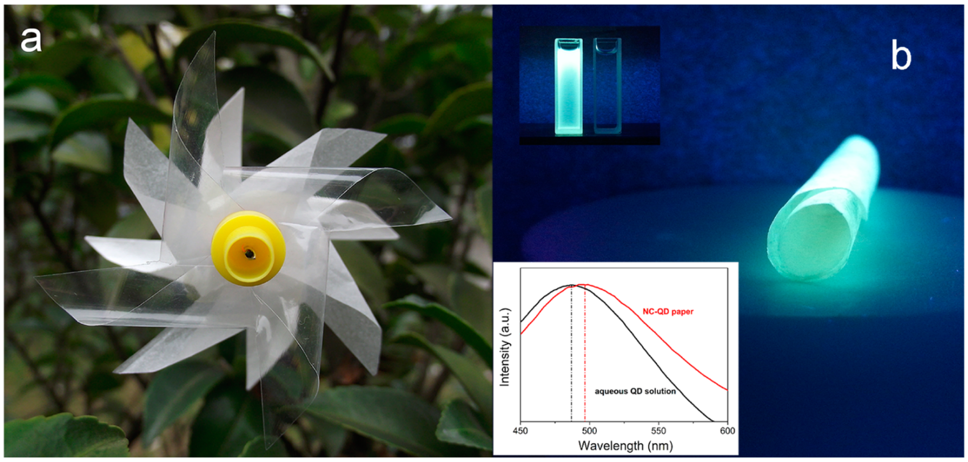

Figure 3. (a) Optical images of normal filter paper (bottom layer), and NC-QD paper (middle layer) and coating with acrylic resin coating (top layer). (b) Photo of NC-QD paper at luminescent state with an excitation at 365 nm. Inserted are the images of aqueous ZnSe QD solution and water excited under the same condition as well as fluorescence spectra of ZnSe QD solution and NC-QD paper.

underlying picture could still be clearly seen, which meant the appearance of NC paper was not obviously influenced by the incorporation of QD. Besides that, the presence of ZnSe QD did not affect flexibility of the NC paper, which could be still rolled without any crack at both normal and light-emitting states (Figure 3a, b). Because of the photoluminescence of ZnSe QD, the composite paper can emit a cyan fluorescence. Compared with the neat QD, the fluorescence spectrum of NC-QD paper just presented a slight 8 nm red-shift (Figure 3b and Figures S6 and S7 in the Supporting Information), indicating that nearly no difference in photoluminescence existed between them. As a display material, furthermore, a good mechanical property as well as a dimensional stability is generally required. NC paper possessed a good mechanical property with the tensile strength and Young's modulus of 119.3 MPa and 4.4 GPa, respectively. Compared with that, only a slight decrease in mechanical property was brought about after introduction of QD; that is, tensile strength and Young's modulus of the resultant composite paper were maintained at 109.8 MPa and 4.0 GPa. Moreover, the CTE of NC-QD paper was as low as 6.0 ppm/K (Table 1), and its initial degradation temperature

Table 1. Mechanical Property and CTE of NC and NC-QD Papers

sample	tensile strength (MPa)	Young's modulus (GPa)	CTE (ppm/K)
NC paper	119.3 ± 5.7	4.4 ± 0.2	3.7
NC-QD paper	109.8 ± 5.8	4.0 ± 0.1	6.0

was 235 °C that was much higher than general application temperature (Figure S10 in the Supporting Information). It meant the resultant composite paper could be normally used within a wide temperature range from at least 0 to 150 °C and completely met the needs of electronic devices. However, it should still be noted that the water/organic solvent resistance of the paper was not satisfied; that is, the paper presented a decreased fluorescence intensity after being immersed in water or ethanol (Figures S11 and S12 in the Supporting Information), which was attributed to the hydrophilicity of NC as well as easy diffusion of QD out from NC matrix.

In summary, a simple suction filtration method was reported in this work to fabricate a thin photoluminescent NC paper, in which ZnSe QD with a high quantum yield was incorporated as a functional filler. PEI was added in order to enhance the retention rate of ZnSe QD in the composite paper, which was favorable to the photoluminescence intensity improvement of resultant paper. Particularly, the functional paper possessed a good transparency and flexibility, that is, it could be easily rolled. Furthermore, a quite low CTE as well as an excellent mechanical property was detected for the paper, which allowed its application within a wide temperature range and in different occasions. In a word, we believe the environmentally friendly, light, and foldable light-emitting paper can bring us a bright prospect in the field of electronic devices, and development of functional papers emitting various fluorescent colors is under way.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, FTIR, XRD, XPS, Raman and fluorescence measurements. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02011.

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Notes

The authors declare no competing financial interest.

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