Fabrication of Ultrathin ZnO Nanocrystal-nanocellulose Composite Paper

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Abstract: We demonstrated a method to fabricate an ultrathin (~2 μm) ZnO nanocrystal (NC)-nanocellulose composite paper through solvent exchange. The paper is extremely transparent in visible light and shows photoluminescence under ultraviolet(UV) excitation. It can be applied towards photodetection applications.

I. Introduction

Driven by consumer needs and technology breakthroughs, we are entering an era of flexible devices, which greatly eases our daily life. While we are witnessing the commercialization of devices such as flexible OLED displays and foldable solar cells, they are more based on conventional device structures and materials. Recently, nanocellulose paper[1, 2] has been recognized for its superior performance in light transmittance, material strength and eco-friendliness, and applied towards a lot of optoelectronic applications. Being nano-sized and hydrophilic, nanocellulose can also be readily mixed with other nanomaterials in solution and create composite structures for different functionality.[3] Previously we have demonstrated quantum dot-cellulose composite structures for flexible photodetection in vertical device structures[4, 5]. However, the commercial or natural cellulose structure such as tracing paper or reed membrane have large thickness and fixed porosity, which make it hard to achieve devices with high performance. We discovered that with nanocellulose, we are able to make ultrathin transparent freestanding semiconducting film with the incorporation of water-soluble ZnO nanocrystals and use it for UV detection.

For nanopaper making, people commonly start with filtering the nanocellulose out from a suspension to form a gel cake and then dry the gel to form a paper. The gel can either be dried single-sidedly with one side in contact with a flat surface and another touching a porous structure for water extraction, or dried double-sidedly with both sides in contact with porous materials. For a film that is fairly thick, tens of micrometers, either way works well since the strength of the paper is able to hold the gel structure. However, when it comes to ultrathin (~2 μm) paper making, the adhesion between the gel and filter or drying surface is much stronger than the inner tension between nanocelluloses. Hence it's almost impossible to dry the nanopaper single-sidedly. Also the strong surface tension of water will easily crank the freestanding film. Thus we also need to modify the double-sided drying method.

II. Fabrication

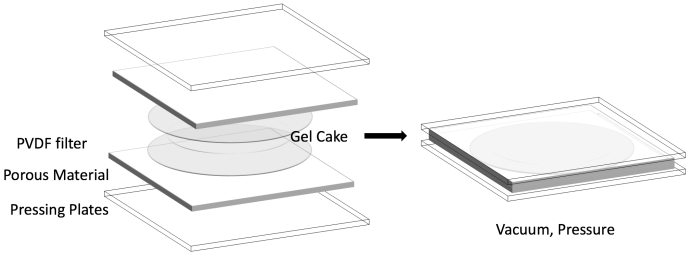


Fig. 1 Drying setup of ZnO NC-nanocellulose paper

The ZnO nanocrystals are synthesized through well-developed wet-chemistry methods. They have a size of 6-8 nm and are suspended in DI-water. Nanocelluloses are also suspended in DI-water after TEMPO-mediated oxidation and high pressure microfluidizing. These two materials are mixed proportionally depending on the need of performance, typically 1:1 in mass ratio in our case, with ultrasonication. The

mixed aqueous suspension's vacuum filtered to leave a thin gel cake which is later quickly peeled off from the filter on a plain acrylic plastic. Then the gel/acrylic is soaked in isopropanol alcohol to do a solvent exchange and to suspend the gel cake which would be otherwise difficult to achieve in free space or in water. Eventually the freestanding gel is sandwiched between two PVDF filters and placed under vacuum with pressing, as is shown in Fig. 1, for drying overnight.

III. Results and Discussion

The results for the end product are shown in Fig. 2. More than 97% of visible light is transmitted through the nanopaper. We can clearly see that the paper is more transparent than cover glass slides and tracing paper. With it's ultrathin edge, it's actually hard to notice without careful searching. The paper shows uniform photoluminescence(PL) under UV excitation. The PL wavelengths are in cope with the PL of ZnO NCs and thus indicating that the ZnO NCs are still functional. The non-uniformity and bright spots in the picture are more due to the background table surface because the nanopaper is very transparent.

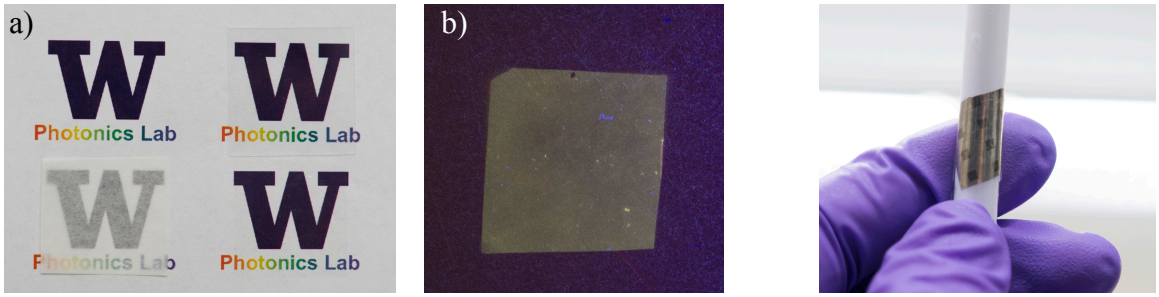


Fig.2 a) Transparency comparison of between air, cover glass slides, tracing paper and ultrathin ZnO NC embedded nanopaper (from left to right, up to down); b) Yellowish green color photoluminescence of the ultrathin nanopaper under 365nm UV excitation

Fig. 3 Ultrathin flexible UV photodetector on nanopaper wrapped around a pen

We also managed to fabricate flexible photodetectors on the ultrathin nanopaper. The image of an array of photodetectors on nanopaper is shown in Fig. 3. The devices can be bent freely around cylindrical surfaces.

IV. Conclusion

We have developed a new way of fabricating nanocellulose papers through solvent exchange to achieve ultrathin film thickness. ZnO NCs can be readily mixed with nanocellulose to prepare ZnO NC-nanocellulose composite papers. The ultrathin paper appears to be extremely transparent in visible wavelength range and shows photoluminescence under UV excitation. The nanopaper can also be used to fabricate photodetector arrays for UV detection.

References

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