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Strongly reduced thermal conductivity in hybrid ZnO/nanocellulose thin films

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ABSTRACT

Utilizing a combination of atomic layer deposition and dip-coating techniques, we have incorporated natural nanocellulose fibers into an inorganic matrix in order to create a layered hybrid inorganic–organic thin-film structure. Such layer-engineered hybrid materials with an unorthodox combination of components are highly potential candidates for exciting new properties. Here, we show a more than an order of magnitude reduction in the cross-plane thermal conductivity for ZnO thin films achieved with the regular inclusion of the cellulose nanofiber layers. We foresee that a similar approach as presented here for ZnO could also be applied to other inorganic materials based on earth-abundant elements to influence their thermal transport properties.

Introduction

In the form of plant fibers, cellulose has traditionally been exploited in materials such as paper and textiles, but the focus has somewhat shifted after modern technology enabled the effortless isolation of the smallest supramolecular units, dubbed nanocellulose, from the fiber matrix [1, 2]. Within the past decade, the potential of nanocellulose has been demonstrated in diverse applications, including nanocomposites [3], self-healing materials [4], responsive membranes [5], cage-like microcapsules [6] and biosensors [7]. There are, however, as of yet relatively few reports on incorporating nanocellulose into inorganic–organic hybrid materials [8–10]. In this paper, we demonstrate how layers of cellulose nanofibers, isolated via 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical-catalyzed oxidation, can be used to greatly suppress the thermal conductivity of ZnO thin films. The TEMPO-oxidized cellulose nanofibers (TOCN) are well suited for such a purpose: Besides the undisputable renewability, their small width (3–4 nm) coupled with a considerable length (µm scale) provides a strong case for phonon scattering at the inorganic–organic interfaces for subduing the thermal conductivity, as reported for other hybrid materials [2, 11–14]. In addition, the

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high charge density introduced by TEMPO-oxidation allows the effortless manipulation of TOCNs in water instead of hazardous solvents, and their controlled deposition from a dispersion onto solid surfaces is straightforward [2, 15, 16].

Hybrid materials are attractive candidate materials for thermoelectric energy harvesting, since it is possible to fabricate layered hybrid superlattice structures in such a way that the thermal conductivity of the material is reduced, while the electrical properties are maintained, or even improved [17–21], a goal which has proven very challenging to achieve in conventional materials [22]. This could in particular provide us the means to enhance the thermoelectric characteristics of inorganic materials such as semiconducting oxides that are based on cheap and safe earth-abundant elements only but often suffer from too high thermal conductivities. Recently, we successfully employed a combination of two state-of-the-art gas-phase thin-film techniques, i.e., atomic layer deposition (ALD) for inorganic layers [23] and molecular layer deposition (MLD) for simple monomolecular organic layers [24–26], to fabricate hybrid superlattice thin-film structures with enhanced thermoelectric characteristics [18, 19, 21, 27]. The MLD technique, however, is not ideal for depositing polymer layers, particularly from native polymers and their respective nanosized supramolecular entities. Therefore, we introduce here a process consisting of ZnO ALD and TOCN dip-coating steps to demonstrate a large reduction in the thermal conductivity of ZnO and compare it to previously employed organic monolayers.

Experimental procedure

Hybrid inorganic–organic thin-film structures were fabricated using a process consisting of multiple zinc oxide ALD depositions separated by steps of dip-coating in a water dispersion of TEMPO-oxidized cellulose nanofibers. The ALD depositions were performed at 170 °C in a Picosun R-100 ALD reactor, using diethyl zinc and water precursors, with pulse/purge times of 0.1 s/4 s and 0.4 s/4 s, respectively. Each film consisted of x ALD cycles of ZnO deposited on sapphire substrates, followed by N number of steps where the films were removed from the ALD reactor, dip-coated by insertion into a 0.01% water dispersion of TOCN and re-inserted into the ALD reactor, where x cycles of ZnO were deposited on top

of the organic layer. A series of depositions were performed where N was set at 3, 5 or 9, and x was varied so that the total number of ALD cycles in a film would be 600 (i.e., N values of 3, 5 and 9 corresponded to x values of 150, 100 and 60, respectively), resulting in a total film thickness of approximately 100 nm (see illustration in Fig. 1c).

The structure of the hybrid films was analyzed using X-ray reflectivity (XRR, PANalytical X'Pert MPD Pro Alpha) and Fourier transform infrared spectroscopy (FTIR, Nicolet Magna 750), and atomic force microscopy (AFM) was used to observe the morphology of deposited TOCNs on ZnO before the subsequent ALD step. The AFM images were collected with an E scanner in intermittent contact mode with NSC15/AIBS silicon cantilevers by Ultrasharp μmasch (Tallinn, Estonia) on a MultiMode 8 scanning probe microscope by Bruker AXS Inc. (Madison, WI, USA).

The cross-plane thermal conductivity of the films was determined with the time-domain thermoreflectance (TDTR) technique at room temperature, and the thermal conductivities of the samples were obtained by fitting of the measurement data with a three-layer thermal model that account for: (1) an Al film transducer (necessary for TDTR measurements to relate the measured reflectivity to temperature); (2) the ZnO/TOCN sample; and (3) the sapphire substrate. The pertinent details of the experimental setup and the analysis procedure to determine the thermal conductivity of the hybrid thin films can be found in Refs. [12, 13].

Results and discussion

The XRR patterns and FTIR spectra, along with schematics describing the layer structure of the sample series, are shown in Fig. 1. Clear signs of a superlattice structure can be seen in the XRR data, as evidenced by the larger superlattice peaks visible in the patterns along with the smaller peaks arising from the entire hybrid thin film (for a quantitative treatise, see Table S1). The separation of the super-lattice peaks between the $N = 3$ and $N = 5$ patterns can also be seen to grow larger as the TOCN layer separation becomes smaller, as expected. The somewhat messy pattern of the $N = 9$ sample, however, could be a sign that some of the TOCN layers in that sample are not formed completely. The XRR patterns
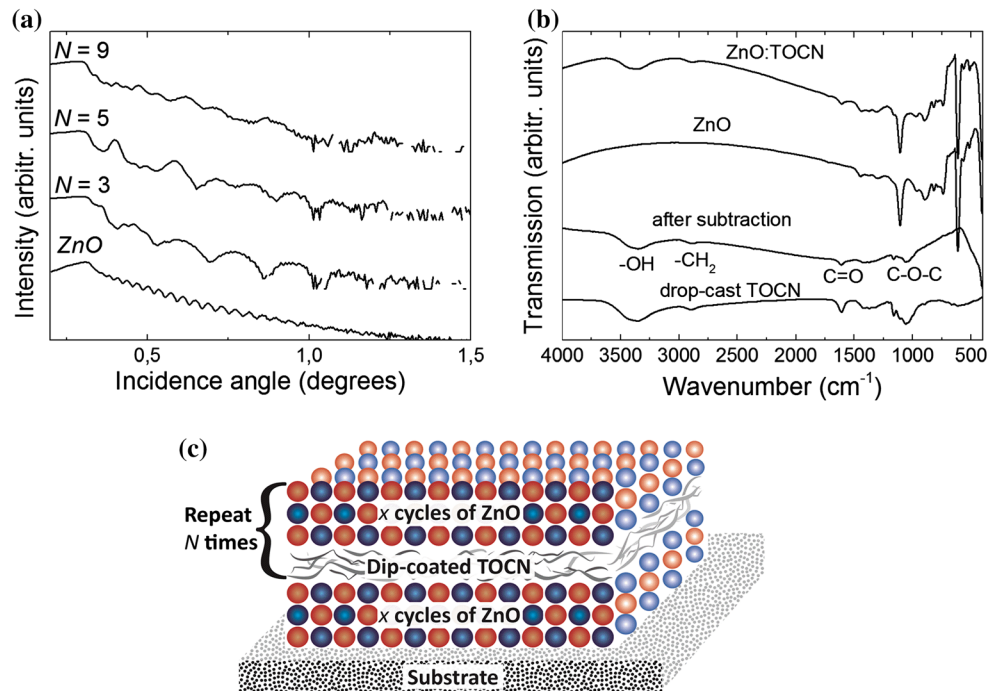
Figure 1 **a** XRR patterns and **b** FTIR spectra of representative ZnO/TOCN films, including **c** a schematic illustrating the film composition.

of the hybrid films as a whole are also not very sharp, which could be seen as a sign that the interfaces between the ZnO and TOCN layers are not perfectly defined. In fact, AFM images taken from the dip-coated TOCN layers, obtained before the ZnO over-layer deposition, revealed a rather loose network of individual TOCNs on ZnO (Fig. 2), suggesting that ZnO could also grow between the cellulose nanofibers during the ALD process. It is somewhat surprising that the cellulose nanofibers do not coat the ZnO surface more completely, considering that the electrostatic attraction between the negatively charged TOCN and the positive ZnO surface [28] would be expected to facilitate the coating of the surface. The FTIR spectra in Fig. 1b compare the peaks from a ZnO/TOCN film to those of ZnO and a drop-cast TOCN film (the intensity of which has been reduced by a factor of 10) to confirm that the characteristic functional groups of the cellulose nanofibers are detected from the hybrid films. Although very much suppressed, the same peaks that are detected from the drop-cast cellulose nanofibers can be seen in the ZnO/TOCN films as well, suggesting that there is no deterioration of the cellulose taking place during ZnO deposition. Taken together, the XRR, AFM and FTIR

measurements confirm that a layered hybrid material of ZnO and cellulose nanofibers was successfully fabricated.

The thermal conductivity values obtained from the TDTR measurements are listed in Table 1 along with values for ZnO and a number of ALD/MLD-grown ZnO/hydroquinone (ZnO/HQ) superlattices from a previous publication [19] for comparison purposes. It should be noted that while the organic layers are different, the methodology for the ZnO depositions and thermal conductivity measurements are exactly the same in this study and in Ref. [19]. All the ZnO/TOCN films display large reductions in their thermal conductivity of more than an order of magnitude compared to that of a ZnO thin film [29], and the effect becomes larger as the number of cellulose nanofiber layers is increased. This is expected, since the total number of ZnO ALD cycles in the films was kept constant at 600, so as the number of organic layers increases, the separation between individual TOCN layers decreases; more specifically, the period thickness changes from ~25 nm in the $N = 3$ film to ~10 nm in the $N = 9$ sample. Thus, not only were there more interfaces to scatter phonons in the films with the higher TOCN content, the layer thicknesses of the inorganic constituent start to become more
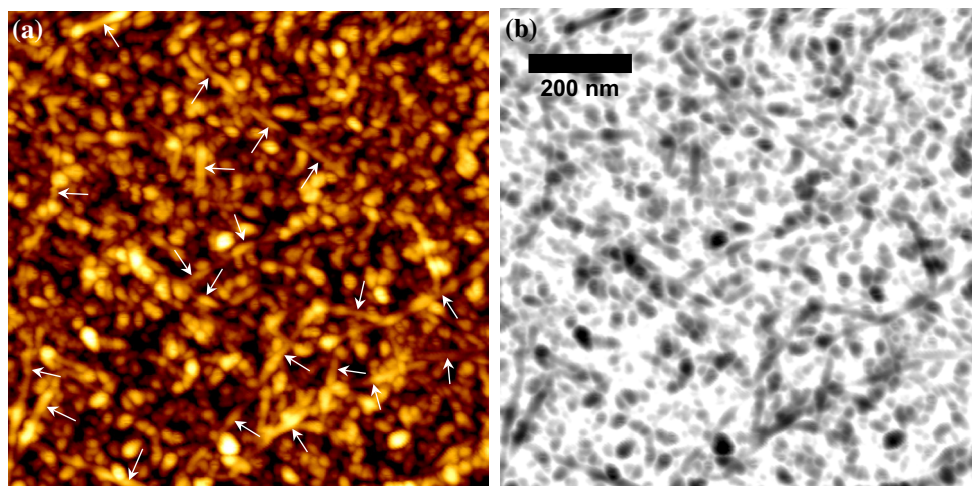
Figure 2 1×1 µm² AFM height images of a ZnO film with TOCNs deposited on top, before the concluding deposition step of the topmost ZnO layer: **a** typical gold-brown AFM image, **b** inverse gray scale image. *Arrows* perpendicular to the longitudinal dimensions indicate the positions of TOCNs, otherwise difficult to discern from the relatively rough ZnO surface.

comparable to the intrinsic phonon mean free paths in zinc oxide.

Compared to the ZnO/HQ hybrid films investigated previously, the TOCN layers appear to be more effective in limiting thermal transport in ZnO thin films, as can be seen from the reduction in the measured thermal conductivities in Table 1. The hydroquinone layers in the ZnO/HQ hybrids were deposited with MLD, and thus consist of a single organic monolayer, so it is not surprising that the TOCN layers would be more effective in reducing thermal conductivity due to the thicker size of the cellulose nanofibers formed during dip-coating as compared to the MLD-grown HQ monolayers. There is in fact a significant difference between the thicknesses of the two organic layers, which was determined by fitting XRR patterns obtained from the different hybrid samples, and the higher thickness of the TOCN layers appears to be the main factor in causing the difference in thermal conductivity. To illustrate this, the thermal conductivity values from Table 1 were plotted based on the films' superlattice periods (again, the separation between the organic layers) and are presented in Fig. 3a. In addition, the thermal conductivity of a ZnO/TOCN sample with a 49:1 layer ratio, extrapolated from Fig. 3a, was compared with ZnO/HQ samples having the same layer ratio but varying organic layer thicknesses (obtained from Ref. [12]), and the results are plotted in Fig. 3b. First of all, from Fig. 3a, it is clear that if the same superlattice is fabricated from TOCN and MLD-

Table 1 Thermal conductivity values measured from the ZnO/TOCN compared with previous results from ZnO/hydroquinone hybrids

N	κ (W m⁻¹ K⁻¹)	Reference
0	43	[29]
3	3.63 ± 0.27	This work
5	2.74 ± 0.18	This work
9	1.94 ± 0.14	This work
6 (ZnO/HQ)	7.16 ± 1.44	[19]
12 (ZnO/HQ)	4.15 ± 0.43	[19]

grown HQ monolayers, the TOCN layers result in a lower thermal conductivity, as listed in Table 1. Secondly, the thickness comparison in Fig. 3b reveals that there is a strong correlation between the thickness of the organic layer and the thermal conductivity of the hybrid superlattice film, irrespective of whether the organic layer consists of hydroquinone or cellulose nanofibers. It should be noted that the thickness value obtained for the cellulose nanofiber layers, 1.9 nm, is an underestimation because typical cellulose nanofibers have thicknesses over 3 nm. This discrepancy most likely arises from a combination of incomplete TOCN layer coverage (Fig. 2) and limitations in the simulation of XRR patterns when the interfaces are potentially very irregular.

One might have expected a larger difference between the thermal conductivity of the ZnO/TOCN
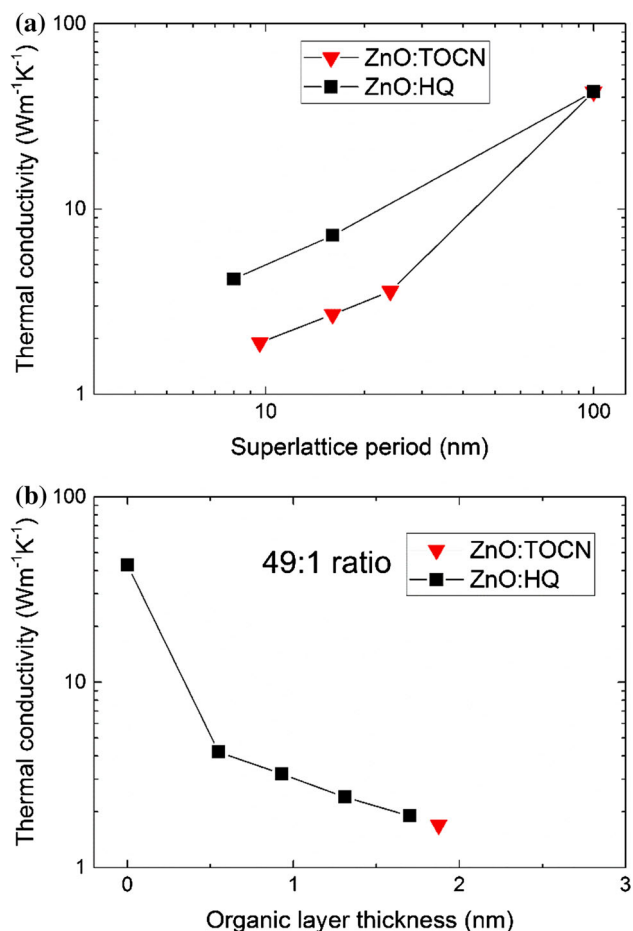
Figure 3 Thermal conductivity values of the ZnO/TOCN films compared with ZnO/hydroquinone hybrid films, based on **a** superlattice period or **b** thickness of the individual organic layers. ZnO/HQ data were taken from references [13, 19].

electrical properties of hybrid materials would be to use very large organic molecules with good electrical properties. However, simultaneous comparison of cross-plane thermal conductivities and electrical resistivities for a variety of hybrid inorganic/organic superlattices with varying structures and thicknesses of the organic layers are necessary before any definitive statements can be made on the matter.

Conclusion

Layered hybrid inorganic–organic thin films were fabricated from ZnO and cellulose nanofibers, and the TOCN layers were found to cause large reductions in the thermal conductivity of ZnO. The effect on thermal conductivity was larger than with the hydroquinone-based monomolecular organic layers investigated previously, which we hypothesize is due to the higher thicknesses of cellulose nanofibers compared to the monomolecular organic layers. The results suggest that the application potential of renewable materials can be further expanded into the field of sustainable thermoelectric materials.

Supplementary information

Thickness, roughness and density values obtained for the individual ZnO and TOCN layers through fitting of XRR patterns are provided in Table S1.

Compliance with ethical standards

Conflicts of interest   The authors declare that they have no conflict of interest.

and ZnO/HQ samples due to the rather different structures of the two organic constituents. The rigid and highly conjugated benzene ring that forms the backbone of the hydroquinone molecule could facilitate thermal transport across the organic layers, at least compared to the long carbon chains of the cellulose nanofibers. The similar results from the two organic substances could be explained by the sparsity of cellulose nanofibers deposited in the dip-coating process; it is feasible that an otherwise larger thermal conductivity reduction was offset by having an incomplete surface coverage of the nanofibers. Nonetheless, it appears clear that molecular size and organic layer thickness are the major parameters affecting the thermal conductivity of a layered hybrid material. This suggests that a good approach for minimizing thermal conductivity while maintaining

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