Preferred citation: C. Czibula, C. Ganser, M. Kratzer, F. Brumbauer, M. Kräuter, K. Shanmugam, W. Batchelor, M. Penn, M. Ebner, M. Pramstrahler, F. Pilat, H.-T. Chien, R. Schennach, B. Friedel and C. Teichert. Silver nanowires: A versatile tool for conductive paper. In **Advances in Pulp and Paper Research, Oxford 2017**, *Trans. of the XVIth Fund. Res. Symp. Oxford, 2017*, (W. Batchelor and D. Söderberg, eds), pp 723–737, FRC, Manchester, 2018. DOI: 10.15376/frc.2017.2.723.

SILVER NANOWIRES: A VERSATILE TOOL FOR CONDUCTIVE PAPER

C. Czibula[1,2], C. Ganser[1,2], M. Kratzer[1], F. Brumbauer[3], M. Kräuter[3], K. Shanmugam[4], W. Batchelor[4], M. Penn[3], M. Ebner[3], M. Pramstrahler[3], F. Pilat[3], H.-T. Chien[3], R. Schennach[2,3], B. Friedel[3,5] and C. Teichert[1,2]

[1] Institute of Physics, Montanuniversitaet Leoben, Austria
[2] CDL for Fibre Swelling and Paper Performance, Graz University of Technology, Austria
[3] Institute of Solid State Physics, Graz University of Technology, Austria
[4] Department of Chemical Engineering, Monash University, Victoria, Australia
[5] Energy Research Center, Vorarlberg University of Applied Sciences, Dornbirn, Austria

INTRODUCTION

Paper has a long tradition as a material in electronic components, for example, it is still used today as a dielectric in capacitors [1]. Here, like in many other applications of paper, one of the most important properties is that it is cheap. However, today many people consider paper as a renewable resource that should be used in a much broader scale in advanced materials (e.g. [2]). To get paper and other cellulose based materials established as an important building block in sustainable advanced materials, one needs to not only rethink paper properties. If paper should replace other materials, possibilities to adjust its properties to a certain device structure need to be further explored and investigated. Established views should be widened to allow a revival of paper as a material which is more than just a cheap substrate.

Applications of paper for microfluidic devices, e.g. [3], in sensors [4], in solar cells [5, 6] or as a dielectric in transistors [7] have been published recently. This demonstrates that paper can enter new scientific disciplines and markets successfully. In this

article, we will show that silver nanowires (AgNWs) are a very versatile tool to turn wood pulp paper [6], nanofibrillated (NF) paper, viscose fibres [8] and films made of regenerated cellulose conductive. Since all these various materials consist mainly of pure cellulose, a composite of an organic and an inorganic material is studied in detail. Our approach will increase the possible applications of paper in areas ranging from dielectrics towards conductors. Furthermore, results of the surface investigations of this interesting and exciting material combination with a special focus on atomic force microscopy (AFM) methods are presented giving a deeper insight into the surface morphology [9].

MATERIALS AND METHODS

Kraft pulp paper + AgNWs sample

20 × 20 mm^2 laboratory paper sheets with 16 g/m^2 were made of unbleached and unrefined kraft pulp (Monopol X, Frantschach, Austria) with a Rapid-Köthen sheet former (DIN EN ISO 5269–2:2004).

The AgNWs (diameter: 115 nm, length: 20–50 μm) were supplied by Sigma-Aldrich and dispersed in isopropanol (0.5 wt%). Via dip-coating (SDI company, Nano-DIP ND-0407) the AgNWs were deposited on the paper sheet [10].

NF paper + AgNWs sample

The nanofibrillated paper was produced by a rapid spray coating technique. A nanocellulose (Celish KY 100S, DAICEL Chemical Industries Limited) suspension with 1.5 wt% concentration was sprayed onto a polished stainless steel plate, which was moving on a conveyor at a velocity of 0.32 cm/s. After spraying, the sheet was air dried under restraint. The processing time to prepare spray coated nanofibrillated paper was approximately 1 min. The aspect ratio of the nanocellulose from sedimentation is 147 and the average fibre diameter obtained from SEM measurements is 73 nm [11, 12].

Ethylene glycol (>99 %), copper (II) chloride (99 %), polyvinylpyrrolidone (360,000 g/mol) (PVP) and silver nitrate (>99 %) have been purchased from Sigma-Aldrich and used without further purification. The AgNWs were synthesized similar to [13]. In brief, to the volume of 100 mL ethylene glycol as solvent, 0.6 mL of copper chloride solution (1.14 mg/mL) were added under stirring and heated to 144 °C. After adding 22.5 mL of PVP solution (25 mg/mL) the solution was cooled to 126 °C. Finally, growth of the silver nanowires was initiated by adding the precursor in form of 5 mL of silver nitrate solution (100 mg/mL) and heating at 150 °C for 50 min. After cooling to room temperature, the obtained AgNWs were

washed 5 times via centrifugation and dispersion in deionized water. The AgNWs were kept as a suspension in deionized water until further processing. Where applicable, the water was exchanged by ethanol for easier deposition.

Viscose fibre + AgNWs sample

Hollow viscose fibres with a length of about 40 mm were provided by Kelheim Fibres GmbH (Kelheim, Germany) and glued with nail polish [14] to a glass for better surface access for the AgNWs during the AgNW deposition.

The same AgNWs as for the kraft pulp paper sheet were used and deposited via dip-coating [10].

Cellulose film + AgNWs sample

The thin films of pure cellulose [15] were fabricated by spin coating a toluene solution of trimethylsilyl cellulose (TMSC) onto glass substrates according to the method published in [16]. After solvent exchange, the AgNW were added to the toluene solution. Subsequently to spin coating, these films were regenerated to cellulose by hydrolysis with gaseous HCl.

Characterization methods

Optical microscopy in reflection mode was performed using a Zeiss Axio Lab.A1 with an integrated Axiocam 105 color digital camera. Electron microscopy images were obtained with a NOVA 200 Nanolab FIB/SEM dual beam microscope. X-ray photoelectron spectroscopy analysis (XPS) was done at the Institute of Chemistry of Polymeric Materials at Montanuniversitaet Leoben, Austria using a K-Alpha™ + XPS system from Thermo Fisher Scientific Inc. The spectrometer is equipped with an Al X-ray source (1486.6 eV) operating at a base pressure in the range of 10^{-8} to 10^{-10} mbar. High resolution scans were acquired at a pass energy of 50 eV and a step size (resolution) of 0.1 eV. The instrument work function was calibrated to yield a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold. All measurements were performed at room temperature. The peaks were fitted utilizing Gaussian/Lorentzian mixed functions employing a linear background correction (program XPSPEAK41).

Electrical characterization of the AgNW-coated viscose fibre and regenerated cellulose films was carried out with electrical microprobes in argon atmosphere, using a Keithley 2636A source-measure unit. Here, droplets of silver paste are deposited on the sample in a distance of 2 mm and contacted by the microprobes. The electrical resistance of the kraft pulp and NF paper with AgNWs was measured using a home built two-point-probe measurement apparatus [10] (see Figure 4). It

consists of two metal clamps and an electrically isolating bottom plate. The distance between the clamps was about 1 cm. Due to the typically high contact resistance the sensitivity of the setup is limited and it is difficult to make clear statements about the influence of surface roughness and contamination effects.

AFM [17] was performed employing an Asylum Research MFP-3D device (Santa Barbara, CA, USA). The AFM system was equipped with a closed-loop planar x-y-scanner with a scanning range of 85 × 85 μm^2 and a z-range of 15 μm. Standard topography measurements were obtained in tapping mode with Olympus AC160-TS silicon probes. The cantilevers had a spring constant of about 30 N/m and the tips a radius of about 10 nm. Kelvin Probe Force Microscopy (KPFM) [18, 19] is an AFM based method for the determination of local contact potential differences (CPD) between probe and substrate. Here, probe tips with a conductive Pt/Ir coating and a tip radius of about 25 nm were used (Access EFM, AppNano). Bringing two materials with different work functions into contact results in a charge transfer between them in order to align their Fermi levels. As a result, a potential (CPD) is generated between them. The same holds true for the conductive AFM probe and the surface. The CPD between them causes an electric field influencing the tip movement. In KPFM, the CPD between tip and sample is compensated by applying a dc-voltage. Unlike in classical Kelvin probe, where the compensating current upon variation of the distance between substrate and electrode is nullified, KPFM uses the electrostatic force between tip and substrate. Since an AFM probe is a highly sensitive force sensor, this allows for high sensitivity in CPD measurement. In this case, the so called two-pass method is applied. First, the topography is scanned in standard intermittent contact mode and in a second pass this topography is retraced at a set lift height. During the second pass, the cantilever is electrically excited by the superposition of a DC voltage and an AC voltage close to the cantilever's resonance frequency ω. The DC voltage is adjusted by a feedback to nullify the capacitive force F_ω at frequency ω. The DC voltage – necessary to compensate F_ω at each tip position – corresponds to the CPD.

The mechanical shifting tests of the AgNWs were performed by taking advantage of the lithography and manipulation abilities of the MFP-3D software. In this software, it is possible to draw lines on the topography images which represent tip paths. Here, the applied force was about 18 μN, and the tip was dragged across the surface with a velocity of 1 μm/s. The data from all AFM measurements was processed with the open-source software Gwyddion [20].

RESULTS AND DISCUSSION

Electrically conductive paper can be fabricated in many different ways. One can metallize the surface of a sheet of paper, integrate carbon black, carbon nanotubes,

and graphene into paper sheets, or one can coat the paper with conductive inks as well as with conducting organic polymers. In all cases, one of the main problems is the adherence of the additives to the paper. Especially when aiming for a flexible device, it is crucial that the electrically conductive material adheres well to the paper. Another important problem is that if one needs specific optical properties, most of these methods fail because they darken the paper. Conductive inks and organic polymers lead to high conductivities, but always at the expense of transparency.

We have shown recently that a laboratory hand sheet made of unbleached kraft pulp fibres can become electrically conductive by integrating AgNWs [6]. Like all metallic nanowires, the AgNWs are stabilized in suspension via surface functionalization. Therefore, the interaction of this surfactant with the paper will determine the adherence of the AgNWs. In the case presented in [6], the commercial AgNWs showed a very good adherence to the paper. The resistivity of paper samples with the best balance between high optical transparency and low sheet resistance reached 38 Ω/sq [6], which is in the range of the common transparent conductor indium tin oxide (ITO). For comparison, an ITO film on glass has a sheet resistance of 5–15 Ω/sq, ITO on a plastic substrate has 30–60 Ω/sq, and most organic conductors like PEDOT:PSS or carbon nanotubes have around 200–800 Ω/sq [21].

Bulk silver has a resistivity of about $1.6*10^{-8}$ Ωm at room temperature. For the AgNW-coated kraft pulp sheet, a well conducting network was already established at low AgNW amounts. By varying the solid content of the AgNW dip-coating suspension between 0.05 and 0.50 wt%, it was possible to adjust the sheet resistance to values between 5 and 160 Ω/sq [6].

The AgNW network on the paper is presented in Figure 1 as optical micrographs and scanning electron microscopy (SEM) images. In Figure 1(a)–(b), one can see that the AgNWs increase the reflectivity of the paper, without much change in the other optical properties. In Figure 1(c), it becomes clear that the AgNWs tend to adhere well to the cellulose fibres and to each other.

A closer look on the AgNWs on the pulp fibre sheet is presented in AFM topography scans in Figure 2. One can clearly recognize the AgNWs on the cellulose fibre. Cellulose fibres are about 30 μm in diameter and have a length of roughly 4 mm. In comparison, the AgNWs diameter is about 115 nm and the length ranges from 20 μm–30 μm. In the SEM image (Figure 1(c)), it seems that the AgNWs are conforming very well to the pulp fibre surface. The AFM scans, however, suggest that the AgNWs have large distances between adjacent points of attachment and do not conform completely to the complex surface structure of the pulp fibres. Therefore, the AFM data suggests a stronger interaction between AgNWs and a weaker interaction between the AgNWs and the paper fibres. This is in contrast to what one would expect and interpret by only looking at the SEM

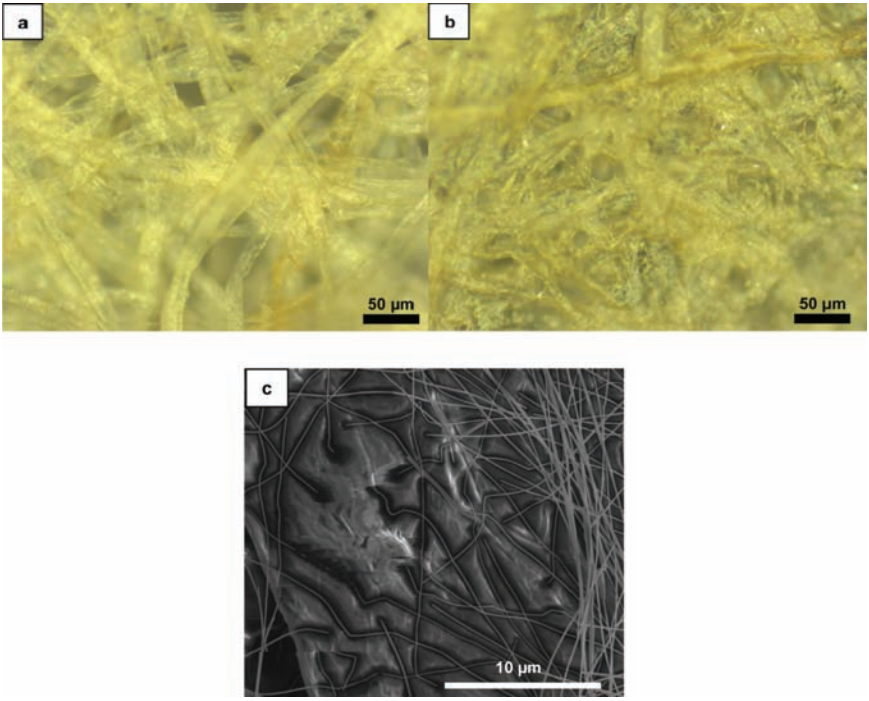

Figure 1. Optical microscopy images of: (a) the pristine soft wood kraft pulp fibre sheet; (b) the same sheet after dip coating with AgNWs; (c) SEM image of one AgNWs decorated cellulose fibre of the sheet shown in (a, b).

image. To further investigate the properties of AgNWs on cellulosic materials, KPFM was applied to measure CPDs as presented in Figure 3(b). The CPD values of the AgNW appear to be 40 mV above the cellulosic background. However, even though some individual AgNW are clearly distinguishable in the morphology, they exhibit a similar CPD value as the cellulose matrix. One explanation could be that these wires are coated by residuals originating from the preparation process (see red arrows in Figures 3(a)–(b)). Another possibility might be that these AgNWs are electrically insulated from the AgNW network. However, even in such a case a stronger difference in CPD values of charged AgNWs in comparison to those of the cellulose would be expected.

In another approach, it was also tried to turn nanofibrillated (NF) paper into a conductor by AgNW deposition. Here, conductivities comparable to standard transparent conducting oxide electrodes have been achieved. Also, bending of the

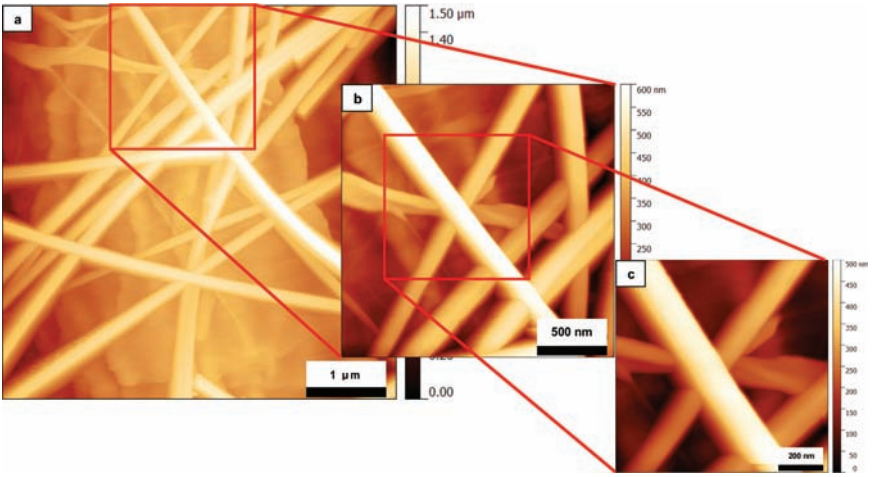

Figure 2. (a)–(c) AFM topography images of a AgNWs dip coated sheet of unbleached softwood kraft pulp [9].

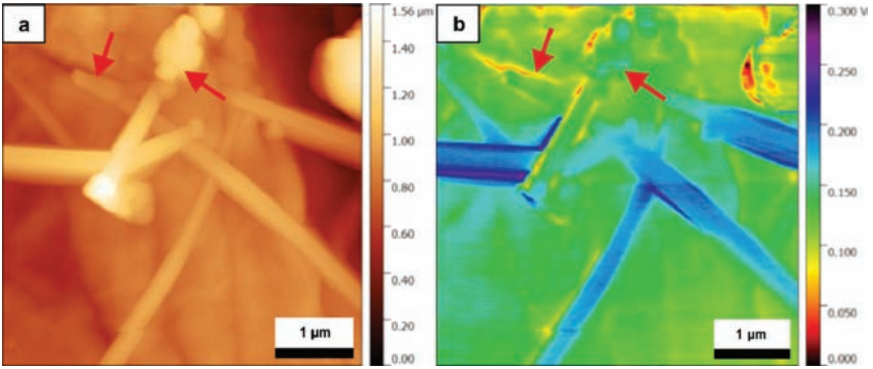

Figure 3. (a) 5 × 5 µm^2 AFM topography and (b) corresponding KPFM CPD image. (b) shows the contrast between AgNWs (blue) and the cellulose substrate (green). The red arrows indicate possible residuals from the preparation process [9].

NF paper sheet based electrode by 180° with a bending radius of about 2.5 mm as demonstrated in Figure 4 resulted in unaltered resistance. Before AgNW deposition, both sides of the NF paper sheet were investigated by optical microscopy as well as AFM to identify any differences in surface roughness. Optically, it was

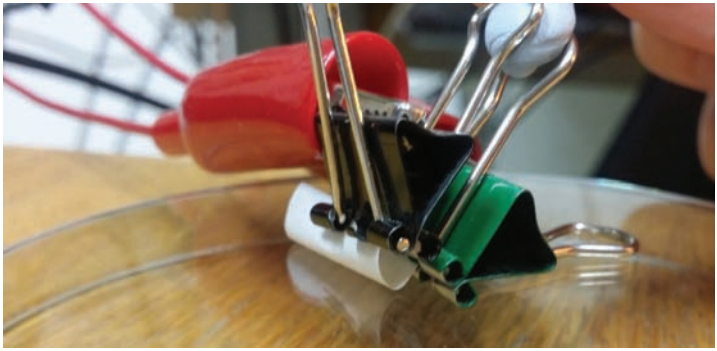

Figure 4. Electrical characterization setup for the AgNW-coated NF paper. Here, also an example for the bending is presented.

possible to distinguish between both sides. This is due to the production of the paper by spray coating.

One side of the sheet seems smoother, which is probably the side in contact with the metal plate. However, AFM measurements revealed only a small difference in surface roughness, but still the apparent smoother side of the paper was used for the AgNW deposition. In Figure 5, optical microscopy images of a bare NF paper and one after deposition of AgNWs are shown.

Comparing Figure 5(a) with Figure 1(a), it is obvious that the kraft pulp paper sheet is a much rougher substrate than the bare NF paper sheet.

For the NF paper, also a detailed AFM topography study has been carried out.

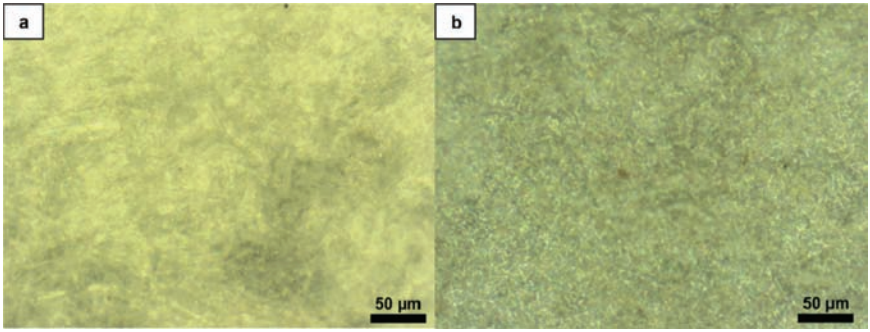

Figure 5. Optical microscopy images of the NF paper before (a) and after (b) the AgNW deposition.

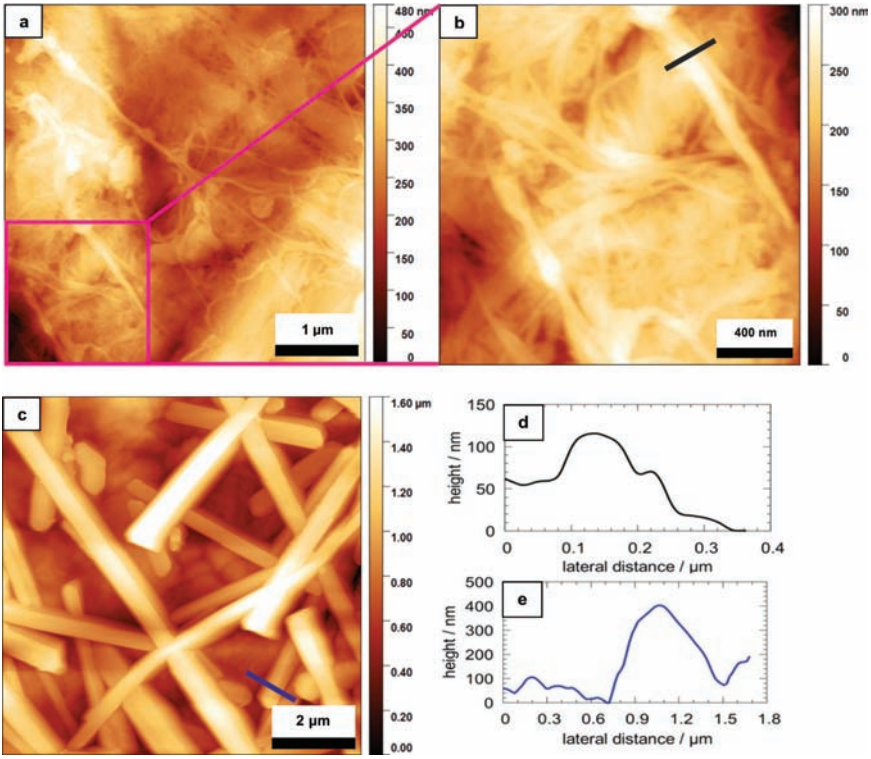

Figure 6. AFM topography images of the NF paper before (a), (b) and after (c) the AgNW deposition. (d) shows the corresponding line profile (indicated by the black line) in (b), (e) represents the corresponding line profile (blue line) in (c).

In Figure 6, exemplary AFM topography images of the NF paper before (6(a), (b)) and after (6(c)) the AgNWs deposition are shown. In larger topography images like in Figure 6(a), fibril bundles of up to 800 nm width and smaller randomly aligned fibrils are visible. Zooming in with an image size of 2 × 2 µm^2 (Figure 6(b)), it is very well visible that the surface is dominated by small fibrils with a lateral size of about 40 nm. The AgNWs are rather randomly distributed and sometimes seem to form agglomerates (Figure 6(c)). From line profiles in the topography images, the height (350 ± 190) nm and the width (310 ± 90) nm of the AgNWs were estimated. In comparison to AgNWs on the kraft pulp paper sample (Figures 2 and 3), the AgNWs deposited on the NF paper are shorter and broader. It should be noted that the dilation effect due to the finite

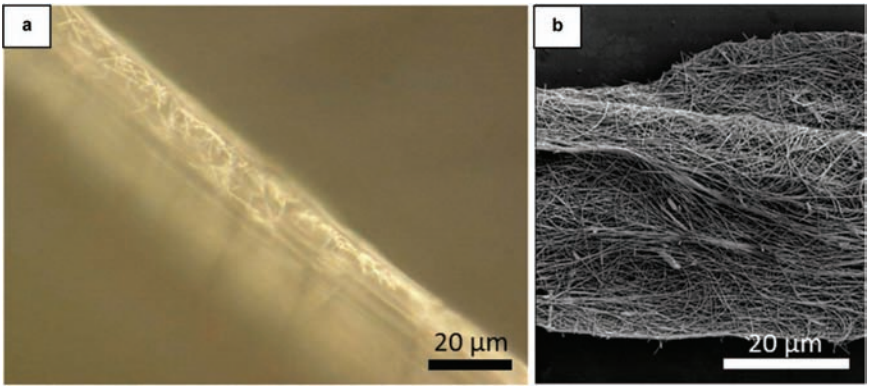

Figure 7. (a) Optical microscopy image and (b) SEM image of a AgNW dip coated viscose fibre taken from [8].

AFM tip size [22] contributes to the apparent width of all the measured surface features.

As expected, the RMS roughness σ increased after the AgNW deposition and showed large deviations. For the bare NF paper, σ = (183 ± 6) nm, with the AgNW on top the roughness increases to a value of σ = (467 ± 182) nm. Those values were obtained from six 10 × 10 μm^2 topography images.

For comparison with other cellulose-based materials, adsorption of AgNWs on viscose fibres has also been investigated [8]. Here, a conducting AgNW network on the fibre surfaces could be established as well. An optical microscopy image and an SEM micrograph of a single viscose fibre coated with AgNWs are presented in Figure 7. The enhanced reflectivity due to the AgNWs shown in Figure 1(b) is also observed on the viscose fibre. Therefore, one can assume a similar adhesion of the AgNWs to the viscose fibre surface. This is also indicated by the perfect Ohmic behaviour that these samples exhibit during electrical measurements. The resistance determined from measuring 11 fibres was (45 ± 11) Ω [8].

To further explore the interactions of AgNW with cellulose, we tried to incorporate the AgNW into thin cellulose films. As can be seen in AFM topography images in Figures 8(a)–(b), the AgNW are integrated within the cellulose film or are located at its surface. The AgNW are also covered by dot-like agglomerates with a lateral size of up to 200 nm. Some of the AgNW do react with the HCl gas forming AgCl which was confirmed via X-ray photoelectron spectroscopy analysis (XPS) of the films (Figure 8(c)). For conductivity measurements, the amount of AgNWs on the surface was not sufficient.

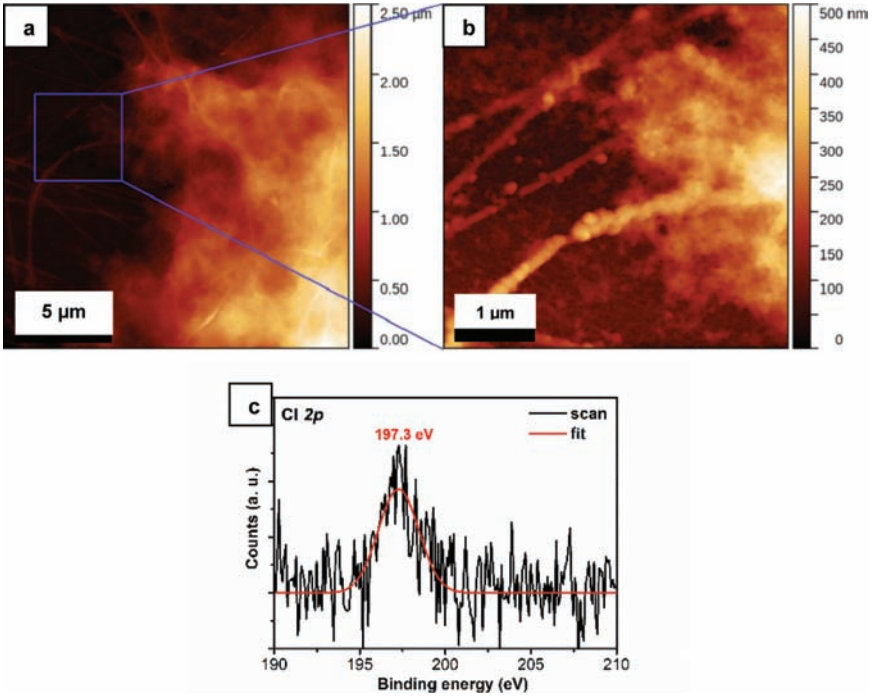

Figure 8. (a) 20 × 20 µm^2 AFM image of a regenerated cellulose film containing AgNWs; (b) A 5 × 5 µm^2 zoom-in AFM scan gives a closer look on the AgCl agglomerates formed on a AgNW; (c) XPS of the Cl 2p region.

OUTLOOK TO MECHANICAL TESTS

Further insight on how strongly the AgNWs are bound to the cellulosic surface can be obtained by pushing the AgNWs with the AFM probe and measure the necessary force. In Figure 9, first results are presented. Trial measurements without recording of the lateral force were performed to explore if it is even possible to move the large AgNWs with the AFM tip.

The AgNWs were mostly laterally moved during these experiments. However, in some cases, AgNWs seem bent afterwards. This is shown in Figure 9(c). Here, a 5 × 5 µm^2 image was recorded to get a closer look. It is still hard to distinguish, but the AgNW might have been broken or bent during the experiment or it was pushed underneath the other AgNW. The line profiles in Figure 9(d) indicate that

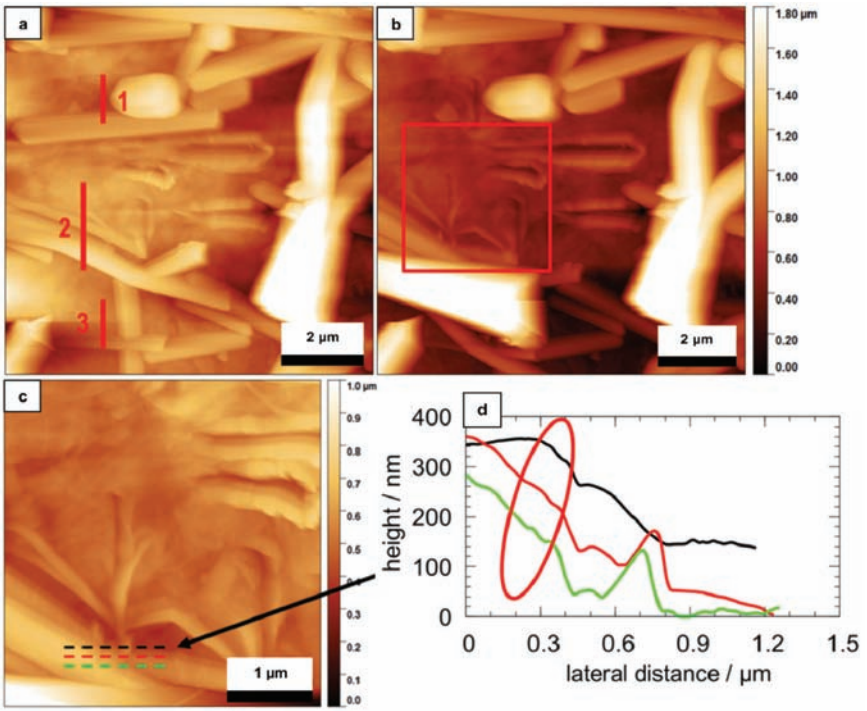

Figure 9. (a)–(b) 10 × 10 µm^2 topography images before (a) and after (b) AFM mechanical shifting experiments of the AgNW on NF paper. The red lines 1–3 in (a) indicate where the tip was dragged across the surface (always from top to bottom). (c) shows a 5 × 5 µm^2 zoom-in of (b) with corresponding line profiles in (d). The red ellipse in (d) indicates a scratch on the AgNW caused by dragging the AFM tip across it.

the tip even produced a notch in the AgNW. This observation of severe damage of the AgNW by the moving AFM probe indicates rather strong adhesion of the AgNWs to each other and to the surface.

By recording the lateral force signal and using different applied forces during these measurements, we expect in future experiments to get more insight on the level of adsorption.

CONCLUSIONS

It has been demonstrated that AgNWs are a very versatile and useful tool to add electrical conductivity to cellulose based materials. Commercially purchased or

self-synthesized AgNWs have been adsorbed to the surface of kraft pulp paper, NF paper sheets and also viscose fibres by dip coating. Together, cellulosic surfaces and AgNWs formed a conductive composite network with resistivity in the range of 38 Ω/sq which is comparable to the commonly used ITO. Additionally, optical and scanning probe microscopy methods have been proven to be appropriate for investigating the surface properties of these complex paper fibre-AgNWs composites. Optical microscopy investigations indicate that the AgNWs increase the reflectivity of the paper, without much change in other optical properties. This is an advantage compared to methods with conductive inks and organic polymers which always lead to a loss in transparency.

Although the samples are fairly rough, we also succeeded to study the surfaces of cellulosic materials with AgNWs by AFM in detail. In topography measurements, it was interesting to explore the alignment of the AgNWs along the rough cellulose fibres. KPFM investigations showed a difference in contact potential, which made it possible to distinguish between the cellulose background and the AgNWs. Finally, mechanical tests with an AFM probe have – at least qualitatively – proven a significant adhesion of the AgNWs to the paper surface.

One of the main future challenges is to build persistently good devices with a flat composite surface to avoid short circuits. Also, the flexibility of the composite needs to be further tested. As was demonstrated, it is possible to bend the AgNW-coated NF paper once and record similar conductivities but the long-term behaviour and cycling stabilities for applications in daily use are not yet clarified. Here, the strength of adhesion between the AgNWs and the cellulosic surface is crucial and needs to be further investigated, with the mechanical AFM tests presented here being the first step in this direction.

ACKNOWLEDGEMENTS

The members of the CD-Laboratory for Fibre Swelling and Paper Performance gratefully acknowledge the financial support of the Austrian Federal Ministry of Economy, Family and Youth and the National Foundation for Research, Technology and Development.

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Transcription of Discussion

SILVER NANOWIRES: A VERSATILE TOOL FOR CONDUCTIVE PAPER

C. Czibula,[1,2] *C. Ganser,*[1,2] *M. Kratzer,*[1] *F. Brumbauer,*[3] *M. Kräuter,*[3] *K. Shanmugam,*[4] *W. Batchelor,*[4] *M. Penn,*[3] *M. Ebner,*[3] *M. Pramstrahler,*[3] *F. Pilat,*[3] *H.-T. Chien,*[3] *R. Schennach,*[2,3] *B. Friedel*[3,5] *and C. Teichert*[1,2]

[1] Institute of Physics, Montanuniversität Leoben, Austria
[2] CDL for Fibre Swelling and Paper Performance, Graz University of Technology, Austria
[3] Institute of Solid State Physics, Graz University of Technology, Austria
[4] Department of Chemical Engineering, Monash University, Victoria, Australia
[5] Energy Research Center, Vorarlberg University of Applied Sciences, Dornbirn, Austria

Georg Goetz SIG CombiBloc

You created a conductive transparent layer with nanowires on the paper surface. What about the conductivity if you start to bend or deform the paper? Does the conductivity still persist, or does it get lowered because you start to get breaks in the nanowire network?

Caterina Czibula Montanuniversität and Graz University of Technology

We did not do cycling, but at least with some of these conductive papers they did bend during the measurement of the conductivity and there was not much of a decrease.

Discussion

Gil Garnier Monash University

First of all congratulations, very interesting work. I think this is the study that holds the record for the most use of AFM modes investigated. Am I correct? Well done! Can you remind us of the dimension of the nanowires particles?

Caterina Czibula

The length varies quite a lot, you saw that in the SEM image, but the width was about 400 nm.

Gil Garnier

So, how much do you use on the composite with cellulose film?

Caterina Czibula

We had a suspension with the volume between 100 µL and 200 µL.

Gil Garnier

So, the volume fraction, as I suspect is the key variable. What is the volume fraction of the composite?

Caterina Czibula

That I would not know. I'm sorry.

Gil Garnier

What is the effect of the length of the wire on the conductivity and how does it compare with silver nanoparticles?

Caterina Czibula

You need these long wires to connect with each other. So, I think there is quite a distribution of longer ones that connect, and it means that the smaller the wires the more you need on the surface. Therefore, you really need to be above the percolation threshold so that you have this conductivity throughout the sample.

Gil Garnier

Have you compared, or how would you expect your silver nanowire composite to compare with graphene oxide cellulose?

Caterina Czibula

I don't know, we did not do anything like that yet.

Gil Garnier

Yes, that could be used to develop clear contacts in cellulose composites.

Caterina Czibula

Yes, it would be certainly interesting to look at that.

Jonathan Phipps FiberLean Technology

What is the advantage of using cellulose as a substrate compared with any other type of material with which you could make a transparent film?

Caterina Czibula

I think it's a very difficult question to answer. I think it's quite well established that you have this environmentally friendly paper production. Nowadays if you look at other processes many are not very environmentally friendly. There is this huge hype for perovskite solar cells for example, and they use lead and it is also quite complicated and here you have with cellulose such a good production process and if you just find a simple way to make it useful for electronics it would be great. You would have environmentally friendly production and they would be easy to recycle.

Akira Isogai The University of Tokyo

In your case, were the silver nanowires sufficiently dispersed in water?

Caterina Czibula

The suspension was kept in deionized water.

Discussion

Akira Isogai

Oh, I see. How strong is the adhesive between the cellulose nanofibre and the silver nanowire? Is it very strong?

Caterina Czibula

So, you already have this surface roughness from the nanofibrillated paper and it depends on the size of the nanowires, so the width and the length of it, as to how well it establishes contact with the surface.

Akira Isogai

Is it possible to bend like this?

Caterina Czibula

Yes, it was possible to bend it.