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Photoconductive Zinc Oxide-Composite Paper by Pilot Paper Machine Manufacturing

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Abstract

Smart materials can be used for a wide variety of applications, including sensing and energy harvesting. Implementation of smart materials in large area devices requires scalable manufacturing. The use of paper-making techniques would offer an enormous production capacity, allowing for low-cost and large-scale manufacturing. In this work we present successful pilot scale paper machine manufacturing of functional composite papers (100 m/min with a web width of 30 cm) based on cellulose fibres and commercial tetrapodal zinc oxide microwhiskers (ZnO-Ts). Carbon electrodes could successfully be printed on the paper, to form complete electronic devices where the paper itself is the active material. This enabled development of a ZnO-composite paper photosensor, where we characterized its stability, sensitivity and speed. The devices show excellent photosensing properties over a wide range of light irradiances (0.01-1 Sun), including short response times (~10 s) and long-term stability. Under simulated sunlight and a bias voltage of 1V, small (0.5 cm²) two-probe interdigitated photosensor devices provided 12 μ A photocurrent. Under the same conditions, four-probe measurements of the composite paper show a sheet resistance of $6.9 \cdot 10^7 \Omega/\text{sq}$. Four-probe measurements also demonstrates that the paper conductivity varies linearly with light irradiance. To the best of our knowledge, this is the first example of pilot paper machine production of an optoelectronic paper, demonstrating the potential for large-scale paper manufacturing of active smart paper from low-cost industrial bulk materials.

1. Introduction

Scalability in manufacturing and low cost are typical prerequisites for the successful implementation of (smart) materials in large area or large volume devices. The possibility to use paper manufacturing methods would be particularly attractive considering the huge production capacity of paper making machines (more than 100 km/h), the low cost of the starting material (around 0.1 cent/dm²) and its environmental-friendly nature [1]. All paper in the world together form the largest surface ever produced by mankind, with about 400 million metric tons produced by year (2013 data) [2].

The most common current approach to low-cost and large-area electronic devices is printed electronics. The principle takes advantage of low-cost material deposition using printing and coating techniques [3,4]. However, if substrates and printing inks are too expensive, this advantage is lost. Here, we explore an alternative route to low-cost large-area functional devices based on paper machine manufacturing. Optoelectronic papers are produced in a pilot paper

machine and used as active substrates for manufacturing of optoelectronic devices by subsequent screen-printing of carbon electrodes and circuits onto the paper.

The active components in our papers are tetrapodal zinc oxide microstructures (ZnO-Ts). ZnO is an n-type semiconductor with a bandgap of 3.37 eV and it is known for its photoconductive properties. For example, ZnO-based coatings on so-called electrofax papers for electrophotographic processes (xerography) were used for printing and reproduction until the 1980s [5,6]. The mechanism of photoconductivity in ZnO is related to photogeneration of electron-hole pairs and adsorption and (photo-)desorption of oxygen onto the material [7-9]. At dark conditions, oxygen molecules adsorbed on the material capture free electrons and create a low-conductive dark state. Upon illumination, holes from electron-pair generation react with and release the oxygen. This leaves non-paired free electrons and a corresponding high-conductive state. The material has a wide applicability and has been used in chemical sensors, as photosensors, detectors for reducing and oxidizing gases, in filters, as photocatalysts, and in various optoelectronic devices [10-15]. In addition, there is a strong interest in ZnO composites due to its high abundance, low cost and safety, since ZnO is a material generally recognized as safe (GRAS) [16]. Low-cost photosensing, and monitoring of UV exposure in particular, could be important in a many applications. For example, high UV-doses can be harmful to human skin, and is associated with health risks and cancer, while medium and low UV doses can benefit health [17,18]. UV-B radiation also affects plants and primary producers on aquatic ecosystems [19,20]. On the other hand, UV-light exposure can be used to preserve food [21,22] and sterilize water [23]. Availability of low-cost devices that can monitor UV-exposure doses could thus benefit health, crop production, reduce food waste and facilitate water purification.

Photosensors based on ZnO can be manufactured by a variety of deposition and patterning methods [7,24-26], even by simply drawing graphite electrodes by a pencil on top of a ZnO-based coatings [27] or on flexible materials such as cloth [28] or paper [29,30]. However, the ZnO-composite papers reported in the literature were not obtained using large-scale manufacturing, limiting their low-cost and applicability. Here, we present the first ZnO-composite paper made by large-scale paper machining and demonstrate its applicability for photosensing. We characterized the sensors using a light source that emulates solar illumination in order to evaluate the concept for low-cost monitoring of sun exposure. The composite paper shows high photoresponse in a wide range of light intensities (0.01 Sun to 1 Sun) with an excellent stability over time. Moreover, we chose to work with ZnO-Ts, which are manufactured on an industrial scale and available in bulk quantities at a low price (<100 USD/kg), as opposed to more complex forms of nanostructured ZnO that have been used in photosensors and other applications [10].

2. Materials and methods

2.1 Pilot Paper Machine manufacturing

Pilot Paper Machine

The composite paper was manufactured on the FEX pilot paper machine at Innventia AB, in Stockholm, Sweden. A simplified schematic illustration of the manufacturing process is presented in figure 1(a), while figure 1(b) shows a photo of the FEX paper machine, as previously described in works by Roding *et al.* [31] and Nordström [32]. The FEX pilot paper machine is designed so that the machine sections and the material flow is similar to that of a full-scale paper machine. For example, it is possible to recirculate the white water back to the inlet flow. The paper machine was equipped with a hydraulic headbox from Andritz, shown in figure 1(c). To make experiments possible with a suitable quantity of raw materials, the web width of the FEX machine is 30 cm, compared with full-scale paper machines where the web typically is

several meters wide. To avoid potential contamination of ZnO-Ts particles, the drying section was disconnected and paper samples were rolled up on bobbins, shown in Figure 1(d). These bobbins were then transferred to a mobile drying section placed in a compartment confining dust emissions. After drying, the paper roll was cut to approximately one-meter-long sheets. In this experiment, the paper machine was running at a web speed of 100 m/min. Since this is still slow for paper-making, there is potential for further up-scaling. As described in detail below, the pulp composition was changed during production to produce seven paper compositions. Since the white water is re-circulated, paper samples were collected 20 minutes after the composition of the feed was changed. For each sample, approximately 60 meter of paper was collected.

Figure 1. (a) Schematic view of the pilot paper machine. (b) Photograph of the FEX pilot paper machine. (c) Inlet box supplying the composite pulp. (d) Bobbins collecting the composite paper before drying.

Composite pulp materials

Panatetra WZ-0501, “tetrapodal ZnO whiskers” ZnO-Ts (single crystal, 99.999% purity), having an average length of approximately 20 μm , were purchased from AMTEC KK, Osaka, Japan (figure S1). Previous reports have proven the feasibility of using this form of ZnO in paper composites [33]. We used a mixture of 70% bleached sulphate softwood pulp and 30% bleached sulphate hardwood pulp as the cellulose component in the composite. The pulps were co-refined in a 26” double disc mill to 140 kWh/ton using an edgeload of 1.0 Ws/m, resulting in a 28.5 °SR (Schopper-Riegler) drainage rate. As retention agent we used Perkol 1510 cationic polyacrylamide at the concentration 750 g/ton, and for the papers containing the sizing agent alkyl ketene dimer wax (AKD) we used 7500 g/ton. Sizing agents can influence how inks penetrate into the paper. The paper machine was fed with seven different compositions of the composite according to table 1. First, we prepared a reference paper, A, having no ZnO-Ts and no alkyl ketyl dimer (AKD). The ZnO-Ts content was then increased in steps of 15% weight percentage (wt%), first without, and then with AKD for each ZnO-Ts content, to form paper types B-G. In all samples the feed was aimed at a grammage of 60 g/m².

2.2 Electrode printing

To probe the photoconductivity of the composite paper and to develop photosensor devices, we printed electrodes using conducting carbon-based ink (7102, supplied by DuPont) (Figure 2(a)). Two-probe interdigitated electrodes and four-probe square configured electrodes were designed and transferred to a screen-printing mask (figure 2(b) and figure S2 in Supporting Information [SI], respectively). Two-probe interdigitated electrode devices (designed for 0.25 mm electrode width and distance and a total foot print of around 0.5 cm²) were used to measure the photosensing properties of the composite paper while the four-probe electrode devices were used to measure the intrinsic properties of the material, such as the sheet conductance and the bulk conductivity. For the latter, square arrangement of probes was preferred to avoid shadowing of the photoconductor by the probes or electrodes. The screen-printing mask was a 20 µm capillary film trademarked Fotocoat 1177 on a polyester web with 120 threads/cm. After printing, the paper with the ink was dried at 100°C in an oven for 3 minutes.

2.3 Photoconductivity measurements

Photoconductive measurements were performed using a LCS-100 Solar Simulator from Oriel Instruments as the light source. The system uses a 100 W Xe lamp and an AM1.5G filter. The irradiance was 1 Sun (1000 W/m²) unless stated otherwise. The calibration of the light irradiance was done by using a calibrated reference cell and meter (91150-KG5 from Oriel Instruments). The voltage applied throughout the photosensing characterization of the composite paper was 1 V unless stated otherwise. The current was measured and recorded in one-second intervals with a Keithley 2420 sourcemeter. A custom-designed LabVIEW program was used to control the equipment and gather the data on a personal computer. The sheet resistance of the paper material was obtained by illuminating the four-probe structure through a circular shadow mask, where the periphery coincides with the electrodes, and then calculated by using the square four-probe points configuration formula [34].

3. Results and discussion

3.1 Material Fabrication and Structural characterization

ZnO-Ts cellulose composite papers were successfully manufactured on the FEX pilot paper machine, with dry contents of ZnO-Ts up to 45 wt%. The grammage and composition of the composite papers are shown in table 1. In all papers, the grammage is near the target value of 60 g/m², with slightly lower values for sample F and G that had the highest loading of ZnO-Ts. The content of inorganic content in a paper can be provided by the ash content, as the cellulose component leaves very little ash upon combustion. Indeed, the ash content in the reference paper A was only 0.3 %. The ash contents in the ZnO-Ts loaded samples (B-G), are consistent with the targeted compositions. In the papers with the highest loading of ZnO-Ts, one can see a slightly lower ash content than the targeted ZnO-Ts content. This together with a slightly lower grammage than the target value indicates lower retention in papers F and G. Samples D and E, on the other hand, have grammage and ash content consistent with an acceptable retention in the paper making process. Paper E was therefore selected for further characterization.

Table 1. Targeted ZnO-content and measured grammage and ash content of the produced composite papers.

Sample	Targeted ZnO content (%)	AKD addition (yes / no)	Measured Grammage ^a (g/m ²)	Ash content ^b 550 °C (%)
A	0	no	60,8	0,3
B	15	no	62,6	15,9
C	15	yes	63,2	15,7
D	30	no	62,0	30,8
E	30	yes	60,5	31,1
F	45	no	56,1	44,5
G	45	yes	57,3	44,1

^a Determined according to ISO 536:2012.

^b Determined according to ISO 1762, where ashing is performed by vaporizing/combusting organic compounds at 550 °C. ZnO is stable at this temperature.

Figure 2. (a) Photograph of ZnO-composite paper with printed devices. (b) Two-probe ZnO-composite devices, as used for photosensing. (c) SEM image of the ZnO-composite paper (paper E).

The papers functioned well as substrates for screen-printing of carbon-based electrodes, as seen in figure 2(a) and 2(b). In order to study the arrangement of the ZnO-Ts in the cellulose matrix we took SEM images of the ZnO-composite paper (figure 2(c)). It appears that the ZnO-Ts successfully fill voids between the fibers in the paper. One concern about the manufacturing of the composite paper was release of ZnO-Ts particles from the paper during manufacturing. However, very little visible traces of particle release from the paper were observed in the wet stage of the machine and also not at the drying section. This is in agreement with the high retention indicated by the measured grammage and ash content. This may be the result of large ZnO-Ts that become entangled with the wood fiber network composed of both long and short fibers. However, we noticed that some traces of powder can detach from the paper if we shake, bend or crease the paper. This may be minimized in the future through further optimization of the paper production protocol, where we speculate that the addition of finely ground parts of fibers called *finer* may help to further hold the ZnO-Ts together and bind them to the paper [35].

3.2 Photosensing Characterization

We evaluate the ZnO-based paper as photosensor using the two-probe interdigitated electrode configuration shown in figure 2(b). The red curve in figure 3(a) shows the measured current of the device at a bias of 1 V, first without light and followed by illumination at 1 Sun of irradiance. As expected, the averaged dark current exhibits a very low value of $8.5 \cdot 10^{-4} \mu\text{A}$ while illumination results in a dramatic increase in the measured current. This photoresponse behaviour can be explained by the well-known mechanism of oxygen adsorption-desorption, as discussed above [7,26,28]. The results corroborate that the density and connectivity of ZnO-Ts in the material is high enough and favourable, respectively, to allow for long-range conduction through the material. Interestingly, the current immediately reaches high values upon illumination, followed by a slow decrease to a stable signal of $12 \mu\text{A}$ after around 20 minutes. The resulting photo-dark current ratio is well above 14000. The photoresponse behaviour makes sensors based on our composite paper particularly suitable for applications where light doses need to be measured over longer times and on large surfaces, such as food preservation, environmental UV-dosage monitoring, or crop growth control. However, the strong immediate photoresponse will also enable measurements of short light exposures. We note that the stabilization curve (red curve of figure 3(a)) was obtained by first applying the voltage, followed by illumination. If we instead pre-illuminate the device for a given time before applying the voltage (green and blue curves, 10 min and 45 min respectively), the signal becomes stable after correspondingly shorter times (effectively only measuring the last part of the full stabilization curve, see figure 3(a)). This indicates that the stabilization effect is not a bias-stress effect in part caused by the applied voltage, but rather related to the illumination. Our results are in agreement with previous studies that report that the evolution of the photocurrent for low-dimensional ZnO structures includes a fast increase upon illumination, followed by a slow decay that asymptotically stabilizes at a current level given by the specific illumination intensity [36,37]. In turn, the photocurrent decay part has been found related to two processes with distinctly different time constants [37]. The relatively faster process (time constant $\sim 50\text{-}300 \text{ s}$) could be attributed to trapping of photoelectrons by O_2 molecules that are re-adsorbed on the surface, while the relatively slower process (time constant $> 500 \text{ s}$) could be attributed to recombination at native defects [38,39]. The details of these processes have also been found dependent on the substrate onto which the ZnO structure are carried as well as on the presence of H_2O and O_2 in the surrounding environment [39].

Figure 3(b) shows the current response for three consecutive illumination on/off cycles after the stabilization period. The results demonstrate a very repeatable behaviour, with minimal dark current and a stable photocurrent of 12 μA (red curve). The rise time is defined as the time required for the current to increase from 10% to 90% of the saturated value, and the decay time as the time required for the current to decrease from 90% to 10% [26]. The device shows an average rise time and decay time of 15 s and 6 s, respectively (figure 3(c)). The values obtained are highly competitive when compared with other response times reported in the literature on small-scale nanostructured ZnO photosensors. For instance, photodetectors based on ZnO single nanowires showed a rise and decay time of 53 s (80%) and 300 s (1.5%), respectively [40]. ZnO nanorods prepared by sol-gel showed response times of 3.7 s and 63.7 s respectively [41]. ZnO devices prepared by chemical bath deposition showed response times of 9 s and 21 s, respectively [26]. On flexible ZnO-nanoparticle-assembled cloth the reported response times were 3 s and 2 s, respectively [28]. Interestingly, the decay time for our device is lower than the rise time. This finding is opposite to the observations of several previous reports for ZnO-based photosensors, in which the decay time was found longer than the rise time, as attributed to a so-called persistent photoconductivity due to trap states within the ZnO bandgap [26,42,43]. The faster decay time than rise time for our ZnO-Ts paper indicates that the adsorption of oxygen molecules is faster than the desorption process upon illumination. This may be due to defects on the material that causes a slow movement of the photo-generated holes from the bulk to the surface of the material. It should also be noted that the photoresponse was found linear with applied bias potential, indicating ohmic contacts in our device, and that the electrons generated by photon excitation are easily transported into the printed carbon electrodes (see figure S3) [44]. The photoresponse was also measured on a blank sample without ZnO-Ts (Paper A). Upon illumination, the device made from this blank paper shows no observable response beyond the noise level (blue curve of figure 3(b)).

Figure 3. (a) Stabilization curve of the ZnO-Ts paper at a bias of 1V and under an irradiance of 1 Sun (red line). The green and blue lines were measured by pre-illumination of the device for 10 min and 45 min, respectively, before applying the voltage. (b) Photoresponse of the device at a bias of 1V and for alternating dark conditions and irradiance at 1 Sun (red line). The blue curve shows the photoresponse for a blank sample, respectively. (c) Enlarged view of figure 3(b) showing the rise and decay times of one of the cycles (second cycle) of the device.

Next, we characterize the sensitivity of the devices by investigating the photoresponse at different light intensities. These experiments were performed by changing the illumination irradiance while keeping a fixed bias voltage of 1 V (figure 4(a)). Figure 4(b) shows the averaged stable current measured at different irradiances. The device shows a strong photoresponse for light irradiances spanning at least two orders of magnitude (0.01-1 Sun). The dependence of the current on light irradiance can be explained by a model accounting for a total device resistance (R) that is the sum of a constant resistance originating from leads and contacts (R_c), and a light-dependent resistance through the paper (R_p). The latter is set inversely proportional to the irradiance (E), as motivated by four-probe measurements of the ZnO-paper material. The four-probe measurements eliminate effects from contacts and demonstrate that the photocurrent (and hence, the conductivity) of the paper varies linearly with illumination irradiance (inset in figure 4(b)). The stable current (I) of the interdigitated photosensor device should then depend on light irradiance (E) as

$$I = \frac{V}{S/E + R_c} \quad (1)$$

where S is a sensitivity factor determined by both device geometry and the inherent sensitivity of the paper's conductivity to illumination. The experimental data can be excellently fitted to this

expression (red curve in figure 4(b)). The fit enables extraction of the total contact and lead resistance of the device (R_c) as 74 k Ω , while the total resistance within the paper ($R_p=S/E$) is found to decrease inversely with illumination as 11 k $\Omega \times \text{Sun}$. This reflects the significant resistance of the printed carbon in electrodes and leads, a material choice motivated by the low cost of carbon and its ohmic contact to ZnO. The current varies strongly and approximately linearly with irradiance at low light intensities, where R_p dominates the device resistance. This could be beneficial for low light intensity applications. We also note that both S and R_c are dependent on device geometry, enabling the response curve to be modified and optimized for different applications and illumination conditions.

From the four-probe measurements, we extract the sheet resistance of the ZnO-Ts paper as $6.9 \cdot 10^7 \Omega/\text{sq}$ under a bias voltage of 1 V and at 1 Sun of irradiance. For our roughly 100 μm thick paper, and approximating the light intensity as constant through the paper, this gives a bulk conductivity of $1.5 \cdot 10^{-4} \text{ S/m}$ under a bias of 1 V and at 1 Sun.

Figure 4. (a) Current at different irradiances over time of the device under a bias of 1V. The values stated for illumination cycle correspond to the irradiance in Sun. The data points of Figure 4b are extracted from the average of the current at the different intensities of light. (b) Current versus irradiance of the device under a bias of 1V. The fit of the photoexcited current is shown (red line). Inset: Current versus irradiance of a four-probe device under a bias of 1V. The black line is a linear fit of the photoexcited current.

Finally, we demonstrate our device at a large scale, using an over 1 m long ZnO-composite paper with arrays of different printed carbon electrodes (figure 5(a)). To simulate relevant conditions for real applications, we measure the response outdoor on a partly cloudy day. Using the same two-probe interdigitated device and experimental setup as for the examples above, outdoor ambient light conditions gave a stable photocurrent of 9.1 μA under a bias of 1 V (figure 5(b)). This is around 25% lower than that measured for simulated solar illumination at 1 Sun, in agreement with the non-ideal Swedish summer weather. When the device is covered, the current decreased to 0.002 μA (figure 5(c)). It should be noted here that the photocurrent is dependent on device geometry and larger photocurrents could easily be obtained by modifying the device geometry (figure S3), allowing for optimization of the device for a wide range of applications.

Figure 5. (a) Outdoor setup using a large scale ZnO-composite paper sample. (b) Photocurrent of the device under ambient illumination. (c) Photocurrent of the device when light is blocked.

4. Conclusions

To our knowledge, this work presents the first production of an optoelectronic paper material with a pilot paper machine. More specifically, we successfully made functional ZnO–cellulose composite papers with a high content of ZnO-Ts (up to 45 wt%). The production rate of 100 m/min corresponds to the lowest speed of the pilot paper machine, indicating additional potential for up-scaling. Furthermore, the material flow and processes in the pilot paper machine are very similar to that of a full-scale paper machine, and the raw materials are both available in bulk amounts and cheap compared to typical active optoelectronic materials. Hence, the manufacturing experiment shows that scaling also to full-scale paper machines is technically and economically viable.

The optoelectronic functionality of the composite paper was demonstrated by application as a photosensor. The measured photoresponse of a two-probe interdigitated carbon electrode printed on the paper (with only 0.5 cm² footprint) showed strong and repeatable photocurrent signals upon illumination with simulated sunlight, with values of 12 μA at 1 V. The device showed fast response times, sufficient for monitoring of, for example, the sunlight exposure during a day, and to monitor illumination of light sensitive applications, such as food preservation, human health, crop control, or water purification.

Scalability to paper-machine manufacturing of papers with optoelectronic functionality opens up for a new concept in large area smart materials, in which composite papers provide functionality within its bulk, and not just act as passive printing substrates. Together with other printed materials and conventional silicon-based devices, this type of smart composite papers can be useful for a large variety of low-cost and large-area devices.

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