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Improvements in purification of silver nanowires by decantation and fabrication of flexible transparent electrodes. Application to capacitive touch sensors

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Abstract

Transparent flexible electrodes made of metallic nanowires, and in particular silver nanowires (AgNWs), appear as an extremely promising alternative to transparent conductive oxides for future optoelectronic devices. Though significant progresses have been made the last few years, there is still some room for improvement regarding the synthesis of high quality silver nanowire solutions and fabrication process of high performance electrodes. We show that the commonly used purification process can be greatly simplified through decantation. Using this process it is possible to fabricate flexible electrodes by spray coating with sheet resistance lower than $25 \Omega \text{ sq}^{-1}$ at 90% transparency in the visible spectrum. These electrodes were used to fabricate an operative transparent flexible touch screen. To our knowledge this is the first reported AgNW based touch sensor relying on capacitive technology.

 Online supplementary data available from stacks.iop.org/Nano/24/215501/mmedia

(Some figures may appear in colour only in the online journal)

Transparent electrodes are widely used in technologies like photovoltaics, displays, touch panels, and many other devices. The fabrication of such electrodes is currently realized with thin films of transparent conductive oxides (TCOs), and notably indium tin oxide (ITO). Besides excellent optoelectronic properties, the as-made ITO transparent electrodes suffer from major limitations like a costly fabrication process and brittleness. The use of solution-processable nanomaterials appears as a promising alternative since it affords a low-temperature, large area and low-cost deposition method. Recently significant work has been carried out using carbon nanotubes [1–3], graphene [4, 5], and metallic nanowires [6–20] for fabricating transparent flexible electrodes with good performances [18, 19]. Silver nanowires (AgNWs) are very attractive since they are easily produced in

high quantity in solution and give results at the best level, in particular with respect to reported figures of merit [21, 22].

A significant drawback with the synthesis of AgNWs arises from the tedious and lengthy purification process which is hardly reproducible. The common purification technique is a succession of centrifugation and washing steps to remove co-produced nanoparticles and organics [23–26]. Some other techniques have been proposed but the amount of purified nanowires remains relatively low [27]. We report herein on a straightforward purification process of AgNWs by simple decantation. This technique allows easy production of a high quantity (few g) of nanowires in a single run. Spray coating of as-processed AgNWs leads to a homogeneous deposition with low sheet resistance, typically less than $25 \Omega \text{ sq}^{-1}$ at 90% transparency in the visible spectrum.

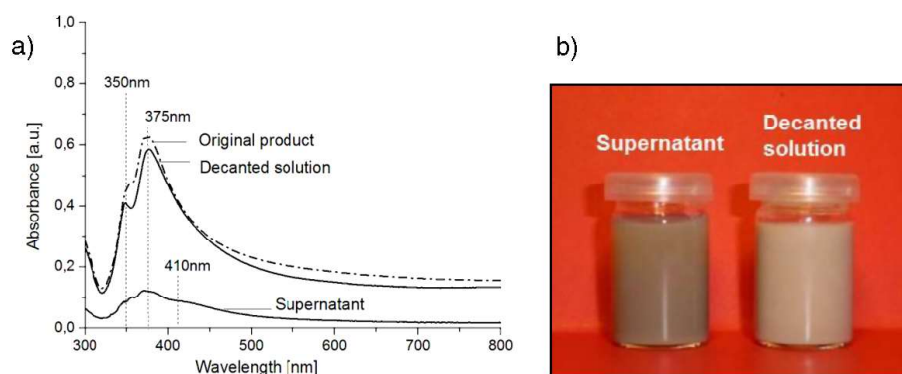


Figure 1. (a) UV-vis-NIR spectrum of crude solution, and after decantation lower phase and supernatant. (b) Sample images of decanted solution and supernatant.

Among optoelectronic product segments with the fastest growth, touch screens are used in a rising number of applications like smartphones, intelligent floors or walls, specific human-machine interface (HMI) for operators, etc. Touchscreen cost is usually a main part of the overall price of such devices since none of the current touchscreen technologies has been realized with low-cost fabrication and printing technologies so far, mainly due to the lack of a printable, flexible and low resistivity transparent conductor. Recent papers about touch panels using AgNW based electrodes have shown that this material could be well adapted, but up to now only resistive systems were reported [13, 28]. Capacitive technology is an alternative with noteworthy advantages. For instance, iPhone™ uses a capacitive touchscreen, which gives the smartphone an excellent response to extremely soft touching. We fabricated electrodes with decanted AgNWs to establish the feasibility of flexible transparent capacitive touch panels. Our results demonstrate that these devices can be easily prepared, with very high sensitivity even under flexion, and they could eventually work without the need for contact.

The most developed fabrication process of AgNWs relies on the polyol synthesis. Different studies have been carried out to improve the yield, the aspect ratio, the seeding effects and other parameters [24, 29, 30]. In this study, AgNWs were synthesized according to a modified published procedure [25]. A 160 ml ethyleneglycol (EG) solution of NaCl (1 mM) and PVP (3.54 g, $M_w = 40\,000$) was vigorously stirred at 120 °C and then cooled down to room temperature. This cooled solution was injected slowly using a syringe pump into 80 ml of a magnetically stirred EG solution of AgNO₃ (1.36 g, 0.1 M) at 120 °C. The injection rate was set to inject the entire solution in 8 min. At the end of the addition, the reaction mixture was further heated at 160 °C, refluxed for 80 min and cooled down to room temperature in ambient air. The diameters of the nanowires were in the range 40–80 nm, and the lengths between 2 and 25 μm, with an average value of 10 μm. At this stage, the solution also contains many nanoparticles and remaining organics used for the synthesis. One of the main issues after synthesis of nanowires is their separation from the raw medium, which is generally performed using tedious cycles of centrifugations

and washing steps with methanol and acetone [8, 24]. We have carried out various experiments in order to improve both the process simplicity and the final performances of the random networks of AgNWs. We performed cross-flow purification of nanowires. This technique gives good purification but we came to the fact that it is rather time consuming and it delivers a moderate amount of product. We have found by chance that decantation can lead to straightforward purification of the solution. Indeed, after a common synthesis of AgNWs, we let the crude reaction mixture settle for few days before treatment. We observed that a grey phase separated from the supernatant. The latter could be easily separated, for instance by pipetting. We performed UV-vis spectra of both phases (figure 1). They are very different, indicating that the upper phase was mostly composed of nanoparticles whereas nanowires were essentially present in the lower phase. The two main peaks at 350 and 375 nm are respectively ascribed to the out-of-plane quadrupole resonance and out-of-plane resonance of the nanowires [31, 32]. They are mostly visible for the crude reaction mixture and the settled phase. We can observe that the supernatant phase spectrum presents also some similar peaks with much lower intensity, indicating the presence of some nanowires, but interestingly these peaks are not well defined. This is obviously related to the fact that they are mixed with a high density of pseudo-one-dimensional nanoparticles. This is confirmed by the presence of a significant absorbance between 410 and 460 nm, with a peak having broad full-width at half maximum. The red shift of the peaks in energy is attributed to the growth of some Ag nanoparticles into larger ones [31].

We repeated the protocol several times and we observed a reproducible behaviour. After reaction, the solution is transferred in a lipless beaker, covered with a watch-glass, and settled for two days. The settlement is noticeable after few hours, but best results are obtained after two days. The remaining grey residue containing nanowires is then washed with acetone to ensure the removal of organics. The obtained AgNW solution is stable for months. It was further confirmed by SEM images (figures 2 and S1 available at stacks.iop.org/Nano/24/215501/mmedia) that most nanoparticles remain in the withdrawn liquid phase whereas the settled grey product contains almost exclusively nanowires. Eventually but not

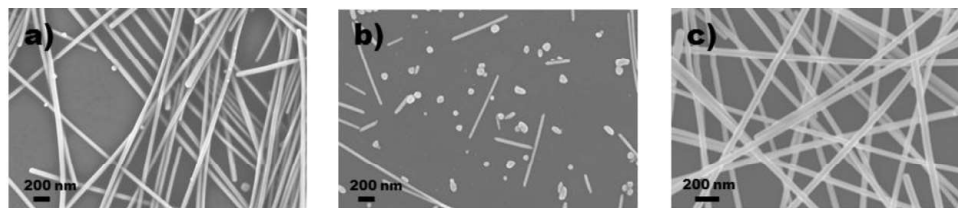


Figure 2. SEM images of AgNWs obtained after decantation (a) in the crude settled product and (b) in the supernatant phase. Image (c) corresponds to product shown in (a) after the removal of organics through acetone washing.

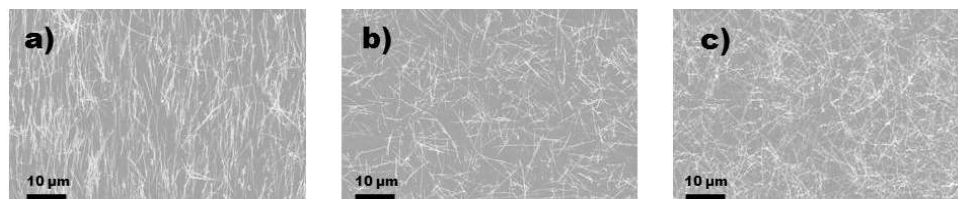


Figure 3. SEM images of (a) outer part and (b) inner part of a 1500 rpm spin coated AgNW random network and (c) after spray-coating (representative coating).

necessarily, more decantation steps can be carried out. We did not find any significant improvement by repeating the decantation process. Flexible transparent electrodes fabricated from AgNWs purified either by the common centrifugation method or by the proposed decantation protocol led to similar results on various runs, indicating that the two purification processes provide products with excellent performances.

The AgNWs are then dispersed in methanol at a desired concentration, typically from 100 to 500 mg l⁻¹ of silver content for deposition experiments. The fabrication of electrodes was realized on Eagle XGTM glass substrates of alkaline earth boro-aluminosilicate type glass or 125 μm thick PEN (i.e. poly(ethylene 2,6-naphthalate)) substrates obtained from Dupont Teijin (Teonex Q65FA). Despite the fact that spin-coating could lead to the fabrication of transparent electrodes, we observed that optical and electrical properties were not homogeneous all over the surface. In particular, values measured on the external parts of the samples presented high discrepancy. As observed in SEM images of figure 3, this can be related to the arrangements of nanowires which are different in the center or at the periphery of the spin-coated sample. As already reported, spray coating is a very suitable technique [13, 21, 33]. Compared to the spin-coating deposition process, spray coating allows reproducible homogeneous coatings on large areas. Deposition was carried out by air-brush spraying, using a vertically mounted commercial airbrush (ExactaCoat Benchtop ultrasonic spraying system, from Sono-Tek corp.). In a typical spray-coating experiment, substrate is placed on a hot plate at 80 °C. The entire process is realized in air as previously described [20]. We were able to obtain, on more than 250 cm², a very low sheet resistance at high transparency with an excellent homogeneity, typically 90 ± 12 Ω sq⁻¹ at 92% transmittance, 23 ± 4 Ω sq⁻¹ at 90% transmittance, 20 ± 4 Ω sq⁻¹ at 86% transmittance. The sheet resistance was obtained as the mean value of at least 5 measurements

by using a four pin probe with a Loresta EP resistivity meter, and the transmittance was measured on a Cary 5000 Varian spectrophotometer using the substrate as a reference. The nanowire density is approximately 1.0 ± 0.5 AgNW μm⁻² at 90% transmittance.

The fabrication of capacitive touch screens was realized using spray deposition on PEN substrates. Silver paste (Ag L200 from Ferro) electrodes were deposited on the edges of the device for contacts with external electronics. In order to prevent destruction of the AgNW networks, and to avoid direct contact of the operators with nanoparticles for safety precautions, the conductive layer was encapsulated through lamination at 4 bar of PSA film from 3MTM. After encapsulation, the performances of the electrodes were measured regularly. They were found to be stable for months. The electrodes play the role of the sensitive part of the capacitive sensor. Capacitive sensing was performed using the relaxation oscillator method integrated with a MSP430 microcontroller from Texas Instruments. When the pin oscillation is enabled, its frequency depends on the capacitance connected to the pin, typically 1 MHz at 20 pF and 0.5 MHz at 50 pF. The frequency is measured using a counter and an interruption mechanism, enabling to perform the measurement while the microcontroller is in a sleep state, thus consuming almost no energy. For instance, during 5 ms at 50 pF, 2500 clock pulses are counted. In this case, 10 clock pulses (about the observed noise level) correspond to 0.2 pF.

Four electrodes were used, each connected to one pin oscillator pad. The four electrodes are surrounded with a fifth electrode which is connected to the ground (figure 4).

When a conductive object such as a finger is approaching or touching the electrode through the protective coating, the electric field is modified, corresponding to a capacitance change. As the surroundings may change, and so the capacitance, a calibration is carried out when resetting the microcontroller. Then only changes are taken into account,

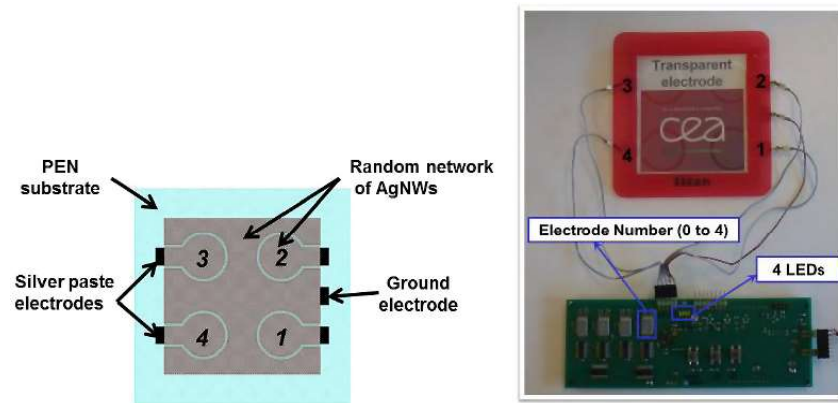


Figure 4. (a) Design of the 4 electrodes with connecting pads. PSA film (not shown) is applied on the entire surface of the device. (b) Transparent electrode on PEN connected to the electronic system.

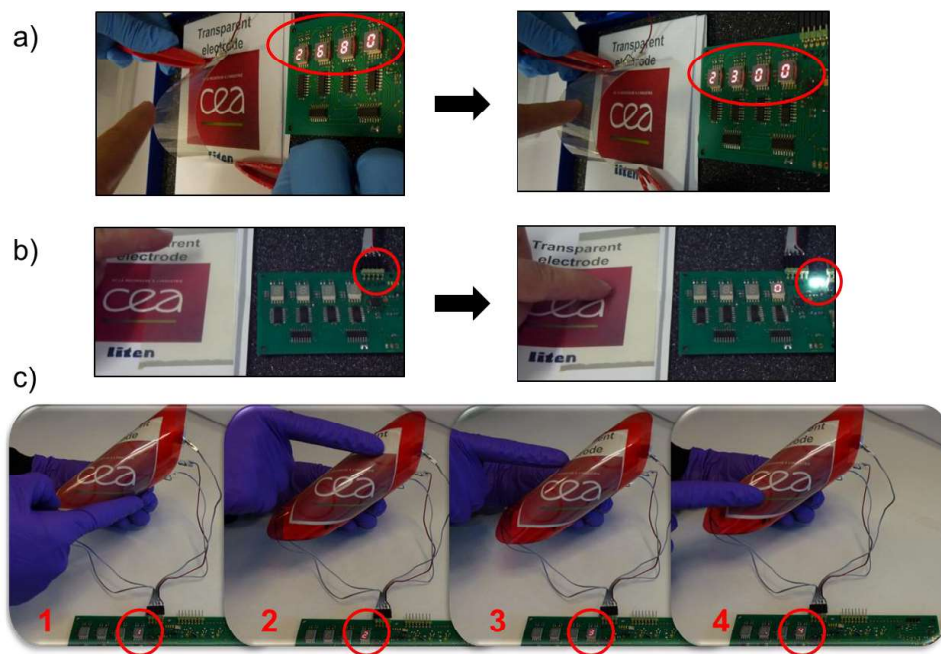


Figure 5. (a) Left, the finger does not touch the sensor surface and oscillation value is 268 and right, the finger touches the surface and oscillation value is 230. (b) Left, the finger is far from the surface thus the LED is off, right the finger is touching the sensor which switches on the LED. (c) Recognition of each electrode (1, 2, 3, 4). See also movie S1, movie S2 and movie S3 in the supplementary material (available at stacks.iop.org/Nano/24/215501/mmedia).

such as a finger approaching. With our configuration, touching corresponds to tens of pF change, and so is easily detected. If the capacitance change is above a predefined threshold, then the corresponding number is displayed. If several electrodes are touched at the same time, only the highest change can be kept, or all of them if we allow multitouching. Proximity detection is trickier because the capacitance change is extremely low, quickly decreasing with the distance and the area: the plate capacitance formula applies. For instance, the capacity of a hand (about $10 \times 10 \text{ cm}^2$) at a distance of 10 cm corresponds to 0.8 pF. The sensitivity of the system was large enough to enable the intensity control of some

LEDs depending on the measured capacitance change. When approaching the hand, the LED intensity increases as shown in movie S1 (available at stacks.iop.org/Nano/24/215501/mmedia). This requires a precise initial calibration to define the zero.

The touch pad was thus able to give absolute responses (yes or no) for specific areas or to modulate responses like lighting (see figure 5 and supplementary information: movie S1, movie S2 available at stacks.iop.org/Nano/24/215501/mmedia) thanks to capacitance variation (see movie S3 (available at stacks.iop.org/Nano/24/215501/mmedia) for real time capacitance variation). During bending experiments,

we did not observe any change in the response of the touch screen, for concave or convex flexions, while applying radius of curvature down to 5 mm.

In summary, we have demonstrated that the protocol to prepare electrodes based on random networks of AgNWs can be improved by simplification of the purification process through decantation. Thanks to high performance sprayed electrodes, we have fabricated a capacitive touch sensor. It shows high sensitivity and can eventually modulate the lighting intensity of connected LEDs. In order to confirm the advantage of this technology to currently used TCOs, we performed experiments with various bendings, and we observed that the device was not sensitive to mechanical constraints even at low radius of curvature. To the best of our knowledge, this is the first report of a transparent capacitive based sensor using metallic nanowires. As we already demonstrated that such electrodes can be obtained on extremely thin films (1.3 μm thick) [20], we think these results could be a useful approach for the engineering of highly flexible or conformable touch screen panels or sensors which are not obtainable by current TCO technologies.

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