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Transparent Conductive Three-Layered Composite Films Based on Carbon Nanotubes with Improved Mechanical Stability

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ABSTRACT

A layered composite coating material with favorable properties for application as a transparent conductor is presented. It is composed of layers of three nanoscopic materials, namely zinc oxide nanoparticles, single wall nanotubes, and graphene oxide nanosheets. The electrically conducting layer consists of single wall nanotubes (SWNTs). The layer of zinc oxide nanoparticles acts as a primer. It increases the adhesion and the stability of the films against mechanical stresses. The top layer of graphene oxide enhances the conductivity of such coatings. Such three-layer composite coatings show better conductivity (without compromising transparency) and improved mechanical stability compared to pure SWNT films. The processes used in the preparation of such coatings are easily scalable.

INTRODUCTION

The development of highly transparent films containing single wall carbon nanotubes (SWNTs) is of large interest as these materials may potentially replace indium tin oxide (ITO) in the field of optoelectronic materials [1]. An additional benefit is the possibility to prepare such films by solution-based processes. Previously, it was shown that the application of a thin layer of highly oxidized graphene oxide nanosheets on such SWNT films results in a distinct increase of conductivity since graphene oxide acts as a p-doping agent [2]. In addition, the transparency of films modified in this way remains nearly constant as compared to pure SWNT films.

A serious disadvantage of carbon nanotube films is their poor adhesion on different substrates. We found that films applied on not-pretreated substrates (as glass or foils) may be easily washed off with water or be removed by wiping. This limits the possible application of these materials in technical processes as post-preparation or cleaning steps are restricted. To improve the adhesion and overall mechanical stability of the films, we have introduced a layer of zinc oxide nanoparticles on the substrate which acts as an adhesion promoter for the SWNT layer and does not influence the transparency of the films. Hence, transparent conductive films with increased adhesion and resistance towards water and mechanical stress can be obtained.

For such transparent conductive films, we thus propose a three-layered composite material consisting of a primer layer of zinc oxide nanoparticles, a layer of SWNTs and a final layer of graphene oxide nanosheets. Here, we describe the preparation of such constructs using easily scalable spray-coating techniques in all steps. The prepared coatings are characterized by electron microscopy as well as transparency and conductivity measurements. In addition, we also report on the results of the durability of the films in scratching and wiping tests, especially in comparison to films created without a primer layer.

EXPERIMENTAL DETAILS

Preparation of zinc oxide primer layer

To obtain zinc oxide nanoparticles, we carried out a sol-gel like reaction following the instructions according to JACOBSSON and EDVINSSON [3]. The synthesis was performed by dissolving 1.1 g (5 mmol) $Zn(OAc)_2{\cdot}2\ H_2O$ in 50 mL of boiling ethanol. Then, the solution was cooled in an ice bath and a mixture of 0.3 g (7.1 mmol) $LiOH{\cdot}H_2O$ and 25 mL ethanol was added slowly. The mixture was kept at 2 °C for 18 hours. After addition of approx. 700 mL heptane, a white precipitate was formed which was isolated by centrifugation. This residue was mixed with 50 ml ethanol. After stirring for several minutes a clear and colorless suspension was obtained.

To create the zinc oxide priming layer, a standard microscope slide was cleaned with water and subsequently ethanol followed by wiping with an optical grade cleaning paper. The cleaned slide was heated up to 80 °C and then the ethanolic ZnO nanosuspension was sprayed onto the glass, using a standard airbrush gun (AFC-101A, Conrad GmbH, Germany).

SWNT layer

SWNT paste was obtained from Fraunhofer IWS in Dresden, Germany. Besides single wall nanotubes and water, this paste contains a large amount of catalyst material, e.g. cobalt, iron or nickel. To remove these catalysts and to oxidize the nanotubes, the material was treated with concentrated nitric acid under reflux conditions for several hours. Afterwards thorough washing and centrifugation steps were performed. A subsequent dialysis resulted in a black aqueous solution with a SWNT content of 0.08 %.

The solution was further diluted to a SWNT content of 0.01 % and then sprayed on the heated ZnO-coated substrate at 100 °C. This step was repeated for a various number of times for each sample to obtain a variety of samples with different thicknesses of the SWNT film. This was done with regard to the investigations on electrical conductivity and optical transparency, respectively.

Graphene Oxide top layer

In order to improve the conductivity, a third layer consisting of graphene oxide (GO) nanosheets was deposited on top of the SWNT layer. Graphene oxide was prepared following an instruction published by MARCANO in 2010 [4]. The synthesis was carried out by adding slowly 4.5 g (28.5 mmol) of $KMnO_4$ to a mixture of 2.5 g (62.5 mmol) graphite and 100 mL H_2SO_4:H_3PO_4 (9:1). Once the addition of $KMnO_4$ is complete, the mixture was stirred for 12 hours at 50 °C. Afterwards, 100 mL of a water ice mixture was added and stirred for several minutes. Then, 3 mL of H_2O_2 (30 %) solution and 200 mL water were added. The precipitate was centrifuged, washed with water repeatedly and finally freeze-dried under vacuum to obtain the GO powder.

40 mg of GO powder were dispersed in 100 mL of water to receive a sprayable suspension. This suspension was treated with an ultrasonic finger (Branson Digital Sonifier 450) with a power output of 120 W for one hour. Nano sized graphene oxide sheets with a size of about 500 nm were obtained from the supernatant after a centrifugation step [2]. This solution was further diluted and then sprayed on top of the heated (80°C) SWNT layer.

RESULTS AND DISCUSSION

Characterization of zinc oxide nanoparticle suspension and primer layer

The ethanolic nanosuspension was clear and colorless and showed no visible TYNDALL scattering during laser irradiation. To determine the particle size and size distribution of the zinc oxide nanoparticles, the particles were investigated with transmission electron microscopy (TEM) and dynamic light scattering (DLS). As shown in figure 1, the solution consists of particles with a monomodal size distribution at approx. 5 nm. Larger agglomerates of particles were not detectable, neither by TEM nor by DLS investigations.

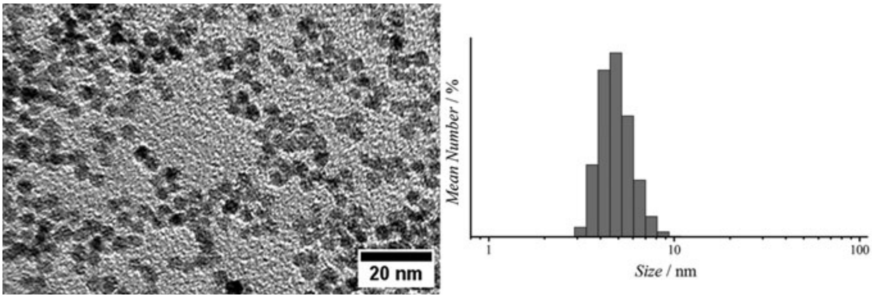

Figure 1. The transmission electron micrograph reveals a particle size of 5 nm (left). Dynamic light scattering measurements show a narrow size distribution with a mean value of 5 nm (right).

Investigations of the zinc oxide layer with a confocal microscope showed that the nanoparticles are not homogenously spread on the substrate, but form circular shaped agglomerates with a thickness of about 80 nm at the edges and a width of several microns (figure 2).

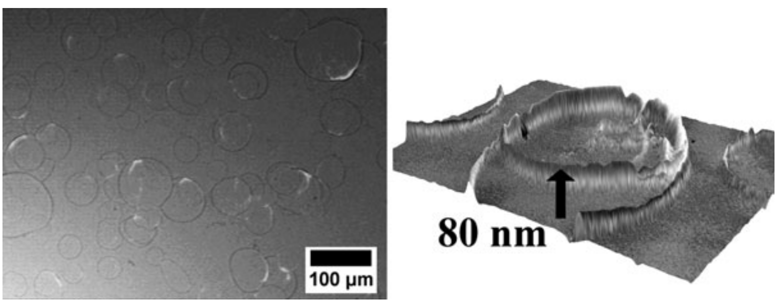

Figure 2. Confocal microscopy of zinc oxide primer layer. Left: Bright field image of zinc oxide nanoparcticle agglomerations on the substrate. Right: Stacked confocal images with height informations.

SWNT layer

Investigations via light microscopy showed that the sample is completely covered with carbon nanotubes but shows circle-shaped inhomogeneities with a diameter of several microns (cf. figure 3, left image).These distortions are caused by the formation of very small droplets during the spraying process. At a very high magnification, using a scanning electron microscope, a dense network of interwoven single wall nanotubes is visible as shown in the right image of figure 3. Besides the network of SWNTs several light spots with a diameter of 20 to 100 nm were found during SEM investigations. These impurities may be dried inorganic salts from the spraying solution or residual catalyst material from the SWNT paste which could not be removed completely during the purification treatment.

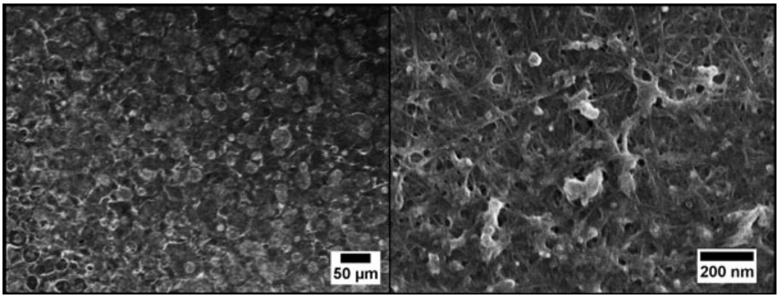

Figure 3. Microscopic investigations of the SWNT layer. Left: Light microscope image, showing circle-shaped structures, caused by the spraying process. Right: SEM image showing dense network of intertwined nanotubes.

To verify whether or not the zinc oxide priming has an influence on the electrical conductivity or optical transparency of the films, several samples with and without priming layer were prepared. Additionally the amount of applied SWNT material was varied as mentioned earlier. The transparency of each sample was measured with a spectrophotometer (Varian Cary 5R) at a wavelength of 540 nm. The electrical characterization was performed by measuring the sheet resistance (R_S) using a four-point-probe arrangement and a digital multimeter (Keithley 2100). As shown in figure 4, the sheet resistance and the film transparency is hardly influenced by the zinc oxide primer.

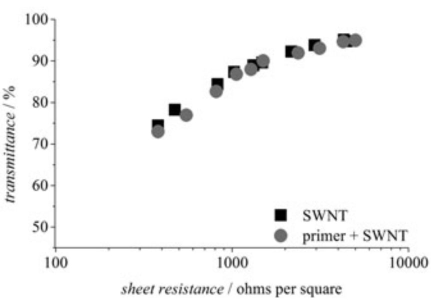

Figure 4. Samples with a primer layer show the same performance with regard to sheet resistance and transmittance as the samples prepared without priming.

To evaluate the stability of the primed SWNT layer in terms of scratch resistance, pencil scratch tests following ISO standard No. 15184 were performed [5]: Different types of pencils were scratched over the coated surfaces. Even though it is not possible to determine the exact pencil hardness of each coating, qualitative statements regarding the mechanical stability of the films are possible. Samples with and without primer were scratched with the same pencil and afterwards characterized via optical microscopy. It can be seen in the left part of figure 5 that the films equipped with a priming layer show significantly less scratches on the surface after the pencil tests using a 6B pencil.

Additionally, a sample partially coated with the ZnO primer but fully covered with a SWNT layer was prepared. Wiping this sample with a wet cotton swab provides a test of the adhesion of the different surfaces under wet conditions. The right part of figure 5 shows the border between the area with zinc oxide primer and the part of the film with only SWNTs. Whereas the area with zinc oxide shows only little defects within the film, the part without primer has nearly been completely wiped off.

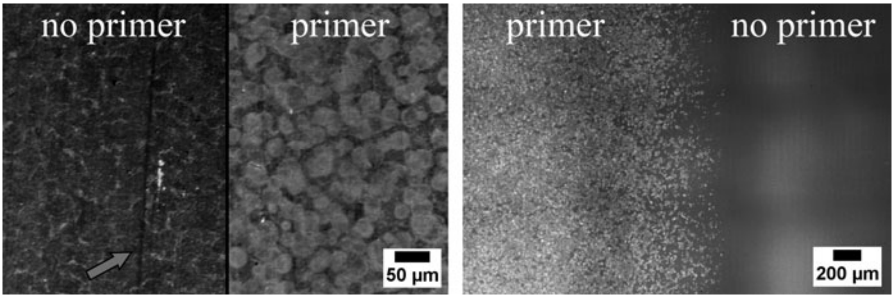

Figure 5. Light microscope images of the films after scratching tests (left) and after wiping tests using a wet cotton swab (right).

One reason for the good adhesion of the SWNT layer on the zinc oxide primer may be the strong electrostatic attraction between the oxidized surfaces of the nanotubes and the polar surfaces of the zinc oxide nanoparticles. Additionally, the formation of the circle-shaped agglomerations of the ZnO nanoparticles increases the surface roughness and could potentially enhance the adhesion of the nanotubes.

Graphene oxide layer

Both – conductivity and transparency measurements – were carried out to confirm the p-doping effect of an added graphene oxide layer on top of the SWNT network. As shown in figure 6, a distinct reduction of the sheet resistance is noticeable. These results are in good agreement with a previous publication [2].

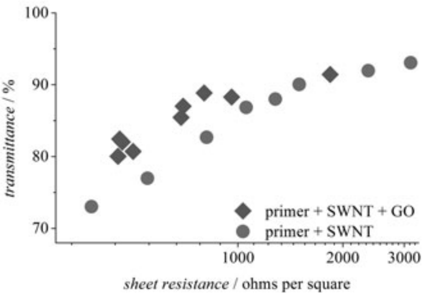

Figure 6. Samples with a top layer of graphene oxide show a better performance than those without such a layer, i.e. at a certain transmittance their sheet resistance is smaller or at a certain sheet resistance their transmittance is higher.

CONCLUSIONS

We have shown how the combination of three different nanoscopic materials – zinc oxide nanoparticles, single wall carbon nanotubes and graphene oxide nanosheets – leads to a composite layered material which has favorable properties for application as a transparent conductor. The layer of zinc oxide nanoparticles is crucial as it acts as a primer and increases the overall film stability against mechanical stress under both dry and wet conditions. The SWNT layer, which forms the conductive regime of the material, consists of a dense network of highly interwoven single wall nanotubes. Finally, the conductivity of such films could further be raised by applying a layer of graphene oxide nanosheets. Overall, this composite layer material does not only show a better conductivity without compromising transparency, but also a much better mechanical stability compared to SWNT films on pristine surfaces. The processes used in the preparation do not need a vacuum and demand for only slightly elevated temperatures; the spray processes can easily be scaled to larger surfaces and can also be used for patterned coatings.

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