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Functionalization of carbon fiber tows with ZnO nanorods for stress sensor integration in smart composite materials

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Abstract. The physical and operating principle of a stress sensor, based on two crossing carbon fibers functionalized with ZnO nanorod-shaped nanostructures, was recently demonstrated. The functionalization process has been here extended to tows made of one thousand fibers, like those commonly used in industrial processing, to prove the idea that the same working principle can be exploited in the creation of smart sensing carbon fiber composites. A stress-sensing device made of two functionalized tows, fixed with epoxy resin and crossing like in a typical carbon fiber texture, was successfully tested. Piezoelectric properties of single nanorods, as well as those of the test device, were measured and discussed.

Keywords: carbon fibers, stress sensors, piezoelectric, ZnO, smart materials

1. Introduction

It is widely acknowledged that carbon fiber (CF) composites are a fundamental class of materials in applications where both light weight and high mechanical properties are required. They are in fact widely used in high-level automotive and their employment in civil engineering and aerospace is growing increasingly [1-4].

Unfortunately, it is also well known that, despite their unique properties, in these composite materials the mechanical response to an applied stress is strongly dependent on the relative arrangement of each resin/ CF patch layer. Since this behavior is different for each single CF composite object, univocal mechanical models and simulations are hard to realize [5-8]. Therefore, it would be very important to monitor in real-time a CF composite structure by means of deformation sensors during its application. [9-10].

Nowadays resistive strain gauges [11,12], fiber Bragg gratings [10,13,14] and piezoelectric lead zirconate titanate (PZT) inserts [15,16] are the most common devices used for this purpose. Nevertheless, all these technologies have still today significant drawbacks: the large dimension (compared to the one of a single CF) can lead to delamination, while the need to monitor several spots on large areas forces an unwanted weight addition (e.g. in aircrafts).

Among the mentioned properties, piezoelectricity is the ideal physical property for sensing mechanical stress, because in a piezoelectric material deformation and electrical properties are deeply correlated. Furthermore, beside the “direct” piezoelectric effect, when displacive charges arises from deformation, there is also a corresponding “inverse” piezoelectric effect, which leads to a deformation when an electric field is applied. The inverse effect is generally exploited for actuating applications. So if both properties are combined with a feedback system within a CF composite, it should be possible to measure and damp vibrations and deformations in real-time.

Stress sensors based on zinc oxide (ZnO) 1D nanostructures grown on CFs have been recently proposed and studied [17]. ZnO is indeed a piezoelectric cheap and lead-free material that can be easily grown on different substrates. We have demonstrated that it is possible to realize a stress sensor with a single CF coated with ZnO nanostructures and that it doesn't need expensive noble metal contacts for Schottky barrier formation. Beside the concept demonstration, a novel approach for the piezoelectric characterization of this type of sensing structure was also reported.

Beside these experiments, however, a few fundamental steps towards the possible integration in real applications and in an industrialization process were still needed. On one hand it was very important to scale up the functionalization process and the whole device design from a single and fragile fiber to larger and more handy CF tows. On the other hand, a more precise quantification of the piezoelectric effect in the synthesized ZnO nanostructures and a test of the obtained devices were required. The results of these studies are herein reported, stepping these devices higher and closer to the industrialization process.

More in detail, the growth technique was optimized for the depositions of ZnO nanorods (NRs) on whole CF tows. The growth techniques commonly used for high quality ZnO NRs need high temperatures, but at high temperature, and in presence of water vapor or oxygen, CFs are subject to oxidative degradation. So a low temperature process has to be always preferred in order to preserve them. Chemical Bath Deposition (CBD) is generally a high-yield, and hence low-cost, and low temperature synthetic method that may be exploited to grow ZnO nanostructures on large scale. It is indeed both not so aggressive towards CFs and suitable for an industrial scale-up.

By the way, piezoresponse also needed to be quantified and then tested on the “tow” system, whose behavior is much more complex than the one of a single-CF in a “proof of concept” experiment.

Piezoelectric characterization of single ZnO-NRs was carried out through piezoresponse force microscopy (PFM), while Dynamic Hysteresis Measurement (DHM) was used in combination with capacitance analysis to test the finished CF-tow-scale sensor.

The piezoelectric coefficient of the samples grown by the chemical solution were also compared with the one arising from ZnO NRs grown by vapor phase method to quantify the potential losses introduced by a cheaper but large-scale oriented growth process.

2. Experimental

2.1 Functionalization of CFs with ZnO NRs

CF tows made of about 1000 fibers were functionalized with ZnO-NRs following a two step CBD process. The first one is needed to form a seed-layer made of ZnO nanoparticles all around the fibers, while the second one is for the growth of ZnO-NRs (Fig. 1a)

The continuous layer of ZnO nanoparticles was deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method. This technique involves subsequent fast immersions in zinc salt solution and ammonia solution, alternated with rinsing in distilled water (Fig. 1b). About 20/30 fast cycle repetitions in zinc acetate and ammonia solutions with 100 mM concentrations were used to obtain a good coating on the CFs. This process can be easily scaled up using a long CF tow in a roll-to-roll system that brings the tow through the different solution containers (Fig. 1c).

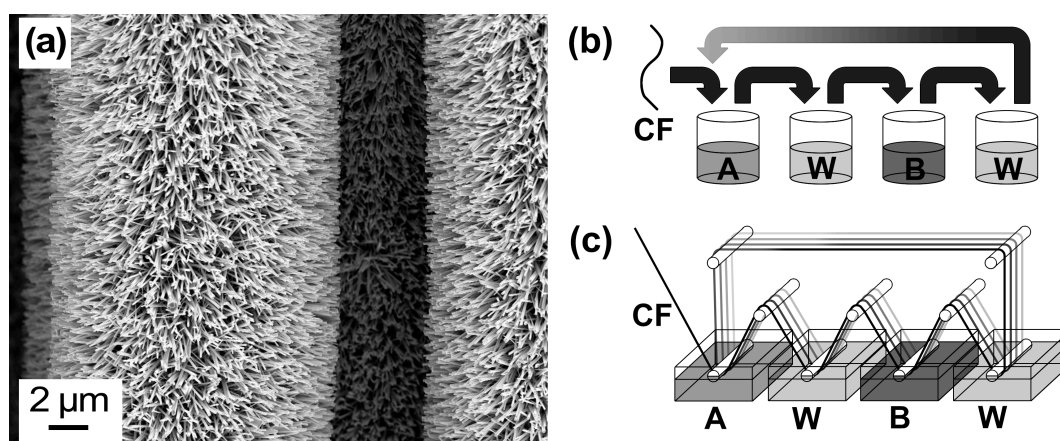


Figure 1. (a) SEM image of CF functionalized with ZnO-NRs (b) scheme of SILAR process, where a piece of CF-tow is cycling immersed in zinc salt solution (“A”), distilled water (“W”) and ammonia solution (“B”); (c) scheme of the possible extension of the previous SILAR process to a “roll-to-roll” system for a long and continuous CF tow.

ZnO-NRs were then grown on the obtained seed layer thanks to a CBD process. The coated CF tows were immersed in an equimolar 20 mM aqueous solution of hexamethylenetetramine (HMTA) and zinc acetate at 95°C for 4 hours. The obtained functionalized CF tows were finally rinsed in distilled water.

2.2 Growth of reference ZnO-NRs by vapor phase technique

A reference sample with high purity ZnO-NRs grown from by vapor phase was prepared following the procedure described in Refs. [17,18]. In this way, ZnO-NRs can be grown homogeneously on a flat and conductive Al:ZnO (AZO) layer using only a metallic Zn source and oxygen. The wanted lack of any catalyst, salt or low-temperature precursor is intended to minimize the possible contamination in the growth of metal-oxide nanostructures like these [19-23].

It was not possible to grow ZnO-NRs on CF by this vapor phase technique because CF quickly degrade at the used temperature (almost 500°C) in presence of oxygen [24].

2.3 2.3. Device preparation and piezoelectric characterization

The piezoelectric response of a single ZnO-NR was measured by PFM (Fig. 2), one of the available operating modes of an atomic force microscope (AFM). PFM is generally used to measure piezoelectric constant through the converse piezoelectric effect. In our experiment piezoelectric constant of ZnO-NRs was characterized by the Park Systems XE-100 PFM. An AFM disc was coated with Ag paste and one of the functionalized CFs was half immersed (laying horizontally) in the conductive paste (Fig. 2b) until complete drying. A Pt coated silicon tip (Multi 75E-G, Budget Sensors, 3 N/m of force constant and 75 kHz of resonant frequency) was then placed on the top of a ZnO-NR with contact force of 10 nN and AC voltage from 0 to 5 V with 17 kHz was applied with a lock-in amplifier (Stanford Research, SR830). The subsequent axial deformation due to the piezoelectric effect was measured. Different NRs were analyzed in sequence in order to obtain statistically valid data.

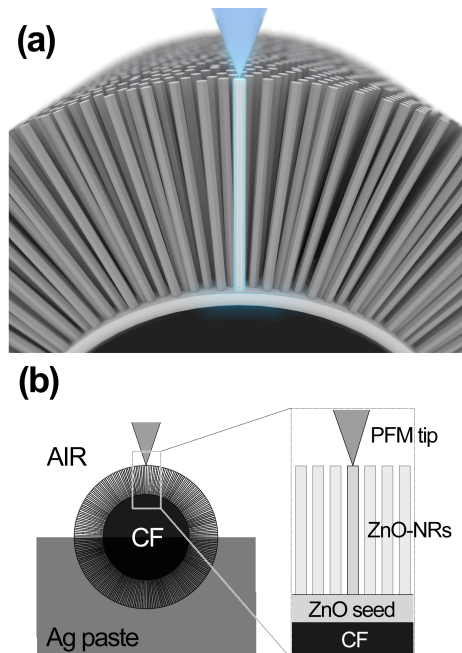


Figure 2. (a) visual and (b) schematic cross-section drawings of the PFM measurement configuration to measure the piezo-response of a single ZnO-NR.

Measurements on single ZnO-NRs grown by vapor phase were also performed by applying the same probe stress, in a similar configuration, with the only exception that NRs were on the flat substrate with AZO back contact instead of the wire-shaped CF.

Two CF tows, made of one thousand CFs each, were arranged perpendicularly one above the other, forming a cross intersection, to realize the test device (Fig. 3). To emulate a finished composite, they were soaked in epoxy resin, which stiffens the structure and prevents short-circuits. A pressure was then applied by means of a micro-controlled pushing system and the piezoelectric signal was measured. The piezoelectric response was discriminated by selecting the dielectric branch of the system through the dynamic hysteresis measurement (DHM) protocol and then by recording the capacitance vs. staircase voltage time dependence under intermittent and variable pressure application, as comprehensively described in Ref. [17]. The utilized instrument is the Ferroelectric Tester TF Analyzer 2000E by AixACCT GmbH equipped with the Ferroelectric module

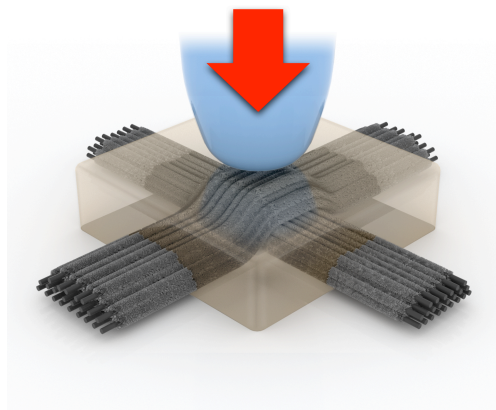


Figure 3. Drawing of the test configuration for the device made with crossing CF-tows. The two tows are embedded in an epoxy resin layer to simulate the final configuration in a CF composite. Pressure is applied along the direction that is perpendicular to the crossing plane.

3. Results and discussion

By varying the different synthesis parameters (precursors concentration, temperature, time) it is possible to tune the aspect ratio on ZnO-NRs. Although these parameters are often dependent on each other, as a general observation it is possible to state that NRs can be grown shorter and less dense mainly by lowering the concentration of precursors.

The ZnO-NRs that were chosen for these experiments have a lateral dimension between 50 and 200 nm (NR diameter shows a Lorentzian distribution with a mean value of 60 nm), while their length is about 1.5-2 μm . The mean density of NRs is about fifty units per μm^2 .

ZnO has piezoelectric properties thanks to the wurtzitic structure (spatial group P63mc) that was confirmed for the grown nanorods by XRD. The piezoelectric behavior of a single ZnO-NR is analyzed by means of PFM technique.

Piezoelectric coefficient d_{33} of ZnO can be calculated as the ratio between the slope of the measured PFM curve and the one of a quartz reference sample (x-cut in this case). In Figure 4a it is possible the response of a typical ZnO-NR grown on CF is reported.

The obtained value of 4.4 pm/V, in agreement with the mean value obtained on different NRs, fits with the known range of 0.4 and 45 pm/V for ZnO [25-34]. This wide compass of values reported in literature can be attributed to the different characterized crystals (nanostructures, bulk, thin film, etc.), but also to the different growth methods. These can, indeed, produce different concentrations of defects or, more often, of free charges that screen the piezoelectric effect.

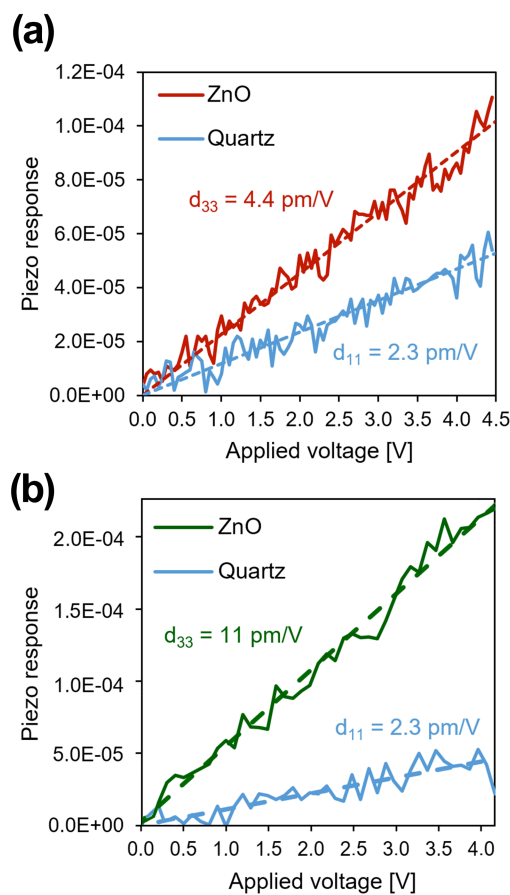


Figure 4. (a) Piezoelectric response of ZnO (red) and reference quartz (blue). (b) Comparison between piezo response of vapor phase grown ZnO NRs (green) and quartz reference (blue). d_{11} of x-cut quartz is 2.3 pm/V. Piezo response is a dimensionless quantity since it is related to the reference's. For both measurements the linear regime is evaluated.

A more accurate quantification of this behavior can be obtained by comparing PFM measurements of samples with similar size but grown by means of different techniques. Figure 4b shows that ZnO-NRs grown by vapor phase exhibit a higher d_{33} value (11 pm/V). This technique allows indeed to obtain ZnO with lower concentration of impurities and defects, so the piezoelectric response is expected to be less screened by the lower concentration of free charges.

Although a slightly lower d_{33} value is measured in the case of the ZnO-NRs grown on CBD because of the higher impurities and/or defects concentration, the value was high enough to produce a good and measurable response in the tow-scale piezoelectric sensor device.

The properties of the test-device made of two crossing CF-tows were characterized by DHM measurements.

As said before, the obtained ZnO-NRs have low resistivity because of the significant presence of intrinsic dielectric leakage currents of the dielectric but for the presence of defects and impurities. Under this condition, free charges can flow through them when DC voltage is applied, shielding the I-V signal coming from the static piezoelectric charges. On the contrary, if fast triangular voltage pulses are used, it is however possible to significantly reduce the free charge contribution moving to a frequency range where material acts as dielectric. For such operational frequency capacitance measurements can be exploited to investigated piezoelectricity.

Once resin is completely dry the object becomes stiff, force is applied perpendicularly to the crossing point and it is transferred rigidly from the outer structure to the ZnO NRs, which are compressed and bent. Deformation of the ZnO crystal causes a variation of dielectric constant, on which capacitance is dependent. This means that within the elastic range, when the relation between applied stress and crystal deformation is linear, a capacitance variation can be correlated with the applied stress.

Crystal facets of ZnO-NRs pointing towards outside are usually [0001] zinc-terminated faces (positively charged), while the opposite [000-1] oxygen-terminated (negatively charged) faces are those pointing towards the corresponding CF [35-37]. In this configuration the piezoelectric signal collected from each wire is added constructively to the others and increases the overall output (Fig. 5a). Figure 5b shows the typical DHM plot obtained on the test device made with functionalized CF tows. In the presented case, the system highlights the typical “banana” loop [38] indicating a substantial balance between the intensity of the displacement current (which gives information of the dielectric/piezoelectric character of the system) and leakage currents.

The frequency (f) range was determined by maximizing dielectric response with respect to the leakage (resistive) one. It was observed that the best results are obtained for $f > 3000$ Hz, even though pure dielectric response cannot be achieved for the tested devices and the leakage effects cannot be reduced less than the 25% of the overall signal. However in this conditions capacitance measurements retain a sufficient dielectric reliability as demonstrated by the expected capacitance vs. voltage invariance.

Hence, piezoelectricity was investigated by measuring real time variations of the capacitance induced by an application of an external mechanical stress. It is possible to see in Fig. 6, that each time a force is applied the capacitance displays a sharp peak whose intensity is proportional to the intensity of the stimulus. A maximum capacitance increase of 508% (respect to the value observed in the state of non-stressed device) is observed during these measurements when a force of about 0.5 N is applied. Under such a force application

intensity, a smaller phenomenon is observed to be superimposed: i.e. the extrinsic capacitance enhancement, due to the overall reduction of mean distance between CFs. However such spurious signal was estimated to be about 50-100% larger than the baseline invariant signal at 0.5 N (as characterized on a ZnO-NRS free sample), quantitatively five and ten times smaller than the piezoelectric one. Consequently, these measurements confirm that the device made with crossing tows of CFs functionalized with ZnO-NRs can act as a stress sensor and paves the way for the production of fully integrated stress-sensing CF composites.

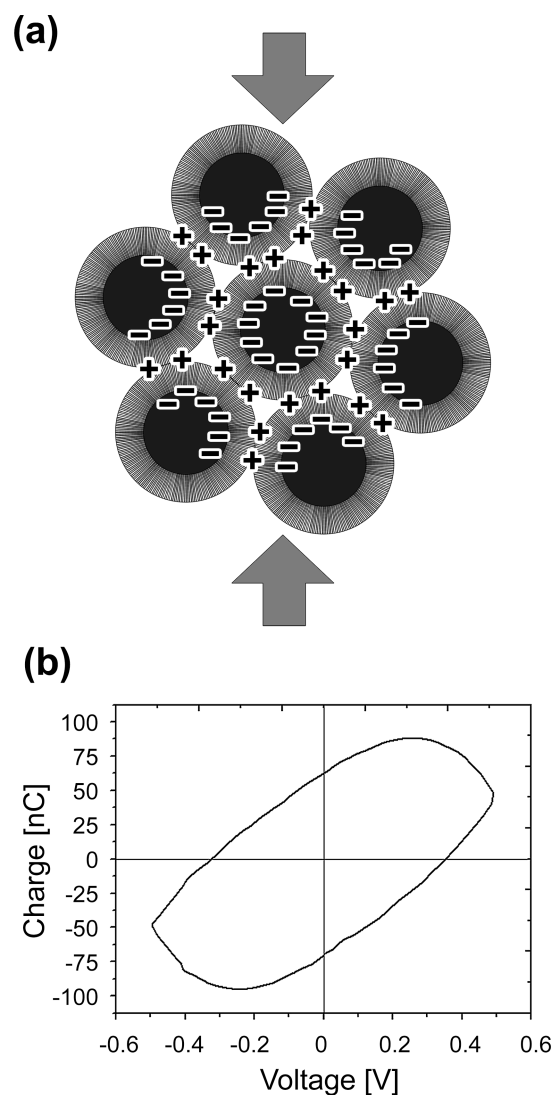


Figure 5. (a) Piezoelectric response of ZnO (red) and reference quartz (blue). (b) Comparison between piezo response of vapor phase grown ZnO NRs (green) and quartz reference (blue). d_{11} of x-cut quartz is 2.3 pm/V. Piezo response is a dimensionless quantity since it is related to the reference's. For both measurements the linear regime is evaluated.

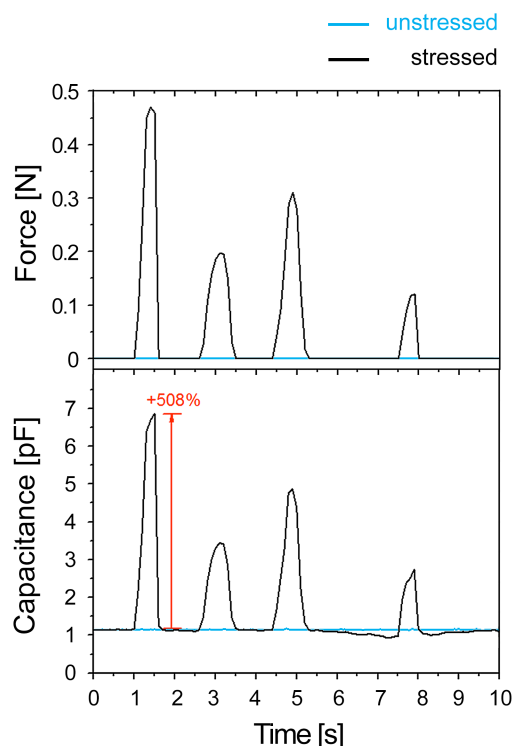


Figure 6. Force intensity and resulting capacitance peaks for randomly applied stress on the device made with functionalized CF tows (collected with staircase signal of maximum amplitude of 1V and modulation frequency of 3KHz).

4. Conclusions

CF tows containing one thousand CFs each were functionalized with a ZnO seed-layer and then with ZnO-NRs by means of an optimized aqueous and low-temperature CBD, suitable also for large scale production.

Piezoelectric characterization was carried out both on single ZnO-NRs and on the test device, made of two crossing CF tows functionalized with ZnO-NRs and immersed in epoxy resin (in order to realize a composite).

Single NRs were characterized by PFM showing that the d_{33} value of these nanostructures grown by CBD is 4.4 pm/V, which is consistent with the known range of 0.4 and 26.7 pm/V. As a term of comparison, also ZnO-NRs grown by vapor phase were characterized, resulting in a higher 11 pm/V value. The difference was reasonably attributed to the higher concentration of defects and impurities in the CBD grown nanostructures. Although this value is not close to the maximum reported one, CBD can be easily applied on a large industrial-scale production and the recorded d_{33} value is sufficient to obtain highly sensitive piezo-sensors.

The test piezo-sensor device, instead, underwent a DHM + capacitance analysis. Measuring at frequency higher than 3 KHz, it has been possible to remove spurious leakage contribution and to detect capacitance peaks induced by the applied stress and proportional to the stimulus intensity, showing a 508% capacitance increase for an applied force of about 0.5 N.

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7 These results with crossing CF tows functionalized with ZnO nanostructures are an
8 important advance on the preliminary experiments on single CFs and an effective
9 improvement toward the industrialization process of integrated stress-sensors in CF
10 composites.
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