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GO/glucose/PEDOT:PSS ternary nanocomposites for flexible supercapacitors

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Abstract

Poly(3,4 ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS), among the most used conductive polymers, shows properties easily modulating by adding fillers as Graphene Oxide (GO). Recently, PEDOT-based polymers have been used with encouraging results as electrodes for flexible supercapacitors. We have already developed a green ternary nanocomposite based on PEDOT:PSS doped with GO and glucose (GGO-PEDOT) with a specific capacitance of 16 F/g, indicating how this nanocomposite is potentially suitable to be used as an electrode material for a supercapacitor. In this work, a free-standing nanocomposite film was realized by drop casting the solution in a proper silicone mould, followed by peeling and thermal annealing. Specific analyses, such as thermogravimetric, colorimetric and contact angle measurements, have been performed aiming at assessing the stability of the thermal and of the surface properties, even in severe moisture and UV aging conditions.

Finally, The capacitive performance of PEDOT:PSS and of GGO-PEDOT was investigated by means of cyclic voltammetry (CV), in the pristine conditions and under UV aging. The deposited GGO-PEDOT film showed a good conductive behaviour and stability under UV treatment of 4 hours.

Keywords

Ternary GO/glucose/PEDOT nanocomposite, durability, flexible supercapacitors

Introduction

PEDOT-based conducting polymers are among the most promising materials to be used as electrodes for flexible supercapacitors[1]. As an example, the supercapacitors realized with nanofibrillar PEDOT films by D'Arcy et al. [2] exhibited high specific capacitance and outstanding electrochemical stability. The supercapacitors based on the PEDOT papers, prepared by Anothumakkool et al. [3] showed both high specific capacitance and energy density. Furthermore, Zaifang Li et al. [1] reported a novel successful approach to prepare a uniform, highly conductive, thick PEDOT:PSS film, suitable for energy conversion and storage devices, such as solid-state flexible symmetric supercapacitors, presenting a good volumetric energy density. However, a potentially higher conductivity is expected to further improve the performances of the conductive polymeric matrices and, in turn of the supercapacitors. To this aim, polymer composites based on three-dimensional lamellar fillers (such as graphene oxide) have been recently largely proposed and examined in literature. In particular, graphene based reinforced polymers are versatile engineering materials that can be employed in several industrial fields, thanks to their high specific strength-to-weight ratio, ease of forming different shapes by one-step manufacturing process and less sensibility to corrosion [4]. Furthermore, polymer thermoelectric/graphene nanofiller composites have attracted increasing attention and exhibited great potential in green energy conversion due to their mechanical flexibility and thermal conductivity [5].

Recently, we developed a green ternary nanocomposite based on PEDOT:PSS doped with GO and glucose for greatly efficient perovskite solar cells [6]. In a subsequent work [7], the electrochemical properties of ternary nanocomposites, i.e. GO/PEDOT with different kinds of green dispersing agents belonging to the family of oligosaccharides and polysaccharides, such as cyclodextrin and cellulose were also, investigated using cyclic voltammetry (CV). The CV results revealed that GO/PEDOT with glucose exhibited the highest specific capacitance among the systems investigated, indicating how this nanocomposite is potentially more suitable to be used as an electrode material for a supercapacitor. Because of its high conductivity and flexible properties, the GO/glucose/PEDOT nanocomposite film could be, hence, proposed for flexible supercapacitors. In order to confirm the

experimental evidence formerly obtained [7] and to verify the suitability of the ternary nanocomposite previously developed for the selected application, in this paper further specific analyses have been performed aimed to assess the durability of the thermal stability and the physical and electrochemical properties, even in severe aging conditions.

Experimental

Materials

PEDOT:PSS (Clevios PVP Al4083) was purchased from Heraeus, α-D-glucose anhydrous 96% was purchased from Sigma Aldrich.

GO, prepared by using a modified Hummers method [8, 9] from graphite flake, was synthesized following an innovative and experimental method largely explained in our previous papers [6, 7].

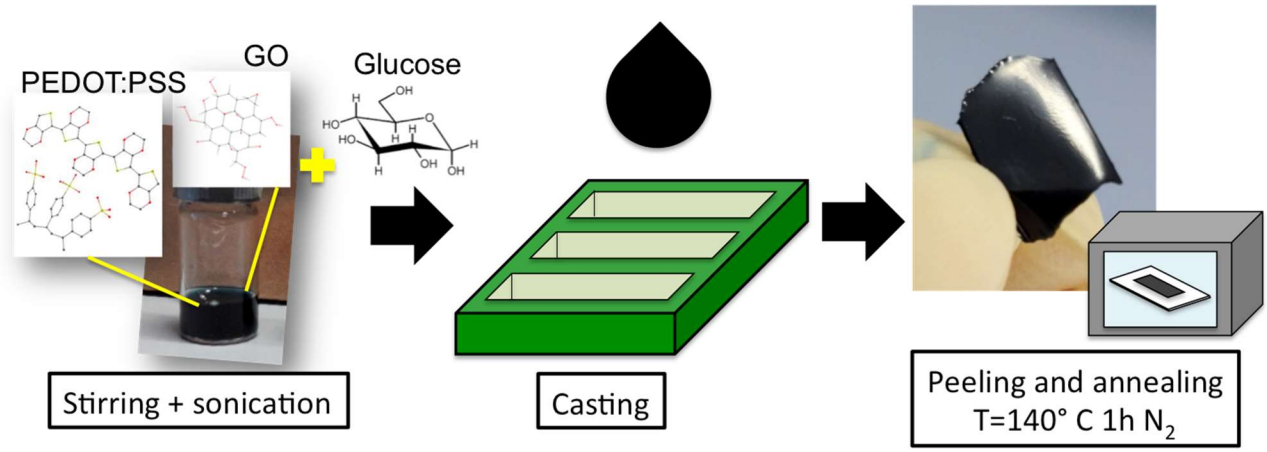
Nanocomposite solution preparation

GO was dispersed into PEDOT:PSS by the solvent swelling method, as discussed in detail in our previous papers [6, 7]. In particular, a GO/PEDOT:PSS dispersion (0.05% wt/V) was stirred (90′) and sonicated (15’) at room temperature. 1% wt/V of glucose was added to the mixture that was stirred and sonicated for others 15′ respectively, obtaining a good dispersion of GO into PEDOT:PSS favoured by the use of glucose, according to previous results [7].

Film preparation

A novel deposition method was explored for PEDOT:PSS+GO+glucose (GGO-PEDOT) nanocomposite solution, developed in our previous work [6, 7], in order to assess the processability of the solution. In particular, the nanocomposite solution was drop casted into a silicone mould and dried in air for 72h. Free-standing films were obtained by peeling off the samples from the silicone substrate, demonstrating that the nanocomposite solutions prepared are suitable to be deposited by a very easily processable method. The films were annealed for 1 h at 140° C on a hot plate in N_2 atmosphere in order to induce the GO reduction by using glucose as green dispersing agent [6, 7]. The preparation method of both nanocomposite solution and film is shown in Scheme 1.

Scheme 1: GGO-PEDOT solution and film preparation



After cooling, all the nanocomposites samples were characterized by several techniques, in order to evaluate their thermal and physical properties before and after artificial weathering tests. PEDOT:PSS films were tested as reference samples, too.

Characterization techniques

Jeol JSM-6550F Scanning Electron Microscopy (SEM) was used to analyse the morphology of the samples.

The XRD spectra of the annealed films were acquired with a PW 1729 Philips, using Cu Kα radiation in reflection mode ($\lambda = 0.154$ nm) at room temperature from 2θ values of 5°- 60°.

The wettability of the films was evaluated by measuring the contact angle of the water on each film, drop casted on glass substrate and annealed at 140°C in N2 atmosphere, by using a First Ten Angstroms FTA1000 quick start instrument. The results were averaged from at least five independent measurements.

The thermal stability of the films was determined by thermogravimetric analysis (TGA/DSC 1 Mettler Toledo). About 7 mg of each samples were heated from room temperature (25°C) up to 900°C at 10°C/min in N_2 atmosphere. The thermogravimetric measurements were repeated at least three times.

Water vapour absorption tests were performed by measuring the weight of the films as a function of the time up to 48 h, by keeping the samples in a controlled climate chamber (KBF 115 by Binder) at relative humidity of 75 % and temperature of 23 °C.

Four annealed films for each sample were tested and the average weight versus time curves were reported in Figure 2(b). The water vapour absorption coefficient α was calculated by the equation (1):

$$\alpha\,(\%) = \frac{W_f - W_0}{W_0} \times 100 \qquad (1)$$

where W_f is the weight at final test time (48 h) and W_0 is the initial weight of the sample. The α average values, for each sample, were reported in the inset of Figure 2(b).

The water vapour absorption rate of all the films, was calculated from the slope (ms) of the initial portion of the curves, and the average values were reported in the inset of Figure 2(b).

The colour of the films, drop casted on glass substrate and annealed at 140 °C in N2 atmosphere, was evaluated by using a colorimeter (CR-410 Konica Minolta) in total reflectance and double channel mode, using a Xenon lamp as light source. The total colour changes expressed as ΔE*, defined by the L*a*b* system (ASTM D-1925, CIE 1976) according to the equation (2):

$$\Delta E^* = \left(\sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}\right) \qquad (2)$$

was calculated by taking, for each sample, the correspondent films before aging tests, as reference at time t=0. The results were averaged from at least three independent determinations.

Electrochemical measurements were carried out with a PARSTAT 2273 potentiostat/galvanostat, employing a three-electrode electrochemical cell. The working electrode was a film of PEDOT:PSS or of GGO-PEDOT prepared by drop casting the respective solutions on a substrate of AISI 304 stainless steel followed by annealing on a hot plate for 1 h at 140 °C in a N_2 atmosphere. The substrates were insulated using Teflon to mask their cut edges, peripheries and back sides, in order to leave only a surface area of 1 cm^2 exposed to the electrolyte. A platinised titanium expanded mesh electrode was used as counter electrode and a Ag/AgCl (KCl 3 M) was employed as reference electrode. All the potentials were referred to Ag/AgCl. The capacitive performance of PEDOT:PSS and of GGO-PEDOT for supercapacitor was investigated in a 1 M H_2SO_4 aqueous solution at 25 °C at a scan rate of 100 mV s^{-1}, using cyclic voltammetry, where the potential range applied was -0.4 V to 0.6 V.

The analysis of the durability of the films in outdoor conditions was obtained by comparing all the physical and thermal properties previously measured (thermal stability, wettability, colour electrochemical properties) before and after two different artificial weathering treatments. In particular, the ambient conditions related to an outdoor utilization were simulated by studying the effect of UV irradiation and humidity separately. The influence of moisture was evaluated by keeping the samples in a controlled climate chamber (KBF 115 by Binder) at relative humidity of 75 % and temperature of 23 °C for 48 h. The influence of UV aging was simulated in a QUV chamber, distributed by Q-LAB and equipped with UV-A (340 nm) fluorescent lamps. The samples were exposed to an accelerated cycle, performed according to a code [ISO 4892-3 METHOD Cycle K], consisted of an UV-light exposure (irradiance equal to 0.76 W/m^2) at 60 °C for 8 hours.

Results and discussion

The physical and morphological characterization of the pristine films is reported in Figure 1, showing that there are no differences between the XRD spectra of PEDOT:PSS and GGO-PEDOT (see Figure 1(a) and (b) respectively). On the other hand, no GO characteristic peak is observed, confirming that the method used to prepare the nanocomposite solutions was suitable to obtain an homogenous dispersion of the nanofiller GO into the polymeric PEDOT:PSS matrix, thanks to the presence of the dispersing agent glucose, as already demonstrated [6, 7]. Furthermore, the absence of the sharp peaks in both XRD spectra (Figure 1(a) and 1(b)), indicates the mainly amorphous nature of the PEDOT:PSS film. A broad band around 2θ~24° can be attributed to the low-ordered interchain planar ring stacking [10] meanwhile, the weak peak around 2θ =12° indicates the distance between two stacks in the two-dimensional stacking arrangement of polymer chains due to the deposition conditions of the films [10].

The morphology of PEDOT:PSS film analysed by SEM is reported in Figure 1(c) and compared with that of GGO-PEDOT film in Figure 1(d). The surface PEDOT:PSS film appears continuous, as well

as an homogeneous dispersion of GO into PEDOT:PSS was observed for GGO-PEDOT film, confirming the XRD results.

The wettability of both the neat and ternary nanocomposite films was analysed by measuring the water contact angle as function of drop deposition time ranging from 0 to 60 s. The results are reported in Figure 1(e) and 1(f) for PEDOT:PSS and GGO-PEDOT, respectively. Referring to the initial time (t=0), comparing the pictures of Figure 1(e) and 1(f) it is evident that both films analysed show a slightly hydrophobic behaviour with a contact angle of about 99° for PEDOT:PSS and 92° for GGO-PEDOT. This latter behaviour seems to be almost stable for nanocomposite film with a contact angle mildly decreased from 92° to 81° after 60 s of drop deposition, still evidencing a regular drop shape. On the other hand, the neat PEDOT:PSS film shows a contact angle highly decreased from 99° to 43° up to 60 s with an irregular drop shape confirming the more hydrophilic behaviour of the unfilled matrix. The improved wettability of the nanocomposite film was attributed to the presence of both glucose and reduced GO into PEDOT:PSS [6].

This stable wettability characteristic of the nanocomposite represents an important advantage for the selected application and together with the excellent electrochemical properties already measured for this system [7] suggest that the ternary nanocomposites developed could be suitable to be proposed as a supercapacitor.

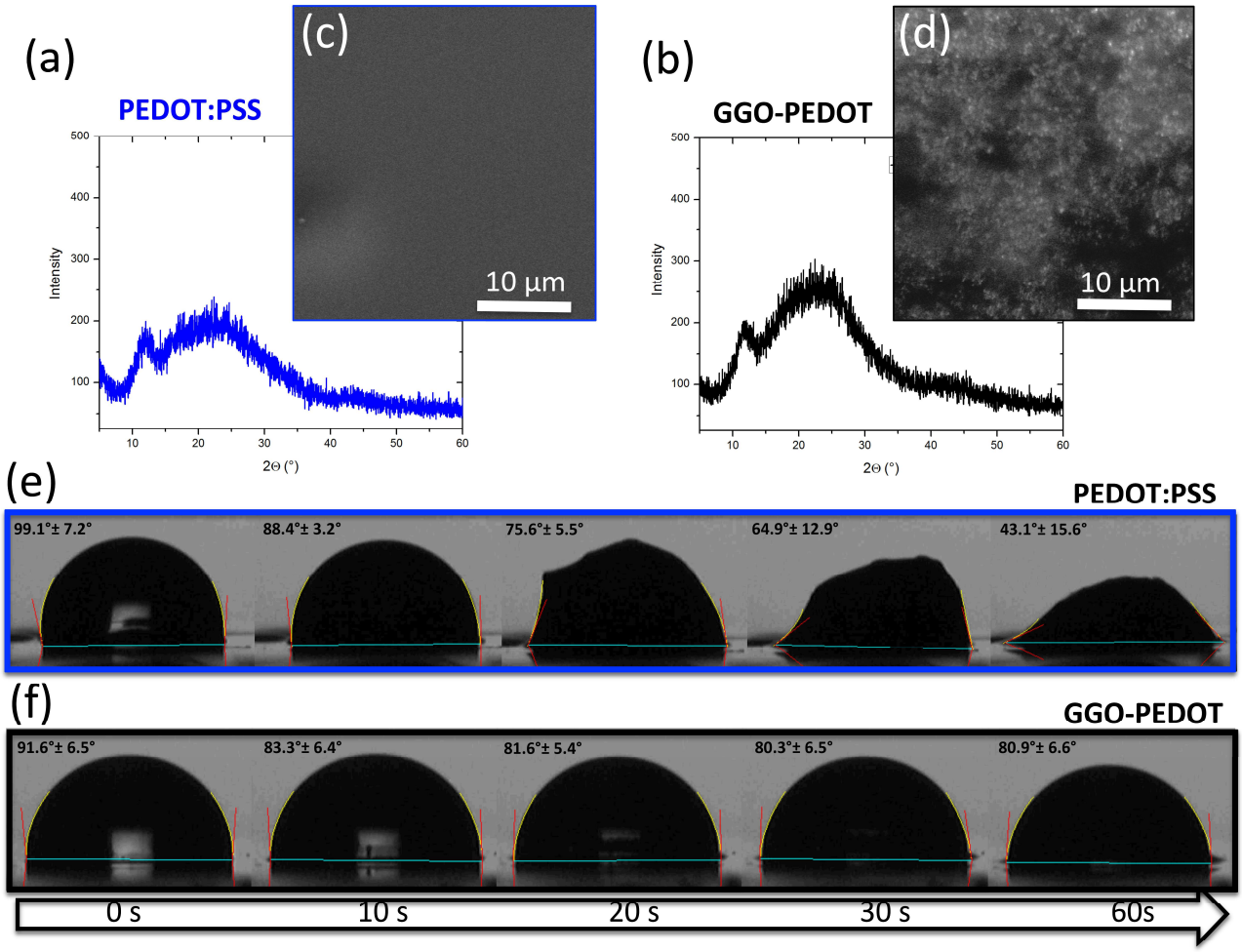


Figure 1 XRD spectra of PEDOT:PSS(a) and GGO-PEDOT(b) films; SEM images of pristine PEDOT:PSS(c) and GGO-PEDOT(d) films; water contact angle as function of drop deposition time on PEDOT:PSS(e) and GGO-PEDOT(f) films.

The thermal stability and the moisture absorption behaviour of both neat and ternary nanocomposite annealed films was also evaluated and reported in Figure 2(a) and (b) respectively.

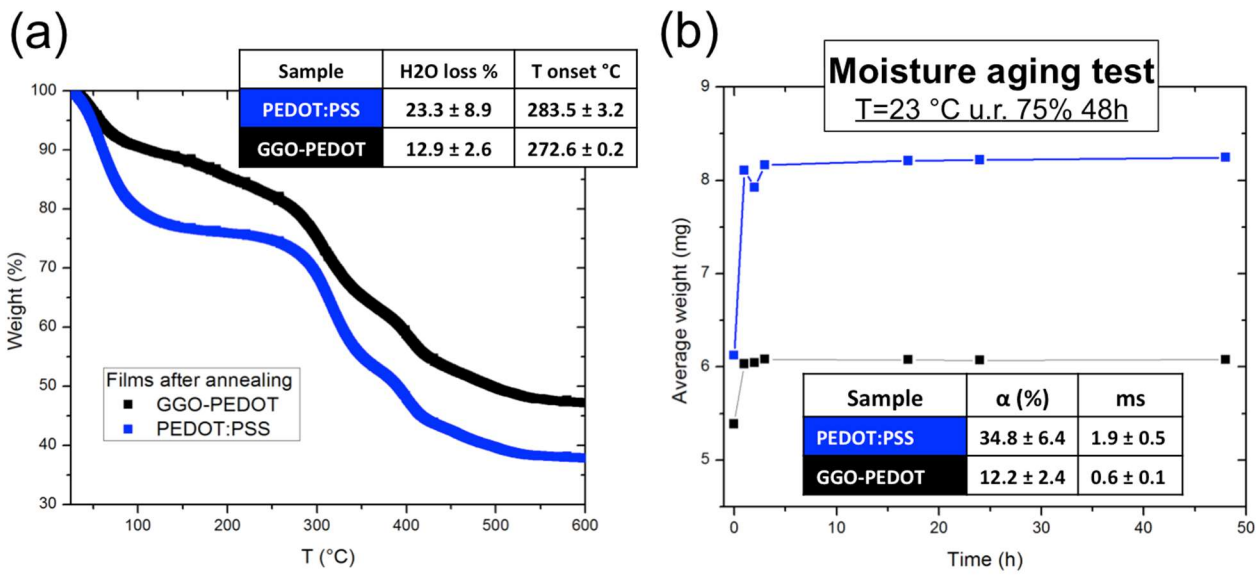


Figure 2 TGA (a) and moisture absorption curves (b) of PEDOT:PSS and GGO-PEDOT

The TGA curves of Figure 2(a) and the weight loss results referred to the first step and reported in the inset Table of the same Figure, evidence a first degradation step, attributed to water loss with a corresponding weight loss of about 23% for the neat PEDOT:PSS and about 13% for GGO-PEDOT film. This result demonstrates that, after 1 h of thermal annealing at 140 °C in N_2 atmosphere, the ternary nanocomposite film contains a lower amount of water in comparison to that of the neat matrix, even if both films were prepared and stocked in the same conditions process (temperature, time, humidity). This latter behaviour confirms that the water molecules present in the nanocomposite film are able to more easily evaporate, because they are more weakly bounded, as already discussed in our previous work [6]. Otherwise, the moisture absorption results (Figure 2 (b)), together with the water vapour absorption coefficient (α) and rate of absorption (ms), calculated starting from the curves reported in Figure 2 (b), following the equation (1) of the experimental section, confirmed this behaviour, even in the case of vapour water. GGO-PEDOT film presents, in fact, both exceptionally lower water vapour absorption rate (about 0.64) and lower water vapour absorption coefficient (about 12%) in comparison to those of neat PEDOT:PSS (about 2 and 35%, respectively), showing a diminution of 68% in water vapour absorption rate and 23% in water vapour absorption coefficient.

A possible explanation of this behaviour could be found in the simultaneous presence of glucose and reduced GO sheets, homogenously distributed into PEDOT:PSS matrix, and, consequently able to create a tortuous path for water molecules, hindering its absorption. In addition, the partially caramelized glucose on the surface of the nanocomposite, as revealed in a previous paper [6], could act as further barrier to moisture absorption.

Finally, a very high degradation temperature (higher than 270 °C) was measured from TGA curves of Figure 2(a) as the onset temperature of the second degradation step for both neat and nanocomposite films (see the inset table of Figure 2(a)), suggesting an optimal suitability of both systems to be used as supercapacitors, even in outdoor conditions.

In order to evaluate if the experimental films realized are able to maintain their good physical and thermal performances even in outdoor conditions, several aging tests were performed on the pristine films and the same properties were evaluated after each accelerated weathering test.

The aging test were performed separately, by exposing the samples to UV lamp for 8 hours (0.76 W/m^2, 60 °C) into the QUV chamber and for 48 h in a climate chamber at 23 °C and 75% of humidity in order to understand which agent among UV irradiation and moisture could have a worst influence on the performance of the films.

The physical and thermal properties of the samples were firstly analysed after moisture aging test and the results are summarized in Figure 3. The pictures of both neat and nanocomposite samples, unaged and aged into climate chamber are reported in Figure 3(a), evidencing, apparently, any difference between PEDOT:PSS and GGO-PEDOT films, before and after the aging test. On the other hand, the quantitative colour test performed on the unaged and aged films shows a slight decreasing of brightness and a certain variation of the colour of both the films after the moisture absorption cycle, as witnessed by ΔL (about 8) and ΔE^* (about 8) values, respectively, calculated respect to each film before aging test, (see the inset table in Figure 3(a)) probably due to the presence of water vapour absorbed.

TGA results referred to the films after the moisture absorption test (see Figure 3(b) and the relative inset Table), show a higher water loss for both PEDOT:PSS (i.e. 28%) and nanocomposite films (i.e. 22%), compared to that obtained on the same films, before the moisture aging test (see Figure 2(a)) confirming higher amount of water present in both samples after the aging test. On the other hand, the TGA results obtained on the films after the moisture absorption confirm the higher absorption capability of the pristine PEDOT:PSS to absorb water respect to the nanocomposite, as already demonstrated from the TGA results before the aging test. Referring to the degradation temperature (onset temperature) of the second degradation step of the TGA curves of Figure 3(b) it is still evident that both neat and nanocomposites films present very high degradation temperature, almost unchanged, even after 48h of permanence in extremely humid ambient.

By comparing the wettability surface behaviour of both the films before and after moisture absorption test (Figure 1(e)-(f) and 3(c)-(d) respectively), it is evident that at the initial time (t=0) the hydrophobic behaviour of PEDOT:PSS slightly decreases with a contact angle ranging from 99° to 92°, meanwhile it remains almost unchanged for GGO-PEDOT (92°). Referring to the effect of the deposition time of the water contact angle, the same qualitative trend was observed for pristine PEDOT:PSS, with a decreasing contact angle up to 29°, even lower than that measured at the same time (60s) for the not aged film (43°).

On the other hand, the wettability properties of GGO-PEDOT film seem to remain unchanged after moisture aging test, even until one minute of water drop deposition with a contact angle ranging from 92° to 83° (Figure 3(c)). This behaviour confirms the higher moisture absorption capability of PEDOT:PSS if compared to GGO-PEDOT and then it determines an higher deterioration of the wettability of the unfilled film surface as a consequence of the accelerated humidity weathering test. This is a further evidence of the exceptional suitability of the ternary GO based nanocomposite to be used in outdoors applications.

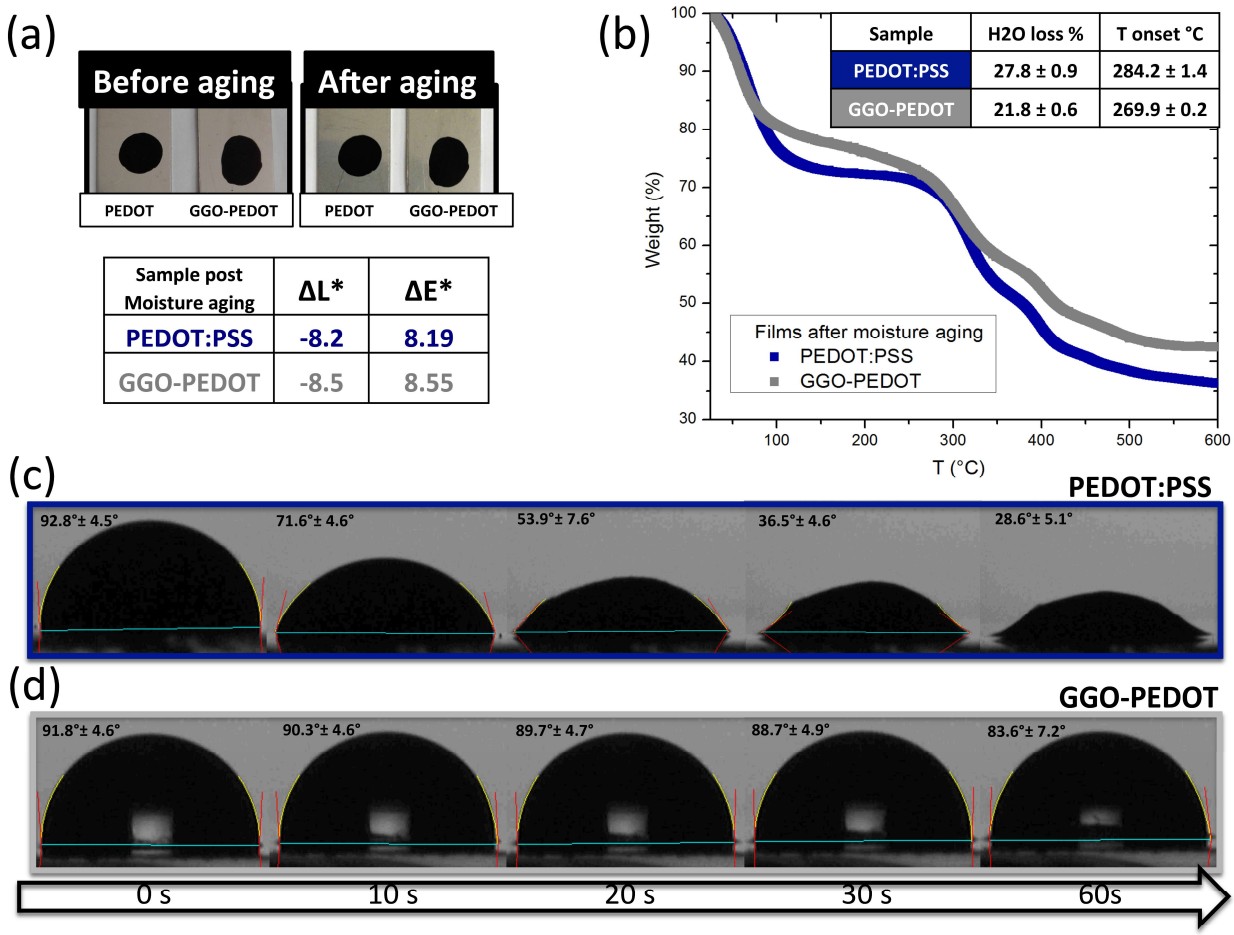


Figure 3 Images and colorimetric test (a), TGA (b) and water contact angle as function of drop deposition time on PEDOT:PSS(c) and GGO-PEDOT(d) films after accelerated moisture aging test.

The influence of a very long UV exposure on physical and thermal properties of both films was also evaluated and the results are summarized in Figure 4. The picture of both samples before and after UV exposure does not evidence differences visible to the naked eye, as confirmed by quantitative colorimetric analyses, too. A slight decreasing of brightness (ΔL ranging from 4 to 7) and an acceptable colour change (ΔE* ranging from 4 to 7), mildly lower than those obtained after moisture aging tests, were registered for UV aged film, as reported in the inset Table of Figure 4(a).

The thermal stability of both films after the UV accelerated aging test continues to be very high, confirming the suitability of both materials to be used in extreme outdoors conditions, without any influence on the degradation temperature, as demonstrated by the degradation temperature, higher

than 265 °C, measured from TGA curves, performed on both films after the UV weathering test (see inset Table of Figure 4(b)). The higher water absorption capability of the neat film compared to the nanocomposite is still confirmed, even after the UV aging, since the water weight loss measured after the first degradation step of the TGA curves of Figure 4(b) evidences a weight loss of about 28% and 20% for pristine PEDOT:PSS and ternary nanocomposite films, respectively.

Referring to the wettability properties of the films, by comparing the water contact angle results obtained on the same films before and after the UV aging treatment (see Figure 1(e)-(f) and 4(c)-(d) respectively), the great influence of UV accelerated aging on the surface wettability properties of both samples are evident, presenting, in turn, an hydrophilic behaviour.

At the initial time (t=0), the contact angle of PEDOT:PSS drastically decreases from 99° to 76° after the UV test, instead, a lower decreasing contact angle was observed for GGO-PEDOT film, ranging from 92° to 83°. Regarding the effect of the deposition time of the water contact angle, the neat PEDOT:PSS film shows a contact angle highly decreased from 76° to 34° up to 60 s with an irregular drop shape, already after 20 s. In this case, even the nanocomposite film seems to be influenced by the UV aging test, presenting decreased water contact angle after the UV exposure as a function of deposition time (ranging from 83° to 40°), however still evidencing a regular drop shape. This behaviour confirms the higher moisture absorption capability, especially after UV accelerated aging test, of PEDOT:PSS respect to GGO-PEDOT and then it determines an higher deterioration of the wettability of the unfilled film surface as a consequence of the accelerated UV test. This is a further evidence that the cooperative presence of glucose and reduced GO sheets, homogenously distributed into PEDOT:PSS matrix, are still able to create a barrier to water molecules absorption, even after so aggressive tests, as accelerated UV weathering test, demonstrating again the exceptional suitability of the ternary GO based nanocomposite to be used in outdoors applications.

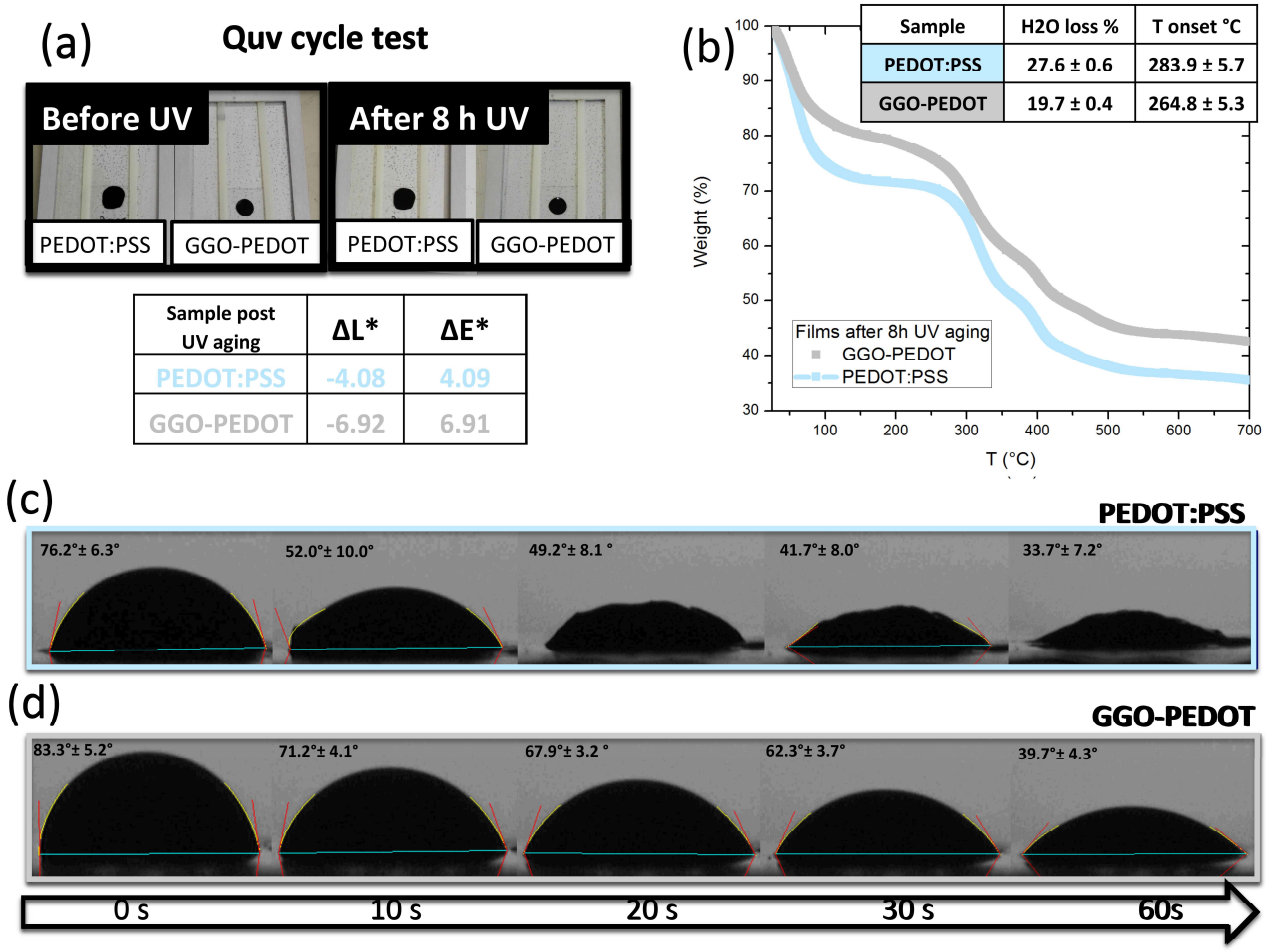


Figure 4 Images and colorimetric test (a), TGA (b) and water contact angle as function of drop deposition time on PEDOT:PSS(c) and GGO-PEDOT(d) films after accelerated UV aging test.

Since the UV test seems to highly influence the surface wettability and hence the physical properties of the films, the UV aged films were selected for further electrochemical characterizations with the aim to predict their electrochemical durability in outdoor conditions.

In details, the capacitive properties of PEDOT:PSS and of GGO-PEDOT film prepared according to the procedure described in the experimental section were studied by means of cyclic voltammetry (CV) in a 1 M H_2SO_4 solution. As described in the literature [11, 12], the enclosed area of CV curves, which corresponds to the charge storage capacity of the electrodes, depends strongly on the material properties. CVs of PEDOT:PSS and GGO-PEDOT pristine films and after an UV treatment performed for 4 h and for 8 h are reported in Figure 5 (a) and (b).

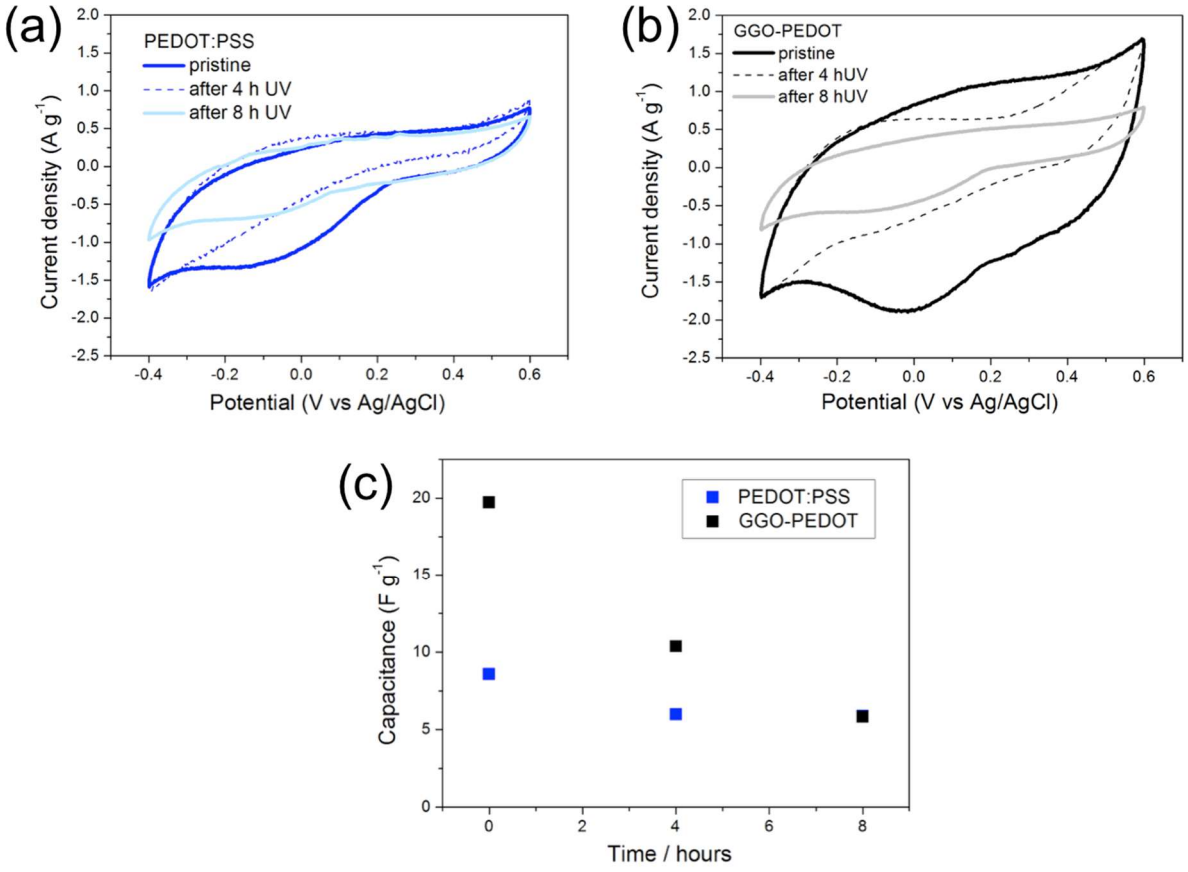


Figure 5 Cyclic voltammograms of (a) PEDOT:PSS and (b) GGO-PEDOT film pristine and after UV aging; (c) estimated specific capacitance as a function of aging time.

For a quantitative assessment of the functional performance of PEDOT:PSS and of GGO-PEDOT film, their specific capacitance C_{sp} (i.e. referred to 1 g of active material) was estimated using Equation 3:

$$C_{sp} = \frac{\int idV}{v \cdot \Delta V \cdot m} \qquad (3)$$

where $\int idV$ is the integrated area of the CV, ν indicates the scan rate (V/s), ΔV is the range of applied potential (V), and m is the mass of the electrode material (g). The calculated values of C_{sp} for the two investigated materials, pristine and after UV treatment, are plotted in Figure 5 (c).

For the PEDOT:PSS film prepared without additives, the specific capacitance C_{sp}, evaluated at a scan rate of 100 mV s^{-1}, is equal to 8.57 F/g in the pristine conditions and is consistent with literature data [13-15]. The C_{sp} value is quickly reduced to 5.98 F/g after a UV treatment performed for 4 h and then it remains almost constant after 8 h of aging. The CV of GGO-PEDOT pristine film presents a broad approximately rectangular shape, due to a large double-layer capacitance provided by GO and its C_{sp} results higher and equal to 19.72 F/g. After 4 h of UV treatment, the C_{sp} value is still fairly high and is equal to 10.37 F/g, whereas after 8 h of UV treatment it is reduced to a value comparable to that of the PEDOT:PSS film in the same conditions. These results reveal a good conductive behaviour of prepared GGO-PEDOT film, indicating that this material is potentially suitable to be used as electrode material for supercapacitor. This evidence should be obviously confirmed by further analysis, assessing the specific capacity at different scan rates. Moreover GGO-PEDOT film presents a good stability after a 4-hour UV treatment, while it loses its capacitive properties after an 8-hour treatment.

Conclusion

In this paper a free standing ternary nanocomposite films, obtained by adding GO nanofiller to PEDOT:PSS by using a green dispersing agent (i.e. glucose), were realized by a simple and low-cost method. The homogeneous ternary nanocomposites solution (GGO-PEDOT) was drop casted into a silicone mould and peeled off after water evaporation, obtaining a flexible film, confirming the easy processability of the preparation method. The films were annealed for 1 h at 140 °C on a hot plate in N_2 atmosphere in order to induce the GO reduction by using glucose. XRD and SEM experimental results evidenced an optimal nano-dispersion of GO in the polymeric matrix, thanks to the use of glucose.

Both the films show a slightly hydrophobic behaviour with a almost stable contact angle of about 92° for GGO-PEDOT, meanwhile PEDOT:PSS film shows a contact angle highly decreased from 99° to 43° up to 60 s with an irregular drop shape confirming the more hydrophilic behaviour.

Thermal analysis demonstrated that, after 1 h of thermal annealing at 140 °C in N2 atmosphere, both films are thermally stable up to a very high temperature (270 °C) and, in addition, the ternary nanocomposite film contains a lower amount of water in comparison to that of the neat matrix. Moisture absorption test confirmed this trend showing a diminution of 68% in water vapour absorption rate and 23% in water vapour absorption coefficient for GGO-PEDOT. The wettability properties of GGO-PEDOT film seem to remain unchanged even after moisture aging tests (contact angle = 92°), differently from PEDOT:PSS that showing an higher deterioration of the wettability of the unfilled film surface. On the other hand, UV aging test seems to highly influence the surface wettability of both unfilled and filled films, presenting decreased water contact angle after the UV exposure as a function of deposition time (ranging from 83° to 40°), still evidencing a regular drop shape, only in the case of nanocomposite.

UV aged films were selected for further electrochemical characterizations with the aim to predict its durability in outdoor conditions. Due to its good conductive behaviour and stability after a 4-hour UV aging, the GGO-PEDOT film has been proved to be a promising candidate as electrode material for supercapacitor.

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References

[1] Li Z, Ma G, Ge R, Qin F, Dong X, Meng W, et al. Free-Standing Conducting Polymer Films for High-Performance Energy Devices. Angewandte Chemie International Edition. 2016;55(3):979-82.

[2] D'Arcy JM, El-Kady MF, Khine PP, Zhang L, Lee SH, Davis NR, et al. Vapor-phase polymerization of nanofibrillar poly (3, 4-ethylenedioxythiophene) for supercapacitors. Acs Nano. 2014;8(2):1500-10.

[3] Anothumakkool B, Soni R, Bhange SN, Kurungot S. Novel scalable synthesis of highly conducting and robust PEDOT paper for a high performance flexible solid supercapacitor. Energy & Environmental Science. 2015;8(4):1339-47.

[4] Hung P-y, Lau K-t, Fox B, Hameed N, Lee JH, Hui D. Surface modification of carbon fibre using graphene–related materials for multifunctional composites. Composites Part B: Engineering. 2018;133:240-57.

[5] Wang L, Liu Y, Zhang Z, Wang B, Qiu J, Hui D, et al. Polymer composites-based thermoelectric materials and devices. Composites Part B: Engineering. 2017.

[6] Giuri A, Masi S, Colella S, Kovtun A, Dell'Elce S, Treossi E, et al. Cooperative Effect of GO and Glucose on PEDOT:PSS for HighVOCand Hysteresis-Free Solution-Processed Perovskite Solar Cells. Advanced Functional Materials. 2016;26(38):6985-94.

[7] Giuri A, Masi S, Colella S, Listorti A, Rizzo A, Liscio A, et al. GO/PEDOT: PSS nanocomposites: effect of different dispersing agents on rheological, thermal, wettability and electrochemical properties. Nanotechnology. 2017;28(17):174001.

[8] Treossi E, Melucci M, Liscio A, Gazzano M, Samorì P, Palermo V. High-contrast visualization of graphene oxide on dye-sensitized glass, quartz, and silicon by fluorescence quenching. Journal of the American Chemical Society. 2009;131(43):15576-7.

[9] Becerril HA, Mao J, Liu Z, Stoltenberg RM, Bao Z, Chen Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. ACS nano. 2008;2(3):463-70.

[10] Zhao Q, Jamal R, Zhang L, Wang M, Abdiryim T. The structure and properties of PEDOT synthesized by template-free solution method. Nanoscale research letters. 2014;9(1):557.

[11] Chang J-K, Huang C-H, Tsai W-T, Deng M-J, Sun I-W, Chen P-Y. Manganese films electrodeposited at different potentials and temperatures in ionic liquid and their application as electrode materials for supercapacitors. Electrochimica Acta. 2008;53(13):4447-53.

[12] Mele C, Catalano M, Taurino A, Bozzini B. Electrochemical fabrication of nanoporous gold-supported manganese oxide nanowires based on electrodeposition from eutectic urea/choline chloride ionic liquid. Electrochimica Acta. 2013;87:918-24.

[13] Azman NHN, Lim HN, Sulaiman Y. Effect of electropolymerization potential on the preparation of PEDOT/graphene oxide hybrid material for supercapacitor application. Electrochimica Acta. 2016;188:785-92.

[14] Liu Y, Weng B, Razal JM, Xu Q, Zhao C, Hou Y, et al. High-performance flexible all-solid-state supercapacitor from large free-standing graphene-PEDOT/PSS films. Scientific reports. 2015;5:17045.

[15] Islam M, Chidembo AT, Aboutalebi SH, Cardillo D, Liu HK, Konstantinov K, et al. Liquid crystalline graphene oxide/PEDOT: PSS self-assembled 3D architecture for binder-free supercapacitor electrodes. Frontiers in Energy Research. 2014;2:31.

Figure captions

Scheme 1: GGO-PEDOT solution and film preparation

Figure 1 XRD spectra of PEDOT:PSS(a) and GGO-PEDOT(b) films; SEM images of pristine PEDOT:PSS(c) and GGO-PEDOT(d) films; water contact angle as function of drop deposition time on PEDOT:PSS(e) and GGO-PEDOT(f) films.

Figure 2 TGA (a) and moisture absorption curves (b) of PEDOT:PSS and GGO-PEDOT

Figure 3 Images and colorimetric test (a), TGA (b) and water contact angle as function of drop deposition time on PEDOT:PSS(c) and GGO-PEDOT(d) films after accelerated moisture aging test.

Figure 4 Images and colorimetric test (a), TGA (b) and water contact angle as function of drop deposition time on PEDOT:PSS(c) and GGO-PEDOT(d) films after accelerated UV aging test.

Figure 5 Cyclic voltammograms of (a) PEDOT:PSS and (b) GGO-PEDOT film pristine and after UV aging; (c) estimated specific capacitance as a function of aging time.