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Reduced graphene oxide filled poly(dimethyl siloxane) based transparent stretchable, and touch-responsive sensors

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The ongoing revolution in touch panel technology and electronics demands the need for thin films, which are flexible, stretchable, and highly touch responsive. In this regard, conductive elastomer nanocomposites offer potential solutions for these stipulations; however, viability is limited to the poor dispersion of conductive nanomaterials such as graphene into the matrix. Here, we fabricated a reduced graphene oxide (rGO) and poly(dimethylsiloxane) (PDMS) elastomer based transparent and flexible conductive touch responsive film by dispersing rGO honeycombs uniformly into PDMS elastomer through an ionic liquid (IL) modification. Pursuing a simple, scalable, and safe method of solution casting, this provides a versatile and creative design of a transparent and stretchable rGO/IL-PDMS capacitive touch responsive, where rGO acts as a sensing element. This transparent film with ~70% transmittance exhibits approximately a five times faster response in comparison to rGO/PDMS film, with negligible degradation over time. The performance of this touch screen film is expected to have applications in the emerging field of foldable electronics. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4947595]

The rapid development of touch screen devices has enabled effective human machine interaction with an accurate and simple touch input mechanism. Various technologies exist for such man–machine interfaces, of which the most commonly used are capacitive touch panels. For instance, metal oxide such as tin-doped indium oxide (ITO) is preferred for this purpose because of its low cost of production. Meanwhile, metal oxide based capacitive touch devices suffer from their complex design, environmental unfriendliness, expensive high-vacuum deposition process, and mechanical inflexibility. Recently, devices fabricated via incorporation of nanomaterial into other matrices have demonstrated revolutionary performance. As a result, large number of reports have come out in this field using nanowires, nanotubes, graphene, etc., to achieve good electrical conductivity and optical transmittance.

Graphene has great potential in suturing touch panel screens, photovoltaic cells, light emitting diodes, and transistors because of its 2D nature, excellent electron-transfer behavior, chemical and thermal stability, low cost, ultrahigh flexibility, and relatively low sheet resistance (~30 Ω/sq at 90% transmittance). Additionally, the large aspect ratio of graphene sheets reduces the percolation threshold considerably when mixed with a polymer matrix. Thus, recent efforts have focused on fabricating the transparent graphene and graphene filled elastomers for flexible and stretchable electronic devices (e.g., touch screens and displays, sensors, and flexible transistors).

Among elastomers, polydimethylsiloxane (PDMS) is an ideal candidate for flexible electrode fabrication as it contributes additional stretchiness. But nanocarbon (e.g., carbon nanoparticles) filled PDMS films lack efficient filler dispersion as well as matrix-filler interactions due to the respective hydrophobic and hydrophilic natures of carbon and PDMS. Ionic liquids (ILs) address these challenges by improving the dispersion of nanomaterials such as reduced graphene oxide (rGO). ILs are marked by their non-volatility, non-flammability, and thermal stability and facilitate easy fabrication compared to the chemical modifications of nanoparticles. Here, an imidazolium IL, [1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF$_4$)], is used to achieve high rate of dispersion of rGO. This homogeneously dispersed material surface was peeled off as a thin film, and the capacitance of which was measured under stretching. This report elevates the usage of rGO/IL-PDMS touch responsive film that can detect human touch at different stretching ratios with superior optical transparency, durability, and faster response times. In short, this work aims to develop stretchable, matrix-structured, dual functional, and capacitive sensor with the integrated capability of touch sensing under different stretching strains.

Figure 1(a) shows a typical TEM image of the crumpled ultra-thin individual synthesized rGO/IL nanosheets (Figure 1(a)). In addition, an AFM image collected in tapping mode (atomic force microscopy—Veeco MultiMode/NanoScope IIIa instrument) of the samples coated on the oxidized silicon...
wafers shown in Figure 1 and corresponding height profiles reveal the planar morphology of rGO/IL nanosheets. The interplanar distance of rGO/IL was calculated to be around 1.5 nm. Raman spectroscopy reveals that in case of GO, the G band is broadened and shifted from 1567 to 1596 cm\(^{-1}\), and the D band becomes significantly stronger compared to graphite (Figure 1(b)). As expected, \(I_D/I_G\) intensity ratio of rGO was higher (1.05) than GO (0.92) due to the smaller size\(^{24,25}\) and consequently high density of structural defects.\(^{26–28}\) Interestingly, the G band of rGO observed at 1589 cm\(^{-1}\) was shifted to 1596 cm\(^{-1}\) after IL treatment, indicating higher exfoliation of the rGO layers.\(^{29,30}\) XRD (X-ray diffraction) analysis shows the characteristic peaks of graphite at 26.6° corresponding to a d-spacing of 0.335 nm. In the case of GO, this peak shifted to 10.02° gives evidence for a higher d-spacing (0.880 nm) due to oxidation that disappeared after the reduction process. However, a broad peak observed at 24.79° for rGO corresponds to a d-spacing of 0.359 nm. This relatively larger d-spacing of rGO and GO than pristine graphite is attributed to the intercalation/exfoliation (GO) and exfoliation of graphene layers (rGO). In rGO/IL, a peak similar to that of rGO is also observed but with reduced intensity, further confirming the high degree of exfoliation.

To fabricate the touch sensitive films, the rGO modified IL was embedded on PDMS substrate using the layer by layer (LbL) spray method.\(^{17}\) During this process, solutions of rGO and IL in a 10:1 ratio were dispersed into Isopropylalcohol (IPA) (4 mg/10 ml) by sonication. Finally, the PDMS mixture (base:cure agent, 10:1) was softly poured into a petri dish to cover the rGO and rGO/IL film and the mixture was heated for 20 min at ~200 °C on a hot plate. After (after curing), the rGO and rGO/IL embedded on PDMS were carefully peeled off from the substrate and used for further experiments.

The surface morphology of the fabricated touch screens were studied by performing FESEM (field emission scanning electron microscopy—Strata DB235 FESEM/FIB) analysis. As expected, rGO-PDMS exhibits a heterogeneous morphology consisting of both exfoliated and aggregated regions (Figures 2(c) and 2(d)). Its wrinkled structure, with corrugation and scrolling, is intrinsic to graphene due to existing Van der Waals forces.\(^{31}\) In rGO/IL-PDMS (Figures 2(e) and 2(f)), the absence of aggregated domains evidences the homogeneous distribution of rGO/IL over the PDMS, suggesting that IL is able to improve the dispersion and can be applied to large-scale touch screen fabrication.

The optical properties of the rGO/IL-PDMS sensing film were also examined, by plotting the UV-Visible transmittance (Cary 50 UV-Visible spectrometer, Agilent Technologies) with respect to the number of sprayed layers. A transmittance of ~80% was observed at 550 nm for rGO/IL-PDMS.
film consisting of 10 layers of rGO/IL (Figure 3). However, a significant transmittance drop was observed at the same wavelength beyond the deposited 10 layers of rGO/IL. For 30 and 40 layers, the transmittance values were ~54% and ~45%, respectively, indicating a strong effect of stacks of the rGO platelets on transmittance. This significant drop in the transparency of rGO/IL-PDMS films is mainly attributed to the high thickness of the deposited rGO/IL film, as an individual graphene layer can absorb approximately 2.7% of transmitting light. However, in the case of LbL deposited films, the effect of the size and distribution of rGO flakes, density of scattering particles, scattering mean free path, and the rate of dispersion also limit the transmittance.

The capacitive touch sensing characteristics of the rGO/IL-modified PDMS films (20 Layers) were analyzed via online monitoring of the capacitance of the film using an LCR meter (Hioki 3522-50 LCR Meter). The capacitance was recorded under normal conditions and at different stretching ratios. Figure 4(a) schematically shows the experimental arrangement in which the film was placed between two electrodes, one movable and the other fixed. The rGO/IL embedded PDMS film, shown in Figure 4(a) and represented in Figure 4(b), has nine touching points marked on it. The capacitive touch responses of the rGO-PDMS and rGO/IL-PDMS were noted by simply finger tapping at each point (e.g., point 5), and the results were plotted as relative capacitance ($A_c$) change versus time as shown in Figure 4.
The $A_C$ values were calculated according to the following equation:

$$A_C = \frac{C - C_0}{C_0},$$  
(1)

where $C$ is the film capacitance at the known position (e.g., point 5 during finger touching), on the test films, and $C_0$ is the initial capacitance. The initial capacitance values of rGO-PDMS and rGO/IL-PDMS were, respectively, 0.1 pF and 1.5 pF.

Figure 4(c) shows the sensing performance of rGO/PDMS and rGO/IL-PDMS films consisting of similar numbers of layers (i.e., 20). The magnitude of the $A_C$ for the rGO/IL-PDMS is more than three times higher in comparison to the $A_C$ measured for an rGO/PDMS sensing film. The results suggest that, when touched, the conductance between the electrodes changes, as the human skin is conductive and can influence the rGO/IL conductivity network better than rGO alone (Figure 4(c)). The higher performance of rGO/IL is attributed to the excellent dispersion and conductive network compared to the rGO film. rGO/IL induces a significant and detectable decrease in the effective capacitance and the capacitance remains in the range of 1–1.76 pF with touching and in the range of 1.76 pF without touching during cyclic touch tests. The film capacitance was also noted with a gloved finger as well, and a decrease in the capacitance value was observed. The sensitivity was checked by touching a finger to all the points, as shown by numbers 1–9 in Figure 4(c). The response obtained from point 5 was the best, due to its equal distance from the electrodes. When the demonstrator’s finger contacted the film, the capacitance of the sensor decreased suddenly distinguishing every single slight touch. Figure 4(d) gives the sensing pattern by finger touching at different points and thereafter keeping as such for 10 s. The capacitance returned to the initial value once the fingers were completely removed. It is also noteworthy that the sensor’s capacitance remained constant upon finger contact at a certain point, proving the excellent stability and reliability of the developed capacitive touch sensor.

The flexibility of the electrodes is also crucial for the touch sensing performance of the final device. Therefore, the endurance of rGO/IL-PDMS was investigated under repeated touching tests where the sample was stretched at 0%, 0.3%, 0.6%, and 0.9% strain by moving the mobile head of the homemade device shown in Figure 4(a). The capacitive touch response, affected by strain, was almost instantaneous and recovered without a time delay (Figure 4(e)). The sensitivity decreases with increasing strain and the capacitance variation upon contact (rising) and removal (dropping) shows a similar behavior under different stretching ratios. When the sample is stretched, the changes in strain manifest themselves as the changes in capacitance and average relative capacitance change due to a loss of capacitive network.

A simple parallel-plate model predicts a linear capacitive response to the applied strain, provides that the overlap between the opposing graphene films is stable. The capacitance ($C$) of such a capacitor is defined by the following equation:

$$C = \frac{e_1 e_2 A}{d},$$  
(2)

where $e_1$ and $e_2$ are the dielectric constants of the two electrode plates of area $A$, separated by a distance, $d$. Due to the inverse relationship between $C$ and $d$, the shortened or lengthened distance, caused by the application of strain, results in linear changes of capacitance (Figure 4(e)).

Figure 4(f) illustrates the durability of the rGO/IL-PDMS touch sensor, investigated by repeatedly keeping a finger at 0.9% strain. The results show a steady response to the cycling field with slight variation examined for 1000 s. Here, the elongation by strain in the $y$-direction (stretching direction) decreases the capacitance. It is also worthy to note that the fringing effect plays a role in capacitors with finite-size electrodes. Thus, transparent capacitive touch-strain sensors with very fast, stable, predictable, and deterministic capacitive responses can be remarkably useful in applications like touch pads.

We also study the variation in the capacitance with respect to the applied voltage, as well as frequency, for the rGO/IL embedded PDMS films (Figure 5). The capacitance variation of the films was measured between −40 V and 40 V, and it mainly presents depletion capacitance by majority rGO flakes carriers (Figure 5(a)). The applied voltage at the edge of the depletion region highly depends on the charge added/removed from the depletion layer. Usually, tunneling of majority carriers through the depletion region is undesirable for any capacitor, and here, diffusion in the rGO facilitates charge increase, resulting in high diffusion capacitance. A transition capacitance appearing by charge accumulation varies at reverse bias, and thus, the film can be utilized...
as a variable voltage capacitor. As the depletion layer width varies with the applied voltage, the capacitance also changes at the metal–semiconductor junction. The lower capacitance at higher applied voltage causes non linearity in low-distortion filters and other analog applications.

In addition, the capacitance of the PDMS and rGO/IL embedded PDMS films has similar frequency-dependent relaxation behavior (Figure 5(b)), decreasing monotonically as frequency increases. The high capacitance of the rGO/IL embedded PDMS at lower frequencies is mainly due to the interfacial polarization occurring in heterogeneous structures by the accumulation of space charges at the interfaces between various regions that differ from each other in their DC conductivities. For rGO/IL-PDMS, the interfacial polarization is caused by the dispersion of islands of conducting rGO/IL-PDMS were also examined to understand the exterior and humidity sensing characteristics of the sample temperature and humidity variation might affect the capacitive aspect ratio, are responsible for the high charge capacity (ion accumulation) near the rGO/IL-PDMS interface, and it enables the long-range electronic responses, along the longitudinal axis, enhancing the polarization. The efficient dielectric screening of the rGO phase does not permit the penetration of electric fields into the material. Moreover, the insulating PDMS surface layers wrapped around the rGO/IL increase the electric breakdown threshold and reduce the overall capacitance of the composites. In the composite, a continuous conductive pathway exists between rGO clusters and the movement of these free charge carriers increases the permittivity. In short, the strong rGO/PDMS interfacial polarization increases the loss tangent as a function of the frequency and its variation over the entire frequency range is attributed to the homogeneous rGO dispersion in PDMS.

The temperature and humidity sensing characteristics of the sample rGO/IL-PDMS were also examined to understand the external effects, which are shown in the supplementary material. The results suggest that the rGO/IL-PDMS film is not sensitive to the variation in the humidity, and the application of the film will not be disrupted by the variation in the humidity under ambient conditions.

In conclusion, our prototype sensors exhibit excellent linearity throughout the whole strain range which is necessary for stretchable and wearable intelligent electronics. Systematic and elaborate strain tests confirmed the superior stability, durability, and reliability of the reusable rGO/IL-PDMS capacitive touch responsive films. However, temperature and humidity variation might affect the capacitive response due to thermal expansion and contraction, and this aspect will be the subject of future investigation. Unlike the widely used ITO and PDMS based touch responsive films, the sensing elements developed here allow easy and multiple integration into stretchable devices that can be used to construct revolutionary multifunctional wearable and implantable electronics for plenty of applications.

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38See supplementary material at http://dx.doi.org/10.1063/1.4947595 for temperature and humidity dependent sensitivity.