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Strain sensing skin-like film using zinc oxide nanostructures grown on PDMS and reduced graphene oxide

Tejus Satish[1], Kaushik Balakrishnan[2], Hemtej Gullapalli[2], Satish Nagarajaiah[*2], Robert Vajtai[2] and Pulickel M. Ajayan[2]

[1]*Department of Biochemistry, Rice University, Houston, Texas, USA 77005*
[2]*Department of Materials Science and Nanoengineering, Rice University, Houston, TX, USA 77005*

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Abstract. In this paper, we present a strain-sensitive composite skin-like film made up of piezoresistive zinc oxide (ZnO) nanorods embedded in a flexible poly(dimethylsiloxane) substrate, with added reduced graphene oxide (rGO) to facilitate connections between the nanorod clusters and increase strain sensitivity. Preparation of the composite is described in detail. Cyclic strain sensing tests are conducted. Experiments indicate that the resulting ZnO-PDMS/rGO composite film is strain-sensitive and thus capable of sensing cycling strain accurately. As such, it has the potential to be molded on to a structure (civil, mechanical, aerospace, or biological) in order to provide a strain sensing skin.

Keywords: strain sensing; flexible; skin; poly(dimethylsiloxane); reduced graphene oxide; zinc oxide

1. Introduction

Dynamic monitoring of structural strain is fundamental to structural health monitoring and maintenance during extreme events (Nagarajaiah and Erazo 2016). Problematically, industry-standard resistance-based foil strain gages measure strain unidirectionally and locally, limiting their utility for large-scale monitoring. To facilitate such distributed monitoring, recent research has explored alternative materials with inherent strain sensing properties (Li *et al.* 2004, Dharap *et al.* 2004, Withey *et al.* 2012, Sun *et al.* 2015, 2016). Piezoelectric materials such as zinc oxide (ZnO) have attracted considerable interest due to their ability to transduce mechanical strain into electrical signals with minimal power requirements (Park *et al.* 2008). Such materials are capable of sensing strain, but are unsuitable for standalone use, as they are typically highly brittle (Klingshim *et al.* 2010). Researchers have found rGO—reduced graphene oxide—thin films (Loh *et al.* 2010, Trung *et al.* 2014, Tang *et al.* 2015) to be effective strain sensors. The possibility of combining ZnO and rGO for strain sensing is investigated in this study.

In order to be utilized in strain sensing, piezoelectric materials must be supported by a scaffold. Previously, we demonstrated a low-temperature solvo-thermal method to fabricate ZnO nanorods on a cellulose scaffold, and demonstrated that the final construct constituted an accurate, flexible, low-cost strain sensor (Gullapalli *et al.* 2010). However, the nature of the cellulose scaffold made

*Corresponding author, Professor, E-mail: satish.nagarajaiah@rice.edu

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scaling the sensor system difficult, essentially requiring a coat of paper over a given sensing area. In addition, we found the cellulose scaffold to degrade easily. Here, we replace the cellulose scaffold with a poly(dimethylsiloxane) (PDMS) base to create a moldable, strain sensitive polymer capable of multipoint sensing using a probing device (such as a four-point probe) to contact the sensing skin at different points and different directions.

PDMS is a hydrophobic, elastic polymer that is essentially inert and flexible. Its elastomeric nature renders it able to coat nearly any shape. Together, these properties suggest that PDMS would be an ideal matrix for a ZnO nanorod-based sensor. However, PDMS is strongly dielectric, complicating the electrical conduction necessary for strain sensing.

Due to its otherwise ideal nature, two approaches were attempted to circumvent this issue. Firstly, we attempted to optimize the solvo-thermal growth method mentioned previously to allow for contiguous growth of conductive nanorods on the surface of the PDMS. Second, we elected to include conductive reduced graphene oxide (rGO) additives in the PDMS to facilitate conduction. To summarize, we aimed to embed ZnO into a resilient PDMS matrix to create a flexible composite material capable of serving as a durable strain sensor.

Although the ZnO-PDMS composite inherited PDMS' flexibility, it did not detect the application of strain. This loss of sensitivity suggested limited charge conduction between the ZnO nanorods due to their noncontiguous deposition. Further optimization of the growth method is necessary to achieve the goal. Upon addition of rGO to the PDMS matrix, conduction issues were resolved. This ZnO-PDMS/rGO sample showed response under cyclic strain. The addition of rGO did not interfere with the composite's inheritance of PDMS' flexibility.

2. Methods

2.1 Poly(dimethylsiloxane) fabrication

Dow Sylgard 184 Elastomer was mixed with Dow Sylgard 184 Curing Agent in a 10:1 ratio to create PDMS. For the fabrication of PDMS-rGO sample, 50 mg reduced graphene oxide was added to the mixture. The PDMS sample was thoroughly mixed and poured onto a Petri dish for circular samples or a glass slide for thin-film samples. The samples were preheated to 100℃ to cure. After 2 hours, the samples were removed from the dish/slide and checked for air bubbles. If air bubbles were present, the samples were placed inside a desiccator for 1 hour to eliminate the bubbles. The samples were subsequently placed on a hot plate heated to 200℃ for 30 minutes to ascertain the thermoresistance of the sample. Zinc application was attempted if the sample resisted melting during testing.

2.2 Zinc (Zn) application

A Torr International FTM-2000 sputter coater was calibrated to a Goodfellow Zn target with density value 7.06 g/cm^3 and Z-factor 0.514 in preparation for Zn seeding. The tooling factor was set to 85. PDMS samples were placed inside the sputtering chamber, which was then evacuated and filled with argon gas. A 100-nm thick layer of Zn was applied at 0.2 Å/sec.

2.3 Zinc oxide nanorod growth

The seeded sides of the PDMS samples were exposed to 0.05 M hexamethylenetetramine (Aldrich) and 0.05 M zinc nitrate hexahydrate (Aldrich) in ethanol at 90°C for 3 hours. Upon removal from the solution, samples were heated at 130°C for 6 hours to evaporate any remaining solution and to soften the PDMS to aid in ZnO nanorod adhesion.

2.4 Incorporation of reduced graphene oxide (rGO) to improve conductivity

A depiction of the proposed ZnO-PDMS/rGO architecture is shown in Fig. 1. It is shown later in Section 3.2 that the addition of rGO improved conductivity, which enabled ZnO-PDMS/rGO sensors to detect strain accurately. ZnO nanorods were grown on an rGO substrate, both of which were embedded in PDMS as shown in Fig. 1(d) and described in Sections 2.1, 2.2, and 2.3.

2.4 Sensor test setup

A four-electrode pattern (similar to a four-point probe mentioned earlier) was established on completed samples by sputter coating a 30 nm layer of gold. A brass sample (cross sectional area 3.17 cm × 0.635 cm, Young's Modulus 166 GPa) was prepared for sensor adhesion by abrading the bond site using acid cleaner and sandpaper. Acid cleaner was neutralized and Hardman Double Bubble epoxy was used to bond sensor samples to the beam. One Micro Measurements CEA 13 conventional strain gage (gage factor 2.1, nominal resistance 120 Ω) was also bonded to the beam to serve as the control. MC Chemicals Pure Silver Epoxy was used to attach leads to the electrodes. Both epoxies were allowed one day to dry. The brass bar was placed between MTS 647 Hydraulic Grips connected to an MTS Load Cell and subjected to tensile/compressive cyclic forces as shown in Fig. 2.

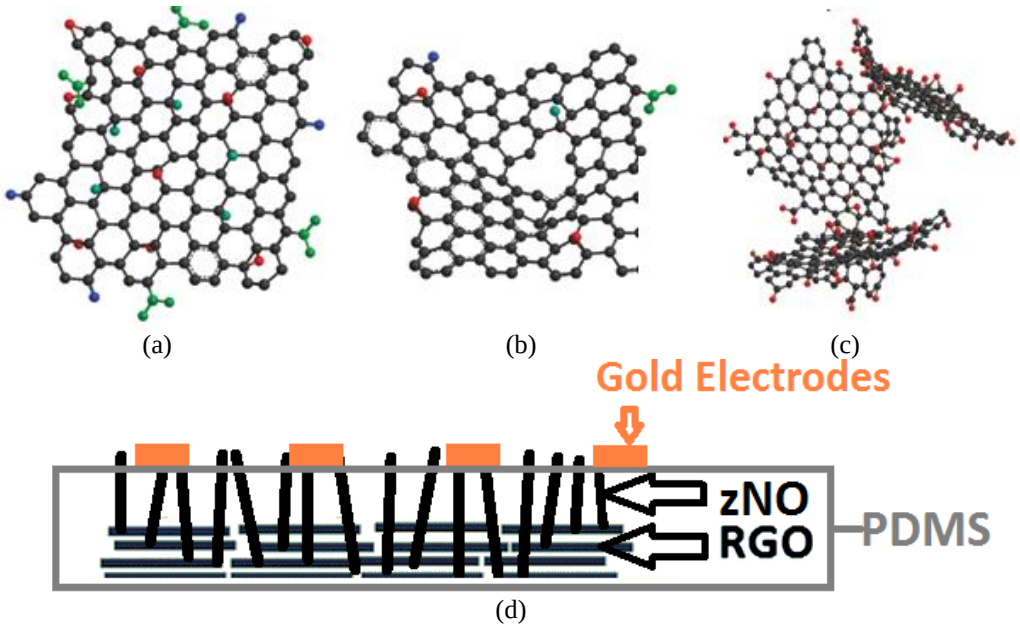


Fig. 1 (a) Graphene oxide, (b) and (c) rGO structure, (d) proposed architecture by which rGO promotes conductivity in the ZnO nanorod layer

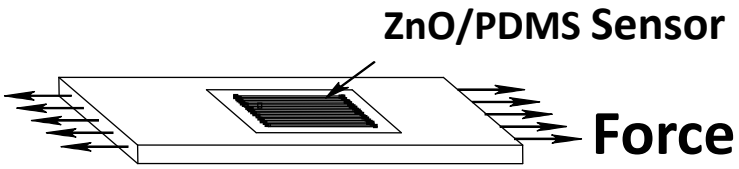


Fig. 2 A diagram of the ZnO-PDMS sensor mounted on the brass specimen

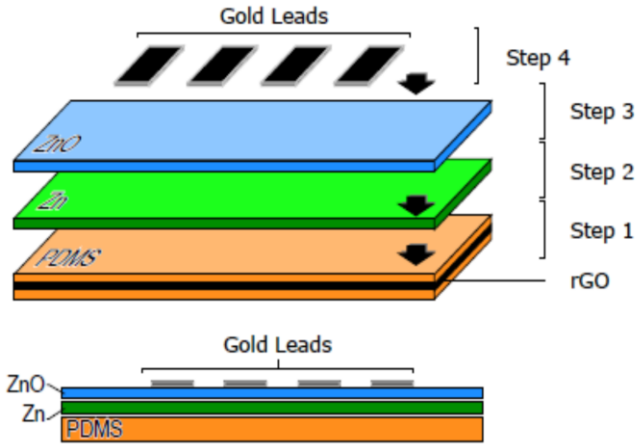


Fig. 3 A detailed diagram of the ZnO-PDMS/rGO sensor at its test-ready phase. All the layers of material are shown. Step 1 corresponds to PDMS fabrication with rGO, Step 2 corresponds to Zn application, Step 3 corresponds to ZnO nanorod growth, and Step 4 corresponds to sensor testing preparation. Note: A ZnO-PDMS sensor would look identical, except for the exclusion of the rGO layer

All sensors were then attached to a Keithley 6430 sourcemeter. The load cell was used to test the ZnO-based sensors and the CEA 13 gage under quasi-static cyclic stress. Results were recorded with LabView. A complete diagram of the sensor in its test ready state can be found in Fig. 3.

3. Results

3.1 Zinc oxide nanorod growth and SEM analysis

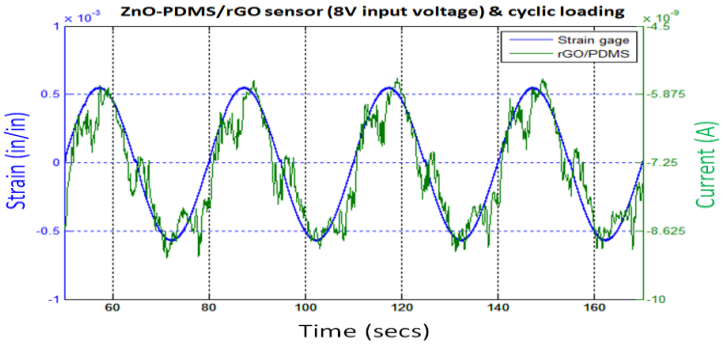
Once ZnO nanorods were grown, SEM was used to visualize the growth (Fig. 4). SEM analysis revealed a relatively continuous growth of ZnO nanorods along the sample. However, some minute deformities of the growth were apparent. The orientation of the layers seemed to be random, and the ZnO nanorods were successfully embedded into the PDMS. ZnO-PDMS and ZnO-PDMS/rGO composites retained PDMS' flexibility.

(a) (b)

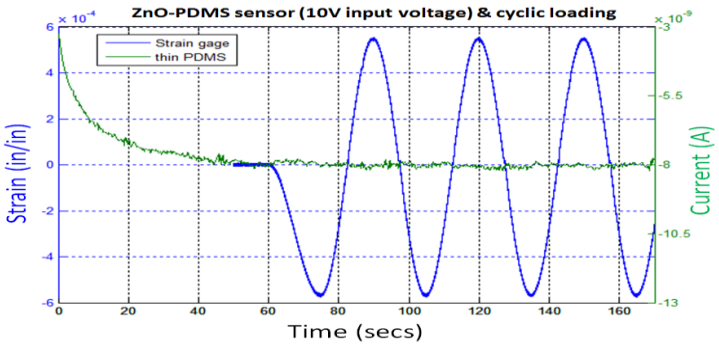
Fig. 4 SEM micrographs of the two types of samples are shown. (a) A view of a ZnO-PDMS sample, exhibiting fairly dense growth, (b) A view of a ZnO-PDMS/rGO sample exhibiting similarly dense growth. Note: the small gaps between the nanorods in both the samples

3.2 Sensor testing

A comparison of the ZnO-PDMS/rGO composite's results and the ZnO-PDMS composite's results is shown in Fig. 5. Both sensors were subjected to cyclic loading. The control strain gage's response is shown for comparison.



(a)



(b)

Fig. 5 A comparison of the response of the ZnO-PDMS/rGO and ZnO-PDMS sensors under cyclic loading is shown. ZnO-based sensor response is shown in green, and control strain gage response is shown in blue. (a) is the ZnO-PDMS/rGO response, and (b) shows ZnO-PDMS response

The ZnO-PDMS sensor registers its initial 10 V charge, and then proceeds to dissipate that charge while showing no further response. Significant background noise is visible, further confirming a lack of strain sensitivity. By contrast, the ZnO-PDMS/rGO sensor accurately registers the strain applied to it both in tension and compression, and its response closely corresponds to the response of the control strain gage. Again, significant background noise is visible, suggesting a need for calibrated software correction. However, the background noise does not interfere with the overall strain pattern.

The early peak in current shown in Fig. 5(b) can be attributed to the initial input of current dissipating through the brass bar and then proceeding to register through the gold electrodes on the ZnO-PDMS samples. However, the steady dissipation of this current indicates that strain was not appropriately detected, especially when compared to the control gage data. As SEM analysis revealed minute discontinuities in nanorod growth, it is probable that the poor sensing capability of the ZnO-PDMS material was the result of a non-contiguous layer of ZnO. In the absence of a completely homogenous coat, the low conductivity of the PDMS matrix would prevent current flow between the sensor electrodes, producing the complete lack of response obtained.

The addition of reduced graphene oxide as an intermediary conductor improved connectivity between the isolated clusters of nanorods. The contacts between the bottom extremities of the ZnO nanorods and the embedded rGO particle network likely created a conductive path throughout the sensor. This improved conductivity is likely what allowed the ZnO-PDMS/rGO sensors to detect strain accurately.

4. Conclusions

In this study, ZnO-PDMS and ZnO-PDMS/rGO flexible film strain sensing skins were developed, fabricated, and tested. Both materials were highly flexible. The strain sensing results demonstrated that the ZnO-PDMS sensors did not appropriately detect strain. However, the addition of rGO as a conducting substrate in the ZnO-PDMS film permitted effective strain sensing.

The tests demonstrate the ability of the ZnO-PDMS/rGO film sensor to accurately measure cyclic strain. Thus, we believe the ZnO-PDMS/rGO composite may constitute a flexible, scalable strain-sensitive polymer capable of multipoint sensing.

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References

Dharap, P., Li, Z., Nagarajaiah, S. and Barrera, E. (2004), “Nanotube film based on SWNT for macrostrain sensing”, *Nanotechnology J*., **15**(3), 379-382, DOI: 10.1088/0957-4484/15/3/026.

Gullapalli, H., Vemuru, V.S.M., Kumar, A., Botello-Mendez, A., Vajtai, R., Terrones, M., Nagarajaiah, S. and Ajayan, P.M. (2010), “Flexible piezoelectric ZnO–paper nanocomposite strain sensor”, *Small*, **6**(15),

1641-1646.
Klingshirn, C.F., Bruno K.M., Andreas W., Axel H. and Johannes M.G. (2010), *Zinc Oxide: From Fundamental Properties Towards Novel Applications*, Springer, New York City, NY, USA.
Li, Z., Dharap, P., Nagarajaiah, S., Barrera, E. and Kim, J. D. (2004), "Carbon nanofilm sensor", *Adv. Mater. J*., **16**(7), 640-643, DOI: 10.1002/adma.200306310.
Loh, K.P., Bao, Q., Eda, G. and Chhowalla, M. (2010), "Graphene oxide as a chemically tunable platform for optical applications", *Nature Chemistry*, **2(**12), 1015-1024, doi: 10.1038/nchem.907.
Nagarajaiah, S. and Erazo, K. (2016), "Structural monitoring and identification of civil infrastructure in the United States", *Struct. Monit. Maint*., **3**(1), 51-69, DOI: 10.12989/smm.2016.3.1.051.
Park, G., Rosing, T., Todd, M.D., Farrar, C.R. and Hodgkiss, W. (2008), "Energy harvesting for structural health monitoring sensor networks", *ASCE J. Infrastruct. Syst.*, **14**, 64-79.
Sun, P., Bachilo, S., Weisman, M. and Nagarajaiah, S. (2015), "Carbon nanotubes as non-contact optical strain sensors in smart skins", *J. Strain Anal. Eng. Des*., **50**(7), 505-512, DOI: 10.1177/0309324715597414.
Sun, P., Bachilo, S.M., Nagarajaiah, S. and Weisman, R.B. (2016). "Toward practical non-contact optical strain sensing using single-walled carbon nanotubes", *ECS J. Solid State Sci. Technol*., 5(8), M3012-M3017, DOI: 10.1149/2.0031608jss.
Tang, Y., Zhao, Z., Hu, H., Liu, Y., Wang, X., Zhou, S. and Qiu, J. (2015), "Highly stretchable and ultrasensitive strain sensor based on reduced graphene oxide microtubes−elastomer composite", *ACS Appl. Mater. Interfaces*, **7**, 27432-27439, doi: 10.1021/acsami.5b09314.
Trung, T.Q., Tien, N.T., Kim, D., Jang, M., Yoon, O.J. and Lee, N.E. (2014), "A flexible reduced graphene oxide field-effect transistor for ultrasensitive strain sensing", *Adv. Funct. Mater.*, **24**, 117-124.
Withey, P.A., Vemuru, V.S.M., Bachilo, S.M. and Nagarajaiah, S. and Weisman, R.B. (2012), "Strain paint: noncontact strain measurement using single-walled carbon nanotube composite coatings", *Nano Letters*, ACS, **12**(2), 3497-3500, DOI: 10.1021/nl301008m.

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