Supporting Information

A well-organized graphene nanostructure for versatile strain-sensing application constructed by covalently bonded graphene/rubber interface

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Figure S1. SEM images of cryogenically fractured surfaces of GO/ENR (2/100) (a) and PA-co-GO/ENR (10/2/100) (b) nanocomposites at different magnification.

Generally, the filler dispersion and interfacial interactions can be concluded from the morphology of fractured surfaces. SEM images of cryogenically fractured surfaces for GO/ENR and PA-co-GO/ENR nanocomposites are given in **figure S1**, respectively. For both two samples, there are no visible aggregates presenting in the fractured surface, indicating homogeneous dispersion of GO nanosheets in ENR matrix. However, in the case of GO/ENR samples, numerous macro holes and evident fractured surfaces can be observed, which are ascribed to the poor interfacial interactions that caused the pull-out of the GO wrapped ENR microspheres. By contrast, the fractured surface of PA-co-GO/ENR samples is more blurry and compact, showing a clear lamellar structure. These observations indicate the strengthened interfacial interactions between GO nanosheets and ENR chains after incorporation of PA molecules.



Figure S2. A comparative study of tensile strength with other related works.¹⁻¹⁴



Figure S3. Raman spectra of GO before and after hydrothermal method.

The reduction of GO was characterized by the Raman spectroscopy via comparing the variation of relative intensities of D band at around 1350 cm⁻¹ corresponding to the breathing mode of k-point phonons of A_{1g} symmetry, and G band at approximate 1600 cm⁻¹ assigning to the E_{2g} phonon of C sp² atoms.^{15, 16} As shown in **figure S3**, after reduction by hydrothermal method, the ratio of D/G increased from 0.68 to 1.01, indicating the successful removal of the oxygen containing groups and the formation of the new domains of conjugated carbon atoms.



Figure S4. XPS analyses of GO and rGO prepared by hydrothermal method: survey scan (a) and C 1s (c) of GO, survey scan (c) and C 1s (d) of rGO.

XPS spectroscopy was carried out to analyze the element composition change and chemical structure variation of GO and reduced graphene oxide (rGO) obtained by hydrothermal method. The XPS spectrum of GO shows the typical peak components of C 1s and O 1s (figure S4a), ascribed to C and O elements presenting in GO nanosheets. After hydrothermal reduction, the ratio of carbon to oxygen increases obviously, indicating the removal of oxygen-containing functional groups. Moreover, the appearance of new peak assigning to P element demonstrates the possible reaction between GO nanosheets and PA molecules (figure S4b). The chemical structure variation was revealed by different chemical states of C and O. The C 1s core-level spectrum could be curve-fitted with four peak components, as shown in figure S4c, d. The main peaks center at the binding energies of approximately 284.5, 285.6, 286.8 and 288.4 eV are assigning to the carbon atoms in aromatic rings, C-OH, C-O (epoxy and alkoxy), and C=O groups, respectively.^{17, 18} After hydrothermal reduction, the intensities of XPS peaks of the carbon atoms bonded to oxygen decreased rapidly, implying most oxygen-containing functional groups were removed during the reduction process. These results demonstrate that the green hydrothermal reduction method is an effective strategy to reduce GO.





In order to intuitively observe the structural evolution of the nanostructured conductive network during stretching, LSCM was carried out by means of labeling GO nanosheets with Rodamine 6G via physical absorption. To ensure the effective fluorescent labeling of GO nanosheets, natural rubber latex (NR) was employed to act as the analogue of ENR. Briefly, 0.001 g rhodamine 6G was dissolved in distilled water and mixed with 0.01 g GO nanosheets. And owing to the abundant functional groups and large specific surface area of GO, the Rodamine 6G was fully absorbed on the surface of GO nanosheets after stirring for 30 min. Then, 1.59 g NR latex (solid content: 1 g) was added to the mixture and sonicated for 5 min to form a homogenous suspension. After removing the residual water quickly, an ultrathin film with segregated nanostructure network could be obtained for the LSCM measurement. The rhodamine-labeled graphene/rubber nanocomposite was excited at 488 nm with a laser attenuation of 5 % and the emission light was recorded using band-pass filter to collect wave length between 500-700 nm. The LSCM images were taken at 200× magnification with a pinhole diameter of 1 Å.

As shown in **figure S5**, a compact segregated nanostructure is clearly observed before stretching. When applied a strain of 50 %, a fraction of disconnected fluorescence region occurs along with the tensile direction owing to the destruction of conductive nanostructure. After removing the applied stress, the distributions of fluorescence recover to its initial conjoint state, indicting the recovery of the conductive path. The results are consistent with our proposed response mechanism.



Figure S6. The response time of our strain sensor, which shows an average response time of 225 ms.



Figure S7. Schematic illustration of the expression recognition based on our strain sensor.



Figure S8. The current signal variation of electronic sensor responding to finger downand up-bending, intorsion, and smiling after bending over 10000 times and placing for 60 days.

Desirable sensing stability and repeatability properties are of great significance for the wide application of wearable electronics. To assess the durability and stability of our electronic sensors, we evaluated the human motion monitoring properties of the sensors after bending over 10000 times and placing at ambient environment for two months. The current signal variation responding to the diverse motions are plotted in **figure S8**. After experiencing those disposal, the corresponding waveforms of our electronic sensor are similar to the initial ones and repetitions of each movements generate the consistent current variation. This observation indicates that our electronic sensors exhibit satisfactory sensitivity and reproducibility, which are quite important for their long-term use.



Figure S9. The current variation of electronic sensor responding to different finger bending degrees.

Table S1. The vulcanization formula for the preparation of S-cu-GO/ENRnanocomposites.

Component	GO	sulfur	Zinc oxide	Steric acid	CBS
Content (phr)	2.00	1.68	3.00	1.80	0.90

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