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STRECHABLE CRUMPLED GRAPHENE PHOTODETECTOR WITH
PLASMONICALLY-ENHANCED PHOTORESPONSIVITY

BY
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THESIS

Submitted in fulfillment of the requirements
for the degree of Master of Science in Materials Science and Engineering
in the Graduate College of the
University of Illinois at Urbana Champaign, 2016

Urbana, Illinois

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ABSTRACT

Graphene has been widely explored for flexible, high-performance photodetectors due to its exceptional mechanical strength, broadband absorption, and high carrier mobility. However, the low stretchability and limited photoabsorption of graphene have restricted its applications in flexible and high-sensitivity photodetection systems. Various hybrid systems based on photonic or plasmonic nanostructures have been introduced to improve the limited photoresponsivity of graphene photodetectors. In most cases, the hybrid systems succeeded in the enhancement of photoresponse, but showed limited mechanical stretchability. Here, we demonstrate a crumpled graphene-gold nanoparticles (AuNPs) hybrid structure photodetector with $\sim 1200\%$ enhanced photoresponsivity compared to conventional graphene photodetector and exceptional mechanical stretchability up to 200% tensile strain. We achieved the plasmonically enhanced optical absorption of graphene-based photodetector by using a hybrid structure of graphene-AuNPs. We crumpled the hybrid structure to realize mechanical stretchability and further enhancement of the optical absorption by areal densification. Our highly stretchable photodetector with enhanced photoresponsivity can be integrated with a contact lens and a spring structure. We believe that our high performance graphene photodetector can find broad applications for conformable and flexible optical sensors and dynamic mechanical strain sensors.

This thesis also explores the fabrication of different degrees of hierarchical crumples of graphene on microstructure array, which can be exploited to control surface wettability. Here, we achieved to create hierarchical structures of graphene in microscale by using three-dimensional (3D) features on a substrate and in nanoscale by compressive pre-strain of the substrate.

“I can do all things through Christ who strengthens me” [Philippians 4:13].

*In the process of the research, I was humbled by my limitations, but I could achieve such things
in the presence of God.*

I dedicate this work to

my family, TaeHong Kim, MyeongSook Kim, and MinSik Kim

for their sacrificial support and limitless love.

ACKNOWLEDGMENTS

I would like to sincerely thank my advisor, Professor SungWoo Nam, for supporting me during these past years and providing me a privileged environment to study and research at the University of Illinois at Urbana-Champaign. I will forever be grateful to my mentor, Dr. Pilgyu Kang, for his scientific advice and insightful teachings. Even though I am still lacking as a scientist and a person, I promise that his sacrifices and teachings are not in vain. I would also sincerely like to thank Juyoung Leem, Jonghyun Choi, Mike Cai Wang, and Sung-gyu Chun for their advice and suggestions; I would not be able to achieve this without their support. I would like to thank all my lab mates: Ali Ashraf, Junghoon Kim, Keong Han Yong, Peter Knapp, Farhad Haque, Chace Cho Satoshi Takekuma, Widi Moestopo, Dawoon Kim, Ryan Han, and Siddhesh Dhanawade. I wish them all the best and hope that their careers succeed.

I am grateful to Steve Chung, Hyunmin Park, Namheon Cho, Hyokang Lee, Seungwon Lee, and JoonHee Kim for always being there, encouraging and supporting me. In addition, I would like to thank my mentors, JunHo Song and Hyongill Lee, and friends, HernSung Kim, Guehyung Kim, ByungJin Kang, KyuNam Kim, MinJae Sohn, HyunKyun Kim, JinHwan Lee, Durkho Park, Seokwon Kang, MinSeok Kwak, DoGun Lee, KwangWoo Kim, BoongKi Kwak and others for providing the support and friendship I needed.

I would especially like to thank my dad, mom, and brother. I am truly privileged to have them as my family. I thank my dad for always sacrificing for me and being my role-model. I am always grateful to my mom for her unconditional love, advice, and prayers. I would like to thank my brother for always being the one I can rely on. I will never forget their love and support.

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CHAPTER 1

INTRODUCTION

Recently, flexible optoelectronic devices have been actively developed for diverse applications, including sensing in biological systems¹⁻³, wearable optoelectronic devices⁴, and flexible integrated photonics⁵⁻⁶. As one of the key components in optoelectronic devices, a highly flexible photodetector with high photoresponsivity has been specifically desired for advanced applications such as human health monitoring devices^{2-3,7} and wearable electronics^{1-2,4}. Graphene, a single layer of hexagonally-bonded carbon atoms⁸, has been considered an attractive optical/optoelectronic material for photodetectors because of its outstanding mechanical strength⁹⁻¹⁰, broadband absorption from ultraviolet to terahertz frequencies¹¹⁻¹³, and high carrier mobility¹⁴⁻¹⁵. Despite its exceptional mechanical, optical, and electrical properties, graphene-based photodetectors have been hardly applied to flexible and stretchable optoelectronic devices for two primary reasons: graphene shows only limited stretchability – specifically, ~6 % for the chemical vapor deposition (CVD) synthesized graphene¹⁶ and 25 % for the mechanically exfoliated graphene⁹ without structural failure; additionally, the low light absorption of a single layer graphene (~2.3 %) ¹⁷⁻¹⁸, attributed to its atomically thin structure, presents another challenge in developing flexible graphene-based photodetectors.

First, the limited mechanical stretchability of graphene can be enhanced by creating an elastically buckled/delaminated structure of graphene (i.e., graphene crumples¹⁹). The crumpled graphene has shown to enable a highly stretchable photodetector with enhanced photoresponsivity¹⁹. During the release of the tensile stress applied to the polymer substrate, graphene becomes buckled and delaminated¹⁹⁻²⁰, and the crumpled structures exhibited high stretchability as well as enhanced photoresponsivity based on optical absorption increase led by

enhanced areal density of graphene. Although high stretchability was demonstrated up to 200% tensile strain, the photoresponsivity of the crumpled graphene photodetector was limited.

Second, to improve photoresponsivity, various approaches to integrating graphene with photonic nanostructures^{13, 21-29} or with other materials (e.g., quantum dots³⁰⁻³², nanowires³³⁻³⁵ and transition metal dichalcogenide monolayers³⁶) have been explored. Despite the high photoresponsivity, the stretchability of most graphene-based photodetectors with the hybrid approaches reported to date was still limited. Recently, Chiang *et al.*³⁰ reported a stretchable photodetector based on the hybrid structure of graphene and graphene quantum dots with high photoresponsivity. However, the photodetector has a limited stretchability only up to 25%. Furthermore, mechanical robustness was shown to be stable only up to 30 cycles of mechanical stretching.

Integrating plasmonic nanostructures with graphene demonstrated the possibility of effectively enhancing optical absorption by a strong field enhancement²⁷⁻²⁹, while also improving stretchability by crumpling graphene. Liu *et al.*²⁹ reported a photodetector with the AuNP array on graphene which exhibited 1500 % higher photoresponsivity compared to that without the AuNP array. The photoresponsivity was plasmonically enhanced by the excited surface plasmons confined in the plasmonic nanostructure. In addition, in our recent studies³⁷, we demonstrated the capability of crumpling the graphene-AuNPs hybrid structure by use of a heat shrinkable polymer for surface enhanced Raman spectroscopy.

Here, we present a photodetector based on crumpled graphene integrated with AuNPs, which shows enhanced mechanical stretchability and photoresponsivity (Figure 1a). To achieve high stretchability, the graphene-AuNPs hybrid structure was crumpled on an elastomeric substrate. Crumpling enables enhanced photoresponsivity at the same time, which is led by optical

absorption enhancement, by the areal densification of graphene¹⁹ and consequently, the number density increase of AuNPs. AuNPs themselves are plasmonic nanostructures, and the increased number of AuNPs per projected unit area further enhances the plasmonic enhancement of optical absorption³⁷⁻³⁸. As a result, our photodetector shows not only over an order-of-magnitude higher enhancement (~1200 %) of photoresponse compared to a flat graphene photodetector, but also outstanding mechanical stretchability up to 200 %, together with the strain-tunable photoresponsivity. Finally, we demonstrate the potential of our stretchable photodetector with plasmonically enhanced photoresponsivity for various applications – for example, biomedical optical sensors³⁹⁻⁴⁰ and dynamic mechanical strain sensors⁴¹.

CHAPTER 2

FABRICATION OF STRECHABLE GRAPHENE PHOTODETECTOR WITH PLASMONICALLY-ENHANCED PHOTORESPONSIVITY

2.1 Graphene Synthesis

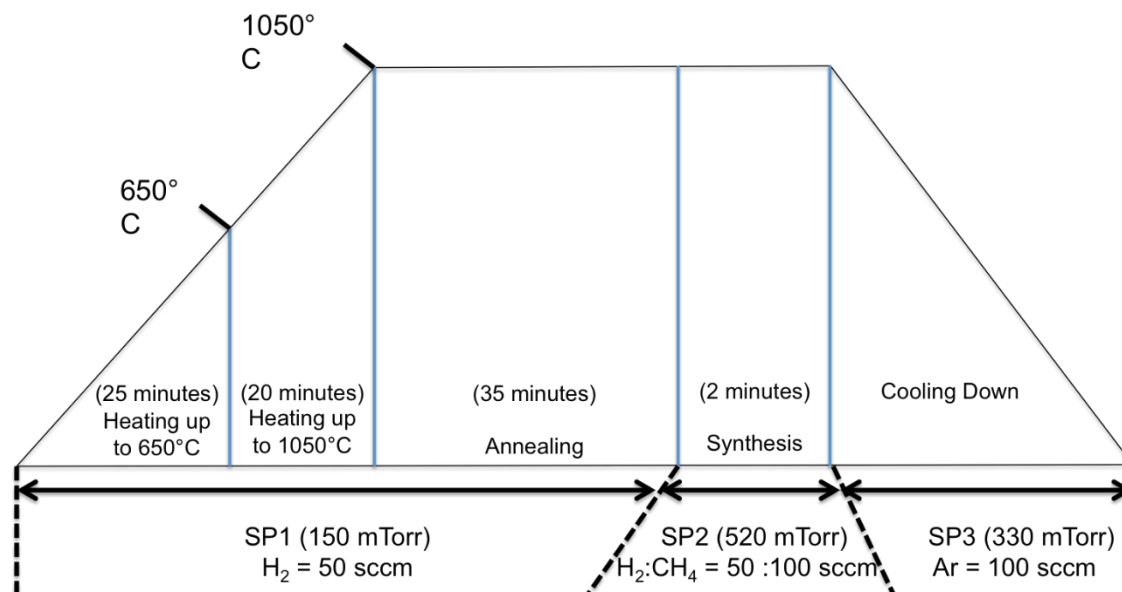


Figure 2.1 A schematic illustration of the graphene growth process by a low pressure chemical vapor deposition (LPCVD) method. The process is composed of heating, annealing a copper catalyst substrate, synthesizing graphene on the substrate, and cooling down.

To fabricate graphene-AuNPs hybrid structure, graphene was firstly synthesized under a low pressure chemical vapor deposition (LPCVD) system (Rocky Mountain Vacuum Tech Inc., CO) using a 25 μ m thick Cu foil (Alfa Aesar, MA) as a catalyst substrate (Figure 2.1). The Cu foil was prepared and immersed in hydrochloric acid (HCl) for 10 minutes to remove native copper oxide layer and impurities on the surface. Then, the foil was cleaned with deionized (DI) water and isopropyl alcohol (IPA) to remove the remaining HCl. The foil was placed in the LPCVD chamber. The LPCVD chamber was vacuumed below 1 mTorr and temperature was raised up to 650 °C in 25 minutes, under hydrogen (H₂) gas injection (50 sccm) at 150 mTorr. Then, the

temperature was raised up to 1050 °C in 20 minutes, and the foil was annealed at 1050 °C for 35 minutes to refine the surface and grow the grain size of Cu. Then, the pressure was increased to 520 mTorr with an inflow of gaseous methane (CH_4) for 2 minutes to synthesize graphene. Then, the chamber was cooled under an inflow of Argon (Ar) gas at 330 mTorr. Graphene was formed at the Cu foil surface as well as at the backside of the Cu foil. For the better quality of transferred graphene, the graphene formed on the backside of the Cu foil was removed by oxygen plasma etching (Diener GmbH, Germany).

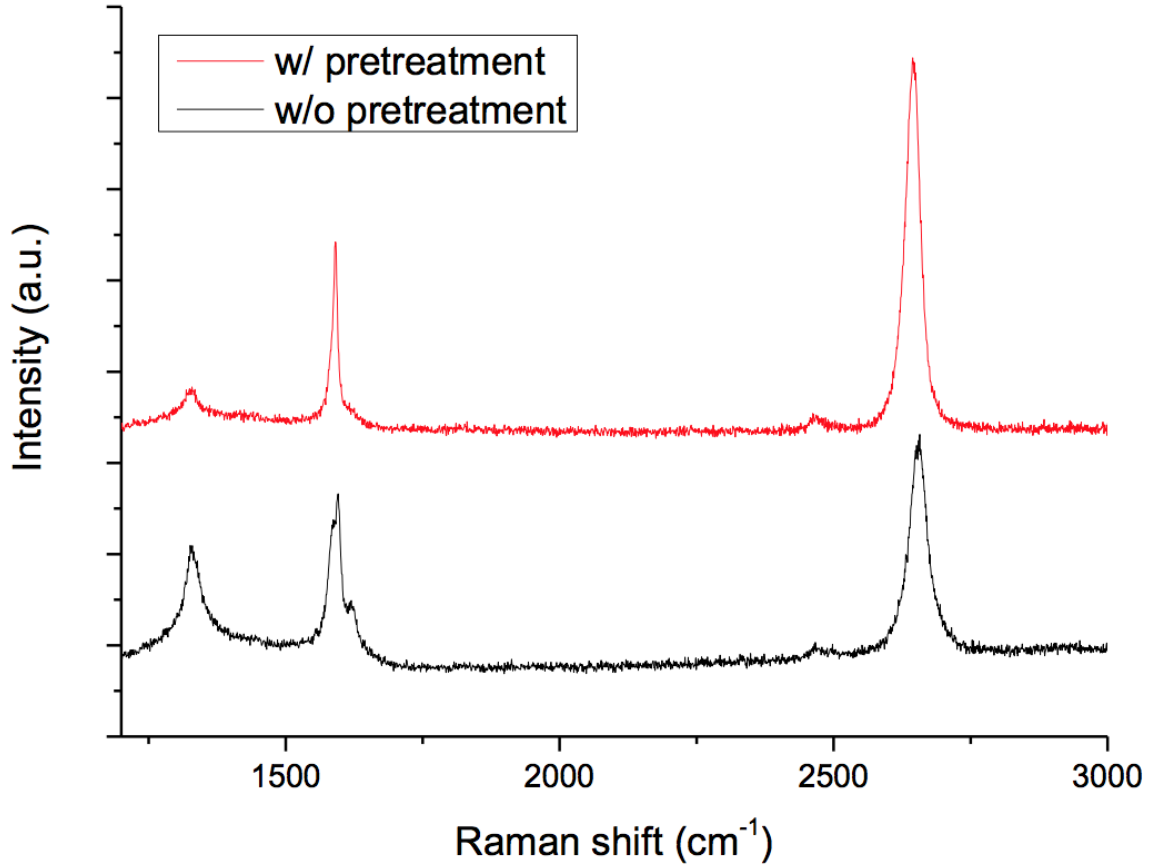


Figure 2.2 Raman spectra of graphene synthesized with pretreatment (red) and without pretreatment (black).⁴² With pretreatment, negligible intensity of D peak was observed and the intensity ratio of G peak to 2D peak is measured to be ~2.3.

The quality of graphene was confirmed by Raman spectroscopy (Renishaw, UK). The Raman spectra of graphene exhibited three characteristic bands at $\sim 1350\text{ cm}^{-1}$, $\sim 1590\text{ cm}^{-1}$, $\sim 2690\text{ cm}^{-1}$ (D, G, and 2D peaks, respectively). The quality of graphene was highly influenced by the pretreatment by HCl. Without the pretreatment, relatively high intensity of D peak and low peak ratio of G peak to 2D peak was observed. With the pretreatment, a graphene sample shows not only the negligible intensity of D peak, which represents the high quality of graphene, but also, the intensity ratio of G peak to 2D peak of ~ 2.3 ; it demonstrates that single or bi-layer of graphene was synthesized (Figure 2.2).

2.2 Fabrication of graphene- AuNPs hybrid structure

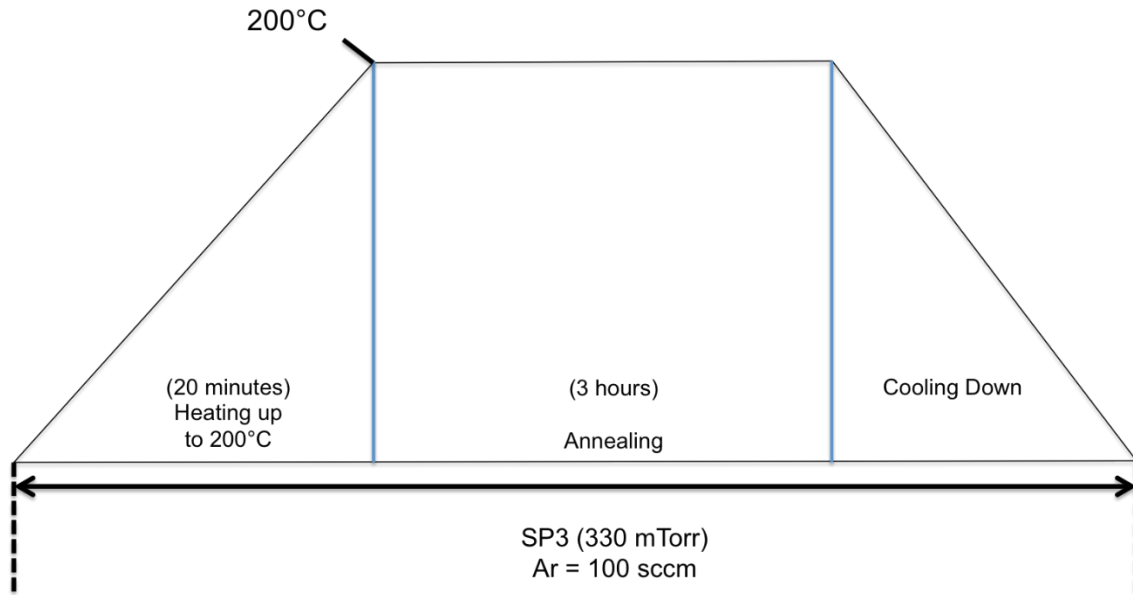


Figure 2.3 A schematic illustration of formation of gold nanoparticles (AuNPs) on graphene process by a low pressure thermal annealing method. The process comprises heating, annealing a gold film on graphene (forming AuNPs), and cooling down.

After graphene is synthesized on a Cu substrate, a 4 nm-thick gold (Au) thin film was deposited on the graphene by a thermal evaporator (Nano 36, Kurt J. Lesker, PA); the deposition rate was 0.1 Å/s . The Au film on graphene/Cu foil was placed in the LPCVD chamber. The LPCVD chamber was vacuumed below 1 mTorr and temperature was raised up to 200°C under

Ar gas injection (100sccm) at 330 mTorr. Then, the Au thin film – graphene – Cu foil was annealed at 200°C for 3 hours to create Au nanoparticles (AuNPs) on the graphene surface (Figure 2.3).

2.3 Fabrication of a stretchable photodetector based on the graphene-AuNPs hybrid structure

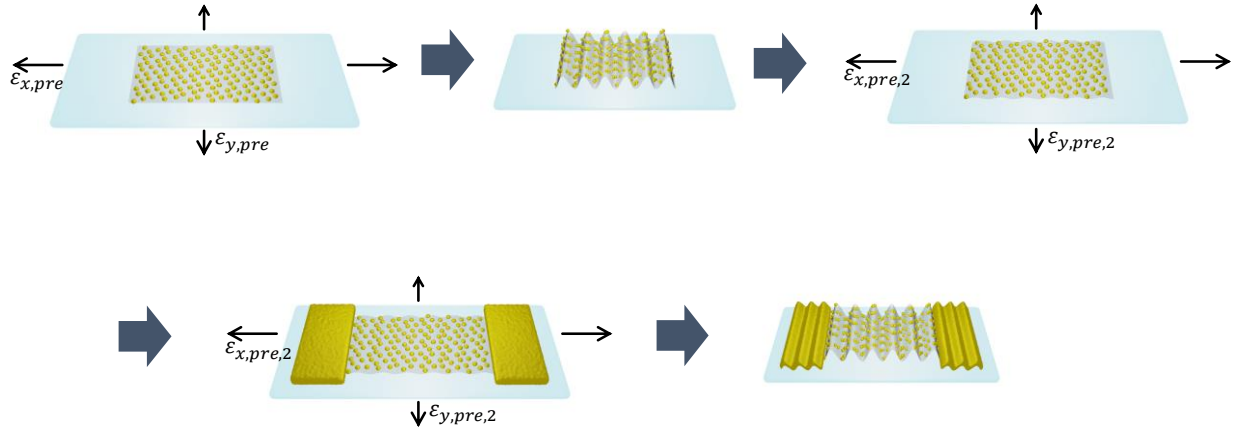


Figure 2.4 Fabrication procedure of the hybrid photodetector. The graphene-AuNPs hybrid film is transferred onto a biaxially pre-strained, highly stretchable polymer substrate ($\epsilon_{x,pre}$ and $\epsilon_{y,pre}$), followed by sequential release that leads to the crumpled hybrid structure. Gold metal contacts are thermally deposited on the biaxially pre-stretched crumpled hybrid film on the stretchable substrate ($\epsilon_{pre2,x}$ and $\epsilon_{pre2,y}$). Sequential release of the pre-stretching allows for the stretchable hybrid photodetector.

The graphene-AuNPs hybrid structure on a Cu foil was transferred onto a polydimethylsiloxane (PDMS) substrate to remove the Cu substrate; AuNPs on the graphene and the PDMS substrate were in contact. The Cu substrate was completely etched by ferric chloride (FeCl_3) aqueous solution, and graphene-AuNPs hybrid structure remains on the PDMS surface. The hybrid structure on the PDMS substrate was transferred by placing the hybrid film on the PDMS substrate onto a biaxially prestrained very high bond (VHB) film (3MTMVHBTM 4910, 3M, MN) and detaching the PDMS substrate. The VHB film was biaxially pre-stretched by 350% in x-direction and 250% in y-direction. The pre-strained VHB tape was released to

deterministically form crumpled structures through delamination-buckling of the hybrid film (Figure 2.4).

For the photoresponse characterization, we fabricated a photodetector device consisting of a photoconductive channel with the crumpled hybrid structures and corrugated gold contacts for collecting photogenerated electrical signal. To fabricate a photodetector consisting of a photoconductive channel of the crumpled graphene -AuNPs hybrid structure and corrugated Au electrodes, the VHB film with the crumpled graphene-AuNPs hybrid structure was re-stretched 300% in the x-direction and 200% in the y-direction. Then, the channel part of the hybrid structure was covered with polyethylene shadow mask and 40 nm of Au was thermally deposited. The pre-strained VHB tape was released to obtain the corrugated gold electrodes.

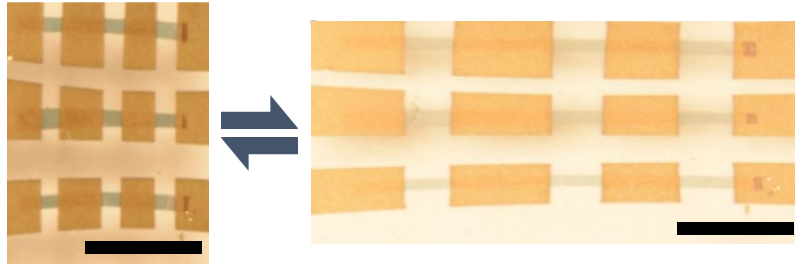


Figure 2.5. Photographs of the fabricated stretchable hybrid photodetector array (an array of 3×3 photodetector devices) (Scale bar = 3 mm). The hybrid photodetectors were fabricated with pre-strains of $\epsilon_{pre1,x}=350\%$ and $\epsilon_{pre1,y}=250\%$. The photographs on the left and the right side show the array device at $\epsilon_{tensile,x}=0\%$ and 200%, respectively.

Finally, the stretchable photodetector with crumpled graphene-gold nanoparticles (AuNPs) hybrid structure was fabricated (Figure 2.5). As the schematic illustration of the stretchable photodetector with the crumpled graphene-AuNPs hybrid structures (Figure 2.6) shows, the uniaxial tensile strain can be applied to the VHB substrate to unwrinkle the crumpled hybrid structure. By stretching the substrate, the areal density of graphene and areal number density of AuNPs decreased.

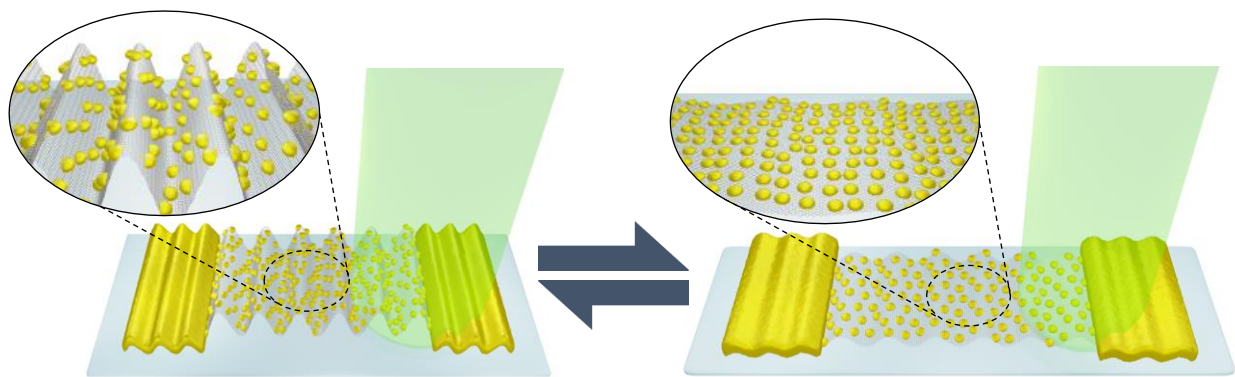


Figure 2.6. The schematic illustration of the stretchable photodetector with the crumpled graphene-AuNPs hybrid structures (left). As uniaxial tensile strain applied, the crumpled hybrid structure is unwrinkled (right).

CHAPTER 3

QUALITATIVE ANALYSIS OF A CRUMPLED GRAPHENE-GOLD NANOPARTICLES HYBRID STRUCTURE

We performed detailed material characterizations of crumpled hybrid structures with scanning electron microscopy (SEM) (S-4800, Hitachi, Japan). Using SEM imaging, morphology of AuNPs on graphene and topography of the crumpled hybrid structures were investigated.

3.1 Flat hybrid structure

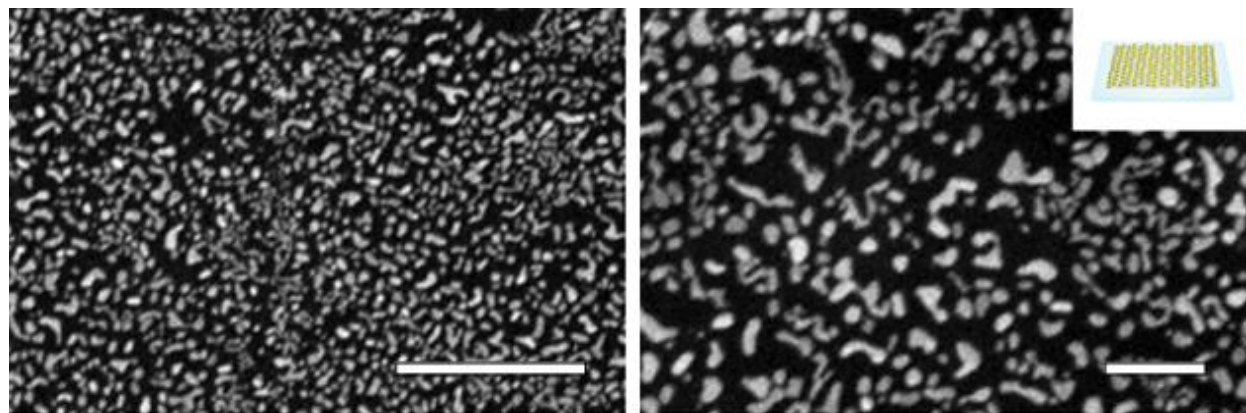


Figure 3.1 Scanning electron microscope (SEM) images of a flat hybrid structure (Left, Scale bar=1 μm) and (right, Scale bar=300 nm)

Figure 3.1 shows a flat hybrid structure. In the SEM image, AuNPs were observed to be highly dense and monodispersed. To further analyze the structure, the SEM image was cropped into the selected area. The cropped image was transformed into an 8-bit image. The area of each particle and number of particles were calculated by ImageJ⁴³ (Figure 3.2). The average diameter and the average number density were 57.0 ± 2.82 nm and 123 ± 12.7 particles/ μm^2 , respectively.

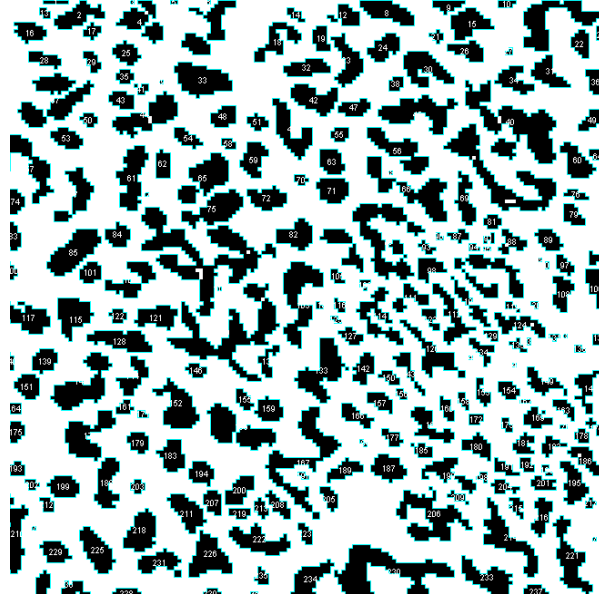


Figure 3.2. Post processed image of the SEM image of a flat graphene-AuNP hybrid structure of Figure 3.1 for analysis of average size and number density of AuNPs.

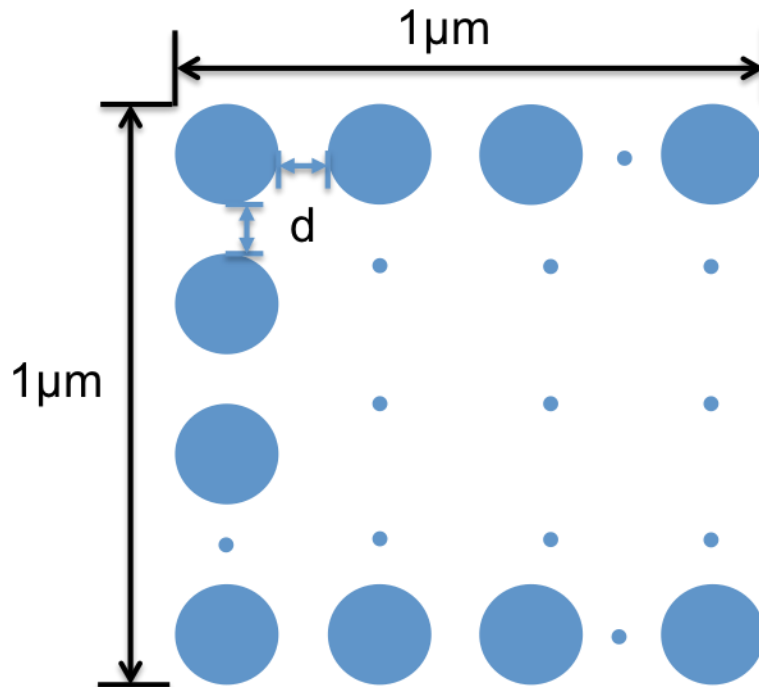


Figure 3.3 A simple particle arrangement model. The distribution of AuNPs in a $1\ \mu\text{m} \times 1\ \mu\text{m}$ square was modeled as an ordered array to make an estimation of a gap distance (d) between particles.

Then, the average gap distance (d) between adjacent particles was estimated to be 36.5 nm based on the simple particle arrangement model (Figure 3.3) and the following equation:

$$d = \frac{1\mu m - N_{1\mu m} \times D_{avg}}{N_{1\mu m} - 1} \quad (1)$$

where $N_{1\mu m}$ is the average number of particles in $1\mu m$, and D_{avg} is the average diameter of a particle. $N_{1\mu m}$ was determined by the number density.

3.2 Crumpled hybrid structure at $\varepsilon_{pre,x} = 350\%$ and $\varepsilon_{pre,y} = 250\%$

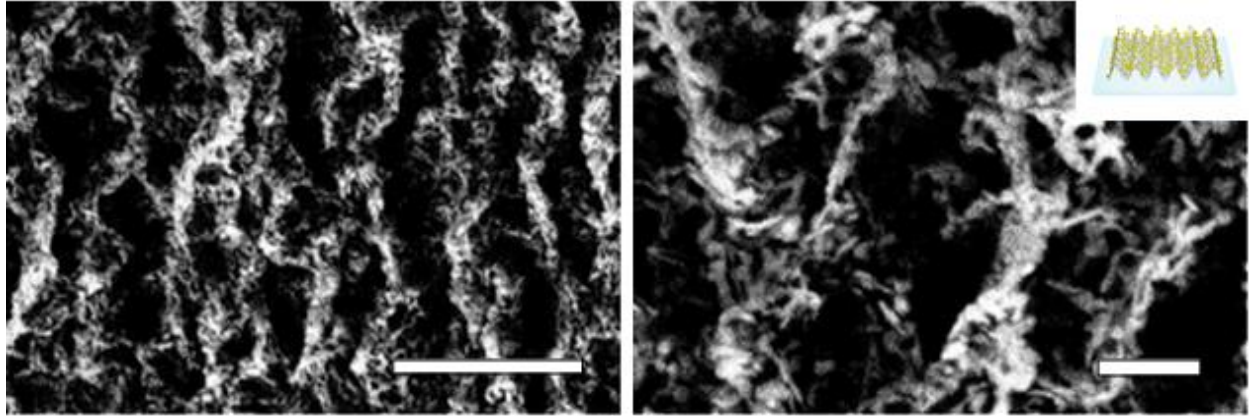


Figure 3.4. Characterizations of crumpled graphene-AuNPs hybrid structures. Scanning electron microscope (SEM) images of the crumpled hybrid structure at $\varepsilon_{stretch,x} = 0\%$. (Left, Scale bar = $1\mu m$) and (Right, Scale bar = 300 nm)

Figure 3.4 shows the SEM image of the crumpled hybrid structure fabricated with prestrains of $\varepsilon_{pre,x} = 350\%$ and $\varepsilon_{pre,y} = 250\%$. The crumpled hybrid structures were highly ordered. First, the wavelengths and amplitude of the crumples were predicted by an analytical model^{9,35,44}. Crumple wavelengths in both x-direction ($\lambda_{c,x}$) and y-direction ($\lambda_{c,y}$) were determined by following analytical formulas, which are based on the assumption of biaxially crumpled structures. The biaxially crumpled structures are mathematically expressed as $z = A \cdot \cos(2\pi x / \lambda_{c,x}) \cdot \cos(2\pi y / \lambda_{c,y})$ ⁴⁴, where A is crumpled height, $\lambda_{c,x}$ and $\lambda_{c,y}$ are crumple wavelengths in x and y directions, respectively.

$$\lambda_{c,x}^{-2} + \lambda_{c,y}^{-2} = \frac{1}{(2\pi \cdot h_f)^2} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} \quad (2)$$

$$\lambda_{c,x}^{-2} - \lambda_{c,y}^{-2} = \frac{1}{(2\pi \cdot h_f)^2} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} \left(\frac{3-\nu_f}{3+\nu_f} \right) \frac{\varepsilon_{pre,x} - \varepsilon_{pre,y}}{\varepsilon_{pre,x} + \varepsilon_{pre,y} - \left[\left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} / 2(1+\nu_f) \right]} \quad (3)$$

where h_f is film thickness, $\bar{E}_f (= E_f/(1 - \nu_f^2))$ and $\bar{E}_s (= E_s/(1 - \nu_s^2))$ are respective plane strain moduli of a film and a substrate. ν_f and ν_s are respective Poisson's ratios of a film and a substrate, and $\varepsilon_{pre,x}$ and $\varepsilon_{pre,y}$ are respective prestrains in x and y directions.

The equations are simplified to calculate $\lambda_{c,x}^{-2}$ and $\lambda_{c,y}^{-2}$:

$$\lambda_{c,x}^{-2} = \frac{1}{2(2\pi \cdot h_f)^2} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} \left(1 + \left(\frac{3-\nu_f}{3+\nu_f} \right) \left(\frac{\varepsilon_{pre,x} - \varepsilon_{pre,y}}{\varepsilon_{pre,x} + \varepsilon_{pre,y} - \left[\left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} / 2(1+\nu_f) \right]} \right) \right) \quad (4)$$

$$\lambda_{c,y}^{-2} = \frac{1}{2(2\pi \cdot h_f)^2} \left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} \left(1 - \left(\frac{3-\nu_f}{3+\nu_f} \right) \left(\frac{\varepsilon_{pre,x} - \varepsilon_{pre,y}}{\varepsilon_{pre,x} + \varepsilon_{pre,y} - \left[\left(\frac{3\bar{E}_s}{\bar{E}_f} \right)^{\frac{2}{3}} / 2(1+\nu_f) \right]} \right) \right) \quad (5)$$

The thickness of a film, h_f , was assumed to be graphene thickness (0.34 nm). We assumed that AuNPs were not a composite layer on graphene because they were not a continuous layer and randomly distributed on graphene. Thus, only graphene was considered in our calculation. Poisson's ratio of graphene and VHB are 0.165⁴⁵⁻⁴⁶ and 0.49 (manufacture's information of 3M VHBTM tape, 3M, U.S.), respectively. The prestrains in x-direction ($\varepsilon_{pre,x}$), and y-direction ($\varepsilon_{pre,y}$) were 3.5 and 2.5, respectively. E_f is 1 TPa of the Young's modulus of graphene⁴⁶, and E_s is 2.2x10² kPa of the Young's modulus of substrate⁴⁷. By inserting the above values into Equations 4 and 5, $\lambda_{c,x}$ and $\lambda_{c,y}$, were estimated to be 298 nm and 346 nm, respectively.

$$A = 4h_f \left(\frac{\bar{\epsilon}_f}{3\bar{\epsilon}_s} \right)^{\frac{1}{3}} \sqrt{\frac{1}{3-\nu_f} \left[\epsilon_{pre,x} - \epsilon_{pre,y} - \left[\left(\frac{3\bar{\epsilon}_s}{\bar{\epsilon}_f} \right)^{\frac{2}{3}} / 2(1 + \nu_f) \right] \right]} \quad (6)$$

The amplitude of the structure (A) was estimated to be 209 nm by Equation 6. The crumple height was calculated to be 418 nm (2×A).

To compare analytical values with experimental results, $\lambda_{c,x}$ was determined to be 277.67 nm by the analysis of SEM images, which was very close to the analytically estimated value of 298 nm. Our fabricated structure is well-matched with the analytical model. The small discrepancy between the analytically calculated value and the experimental value is attributable to our assumption that AuNPs were not considered as a composite layer on graphene.

3.3 Crumpled hybrid structure at $\epsilon_{pre,x}= 350\%$, $\epsilon_{pre,y}= 250\%$, and $\epsilon_{pre,x,2}= 200\%$

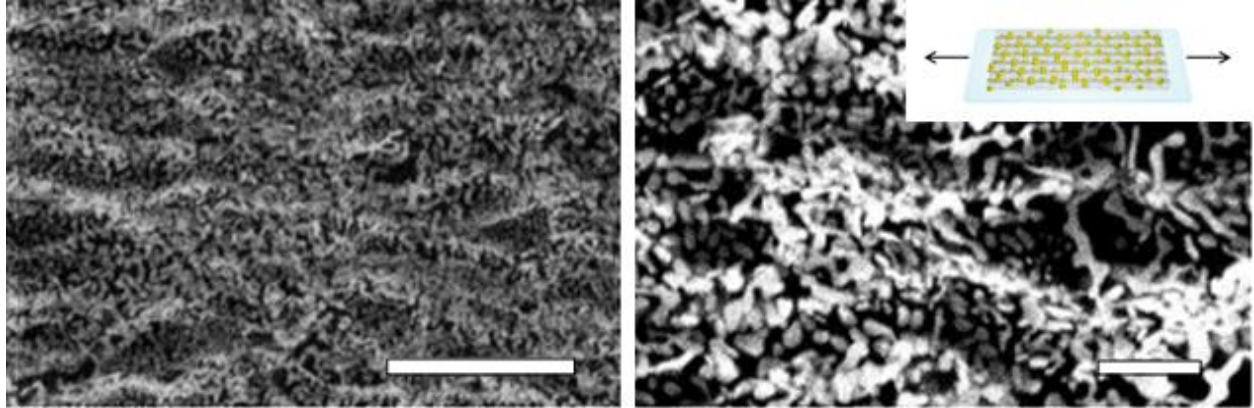


Figure 3.5 Scanning electron microscope (SEM) images of the crumpled hybrid structure at re-stretching strains, $\epsilon_{stretch,x}= 200\%$. (Left, Scale bar=1 μm) and (Right, Scale bar=300 nm)

Figure 3.5 shows a SEM image of the crumpled hybrid structure taken with uniaxial stretching in the dominantly crumpled direction. The structures shown in Figures 3.4 and 3.5 were prepared with the same amount of prestrains, but the hybrid structure shown in Figure 3.5 was re-stretched ($\epsilon_{pre,x,2}= 200\%$) after a hundred cyclic re-stretching strains. The dominantly

induced crumples were unwrinkled, whereas crumples in the other direction were formed due to Poisson's effect. It is notable that the morphology of AuNPs was retained over the cyclic re-stretching strains. Importantly, it was revealed in the SEM characterization that structural integrity between graphene and AuNPs is robust with respect to stretching strains so as to develop the crumpled hybrid structure for stretchable devices.

3.4 Number density calculation

The number density of AuNPs at $\epsilon_{\text{tensile},x} = 0\%$ and 200% were estimated based on the average number density of flat graphene-AuNPs hybrid structure and the ratio of the surface area to the projected area (d_b) (Equation 7)⁴⁸.

$$d_b = 1 + \frac{\pi^2 A^2 \lambda_{c,x}^2 + \lambda_{c,y}^2}{2 \lambda_{c,x}^2 \cdot \lambda_{c,y}^2} \quad (7)$$

The d_b at $\epsilon_{\text{tensile},x} = 0\%$ and 200% were calculated to be 5.2 and 3.8, respectively. The number density was determined by multiplying the number density of the flat hybrid structure by the d_b . The number density of AuNPs in the crumpled hybrid structure at $\epsilon_{\text{tensile},x} = 0\%$ and 200% were estimated to be 643 particles/ μm^2 and 467 particles/ μm^2 , respectively. However, the number density of AuNPs at $\epsilon_{\text{tensile},x} = 200\%$ would be more than 467 particles/ μm^2 with consideration of Poisson's effect. With $\nu_{VHB} = 0.2$ of a measured Poisson's ratio in our experiment, the number density of AuNPs is estimated to be 505 particles/ μm^2 . Thus, the difference of number density between $\epsilon_{\text{tensile},x} = 0\%$ and 200% was determined to be 21.5%. It indicates that by stretching 200% of the substrate in x-direction, the structure was expected to absorb ~21.5% less light.

CHAPTER 4

QUANTATATIVE ANALYSIS OF A CRUMPLED GRAPHENE-GOLD NANOPARTICLES HYBRID STRUCTURE

We performed quantitative material characterizations of crumpled hybrid structures with Raman spectroscopy (Renishaw, UK) and ultraviolet-visible spectroscopy (UV-Vis) (Varian Cary 5G, US). Using Raman spectroscopy and UV-Vis, the quality and the photoabsorption of crumpled hybrid structure at varying uniaxial strains between 0 % and 200 % were investigated, respectively.

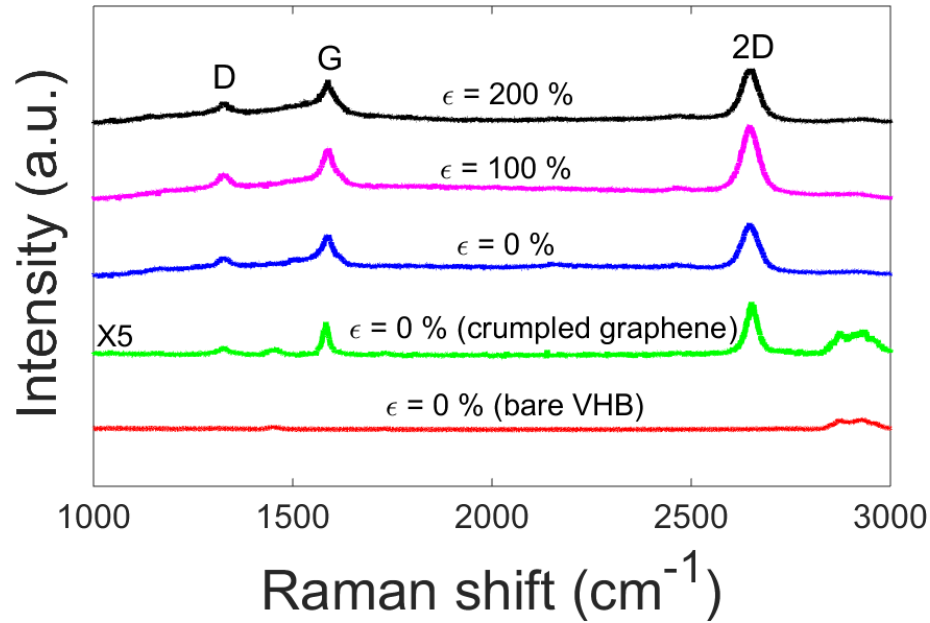


Figure 4.1 Raman spectra of the crumpled hybrid structure on a VHB substrate at varying uniaxial tensile strains ($\epsilon_{\text{tensile},x} = 0\%, 100\%, 200\%$), a flat graphene on a VHB substrate, and a bare VHB film.

For quantitative material characterizations, we further carried out Raman spectroscopy of the crumpled hybrid structures at varying uniaxial tensile strains between 0% and 200% (Figure 4.1). Crumpled graphene exhibited three characteristic bands at 1350 cm⁻¹, 1580 cm⁻¹, and 2650

cm⁻¹ (D, G, and 2D, respectively). The relatively small intensity of the D peak indicated that no significant defects were present in the crumpled graphene. For comparison, Raman spectral intensity of crumpled graphene was multiplied by 5 times. The Raman spectral intensity of the crumpled hybrid structures was intense due to electromagnetic amplification of Raman signal intensity by the plasmonic effect of the AuNPs^{37, 49}. The small peaks in the spectrum of crumpled graphene between ~2900 cm⁻¹ to 3000 cm⁻¹ were attributed to a VHB substrate. The crumpled hybrid structures showed small D peak intensities at varying tensile strains between 0% and 200%, similar to that of the crumpled graphene. This indicated negligible structural defects in the crumpled hybrid structures. It was also notable that the crumpled hybrid structures were mechanically robust in re-stretching strains up to $\epsilon_{\text{tensile},x} = 200\%$.

Then, UV-Vis was performed to investigate tunability and enhancement of photoabsorption and to quantitatively characterize the integrity of the crumpled hybrid structure at varying tensile strains between 0% and 200%. For comparison, optical extinction of crumpled graphene with varying tensile strains between 0% and 200%, as well as that of flat graphene was also measured. First, the transmittance (T) values of crumpled hybrid structure and crumpled graphene on VHB substrates under uniaxial tensile strains (0%-200%), and flat graphene on VHB substrate were measured over the broad range of wavelength (350 nm-800 nm) (Figure 4.2). Then, transmittance values (T₀) of bare VHB substrates over wavelengths (350 nm-800 nm) were obtained for background subtraction. The transmittance values were converted into extinction, which accounts for absorption and scattering, by calculating $1 - T/T_0$. Figure 4.3 shows the optical extinction at a wavelength of 532 nm. $\lambda_{\text{light}} = 532 \text{ nm}$ was selected because the wavelength is widely used in biosensing applications⁵⁰. In addition, the optical extinction at 532 nm wavelength showed a relatively large difference between $\epsilon_{\text{tensile},x} = 0\%$ and 200%.

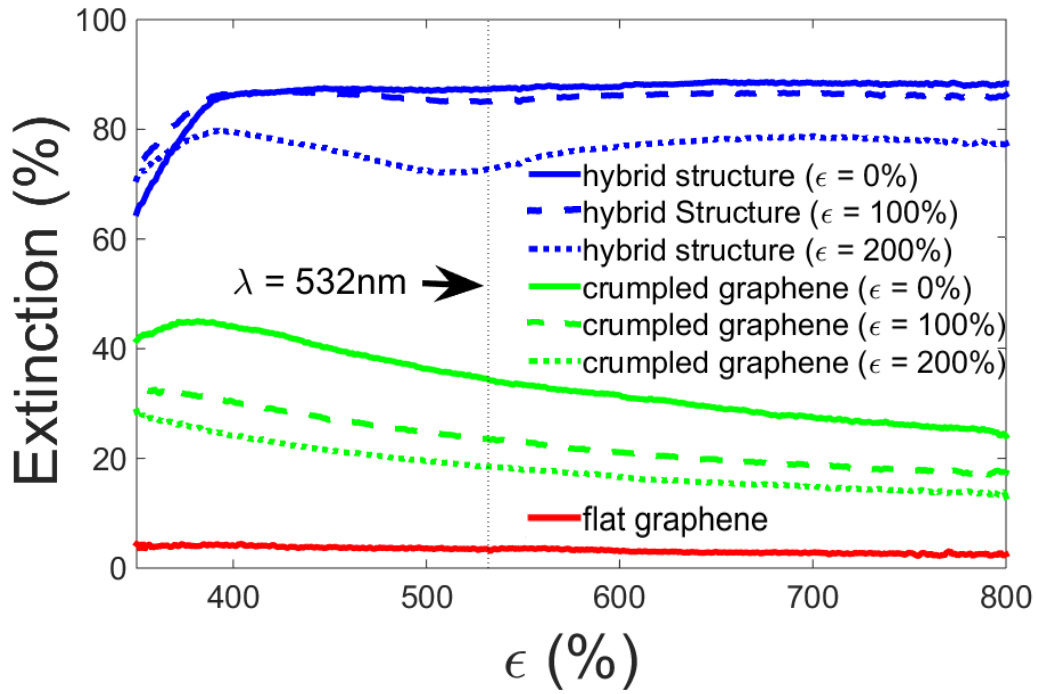


Figure 4.2 Extinction spectrum of a crumpled hybrid structure and crumpled graphene on a VHB substrate at varying tensile strains of 0%, 100%, and 200%, and extinction spectrum of flat graphene on a VHB substrate (a wavelength range between $\lambda=350-800$ nm). The wavelength of 532 nm was denoted by a black dotted vertical line to indicate the relatively large modulation of photo-absorption at $\epsilon_{\text{tensile},x} = 0\%$ and 200%, compared to other wavelengths. It indicates that the largest tunability of the photoresponse can be achievable around the wavelength.

We compared the optical extinction of crumpled hybrid structures at $\epsilon_{\text{tensile},x} = 0\%$, that of crumpled graphene at $\epsilon_{\text{tensile},x} = 0\%$, and that of flat graphene to demonstrate the amount of photoabsorption enhancement. The optical extinction of the crumpled graphene at $\epsilon_{\text{tensile},x} = 0\%$ was 10.2 times that of flat graphene. The areal density increase of crumpled graphene yields higher light absorption. The optical extinction of crumpled hybrid structures at $\epsilon_{\text{tensile},x} = 0\%$ was 2.52 times that of crumpled graphene at $\epsilon_{\text{tensile},x} = 0\%$. Such enhancement is attributable to the two mechanisms of plasmonic enhancement by AuNPs²⁹: 1) localized surface plasmons of AuNPs enhance local electromagnetic fields in AuNPs, and 2) the plasmonic energy absorbed in one nanoparticle decays radiatively and interacts with other neighboring nanoparticles⁵¹.

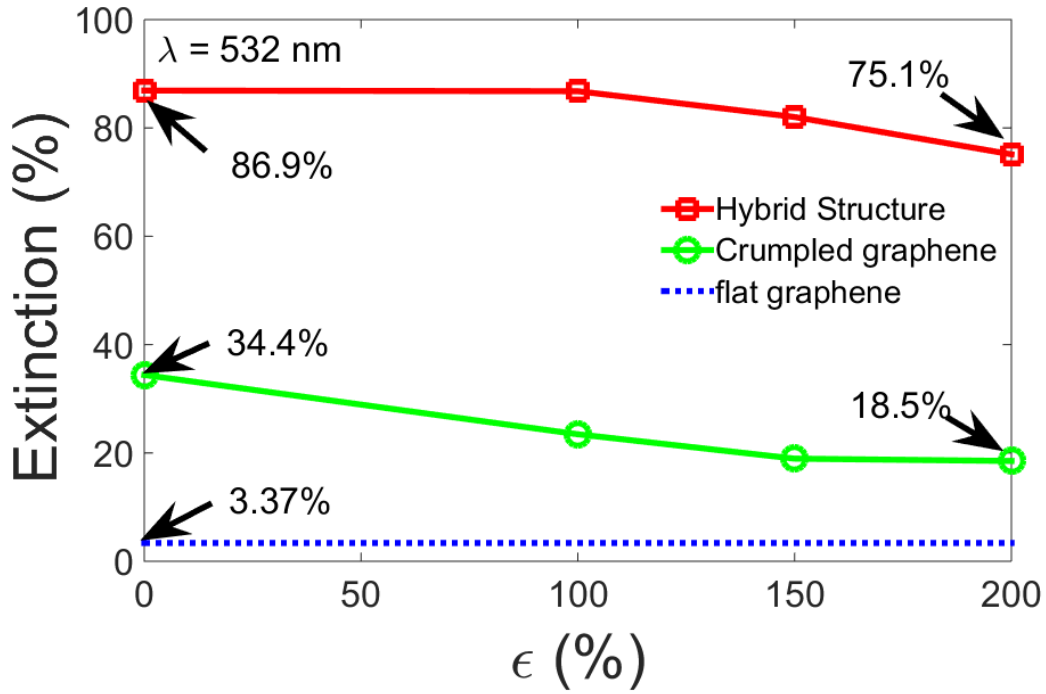


Figure 4.3 Optical extinction at $\epsilon_{\text{light}} = 532 \text{ nm}$ of the crumpled hybrid structure on a VHB substrate, the crumpled graphene on a VHB substrate at varying uniaxial tensile strains ($\epsilon_{\text{tensile},x} = 0\%, 100\%, 200\%$), and flat graphene on VHB substrate at $\lambda = 532 \text{ nm}$. All scale bars are $1 \mu\text{m}$.

The number density of AuNPs in the crumpled graphene-AuNPs hybrid structure was estimated to be $\approx 640 \text{ particles}/\mu\text{m}^2$ at $\epsilon_{\text{tensile},x} = 0\%$ and $\approx 505 \text{ particles}/\mu\text{m}^2$ at $\epsilon_{\text{tensile},x} = 200\%$ (Chapter 3). With consideration of the estimated number density values, optical absorption at $\epsilon_{\text{tensile},x} = 0\%$ was expected to be $\sim 21.5\%$ larger than that at $\epsilon_{\text{tensile},x} = 200\%$, and $\sim 14\%$ difference of photoabsorption was observed between $\epsilon_{\text{tensile},x} = 0\%$ and 200% . The theoretical number density is well-matched to the experimentally measured difference of $\sim 14\%$.

Furthermore, the crumpled hybrid structure showed the consistent optical extinction at varying tensile strains in the UV-Vis measurements with a thousand cycles of uniaxial stretching and release (Figure 4.4), and such results showed robust tunability. These UV-Vis characterization results conclusively showed the enhanced optical absorption of the crumpled hybrid structure and the tunability of the enhancement of optical absorption.

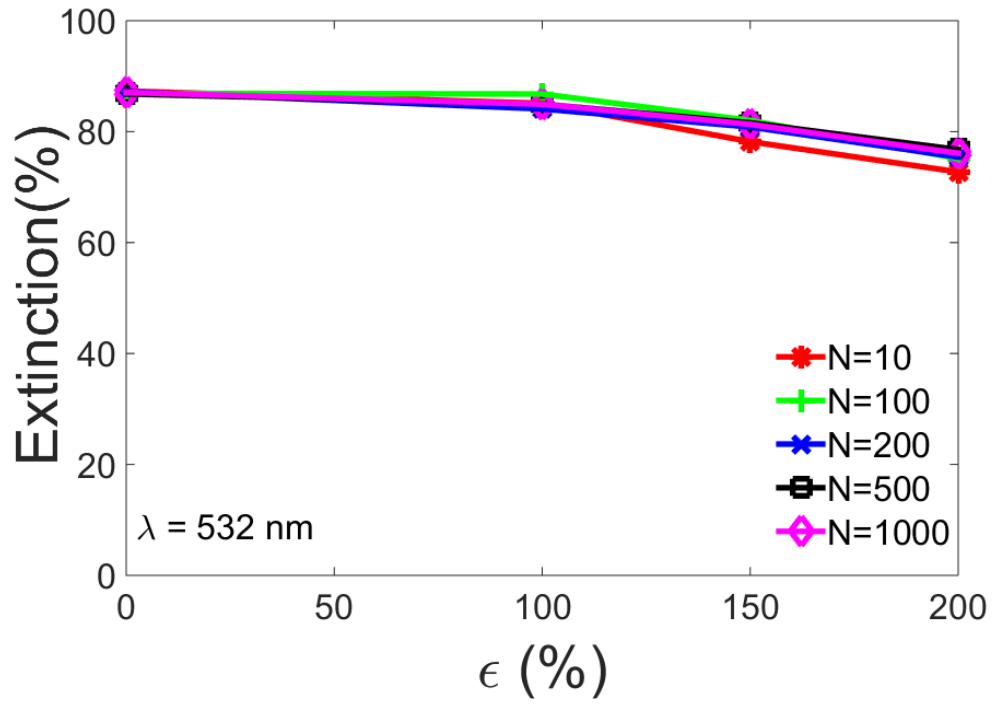


Figure 4.4 Mechanical robustness of the crumpled graphene-AuNPs hybrid plasmonic structure. (a) Measured extinction at $\lambda_{\text{light}} = 532 \text{ nm}$ at four different uniaxial strains (0%, 100%, 150%, and 200%) over 1000 cycles.

CHAPTER 5

DEVICE CHARACTERIZATIONS

To characterize dynamic photoresponse of the hybrid photodetector, the photocurrent of the device generated by the incident beam from a diode laser of 532 nm was measured by a sourcemeter (Keithley 2614B, US) and microprobe station. The beam size of an elliptical laser beam ($\lambda_{\text{light}}=532\text{nm}$, Thorlabs CPS532, NJ) was measured to be $L_{\text{beam}} \sim 760 \mu\text{m}$ and $W_{\text{beam}} \sim 1080 \mu\text{m}$ (Power $\sim 3 \text{ mW}$ through a 5X objective lens). The photodetector was fabricated with the dimensions of channel length (L) and width (W), which were $\sim 350 \mu\text{m}$ and $\sim 500\text{-}700 \mu\text{m}$, respectively. The dimensions were determined to be $L_{\text{channel}} > L_{\text{beam}}/2$ and $W_{\text{channel}} \approx W_{\text{beam}}$ so that the maximum possible photocurrent of a photodetector device could be measured in later analysis. To maintain a consistent power and illumination position, the laser power and beam focus/alignment were calibrated through a 5X objective lens with a photodiode power sensor (S120C and PM100USB, Thorlabs, NJ). The bias voltage of $15 \mu\text{V}$ was applied for electrical potential through the gold electrodes, which is required to induce the current.

We characterized dynamic photoresponse of the hybrid photodetector to a 532 nm laser light at varying uniaxial tensile strains between 0% and 200%. A 532 nm wavelength laser beam was focused at the junction of the photoconductive channel and the gold electrode to measure the maximum photocurrent²⁹. The laser was turned on and off every 15 seconds for 3 cycles. For comparison, a crumpled graphene photodetector and a flat graphene photodetector were fabricated with similar device dimensions, including channel length and width. Dynamic photoresponse of the crumpled graphene photodetector and the flat graphene photodetector was characterized same as the hybrid photodetector. Measured photocurrents were normalized with the maximum photocurrent value of the hybrid photodetector at $\epsilon_{\text{tensile},x}=0\%$ (Figure 5.1).

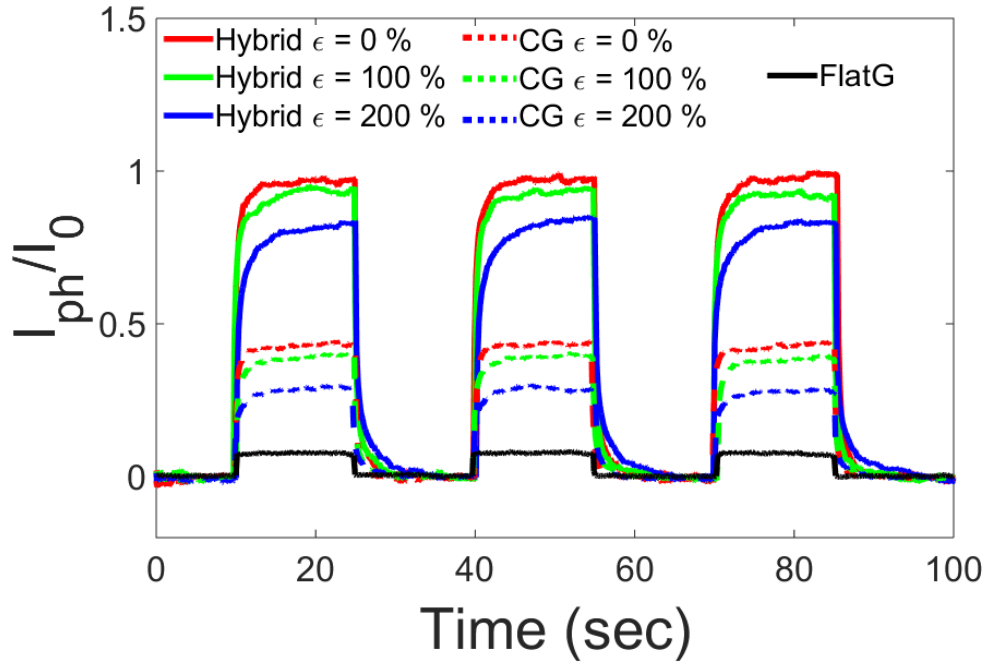


Figure 5.1. Photoresponse characterization of a stretchable hybrid photodetector with crumpled graphene-AuNPs hybrid structures. Dynamic photoresponse at $\lambda_{\text{light}} = 532$ nm of the hybrid photodetector and a crumpled graphene photodetector at varying uniaxial tensile strains between 0% and 200%, and that of a flat graphene photodetector. All measured photocurrents were normalized with the photocurrent of the hybrid photodetector measured at $\epsilon_{\text{tensile},x} = 0\%$, denoted by I_0 .

The photocurrent of the hybrid photodetector was measured to be 110% larger than measured photocurrent of the crumpled graphene photodetector. More notably, the measured photocurrent of the hybrid photodetector was 1570% larger, compared to that of the flat graphene photodetector (Figure 5.2).

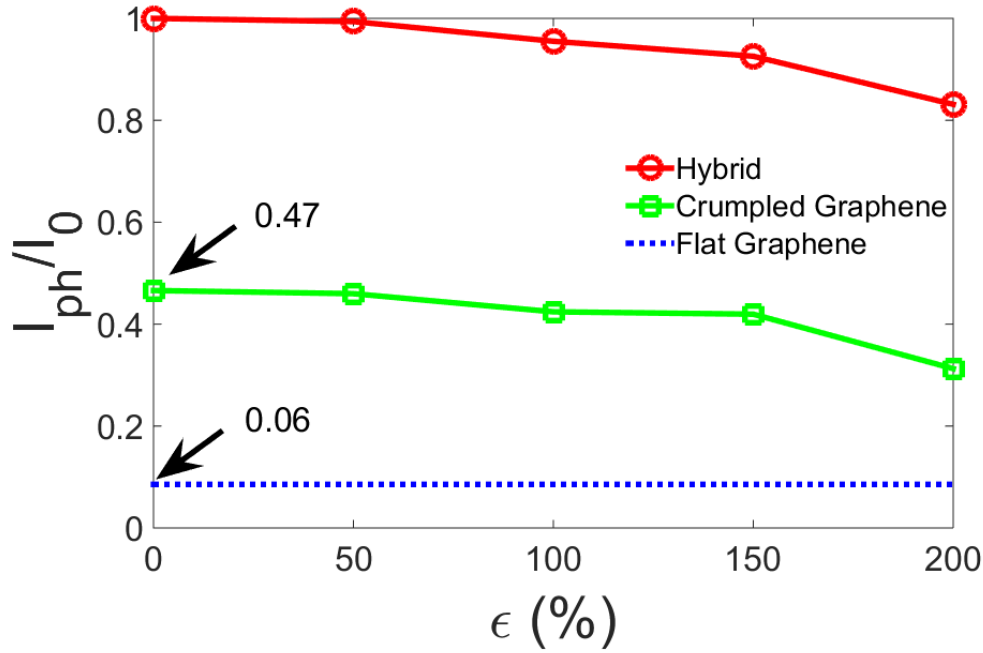


Figure 5.2 Comparison of the photoresponse, normalized measured photocurrents, I_{ph}/I_0 , of the hybrid photodetector and the crumpled graphene photodetector at the varying uniaxial tensile strains, and that of flat graphene device.

In order to calculate the photoresponsivity (R_{ph}) of photodetector devices, photocurrents (I_{ph}) generated with respect to the incident light intensity at $\epsilon_{tensile,x} = 0\%$ was divided by half of the incident power. The incident power was divided by 2 because half of a channel was illuminated by the laser beam. The photoresponsivity ($R_{ph} = I_{ph} / (P_{in}/2)$) of a photodetector based on the crumpled hybrid structure was estimated to be 0.044 mA/W. For comparison, the photoresponsivity of a crumpled graphene photodetector and a flat graphene photodetector was calculated same as that of the photodetector on the crumpled hybrid structure and the photoresponsivity values were 0.0194 mA/W and 0.0034 mA/W, respectively (Table 1). The photoresponsivity (R_{ph}) of the hybrid photodetector was $\sim 130\%$ and $\sim 1200\%$ larger than that of a flat graphene photodetector, respectively.

The optical extinction enhancement factor due to crumpling $\sigma_{ext,crumpled}/\sigma_{ext,flat} = 34.4\% / 3.37\% \sim 10.2$ (Figure 4.3), attributable to plasmonic enhancement, was close to the photoresponse

enhancement $I_{ph,crumpled}/I_{ph,flat} = 0.47/0.06 \sim 7.83$ (Figure 5.2). The optical extinction enhancement factor due to AuNPs, $\sigma_{ext,hybrid}/\sigma_{ext,crumpled} = 86.9 \% / 34.4 \% \sim 2.52$ (Figure 4.3), attributable to plasmonic enhancement, was also well-matched with the photoresponse enhancement, $I_{ph,hybrid}/I_{ph,crumpled} = 1/0.47 \sim 2.13$ (Figure 5.2). This consistency in values indicated that enhanced photoabsorption led to the enhancement of photoresponsivity. The small difference between the enhancement factor and photoresponsivity ratio is attributable to the scattering of photoexcited carriers in the crumpled plasmonic hybrid structures.

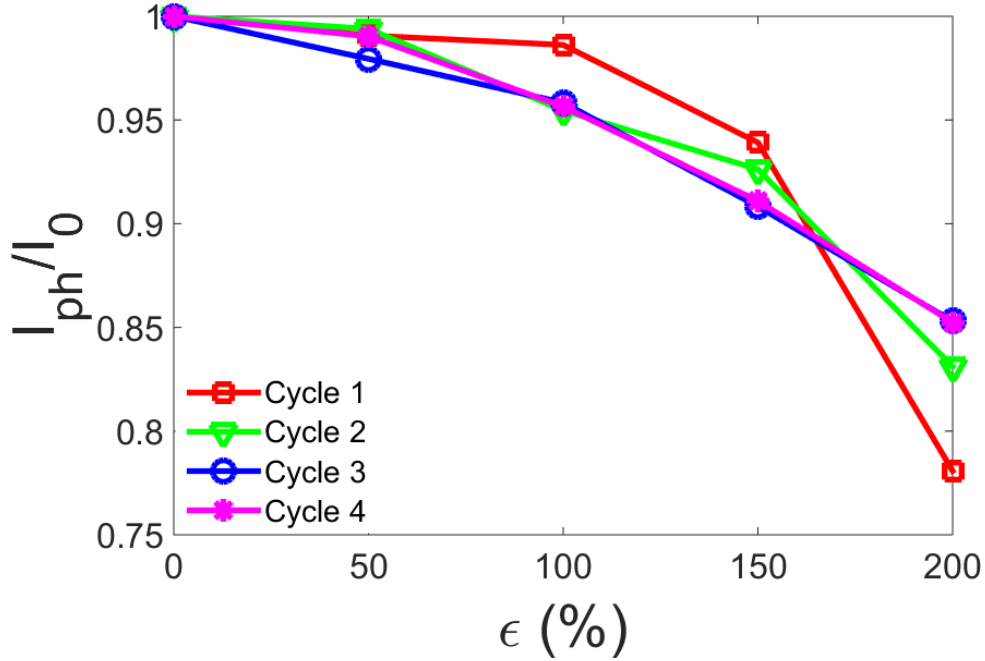


Figure 5.3 Photocurrent measurements of the hybrid photodetector with multiple cycles of the different uniaxial tensile strains between 0% and 200%.

Furthermore, we examined the tunability of photoresponse of the hybrid photodetector by applying tensile strains. The optical extinction of the crumpled hybrid structures at $\epsilon_{tensile,x} = 0\%$ was larger by 15% than that at $\epsilon_{tensile,x} = 200\%$. Measured photocurrent at $\epsilon_{tensile,x} = 0\%$ showed $\sim 20\%$ larger photocurrent, compared to that at $\epsilon_{tensile,x} = 200\%$ (Figure 5.2). The tunable extent of photoresponse was closely matched to that of optical extinction (15%). The strain-tunable

photoresponse was consistent in multiple cycles of stretching and release (Figure 5.3). In addition, mechanical robustness of the hybrid photodetector was tested with respect to a thousand cyclic stretching. (Figure 5.4). Photocurrents measured at $\epsilon_{\text{tensile},x} = 100\%$ were consistent throughout a thousand of the cyclic stretching. Such results showed mechanical robustness of strain-tunable photoresponse of the hybrid photodetector.

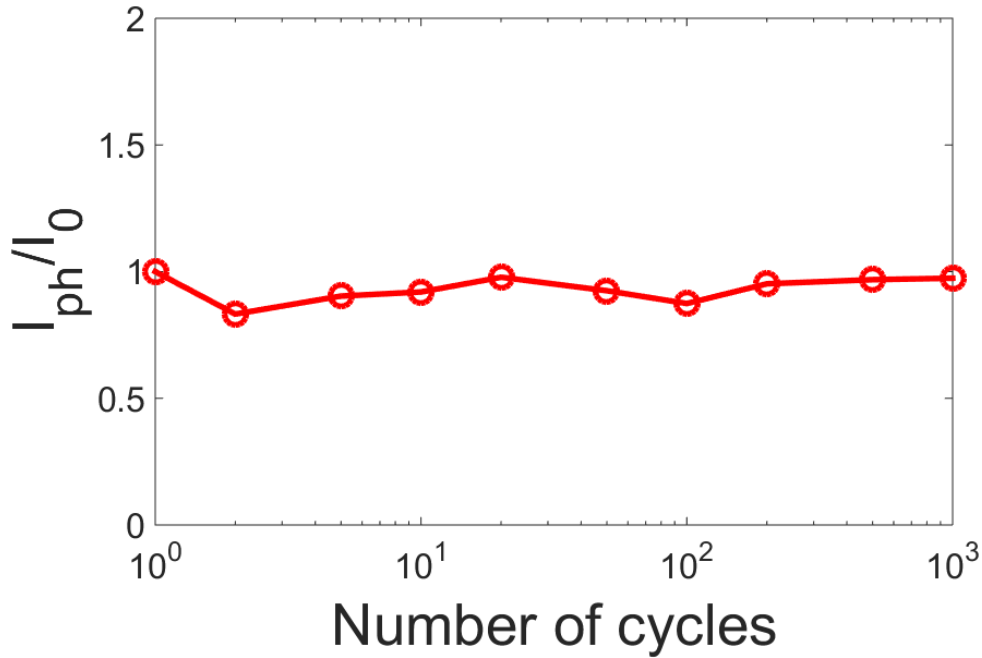


Figure 5.4 Mechanical robustness of a hybrid photodetector with the crumpled graphene-AuNPs hybrid plasmonic structure. Normalized photocurrents measured at $\epsilon_x=100\%$ over a thousand cyclic tensile strains. Measured photocurrents at different cycles were normalized by the photocurrent measured in the first cycle.

Table 1. Comparison of the photoresponsivity (R_{ph}) of a hybrid photodetector with the crumpled graphene-AuNPs hybrid structure, a crumpled graphene photodetector, and a flat graphene photodetector. The photoresponsivity was determined with measured incident power of a $\lambda_{\text{light}}=532$ nm laser light (P_{in}) and measured photocurrent (I_{ph}) respectively.

	P_{in}	I_{ph}	$R_{ph}(= I_{ph} / (P_{in}/2))$
Hybrid Structure	3.052×10^{-3} W	6.73×10^{-2} μ A	0.0440 mA/W
Crumpled Graphene	3.105×10^{-3} W	3.01×10^{-2} μ A	0.0194 mA/W
Flat Graphene	3.225×10^{-3} W	5.52×10^{-3} μ A	0.0034 mA/W

CHAPTER 6

APPLICATIONS

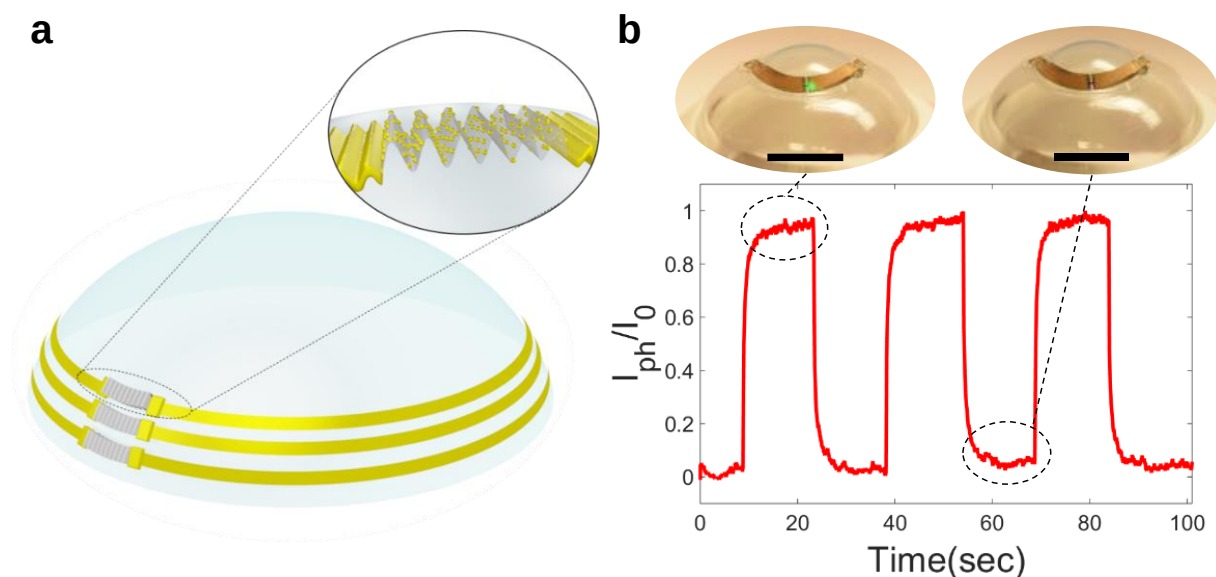


Figure 6.1 Conformability of a hybrid photodetector with crumpled graphene-AuNPs hybrid structures. (a) Schematic illustration of a stretchable hybrid photodetector integrated on a contact lens. (b) Dynamic photoresponse of the stretchable hybrid photodetector on a contact lens. Inset photographs show photoresponse measurements with the integrated hybrid photodetector at the illumination of a 532 nm laser light which is turned on (left) and off (right) (Scale bar = 1 cm).

Finally, we demonstrated the potential of our stretchable photodetector as a flexible and conformal optical sensor. We showed that our hybrid photodetector can be conformably integrated on the curved surface of a contact lens (Figure 6.1a). The dynamic photocurrent was measured with respect to three on-off cycles of a 532 nm laser light. The measured photocurrent exhibited a high signal-to-noise ratio through the cyclic switching of the light (Figure 6.1b). This demonstration shows that our hybrid photodetector with enhanced photoresponsivity and high flexibility has the potential for wearable optical sensors and broad applications of human health monitoring.

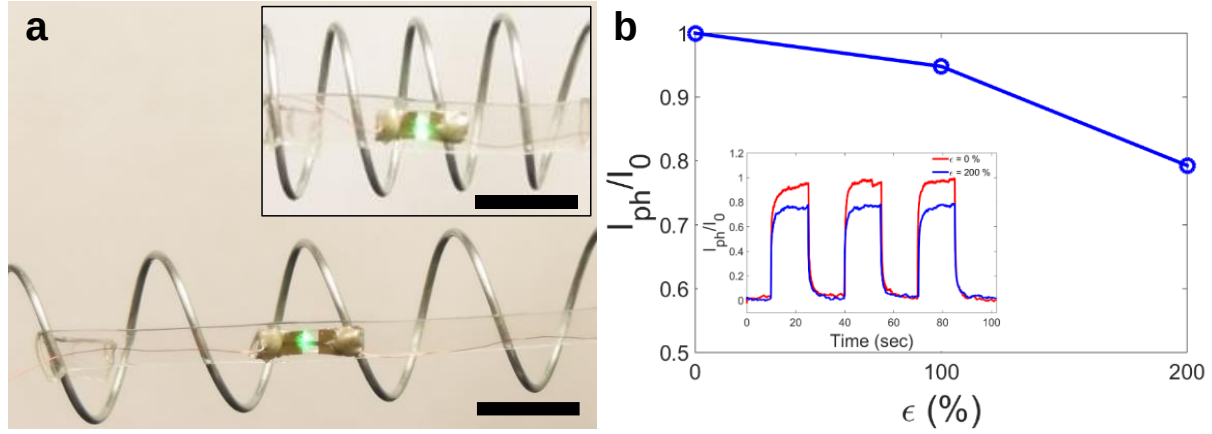


Figure 6.2. High stretchability of a hybrid photodetector with crumpled graphene-AuNPs hybrid structures. (a) Photographs of a stretchable hybrid photodetector integrated on a spring for the demonstration of a dynamic mechanical strain sensing. Inset photograph shows the integrated photodetector at $\epsilon_{\text{tensile},x} = 0\%$ (Scale bar = 1 cm). (b) Measured photoresponse of the integrated hybrid photodetector at varying uniaxial tensile strains between 0% and 200%. Measured photocurrents were normalized by the photocurrent of the integrated hybrid photodetector measured at $\epsilon_{\text{tensile},x} = 0\%$ (I_0). Inset figure shows dynamic photoresponse of the integrated hybrid photodetector at $\epsilon_{\text{tensile},x} = 0\%$ and 200%.

Moreover, we showed a dynamic mechanical strain sensing by using the strain-tunable photoresponse and high stretchability. Our hybrid photodetector was integrated with a spring (Figure 6.2a). Photocurrents were measured with respect to cyclic on-off of a 532 nm laser light at varying tensile strains between 0% and 200% applied to the spring (Figure 6.2b). In the stretching of the spring, the measured photocurrent was decreased as the photoresponse of the hybrid photodetector was reduced at increased tensile strains. The reduction of the measured photocurrent was consistent with our earlier photoresponse characterization results. Our hybrid photodetector has the potential to be applicable to the suspension spring for an automotive vehicle when it is integrated with flexible light emitting diode, and the integrated system can monitor the strain variance from shock loads more efficiently. Moreover, the photodetector with the large strain sensing capability is applicable to structural health monitoring⁴¹.

CHAPTER 7

HIERARCHICAL CRUMPLES OF GRAPHENE ON 3D MICROSTRUCTURE ARRAY

Multiscale, hierarchical patterned surfaces exhibiting multifunctional properties could be abundantly found in nature, such as lotus leaves,⁵² gecko feet,⁵³ and butterfly wings.⁵⁴ To emulate such hierarchical structures using graphene, we fabricated hierarchical patterns of graphene using multilevel tuning of morphologies: 1) microscale tuning by transferring graphene onto 3D microstructured surfaces,⁵⁵ and 2) nanoscale tuning by inducing graphene crumples using pre-strained, stretchable substrates (e.g., Ecoflex).^{20, 56} Ecoflex is a commercially available stretchable elastomer, and we patterned Ecoflex with 3D protruding microfeatures by curing on 3D patterned Si molds. Next, we transferred as-grown graphene onto biaxially pre-strained (40 – 200%) 3D Ecoflex with diluted poly(methyl methacrylate) (PMMA) as a carrier film.⁵⁷ As the pre-strain was carefully released and PMMA was removed by acetone, we achieved hierarchically integrated graphene on 3D microstructured substrate.

SEM images (Figure 7.1) demonstrate the multiscale patterns of graphene, where microstructure was patterned by the underlying feature and nanostructure was developed using the pre-strain of substrate. In particular, by modulating the pre-strain value of Ecoflex, we could control the height and density of nanoscale crumples of graphene both on the apices and base areas of the microfeatures (middle and right panels, respectively, in Figure 7.1). We note that cracks or damages of graphene are expected to induce significant electron charging in the SEM images due to the insulating characteristic of underlying Ecoflex. Therefore, our SEM images with no electron charging demonstrate the damage-free nature of our integrated graphene (Figure 7.1).

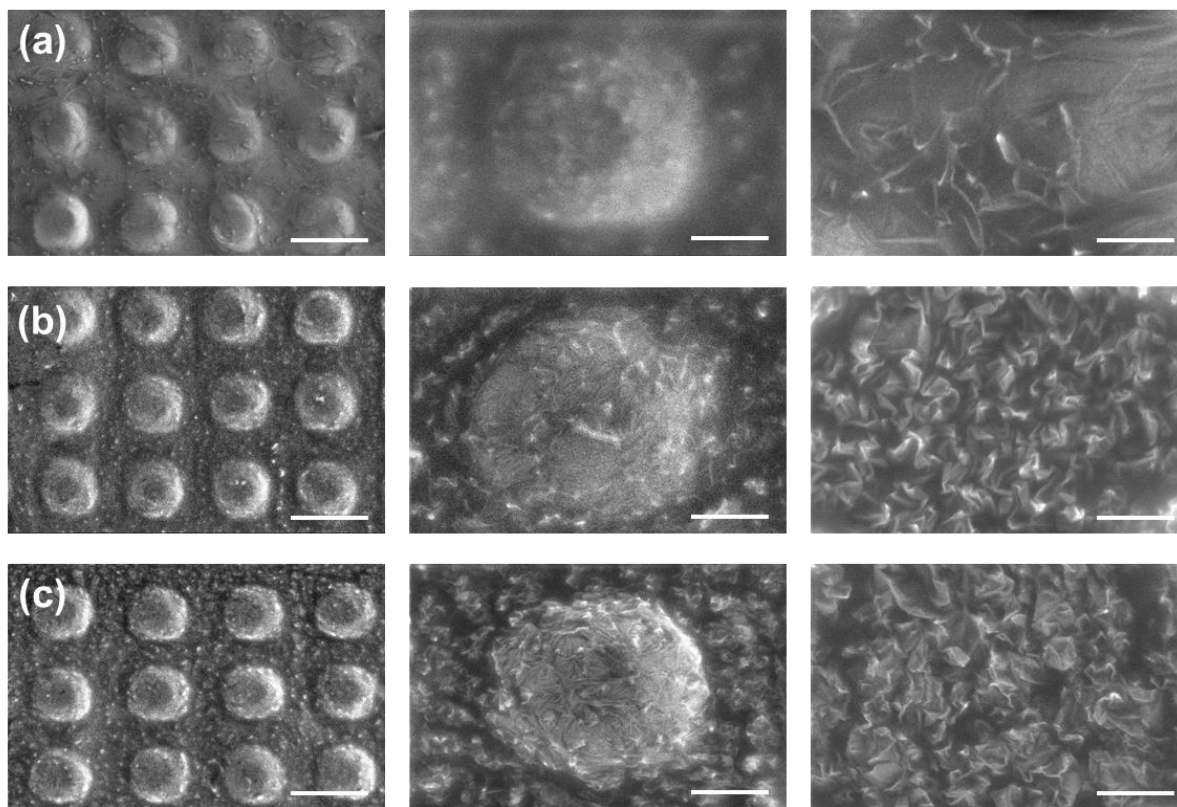


Figure 7.1. SEM images of hierarchically patterned graphene on microstructured surfaces, where the pre-strain of substrate is 40% (a), 100% (b), and 200% (c). Left, middle, and right panel images show the overall area images, apices of domes, and base areas, respectively. Height and density of nanoscale crumple of develop as the pre-strain of substrates increases. SEM images do not show electron charging, demonstrating successful integration of graphene without significant damages. Scale bars: 10 μm (left panels), 2 μm (middle and right panels).

To further demonstrate the integration of graphene and evaluate the strain of graphene, we carried out Raman spectroscopy characterizations (633 nm laser) at the apices and base areas, respectively (Figure 7.2). In Raman spectra, 2D ($\sim 2,650\text{ cm}^{-1}$) and G ($1,580\text{ cm}^{-1}$) peaks with high I_{2D}/I_G ratio (> 2) support the successful integration of monolayer graphene (Figure 7.2a).⁵⁷⁻⁶⁰ In addition, the 2D band position (fitted by a single Lorentzian function) shows blue-shift as the pre-strain of substrate increases (Figure 7.2b). Such blue-shift indicates that the releasing of substrate pre-strain induces compressive strain in graphene. Furthermore, D peak ($\sim 1,350\text{ cm}^{-1}$) intensity shows negligible value at high pre-strain ($> 100\%$) due to the damage-free integration, whereas

large D peak at low pre-strain ($< 80\%$) indicates damages in graphene resulted from the insufficient amount of substrate pre-strain.⁵⁵

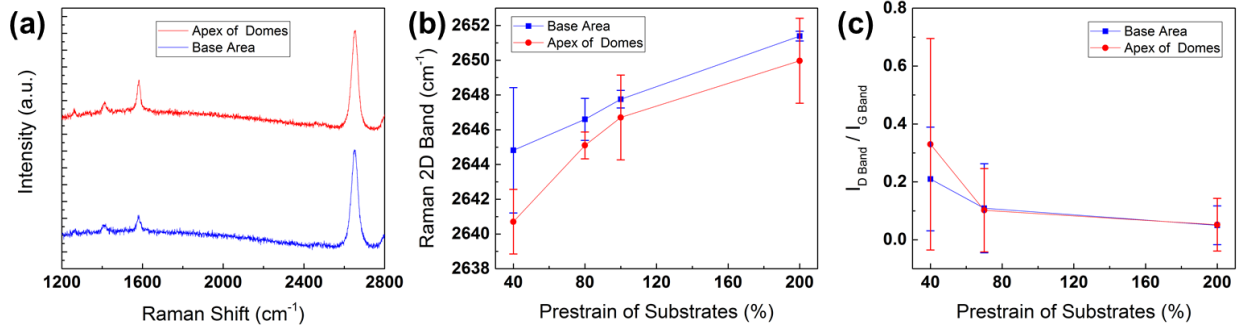


Figure 7.2. Raman spectroscopy characterization of graphene. (a) Raman spectra at the apex and base area of graphene integrated on dome array, exhibiting clear 2D ($\sim 2,650$ cm⁻¹) and G ($\sim 1,580$ cm⁻¹) bands. (b) Blue-shift of 2D band with increasing substrate strain, indicating compressive strain in graphene induced by the releasing of pre-strain. (c) D band intensity compared to G band decreases with increasing substrate pre-strain, owing to the successful integration at high pre-strain.

In conclusion, we have demonstrated hierarchical structures of graphene by multiscale control of morphologies: 1) microscale modulation by underlying 3D features and 2) nanoscale modulation by controlling pre-strain of a polymer substrate. Our hierarchically patterned graphene has future potential for highly sensitive sensing arrays with enhanced surface areas, and water-repellent surfaces with high surface roughness.

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