



### Transparent, Wearable, Broadband, and Highly Sensitive **Upconversion Nanoparticles and Graphene-Based Hybrid** Photodetectors

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Supporting Information

ABSTRACT: Numerous investigations of photon upconversion in lanthanide-doped upconversion nanoparticles (UCNPs) have led to its application in the fields of bioimaging, biodetection, cancer therapy, displays, and energy conversion. Herein, we demonstrate a new approach toward lanthanidedoped UCNPs and a graphene hybrid planar and rippled structure photodetector. The multi-energy sublevels from the 4f<sup>n</sup> electronic configuration of lanthanides results in longer excited state lifetime for photogenerated charge carriers. This



opens up a new regime for ultra-high-sensitivity and broadband photodetection. Under 808 nm infrared light illumination, the planar hybrid photodetector shows a photoresponsivity of 190 AW<sup>-1</sup>, which is higher than the currently reported responsivities of the same class of devices. Also, the rippled graphene and UCNPs hybrid photodetector on a poly(dimethylsiloxane) substrate exhibits an excellent stretchability, wearability, and durability with high photoresponsivity. This design makes a significant contribution to the ongoing research in the field of wearable and stretchable optoelectronic devices.

**KEYWORDS:** upconversion nanoparticles, hybrid photodetectors, stretchable optoelectronics, rippled graphene, broadband response, wearable electronics

n this fast-paced world, science and technology have marched hand in hand toward an enormous paradigm shift in the field of wearable devices.<sup>1</sup> In the past, a major fusion of technologies had paved the way for two-dimensional (2D) hybrid stretchable systems.<sup>2</sup> Particularly, owing to the higher photoresponsivity and low power consumption, 2D hybrid photodetectors have emerged to be the potential indomitable candidates for research, military, medicine, and industry.<sup>3-7</sup> Graphene is a 2D material with high carrier mobility and short carrier lifetime.<sup>8</sup> In addition, graphene is flexible, optically transparent, lightweight, and environmentally friendly, thus making it promising for researchers in the field of optoelectronics.<sup>9,10</sup> Since graphene offers a good optical transmittance (2% absorption of incident photons) and has a

low density of states around the Dirac point, making its conductance influenced by external perturbations from allied materials, a composite structure comprising light-absorbing nanoparticles was developed. In this work, we design, fabricate, and demonstrate a new 2D hybrid photodetector based on lanthanide-based upconversion nanoparticles (UCNPs) and graphene with excellent multifunctionalities, including high photoresponsivity, transparency, wearability, stretchability, and broadband photoresponse.<sup>11</sup>

Lanthanide-based UCNPs exhibit a nonlinear optical phenomenon, which can be described as an anti-Stokes

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Figure 1. (a) Schematic diagram of the UCNPs/graphene hybrid planar structure photodetector. (b) Schematic diagram of the UCNPs/graphene hybrid rippled structure photodetector.

emission, in which a sequential absorption of two or more photons of higher wavelength leads to an emission of photons of lower wavelengths.<sup>12</sup> Lanthanide-based UCNPs comprise a host and an activator. Lanthanides such as erbium (Er<sup>3+</sup>) and neodymium (Nd<sup>3+</sup>) can serve as an activator, as they offer a considerably split energy-level pattern, and NaYF4 serves as one of the most suitable host matrices owing to its low phonon energy that subdues nonradiative multiphonon relaxation processes of activators.<sup>13</sup> In addition, lanthanide-based UCNPs are chemically stable, hydrophobic, and less toxic.<sup>14</sup> Quite recently, upconversion nanoparticles have seen a remarkable experimental progress in the field of optogenetics,<sup>15</sup> bioimaging,<sup>16</sup> biodetection,<sup>17</sup> and displays.<sup>18</sup> So far their applications in the field of energy conversion is limited to solar cells.<sup>19</sup> Recently, Zhou et al.<sup>20</sup> and Niu et al.<sup>21</sup> have reported and exquisitely explained the near infrared (NIR) photoresponse from UCNPs in different hybrid devices fabricated on solid substrates. Although, Li et al.<sup>22</sup> reported a flexible photodetector based on UCNPs/perovskite microarray composites where the UCNPs were incorporated only for infrared photodetection. Here, the challenge lies in improving the photoresponsivity and a novel design to incorporate the unique features of UCNPs, such as broadband photoresponse and transparency. Also, there is a need for fabricating a stretchable, flexible, and durable UCNPs-based photodetector to meet the desired trend of the next-generation technology. Although graphene alone has a limited stretchability of about 6% as reported by Lee et al.,<sup>23</sup> recently Kim et al.<sup>24</sup> reported a stretchable crumpled graphene photodetector on very high bond (VHB) film, which could be stretched up to 200% taking into account likewise crest and trough formations of graphene on a polymer substrate when the already applied tensile strain is released from the polymer substrate.

Here in this work, to circumvent the challenges described above, we have used core-shell-structured UCNPs (NaY- $F_4$ :Yb:Er:Nd@NaYF<sub>4</sub>:Nd) and monolayer graphene on a prestrained poly(dimethylsiloxane) (PDMS) substrate to fabricate a planar structure hybrid photodetector. This prestrained PDMS substrate was later released to get a UCNPs/rippled graphene structure hybrid wearable photodetector.<sup>25</sup> Owing to the broadband absorption by the UCNPs, for the first time a broadband photoresponse was demonstrated using the hybrid planar structure photodetector. We are able to achieve the highest responsivity on the order of 10<sup>2</sup> AW<sup>-1</sup> among UCNP-based hybrid planar structure photodetectors based on the upconversion transitions of the multiple energy sublevels of UCNPs.<sup>12</sup> Notably, the rippled graphene structure enables increasing the optical absorption of photons for UCNPs arising from light trapping due to multiple scattering, which adds to the increase in responsivity for the hybrid photodetector.<sup>25</sup> Large-area, effective low-cost fabrication and its ability to function at lower powers of illumination make this highly stretchable, flexible, transparent, and multiple discrete band hybrid photodetector suitable for our day-to-day optoelectronics applications.<sup>26</sup>

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#### RESULTS AND DISCUSSION

The schematic diagrams for the planar and rippled structure of the fabricated graphene and UCNPs hybrid photodetectors are shown in Figure 1a and b, respectively. The scattering Raman spectrum of PDMS and graphene on PDMS is shown in Figure 2a. The scattering Raman spectrum of graphene with PDMS shows a much less intense D peak around 1327  $\mbox{cm}^{-1}$  and a significant 2D peak as shown in Figure 2, confirming the presence of good-quality graphene over PDMS.<sup>27</sup> The integrated intensity ratio of the 2D to G band is around 1.70, corresponding to 1 or 2 layers of graphene.<sup>39</sup> The scattering Raman spectrum of bare PDMS in Figure 2 shows peaks at 1263.61 and 1413.76 cm<sup>-1</sup>, confirming the Raman signals of PDMS.<sup>28</sup> Insignificant peaks due to defects in PDMS are observed at 1599.35 and 1699.72 cm<sup>-1</sup> in the Raman spectrum of PDMS.<sup>29</sup> The size distribution of UCNPs is confirmed between 20 and 30 nm by a transmission electron microscopy (TEM) image as shown in Figure 2b. The absorption spectrum in Figure 2c shows the broadband wavelength absorption scanning over the ultraviolet, visible, and infrared wavelengths. This makes it suitable for a broadband photodetector owing to the fact that photocurrent response follows the absorption spectra.<sup>4</sup> The photoluminescence emission spectrum shows multiple emission peaks at around 400, 525, 540, 650 nm, etc., under the illumination of an 808 nm laser beam as shown in Figure 2c. The 5s and 5p shells shield the 4f orbital in the case of UCNPs, thus resulting in sharp absorptions and emissions, which are in accordance with the absorption and emission spectra of lanthanide ions.<sup>12</sup> Figure 2d shows the scanning electron microscopy image of the generated rippled graphene structure after being released from applied 100% strain. Figure 2d (i) shows the cross-sectional view of the rippled structure where the average height of each ripple is observed to be  $\sim 70$  $\mu$ m. Also, Figure 2d (ii) shows the top view of the rippled graphene structure, hence confirming the formation of a uniformly spaced rippled structure.

Our hybrid device consists of monolayer graphene decorated with UCNPs spin coated over it as shown in the cross-sectional view of the device in Figure 1. Here, graphene serves as the carrier transport channel<sup>30</sup> and UCNPs serve as the photonabsorbing material. The dynamic broadband photoresponse of the hybrid planar structure photodetector with a channel length 100  $\mu$ m was studied under 325, 532, 657, 808, and 980 nm laser illumination, as shown in Figure 3a, b, c, d, and e, respectively. Also, the photocurrent ( $\Delta I$ ) versus drain—source voltage,  $V_{\rm DS}$ (V), was recorded as shown in Figure 3f. The photographic



Figure 2. (a) Raman spectrum of PDMS and graphene on PDMS. (b) TEM image of UCNPs. (c) Absorption and photoluminescence spectra of UCNPs in cyclohexane. (d) (i) Cross-sectional SEM image of the rippled structure; (ii) Lateral SEM image of the rippled structure. (e) Schematic diagram of multiple internal reflections resulting from the rippled structure of the hybrid photodetector.

image of the hybrid planar structure photodetector is shown in the inset of Figure 3f. The maximum photoresponsivity of  $\sim 21$  $AW^{-1}$  was observed under 325 nm illumination. The next higher photoresponsivity of  $\sim 4 AW^{-1}$  was observed under 808 nm illumination. The photoresponsivities of the hybrid planar structure photodetector under 532, 657, and 980 nm were lower as compared to that observed under 808 and 325 nm illumination, as shown in Figure 3g. This behavior can be well interpreted with the assistance of the absorption spectrum of UCNPs. The UCNPs show comparatively larger absorption in the ultraviolet (UV) range as shown in Figure 2c, thereby resulting in higher photoresponsivity. A significantly slower response of the hybrid UCNPs and graphene planar photo-detector under 325 nm illumination is well explained in the Supporting Information SIII. The UCNPs have comparable absorption coefficients in the visible and infrared range. It is



**Figure 3.** Dynamic photoresponse of the hybrid planar photodetector with a channel length equal to 100  $\mu$ m under (a) 325 nm, (b) 532 nm, (c) 657 nm, (d) 808 nm, and (e) 980 nm laser illumination. (f) Photocurrent of the hybrid planar photodetector with a channel length equal to 100  $\mu$ m under different wavelengths of illumination (power,  $P \approx 4 \mu W$ ) as a function of drain–source voltage (V) (inset: (right, top) photographic image of the device and (left,bottom) magnified image showing photocurrent V/s drain–source voltage (V) for 532, 657, 808, and 980 nm). (g) Dependence of photoresponsivity ( $R_{ph}$ ) on different applied wavelengths of illumination.

observed that under 808 nm illumination the hybrid planar photodetector gives the next higher photoresponsivity. Our UCNPs are composed of neodymium (Nd) in both the core and the shell structure of UCNPs. It is reported that addition of Nd to UCNPs results in higher absorption and emission cross sections, which serves as the possible reason for better photoresponsivity and faster photoresponse of our hybrid planar structure photodetector under 808 nm laser illumination as shown in Figure  $3d.^{31,32}$ 

The device performance and working mechanism of hybrid UCNPs and graphene-based planar structure photodetector (without rippled structure) were studied using an 808 nm infrared (IR) laser as excitation source as shown in Figure 4. The 808 nm IR laser beam was first focused to a spot area of 2



**Figure 4.** (a) Photocurrent of the hybrid photodetector with channel length equal to 25  $\mu$ m (inset) for different optical powers of 808 nm laser illumination as a function of drain–source voltage (V). (b) Temporal photocurrent of the hybrid photodetector with a channel length equal to 25  $\mu$ m under different powers of 808 nm laser illumination. (c) Temporal photocurrent of the hybrid photodetector with a channel length equal to 25  $\mu$ m under 41.625  $\mu$ W of 808 nm laser illumination. (d) Dependence of photoresponsivity ( $R_{\rm ph}$ ) and photocurrent gain (G) on different applied optical powers of 808 nm laser illumination. Temporal response of the hybrid photodetector with channel length equal to 25  $\mu$ m under 41.625  $\mu$ W of 808 nm laser illumination. Temporal response of the hybrid photodetector with channel length equal to 25  $\mu$ m under 41.625  $\mu$ W of 808 nm laser illumination. Temporal response time or rise time less than 200 ms and (f) recovery time or fall time less than 200 ms.

mm<sup>2</sup> and was adjusted to completely fit the channel length of 25  $\mu$ m. Subsequently, change in current or photocurrent ( $\Delta I$ ) versus voltage (V or  $V_{\rm DS}$ ) and  $\Delta I$  versus time (t) measurements at different powers of illumination were recorded (Figure 4). The photocurrent ( $\Delta I = |I_{\rm illumination} - I_{\rm dark}|$  and the total 808 nm IR laser illumination power (P) on the device active area of 37  $\mu$ m × 25  $\mu$ m gives the photoresponsivity of the device according to the following equation:<sup>33,34</sup>

$$R_{\rm Ph} = \frac{\Delta I(A)}{P(W)} \tag{1}$$

Figure 4a shows the  $\Delta I$  versus V plot and dynamic photoresponse with time respectively measured under illumination power ranging from 106 to 507 nW for the UCNPs and graphene hybrid planar structure device. The photocurrent varies linearly with the bias voltage ( $V_{\rm DS}$ ). An ultrahigh responsivity on the order of ~190 AW<sup>-1</sup> is measured at  $V_{\rm DS} = 1$ V under ~10<sup>-7</sup> W 808 nm illumination, which is the highest value ever reported among the UCNP-based hybrid devices (Figure 4d).<sup>20–22</sup> The photocurrent gain is a dimensionless quantity and is defined by the following equation:<sup>35</sup>



Figure 5. Schematic energy band diagram of the UCNPs and graphene, illustrating the mutual transport of photogenerated charge carriers.

$$\Gamma = \frac{\Delta I/q}{P/h\nu} \times \frac{1}{\eta}$$
<sup>(2)</sup>

where  $\Gamma$  is the photocurrent gain,  $\Delta I$  is the photocurrent, q is the electron charge, P is the incident power,  $h\nu$  is the photon energy of incident light, and  $\eta$  is the quantum efficiency for carrier generation per unit absorption. Assuming  $\eta \approx 1$  for simplicity,<sup>35</sup> the highest photocurrent gain measured under  $\sim 10^{-7}$  W 808 nm illumination is  $\sim 300$  (Figure 4d). The device exhibits positive photocurrent, and its response time and recovery time are less than 200 ms, as shown in Figure 4b, e, and f, respectively.

The ultrahigh responsivity of the UCNPs and graphene hybrid planar structure device can be explained in terms of the band structure of graphene<sup>36</sup> and the rich energy level pattern of UCNPs.<sup>12</sup> As we know, in the case of lanthanide-doped UCNPs, the electronic repulsions and spin-orbit coupling split the electronic configurations of 4f orbitals into multiple discrete energy sublevels.<sup>12</sup> These sublevels in turn serve as the ideal contender for observing photon upconversion. When the UCNPs and graphene hybrid device is subjected to 808 nm laser illumination, Nd<sup>3+</sup> and Yb<sup>3+</sup> act as the sensitizers to absorb the 808 nm, as shown in Figure 5. After the absorption of 808 nm photons by the sensitizers, the electron is efficiently transferred from the sensitizer to the activator, i.e., Er<sup>3+</sup>, along multiple energy sublevels. Here two main upconversion mechanisms play a role. The first is the excited state absorption (ESA) and the energy transfer upconversion (ETU).<sup>12</sup> Er<sup>3+</sup> being the activator undergoes ESA and absorbs two or more photons via two-photon absorption and gets excited to higher energy levels.  $Nd^{3+}$  in the shell and the core and  $Yb^{3+}$  in the core act as the sensitizers to absorb the photons and transfer them to various energy levels of Er<sup>3+</sup> of the core as a part of ETU. This absorption of photons and their excitation to higher energy levels lead to the generation of photogenerated charge carriers. Since the UCNPs and graphene hybrid device show a positive photocurrent as shown in Figure 4b and c, we can consider the fact that the absorption of photons leads to the accumulation of holes in the valence band and the accumulation of electrons in the conduction band of UCNPs.<sup>36</sup> Two- or three-photon absorption in UCNPs leads to more and more generation of electron hole pairs, and this in

turn keeps the electrons and holes separated from each other for longer periods of time, thus delaying their recombination. Also whenever the photons are being absorbed, the generated electron hole pairs tend to separate out from each other through a number of metastable states' formation due to the multiple photon absorption. This unique property of discrete energy sublevels in the case of lanthanide-doped upconversion materials is very useful to achieve a highly sensitive photodetector. Since our device is a hybrid of UCNPs and graphene, we can thus take into account the effect of a built-in electric field due to the charge transfer after they are deposited together.<sup>4</sup> When the hybrid device is subjected to 808 nm IR laser illumination, electron/hole pairs are produced. The holes are transferred from the UCNPs to graphene, giving rise to a positive photocurrent, and electrons will stay in the metastable states as described above. As more and more photons are absorbed, more and more holes are being transferred to graphene at a faster rate assisted by the built-in electric field, thus lowering the Fermi level of the graphene layer as shown in Figure 5. The interpretation can be further supported by the photoluminescence measurement. The photoluminescence spectrum of UCNPs and UCNPs/graphene flakes shows a considerable reduction in the upconversion emission intensity on 808 nm illumination when compared with the pure UCNPs owing to the fact that charge transfer happens between graphene and UCNPs as shown in Supporting Information SII (Figure S7).<sup>20,36</sup> In Figure 4d, we plot the responsivity and photocurrent gain of the device of area 925  $\mu$ m<sup>2</sup> as a function of the power of illumination of an 808 nm laser. It is found that as the power of illumination is decreased, responsivity and photocurrent gain increase and subsequently get saturated for lower values of the power of illumination.<sup>4</sup> This saturation of the responsivity at lower powers of illumination can be explained considering the concept of electric fields as explained above. When the hybrid UCNPs and graphene device is subjected to higher powers of illumination, more and more electron/hole pairs are generated. This results in the accumulations of more charge carriers on UCNPs, thus inevitably decreasing the built-in electric field. The net effective electric field decreases with increasing powers of illumination; as a consequence, the responsivity of the hybrid device decreases at higher powers of illumination. Also it is



**Figure 6.** (a) (i) Photographic image of the experimental setup for longitudinal strain dependence study. (ii) Photographic image of the hybrid photodetector with a channel length equal to 100  $\mu$ m. (iii) Electrode mask used for lateral strain dependence study. (iv) Schematic diagram to demonstrate no ripple formation while stretching laterally and formation of ripples under released state. (b) Dynamic photoresponse of the hybrid photodetector with a channel length of 100  $\mu$ m under different longitudinal strains under 808 nm laser illumination. (c) Photocurrent of the hybrid photodetector with a channel length equal to 100  $\mu$ m under different longitudinal strains as a function of drain–source voltage (V) under 808 nm laser illumination. (d) Photoresponse versus longitudinal strain and number of times longitudinal strain applied under 808 nm laser illumination of the hybrid photodetector with a channel length of 100  $\mu$ m. (e) Fatigue test demonstrated by dynamic photoresponse of a hybrid photodetector with a channel length of 100  $\mu$ m. (e) Kan 100 times upon 100% longitudinal strain under 808 nm laser illumination.

experimentally found that the response time and recovery time increase with decreasing illumination power as shown in Figure 4b.<sup>36</sup> This behavior can be attributed to the carrier trapping at the UCNPs and graphene interface and the screening of the built-in electric field. As the power of illumination is increased,

the number of charge-trapping states is reduced in comparison with the photogenerated electrons and holes. Consequently, the recovery time and response time become shorter. A channel length of the device versus responsivity study has also been performed, and it was found that if we reduce the size of the



**Figure 7.** (a) (i) Photographic image of the experimental setup for curvature strain dependence study. (ii) Photographic image of the hybrid photodetector with a channel length equal to 100  $\mu$ m. (iii) Schematic diagram to show the experimental setup for performing a curvature dependence study. The hybrid photodetector is placed over a cylinder with a radius of curvature (r). (iv) Electrode mask used for curvature strain dependence study. (v) Schematic diagram to show the formation of ripples under the released state and ripple formation under the stretching state over a bending radius, r. (b) Dynamic photoresponse of the hybrid photodetector with a channel length of 100  $\mu$ m under different curvature strains under 808 nm laser illumination. (c) Photocurrent of the hybrid photodetector with a channel length equal to 100  $\mu$ m under different curvature strains as a function of drain–source voltage (V) under 808 nm laser illumination. (Inset: Magnified image to show photocurrent under different curvature strains at  $V_{\rm DS} = 1$  V.) (d) Photoresponse versus curvature strain and number of times the curvature strain was applied for the hybrid photodetector with a channel length of 100  $\mu$ m under 808 nm laser illumination. (e) Fatigue test demonstrated by dynamic photoresponse of the hybrid photodetector with a channel length of 100  $\mu$ m under 808 nm laser illumination. (e) Fatigue test demonstrated by dynamic photoresponse of the hybrid photodetector with a channel length of 100  $\mu$ m under bending 20, 40, 60, 80, and 100 times over a radius of curvature of r = 0.35 cm under 808 nm laser illumination.

channel length, then responsivity increases (Figure S6). The reduction in the channel length paves the way for a better recirculation of holes on a graphene channel, which in turn improves the responsivity, thereby making it a suitable candidate for devices that can function even at low powers.<sup>36</sup>

A bigger device of channel length 100  $\mu$ m was designed in order to experimentally demonstrate and study the rippled hybrid UCNPs and graphene photodetector.<sup>24</sup> This would provide a proof of concept of the device performance when it comes to stretchability and wearability of the photodetector. The hybrid photodetector with the rippled structure was



Figure 8. (a) Experimental results of the conductivity ratio versus different lateral strains at  $V_{DS} = 0.1$  V. (b) Photographic images showing the wearable, flexible, and transparent nature of the hybrid rippled structure photodetector {National Taiwan University logo; Copyright 1997 National Taiwan University}. (c) Temporal photoresponse of the hybrid rippled structure photodetector showcasing its durability under 808 nm laser illumination.

studied using an 808 nm laser as excitation source as shown in Figure 6. The 808 nm laser beam was again focused to a spot area of 2 mm<sup>2</sup> and was adjusted to completely fit the channel length 100  $\mu$ m. In order to test the stretchability of the hybrid UCNPs and graphene photodetector, the device was placed on a flat surface and was longitudinally strained as shown in Figure 6a. Subsequently, photocurrent ( $\Delta I$ ) versus time (t) (Figure 6b) and photocurrent ( $\Delta I$ ) versus voltage (V) (Figure 6c) measurements under different longitudinal strain conditions at a 4.5  $\mu$ W power of illumination at  $V_{DS}$  = 0.1 V were recorded. The different longitudinal strain conditions taken into account here include 0%, 20%, 40%, 60%, 80%, and 100% strain. It was experimentally observed that the magnitude of photocurrent increases with decreasing longitudinal strain.<sup>25</sup> The increased photocurrent can be attributed to the formation of a rippled graphene structure, as confirmed by the SEM image shown in Figure 2d. The formation of a rippled structure paves the way for more and more photons being multiply reflected within the crest and trough of each ripple, thus increasing the probability of absorption of photons by the UCNPs as shown in Figure 2e and is experimentally confirmed by the optical transmission measurements shown in the Supporting Information SIV (Figure S8). The height of the ripple is increased with the reduction in strain, resulting in photons trapping in the troughs of the ripples, thereby catalyzing the process of photon absorption by UCNPs, which results in a maximum photoresponse of 31.2 AW<sup>-1</sup> ( $V_{\rm DS}$  = 1 V) at 0% longitudinal strain (Figure 6c). A quantitative analysis of the relationship between strain and the height of the graphene ripples is reported in the Supporting Information SV (Figures S9 and S10). In order to

test the stability of the hybrid UCNPs and graphene photodetector, the device was subjected to stretching in the limits of 100% longitudinal strain and 0% longitudinal strain at multiple times (fatigue test). The photocurrent ( $\Delta I$ ) versus time (t) at a 4.5  $\mu$ W power of illumination at  $V_{\rm DS}$  = 0.1 V was recorded after applying longitudinal strain 20, 40, 60, 80, and 100 times (Figure 6d). The photoresponse is quite consistent and only slightly changes with the multiple application of longitudinal strain, thus accounting for a highly durable and stable photodetector (Figure 6e). Since the device is designed on a PDMS substrate, it provides for a mechanical support to the graphene layer, thereby avoiding free-standing of graphene and folding of graphene in a random fashion when the longitudinal strain is released.

Furthermore, in order to test the bending nature of the hybrid UCNPs and graphene photodetector, the device was placed on different cylindrical objects with different radii of curvature (r), as shown in Figure 7a. The corresponding change in current ( $\Delta I$ ) versus time (t) (Figure 7b) and change in current ( $\Delta I$ ) versus voltage (V) (Figure 7c) measurements under different curvature strain conditions at 4.5  $\mu$ W power of illumination at  $V_{DS} = 0.1$  V were recorded. The different curvature strain conditions along with the radius of curvature (*r*) taken into account here includes 0% (*r* = infinity), 0.1% (*r* = 1 cm), 0.16% (r = 0.6 cm), 0.2% (r = 0.5 cm), and 0.28% (r =0.35 cm) strain. The photoresponse is found to be consistent and only slightly decreases with increasing curvature strain, as shown in Figure 7e. As the strain is applied along the curvature, the rippled graphene structure tends to open up, thus resulting in broader troughs. This decreases the trapping of photons in

the crests and troughs of the rippled graphene structure. As the probability of photon absorption is lessened, we get a lower photoresponse with increasing curvature strain, as shown in Figure 7e. The fatigue test on application of a curvature strain of 0.28% (r = 0.35 cm) was performed. The photocurrent ( $\Delta I$ ) versus time (t) at 4.5  $\mu$ W power of illumination at  $V_{\rm DS} = 0.1$  V was recorded after applying curvature strain 20, 40, 60, 80, and 100 times (Figure 7d). The photoresponse was stable and almost unchanged.

In order to prove that with increasing strain the photoresponse of the device falls due to the reduction in the size of the ripples only and the stretching, folding, or tearing of the graphene layer does not play a role, a dark conductivity test under different longitudinal strain was performed on a specifically fabricated device consisting of graphene and PDMS only. As shown in Figure 8a, the dark conductivity of the graphene is found to increase under subjection of 20% to 100% longitudinal strain, which is similar to the results reported by Chiang et al.<sup>25</sup> As the longitudinal strain is increased, the size of the ripples decreases, thus resulting in the scattering of charge carriers in the graphene layer. The resistivity of the rippled graphene structure is found to decrease nonlinearly with increasing strain. Beyond 100% strain, the graphene tends to break, thereby decreasing its conductivity. This test proves that the only reason for lower photoresponse under a prestrained condition is a lesser number of photons being absorbed by our hybrid UCNPs and graphene photodetector. This proves that out hybrid device is easily stretchable and bendable. Figure 8b shows that our device is flexible, transparent, and quite wearable. In order to test the durability of the hybrid device, the photocurrent ( $\Delta I$ ) versus time (t) at 4.5  $\mu$ W power of illumination at  $V_{\rm DS}$  = 0.1 V was recorded at different time intervals of 1 day, 7 days, 14 days, 30 days, 60 days, and 90 days, as shown in Figure 8c. The photoresponse is stable and consistent, accounting for a great durability of the device. In order to test the wearability and easy usage of the device, the photocurrent ( $\Delta I$ ) versus time (t) at s 4.5  $\mu W$ power of illumination at  $V_{DS} = 0.1$  V measurements was performed keeping the device with various day-to-day essentials in the laboratory, such as a cloth belt of the eye gear, aluminum box, rubber gloves, cardboard box, and Petri dish, as reported in the Supporting Information (Figures S11, S12, S13, S14, and S15). The steady and consistent measurements demonstrate that this device is human friendly and stable.

#### CONCLUSION

In conclusion, we have successfully fabricated a highly stretchable and wearable photodetector suitable for optoelectronics applications. Our hybrid UCNPs/graphene planar structure photodetector is highly sensitive with a responsivity of about  $10^2 \text{ AW}^{-1}$ , which is the highest among UCNPs-based hybrid devices. The multi-level energy system of lanthanidedoped UCNPs makes way for metastable states on absorption of two or three photons, which in turn increases the lifetime of recombination of photogenerated carriers. This allows an efficient transfer of photogenerated carries to the graphene layer, thereby increasing the responsivity. The introduction of a rippled graphene structure further increases the photoresponsivity in UCNP-based hybrid photodetectors. The rippled graphene structure decorated with UCNPs is stable, highly conducting, and wearable under different longitudinal and curvature strain conditions. Since UCNPs are hydrophobic and are best used for biological applications, the UCNPs/

graphene hybrid photodetector turns out to be highly durable and environmentally friendly. The PDMS-based UCNPs/ graphene hybrid device is stretchable and paves the way for the development of stretchable and wearable optoelectronics. The cost-effective fabrication of the device, its transparency, and wearability make it ideal for a wide variety of applications spanning from military to optical communication.

#### METHODS

Device Fabrication. In order to design a planar and rippled UCNPs and graphene hybrid broadband photodetector, the following steps were performed (Figure S1): (Step 1) Graphene was grown on a 99.99% pure copper substrate using the chemical vapor deposition method.<sup>37</sup> (Step 2) Poly(methyl methacrylate) (PMMA) was spin coated on graphene grown on a Cu substrate followed by etching of copper using an FeCl<sub>3</sub> solution. (Step 3) Graphene with a layer of PMMA over it was transferred on a 100% prestrained PDMS substrate. (Step 4) Silver electrodes were deposited using the thermal vapor deposition technique. (Step 5) UCNPs in cyclohexane were spin coated over the 100% prestrained device in accord with the optimized parameters, as discussed in the Supporting Information (Figures S3 and S4). In order to demonstrate an ultra-high-responsive UCNPs and graphene based hybrid broadband photodetector (without rippled graphene structure), a device of area 925  $\mu$ m<sup>2</sup> was fabricated whose cross-sectional view is shown in Figure 1a. Stretchability and flexibility in the UCNPs and graphene based hybrid broadband photodetector (with rippled graphene structure) were demonstrated using the device of area  $10^4 \ \mu m^2$ . (Step 6) The 100% prestrained devices  $10^4 \ \mu m^2$  in area were released, resulting in a rippled graphene structure with UCNPs coated over it, thereby completing the rippled structured device fabrication process, as shown in Figure 1b and Figure S2.

Synthesis of Upconversion Nanoparticles. NaOH and NH<sub>4</sub>F and all lanthanide acetates  $((Y(CH_3CO_2)_3 \text{ hydrate}, Yb(CH_3CO_2)_3 \text{ hydrate}, Tm(CH_3CO_2)_3 \text{ hydrate}, Er(CH_3CO_2)_3 \text{ hydrate}, and Nd(CH_3CO_2)_3 \text{ hydrate}) for nanoparticle synthesis were purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA).$ 

The thermal decomposition method was employed for the synthesis of the oleate-capped NaYF<sub>4</sub>:Yb, Er, Nd core. In a 50 mL three-neck flask, an appropriate mole ratio of lanthanide acetates  $((Y(CH_3CO_2)_3 \text{ hydrate}, Yb(CH_3CO_2)_3 \text{ hydrate},$  $Er(CH_3CO_2)_3$  hydrate, and Nd(CH\_3CO\_2)\_3 hydrate) of total 0.4 mmol was mixed together with oleic acid (3 mL), 1octadecene (7 mL), and a water solution (2 mL). The mixture was heated to 150 °C with continuous stirring under vacuum conditions for 1 h duration to form a homogeneous solution of lanthanide oleate complexes and then cooled to room temperature. Meanwhile, a methanol solution (6 mL) containing NaOH (1 mmol) and NH<sub>4</sub>F (1.6 mmol) was added into the same reaction flask and was stirred continuously for 2 h at 50 °C. After the evaporation of methanol, the solution was heated to 290 °C under a nitrogen atmosphere and kept for 1.5 h under vigorous stirring. Subsequently, a slightly yellowish solution was obtained and allowed to cool to room temperature. The as-synthesized NaYF<sub>4</sub>:Yb, Er, Nd core nanocrystals were precipitated by adding ethanol, isolated via centrifugation, and redispersed in 4 mL of cyclohexane for further use.

 $Y(CH_3CO_2)_3$  and  $Nd(CH_3CO_2)_3$  at appropriate ratio (total lanthanide amount of 0.4 mmol) were mixed with oleic acid (3 mL), 1-octadecene (7 mL), and a water solution (2 mL) in a 50

mL three-neck flask. The mixture was heated to 150 °C under vacuum conditions with vigorous stirring for 1 h to form a homogeneous solution, followed by cooling to room temperature. Subsequently, the as-synthesized NaYF4:Yb,Er,Nd core nanoparticles in 4 mL of cyclohexane were added to the above solution mixture, followed by the addition of 6 mL of methanol containing NaOH (1 mmol) and NH<sub>4</sub>F (1.6 mmol), and the mixing solution was vigorously stirred for 2 h at 50 °C. After the evaporation of methanol and cyclohexane, the solution was heated to 290 °C under a nitrogen atmosphere and kept for 1.5 h under continuous stirring. Subsequently, a slightly yellowish solution was obtained and allowed to cool to room temperature. The as-synthesized NaYF4:Yb,Er,Nd@NaYF4:Nd coreshell nanocrystals were precipitated by adding ethanol, isolated via centrifugation, and redispersed in cyclohexane for further use.<sup>38</sup> The TEM image shows that NaYF<sub>4</sub>:Yb,Er,Nd@ NaYF<sub>4</sub>:Nd core-shell nanocrystals were highly monodispersed and possessed a nearly hexagonal morphology with a diameter of  $23 \pm 0.5$  nm.

**Single-Layer Graphene Synthesis.** A standard chemical vapor deposition (CVD) technique was used to synthesize monolayer graphene. 99.98% pure copper foil manufactured by Aldrich was used. This copper foil was first polished by electrolysis of 85% phosphoric acid ( $H_3PO_4$ ) for 15 min at 1.5 V. A counter electrode of copper was used in order to avoid the doping of the host atom into the copper. Before growing the graphene on the polished copper it was placed into the CVD furnace for 60 min and was exposed to 1000 °C with 60 sccm of  $H_2$  flow. In the next 30 min 3.4 sccm of  $CH_4$  was made to flow through the CVD furnace, keeping the aforementioned parameters the same. The chemical reaction between  $H_2$  and  $CH_4$  at 1000 °C results in deposition of a single layer of graphene on both sides of the polished copper.

In order to transfer the graphene on the PDMS substrate, PMMA was spin coated over Cu/graphene and was then made to float over an FeCl<sub>3</sub> solution so as to etch the copper, leaving behind PMMA/graphene floating over the FeCl<sub>3</sub> solution. Using a glass slide, PMMA/graphene was transferred onto distilled water, thereby washing out the leftover  $Fe_2(NO_3)_3$  solution from it. Finally PMMA/graphene was flipped transferred over PDMS so as to get a hierarchy of graphene/PMMA/PDMS structure for device fabrication.

**Electrode Deposition.** G400 copper mesh (channel length = 25  $\mu$ m) (Figure 4a; inset) and channel length 100  $\mu$ m mask (Figure 6a (iii)) from Electron Microscopy Science were used as a mask to pattern Ag electrodes on the graphene/PMMA/ PDMS structure. Ag electrodes were deposited using a thermal evaporator. The UCNPs were spin coated (Figure S1), and the optimum thickness for UCNPs of 150 nm was achieved (Figure S5).

**Electrical and Optical Measurements.** The transfer characteristics of the hybrid UCNPs/graphene photodetector were measured with the help of a 4156C semiconductor parameter analyzer from Agilent. A Keithley 236 source measurement unit was used to perform the dynamic response measurements. All the measurements were performed under ambient circumstances.

**PDMS Synthesis.** The PDMS solution was purchased from Dow Corning Sylgard 184. The PDMS solution was then mixed with a cross-linking solution in a ratio of 10:1. The PDMS solution was then taken into a Petri dish and was spread uniformly. It was then kept in a furnace for 120 min at 70 °C. This resulted in a high-quality, uniform, and highly stretchable PDMS.

**Instrumentation Detail of TEM.** Electron microphotographs were recorded on a JEOL JEM-1400 (120 kV) TEM.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00141.

Additional information (PDF)

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#### **Author Contributions**

Y.F.C. planned the project and supervised the overall project. M.K. designed the experiments, fabricated the device, and performed electrical and optical measurements. K.Y., Y.-T.C., and H-M.L. did the synthesis and characterization (TEM, SEM, absorbance, PL) of upconversion nanoparticles. Y.F.C. and H.G. contributed to the idea of the project and the Raman spectrum of monolayer graphene. M.K., W.-H.W., and Y.F.C. discussed the mechanism of upconversion nanoparticles and graphene. M.K., Y.H.C., C.-R.P.I., and K.P.B. performed the experiment. M.K., Y.-M.L., H.I.L., Y.-R.L., and S.Y.C. analyzed the data. All the authors contributed to writing the manuscript.

#### Notes

The authors declare no competing financial interest.

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### Transparent, Wearable, Broadband, and Highly Sensitive Upconversion Nanoparticles and Graphene-Based Hybrid Photodetectors

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17 pages, 15 figures



**Figure S1**. Schematic diagram of fabrication process of UCNPs/Graphene/PMMA/PDMS based planar and rippled photodetectors.



**Figure S2**. Schematic diagram of UCNPs/Graphene/PMMA/PDMS based rippled photodetector with electrodes conformably placed on the rippled graphene.

#### SI. Optimization process of UCNPs layer thickness for better photoresponse

A number of steps were followed as a part of optimization process to get the best suitable layer thickness of UCNPs over graphene for better and enhanced photoresponse.<sup>S1</sup> In order to get the thin film of UCNPs over the graphene layer, the UCNPs were spin coated over the graphene layer under optimised conditions. The original UCNPs were first dissolved in cyclohexane in different volume ratios. The five different concentrations of UCNPs in cyclohexane were prepared that includes (i) Original UCNPs, (ii) 1 part of original UCNPs in 1 part of cyclohexane, (iii) 1 part of original UCNPs in 2 parts of cyclohexane, (iv) 1 part of original UCNPs in 3 parts of cyclohexane, (v) 1 part of original UCNPs in 4 parts of cyclohexane. These different concentrations of UCNPs were spin coated at a speed of 1000 RPM for 5 seconds followed by 3500 RPM for 20 seconds on a device with channel length 25  $\mu$ m. The change in current ( $\Delta I$ ) versus time (t) at 41.625  $\mu$ W power of illumination at V<sub>DS</sub>=0.1 V were recorded and the corresponding change in current ( $\Delta I$ ) versus variation in concentration was plotted as shown in Figure S3.



**Figure S3**. Dependence of photoresponse on the concentration of UCNPs in cyclohexane of the hybrid planar photodetector under 808 nm laser illumination.

It was observed that 1 part of original UCNPs in 1 part of cyclohexane gave the better response in comparison to other concentrations. The number of UCNPs and its layers over graphene have a role to play as far as responsivity of the device is concerned. The optimized concentration gives us the idea that a critical amount of UCNPs over graphene can enhance the photoresponse. When the 808 nm photons strike the original UCNPs concentration, we get a poorer response since there lies a large number of UCNPs on the graphene layer thus making the charge transfer difficult between the UCNPs and graphene. As the UCNPs are diluted in cyclohexane, a critical concentration *i.e.* 1 part of original UCNPs in 1 part of cyclohexane is achieved, where the charge transfer between UCNPs and graphene layer is the fastest and we get a better photoresponse. Beyond this critical concentration, the photoresponse is reduced as the number of UCNPs in cyclohexane is decreased. Since UCNPs serve the role of photon absorbing material in our hybrid UCNPs and graphene device, thereby lowering down the number of UCNPs in cyclohexane results in lesser absorption of 808 nm photons by UCNPs. Also the spin coating speed was optimized in order to get the most suitable thickness of UCNPs over graphene layer. Six different rotations per minute (RPM) speeds were taken into consideration as follows: (i) 1000 RPM for 5 seconds followed by 1000 RPM for 20 seconds; (ii) 1000 RPM for 5 seconds followed by 1500 RPM for 20 seconds; (iii) 1000 RPM for 5 seconds followed by 2000 RPM for 20 seconds; (iv) 1000 RPM for 5 seconds followed by 2500 RPM for 20 seconds; (v) 1000 RPM for 5 seconds followed by 3000 RPM for 20 seconds; (vi) 1000 RPM for 5 seconds followed by 3500 RPM for 20 seconds. Experimentally, the maximum photocurrent was recorded at 1000 RPM for 5 seconds followed by 2500 RPM for 20 seconds setting it as the optimized parameter for UCNPs layer thickness over graphene layer (Figure S4).



**Figure S4**. Dependence of photoresponse on the UCNPs layers thickness due to variation in RPM of the hybrid planar photodetector under 808 nm laser illumination.

The thickness of UCNPs layer spin coated under the optimised parameter is found to be 150 nm as shown in the Figure S5.



Figure S5. SEM image showing the optimised thickness of the UCNPs spin coated on the hybrid planar photodetector.

Figure S6 shows the responsivity versus device size. As the device dimension is reduced, responsivity increases. The photocurrent observed under optimised parameter is maximum as it best suits the penetration depth for the photons that are being made incident on our hybrid UCNPs and graphene layer device. Hence, the optimized parameters were taken into account for device fabrication and further studies were performed.



**Figure S6**. Responsivity versus channel length study for the hybrid planar photodetector under 808 nm laser illumination.

#### SII. Photoluminescence spectra of UCNPs and UCNPs/Graphene Flakes

A photoluminescence study was carried out for UCNPs and UCNPs/graphene flakes as shown in Figure S7. An 808 nm laser was made incident on the UCNPs and its upconversion spectra was recorded. It showed emissions at 400, 525, 540, and 650 nm. In order to provide a proof of concept of charge transfer happening between the UCNPs and graphene, a solution of UCNPs and graphene flakes were considered for photoluminescence study. It was found that there was a drop in upconversion intensity when UCNPs and graphene flakes were together used for photoluminescence study.<sup>S2</sup> This drop in upconversion intensity in the case of UCNPs can signify that photogenerated charge carriers have a longer lifetime at its metastable states thus resulting in the lesser upconversion of photons.



**Figure S7**. Photoluminescence Spectra of UCNPs and UCNPs/Graphene Flakes under 808 nm laser illumination.

#### SIII. Dependence of response time on the wavelength of illumination

In Figure 2 under 325 nm laser illumination, the planar structure hybrid UCNPs and graphene photodetector shows maximum photoresposnsivity with significantly slow response. Also, under 808 nm laser illumination the planar structure hybrid UCNPs and graphene photodetector shows significantly faster response. This implies that there lies a strong dependence of response time on the wavelength of laser illumination. This can be explained by taking into account the core-shell structure of the UCNPs under laser illumination. The core-shell structure of UCNPs consists of NaYF4:Yb:Er:Nd in the core and NaYF4:Nd in the shell. Under 325 nm laser illumination, the photons are majorly absorbed by the Erbium (Er) present in the core. Neodymium (Nd) and Ytterbium (Yb) will not be responsive to the 325 nm laser illumination owing to their band structures limited to much higher wavelengths such as 808 nm and 980 nm as shown in Figure 5.<sup>S3</sup> The absorption of photons results in the generation of electron/hole pairs in UCNPs. Since the UCNPs are placed in close proximity with graphene in our UCNPs and graphene hybrid device, the holes are transferred from UCNPs to graphene to give the positive photoresponse. When 325 nm laser photons are made incident on the UCNPs, the photons are absorbed only by the core thus resulting in formation of electron/hole pairs in the Erbium(Er) present in the core. Now, the holes need to be transferred from the core of UCNPs to graphene via the shell of UCNPs thereby contributing towards a slower response in case of 325 nm laser illumination. Similarly, lesser faster photoresponse is observed under 532 nm and 657 nm laser illumination. Under 808 nm laser illumination we observe the fastest photoresponse owing to the fact that Nd and Yb present in the shell of the UCNPs will absorb 808 nm photons and will help in catalysing the response of the UCNPs and graphene hybrid photodetector.

# SIV. Optical Transmission Spectra (Proof of enhancement of photoresponsivity under 0% strain and 100% strain)

In Figure 6, it is well demonstrated that the rippled hybrid UCNPs and graphene photodetector shows a considerable higher photoresponse in comparison to a planar structure photodetector. It is experimentally noted that the photoresponsivity decreases with increasing strain in the case of rippled hybrid UCNPs and graphene photodetector. Optical transmission measurements as shown in Figure S8 were performed for planar graphene/PDMS and rippled graphene/PDMS structure in order to prove the enhancement of photoresponsivity owing to rippled graphene/PDMS structure. The transmission of light is more in the case of planar structure. The reduction in the transmission of light in the case of rippled structure agrees well with the enhancement mechanism explained with Figure 2e.



Figure S8. Optical Transmission Spectra of planar and rippled graphene/PDMS

# SV. Relationship between the strain and the height of the graphene ripples (A Quantitative analysis)

The definition of applied strain is depicted in Figure S9. The strain can be quantitatively explained by using the experimental data. The PDMS originally taken is of 1.8 cm (approximate value) in length. It is stretched up until the length of PDMS becomes twice of original length thereby accounting for 100% strain. The graphene with a layer of PMMA is transferred over the PDMS under 100% strain. The initial length of graphene transferred is 0.8 cm (approximate value). The PDMS with graphene over it is then released such that the PDMS attains back the length of 1.8 cm and the graphene shrinks to 0.4 cm. The rippled structure so obtained is under 0% strain.



Figure S9. Schematic representation of the definition of applied strain

From the SEM image of the ripples under 0% strain shown in Figure 2d, the average height (h) of the ripple is observed to be approximately 70  $\mu$ m. Also, the approximate average distance between two adjacent troughs (2t) is observed to be 61  $\mu$ m (see Figure S10). Then, the periodicity of graphene ripples formed under 0% strain is calculated to be approximately 0.016  $\mu$ m<sup>-1</sup>, where periodicity is defined as the number of graphene ripples formed per unit length. Under 20%, 40%, 60%, and 80% longitudinal strain the length of graphene is observed to be 0.49 cm, 0.58 cm, 0.65 cm, and 0.73 cm, respectively.

Let us consider Strain (S) as a function of crest width (2t) as follows:

$$S = (t - t_0)/t_0$$
 (i)

where 2t<sub>0</sub> and 2t is the crest width under 0% strain and arbitrary strain, respectively.

Then, from equation (i)

$$\mathbf{t} = \mathbf{t}_0 + \mathbf{S} \, \mathbf{t}_0 \tag{ii}$$

Also, from Figure S10

$$\mathbf{l}^2 = \mathbf{h}^2 + \mathbf{t}^2 \tag{iii}$$

Therefore, equations (ii) and (iii) will contribute towards a quadratic function of strain varying with the height of the graphene ripple or the wavelength of the graphene ripples.



Figure S10. Schematic representation of crest width (2t) and height of ripple (h)



Figure S11. Temporal photoresponse of the hybrid rippled structure photodetector on cloth belt under 808nm laser illumination.



Figure S12. Temporal photoresponse of the hybrid rippled structure photodetector on aluminium plate under 808nm laser illumination.



**Figure S13**. Temporal photoresponse of the hybrid rippled structure photodetector on rubber gloves under 808nm laser illumination.



Figure S14. Temporal photoresponse of the hybrid rippled structure photodetector on cardboard under 808nm laser illumination.



**Figure S15**. Temporal photoresponse of the hybrid rippled structure photodetector on plastic pettridish under 808nm laser illumination.

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