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Ultrasensitive broadband photodetector using electrostatically conjugated MoS$_2$-upconversion nanoparticle nanocomposite

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A B S T R A C T

Hybrid or composite nanomaterials have emerged that demonstrates superior optoelectronic performance over pure nanomaterials that lacks broadband usage, or responsivity, or both, mainly because of the limitation of the collection of photogenerated carriers. We have addressed this problem by using a composite of MoS$_2$ and a multi-photon absorbing lanthanide doped upconversion nanoparticles (UCNPs), that emits in the visible, to make a photodetector (PD) device with ultra-high broadband responsivity. Single flake MoS$_2$ electrostatically conjugated with UCNPs were used to fabricate the PD device with platinum, and gold contacts. The device was irradiated with UV-to-NIR illumination, at different power density, to study its broadband photosensitivity. Photosresponsivities in excess of 100 A W$^{-2}$ is easily attained; a highest responsivity of 1254 A W$^{-1}$ is reported for 980 nm at 1,0 V bias. An unprecedented normalized gain of $7.12 \times 10^4$ cm$^2$ V$^{-1}$, and Detectivity of 1.05 $\times 10^{15}$ Jones (@980 nm, 1 V) was obtained which is, to the best of our knowledge, the highest reported till date for this device class. Under vacuum conditions even higher values of these device parameters were obtained, while losing on the response speeds. The photosresponsivity in the nanocomposite followed the trend of the convoluted optical absorption of the individual components. Real application of the PD device was demonstrated using non-laser domestic appliances such as sodium vapour lamp, mobile phone flash light, and air-condition remote controller.

1. Introduction

Hybrids or composites stand to benefit from the combination of individual material properties or even generate attributes inaccessible to the individual components. In the nanomaterials domain two key elements dominate these properties. One is the atomic composition, for example carbon (C) in graphene, or molybdenum (Mo) and Sulphur (S) in molybdenum disulphide (MoS$_2$). The other is the structure or dimensionality of the material, for example 0 dimension (D) of the quantum dot or nanoparticles, 1D for nanowires or tubes, and 2D for MoS$_2$, graphene. Hetero-atomic composites of the same dimension, or hetero-dimensional composites of same or different elemental compositions are under intensive research for different applications in catalysis [1–4], chemical [5–7] and light sensors [8–12], energy materials [13, 14], optoelectronics [15,16], and many others [17,18]. In most cases they have shown superior performance related to output, sensitivity, range, and other parameters critical to the application. Graphene, though electronically an efficient transporter [19], suffer from the lack of optical activity even with doping to open up a reasonable bandgap [20,21]. The other promising single phase 2D material, MoS$_2$, though electronically inferior to graphene, have reasonable optical activity over a specified band [16,22]. These properties inspired researchers to test them as photodetectors (PDs). Indeed, MoS$_2$ worked with high responsivity (R in A W$^{-1}$) albeit over a limited spectral band [22]. The report triggered further activity in MoS$_2$ based composites aimed at compensating the optical sensitivity with efficient absorbers such as quantum dots [10], and upconversion nanoparticles (UCNPs) [9]. Similarly, activity on graphene conjugated photoabsorbers [23] initiated with improved performances that underlined the efficacy of composites. Photoabsorbers that are efficient emitters, such as quantum dots, were the automatic choices for inclusion in the composites. However, their absorption is predominantly in the high energy ultra violet (UV) range. Although a broadband PD is not always desirable, and colour-specific detectors are sought for many applications, we should have the option

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of tunable range of photodetection where the challenge is mostly in the infrared (IR) part of the spectrum. This is where the 0D lanthanide doped UCNPs can contribute by their multiphoton absorption in the 980 nm range [24–26]. These UCNPs absorbs low energy IR light and emits in the visible range depending on the dopant ions [24–26]. Recently, Ji et al., reported a UCNP-perovskite based hybrid PD with an R~303 A W−1 [27]. Another report on UCNP-graphene composite PD showed broadband sensitivity of the device with good device parameters such as, R, optical gain (Γ), and detectivity (D*) values [23]. The positive photoresponse indicates the transfer of photogenerated holes to graphene for transport, and ultimate collection at the electrodes. The challenge is to achieve an optimal composition, and an optophysically stable hybrid, of either chemically bonded, or electrostatically attached components, with reproducible device performance.

In this work, we demonstrate an electrostatic conjugation of chemically exfoliated MoS₂, and UCNPs prepared by thermal decomposition. The electrostatic conjugation is demonstrated by electron microscopy, optical properties, and surface charge measurements. The composite is optimized by varying the ratio of the UCNPs, and MoS₂. Finally, a broadband (325–1064 nm) PD was designed with the optimal hybrid that shows unprecedented values of device parameters such as, R, Γ, normalized Γ (Γ_n), and D*.

2. Materials and methods

2.1. Materials

For the synthesis of chemically exfoliated MoS₂, Molybdenum disulfide powders (MoS₂, 98.5%, CAS 1317-33-5, ACROS ORGANICS, USA), and N-methyl-pyrrrolidone (NMP, 99%, extra pure, CAS 872-50-4, ACROS ORGANICS, USA) were purchased and used as-obtained. For the synthesis of the oleic acid capped NaGdF₄:Yb³⁺, Er³⁺ upconversion nanoparticles (UCNPs), GdCl₃, YbCl₃, ErCl₃, Oleic acid (OA), 1-octadecene (ODE), ammonium fluoride (NH₄F), NaOH and analytical grade chemical such as ethanol, cyclohexane, and methanol were all purchased from Sigma Aldrich, USA, and used as-received.

2.2. Synthesis of UCNPs

The Yb³⁺/Er³⁺-doped NaGdF₄ nanocrystals were prepared according to a thermal decomposition method as reported previously by Liu et al. [28]. In this typical synthesis, GdCl₃ (80%), YbCl₃ (18%), ErCl₃ (2%) were first mixed with 15 ml of OA and 16 ml of ODE in a 100 ml three neck flask. The resultant mixture was then heated to 150 °C under nitrogen atmosphere to form a homogeneous solution. When the above solution is cooled to 50 °C, 10 ml of methanol solution containing NaOH (2.5 mmol) and NH₄F (4 mmol) is added drop by drop, and the reaction chamber is then kept under stirring for 30 min. Subsequently, methanol in the system was removed by keeping the reaction system at 100 °C. Afterwards, formed reaction mixture is heated to 300 °C for 1 h with continuous flowing of nitrogen gas and terminated by cooling the reaction mixture to room temperature. The resultant nanoparticles were then washed with ethanol for 5 times, and finally redispersing in cyclohexane for further experiments.

2.3. Synthesis of few layer MoS₂ nanoflakes

Exfoliation of few layer MoS₂ from the bulk powders was done following a published paper [29]. In short, 7.5 mg of as-purchased MoS₂ powders were mixed with 10 ml of NMP in a 100 ml capacity flat bottom beaker. These samples were sonicated continuously for 120 min using a sonicator (LEO-1502, Leo-Sonic, Taiwan). The beaker was immersed in a cooling bath having a continuous supply of cold water (~5 °C) during sonication. The solution appeared non-transparent black. The solution was poured in a 15 ml plastic centrifuge tube, and centrifuged (Heraeus Megafuge 8 Small Benchtop Centrifuge, Thermo Scientific™, USA) at 1500 rpm for 45 min. The solution separates into a greenish supernatant, at the top fraction of the tube, and a dark precipitate at the bottom. The supernatant is collected by a pipette and stored in a 10 ml glass bottle. This process is repeated thrice before the supernatants were finally collected containing the exfoliated MoS₂.

2.4. Synthesis of MoS₂-UCNP nanocomposites

For the preparation of MoS₂-UCNP nanocomposites, the exfoliated MoS₂ nanoflakes (0.01 mg mL⁻¹ in NMP), was put in the sonicator, and the UCNPs (0.1 mg mL⁻¹ in NMP) solution was slowly added dropwise followed by stirring (300 rpm) for 16 h to allow for the electrostatic conjugation. To separate the free or unbound solutions, the solution was centrifuged at a speed of 6000 rpm for 10 min. Finally, the precipitate of predominantly nanocomposite product is collected and stored in a refrigerator (4 °C) for later use.

2.5. Characterisation of MoS₂-UCNP nanocomposites

The Raman spectra were measured by using a commercial Jobin Yvon LabRAM HR800 (Horiba Ltd.) Raman spectrometer equipped with an Olympus BX-41 microscope, using 532 nm (CNI MSL-III-532) exfoliation with tunable powers. A 50 mm objective was used for focusing and data collection. Exposure time of 10 s, and triple accumulation was used to collect the spectra. The optical absorption/reflectance spectra of free MoS₂, UCNPs, and MoS₂-UCNP composites were recorded by UV-Vis-NIR spectrometer (Jasco V770, USA), equipped with an integrating sphere (ABSN-917) for absolute reflectance, in the range of 200–2700 nm using suitable references. Fluorescence spectra were recorded by a Fluorolog (JY Flurolog 3 with iHR 320, Horiba, Japan) in the range of 375–700 nm using a 980 nm laser excitation (SDL-980-LM-5000T, Shanghai Dream Lasers Technology Co., Ltd., China) having tunable powers up to 5 W. The surface charge of all the materials used, including the nanocomposites, was measured with a Zeta potential machine (NanoPlus Particulate System, USA).

The morphology, and crystal structure of the pure MoS₂, pure UCNPs, and their nanocomposite was imaged by High Resolution Transmission Electron Microscope (HR-TEM, JEM-21010F, JEOL, Japan) with Energy Dispersive X-ray Analyzer (EDAX, OXFORD INCA) to measure their compositions.

The PD device was prepared on a pre-fabricated lithographically patterned Au/SiO₂/Si chip [30] on which the nanocomposites were drop casted. These chips were viewed under a focus ion beam-scanning electron microscope (FIB-SEM, Quanta 3D FEG, FEI, Japan) to locate the nanocomposite flakes within few microns of the Au electrodes of the chip. The nano flake was then electrically connected to the Au electrodes, to serve as source and drain, by platinum (Pt) deposition using FIB. The voltage and current of the FIB for the Pt deposition was 30 kV and 100 pA, respectively.

Electrical characterization was performed in an ultralow leakage current probe station (LakeShore Cryotronics TTP4), using a semiconductor characterization system (Keithley 4200-SCS) for the measurement of the current-voltage characteristics. Different lasers with wavelengths of 325 (He-Cd, Kimmon, Japan), 405 (CNI, China), 532 (Nd:YAG, CNI, China), 808 (CNI, China), 980 (SDL, China), and 1064 nm (Newport, USA) were used for irradiation. The incident laser power was measured by a calibrated power meter (Ophir Nova II) with a silicon photodiode head (Ophir PD300-UV) before and after each measurement. Neutral density filters (NDC-100S-4M, Thor Labs, USA) were used to change the power levels of each laser.

3. Results and discussion

We begin with structural characterization of the MoS₂-UCNP nanocomposites by transmission electron microscopy (TEM). Fig. 1 shows the morphology, crystal phase, and structure of the nanocomposite, as well
as individual materials. Fig. 1a shows the TEM image of a flexible, and folded MoS$_2$ nanoflake and its high resolution version with well-defined hexagonal structure having a lattice spacing of ~0.32 nm [31]. Fig. 1b shows a top view TEM of the MoS$_2$-UCNP nanocomposite where the UCNPs are shown attached to the surface of the MoS$_2$ nanoflakes. HRTEM image of a single UCNP (inset, Fig. 1b) shows a lattice spacing of 0.4 nm corresponding to the hexagonal crystal phase as reported previously [32]. The size of the UCNPs is found to be ~10 - 1 nm, and their size distribution is shown in Fig. S1a (ESI). The interface between the UCNPs, and the MoS$_2$ nanoflakes is revealed under cross-sectional HRTEM (Fig. 1c). The UCNPs are attached on the both side of the MoS$_2$ nanoflakes, including the edges. This attachment is electrostatic in nature that we will prove later. The layer-to-layer distance in the MoS$_2$ nanoflakes is 0.65 nm [33]. We have estimated that the maximum number of exfoliated MoS$_2$ layers stacked together is ~4-6 (Fig. 1c).

From the selected area electron diffraction (SAED) pattern, clear bright spots originating from MoS$_2$, and spotty ring pattern from the UCNPs were observed (Fig. 1d) (JCPDS 27-0699). SAED of individual UCNPs is shown in Fig. S1b (ESI). No interfacial artefacts in the composite were observed under structural investigation.

In the TEM-EDAX mapping of the MoS$_2$-UCNP nanocomposite (Fig. S1c), the presence of all the elements Mo (Fig. S1d), and S (Fig. S1c) from MoS$_2$ nanoflakes, and Na (Fig. S1f), Gd (Fig. S1g), and F (Fig. S1h) from NaGdF$_3$ UCNPs have been confirmed. Due to the very low concentration of the dopant ions, Yb$^{3+}$, and Er$^{3+}$, used in the UCNPs, we could not observe those in EDAX colour mapping. However, the EDAX spectrum (Fig. S1i) confirms the presence of all the elements together with the low concentration dopants, Yb$^{3+}$ and Er$^{3+}$.

Zeta potential, a conclusive parameter for surface charge [34], proves the electrostatic conjugation between MoS$_2$ and UCNPs (Fig. S2).

Fig. 2 represents the optical and vibrational characterizations of MoS$_2$-UCNP nanocomposites. The excitonic absorption peak for MoS$_2$ can be observed (Fig. 2a) near 679 nm [29]. The absorption band for UCNPs at 980 nm (inset, Fig. 2a) can be observed only for the high concentration (MoS$_2$:UCNP 1:10) colloidal solution. The Raman spectrum (Fig. 2b) shows the characteristic phonon bands at ~250, ~298, and ~345 cm$^{-1}$ for the UCNPs [36,37]. MoS$_2$ Raman bands at ~386, and ~410.5 cm$^{-1}$ corresponding to the phonon modes $E_g$ and $A_{1g}$ [38,39], respectively, can be observed. The inter mode separation (in wavenumbers) indicates the approximate number of layers in MoS$_2$ [40]. In this case, the peak separation $\Delta$($A_{1g}$ - $E_g$) 24.5 cm$^{-1}$, indicates 4-5 layers of MoS$_2$ [41]. Multilayer MoS$_2$ will have a lower bandgap to increase absorption, while losing out on the electronic mobility when compared to the single layer MoS$_2$. An optimum layer number, other than 4-5 layers, may exist where the requirement of high optical absorption and high electronic mobility can both be met. Raman spectra for the individual components are shown in Fig. S3a,b (ESI).

Fig. 2c represents the power dependent fluorescence spectra of the MoS$_2$-UCNP nanocomposites. The characteristic emission bands of the UCNPs at 520, 540, and 655 nm increases in intensity with increasing incident powers. However, compared to pure UCNPs (Fig. S3c), a quenching of the UCNP fluorescence [42] was observed upon conjugation with MoS$_2$. The electronic transitions responsible for the emission colors in the UCNP is schematically depicted in Fig. S3d. The observed quenching of fluorescence in the MoS$_2$-UCNP composite, compared to free UCNPs (of same concentration) (Fig. S3c), may be due to several reasons such as excited-state reactions, energy transfer, collisional quenching with solvent environment, and so on [42]. Our results indicate a possible energy transfer from the UCNPs to MoS$_2$ following the previous reports in metal induced quenching in fluorophores [43,44]. This fluorescence quenching is key to the PD application as it indicates an energy transfer mechanism between the component materials. The extent of the green fluorescence quenching in the nanocomposite, compared to UCNP only, under identical concentrations, and measurement conditions is approximately ~51% (Fig. 2d) and can be observed visually by the naked eye (inset, Fig. 2d).

Having characterized the materials, and the nanocomposite we proceed to fabricate the PD device on a specially designed pre-fabricated gold-patterned SiO$_2$/Si substrate as shown schematically in Fig. 3a. After dispersion of the nanocomposite, the device was viewed under a FIB-SEM, and final Pt contacts were extended, to the gold drain (d) and source (s) electrodes, from a suitable composite flake by the FIB to complete the device (Fig. 2b). The effective area of our device is 4.49 $\mu$m$^2$. A live device was selected from the ones showing a linear dark current (I$_{ds}$)-voltage (V$_{ds}$) characteristics under an applied V$_{ds}$ between 0.1 and 0.1 V in the two electrode configuration (no gate electrode). The photoresponse was then measured by illuminating the device with different lasers from UV (325 nm) to NIR (1064 nm) to check the broad band responsivity.

Fig. 4 shows the $\Delta$I$_{ds}$-V$_{ds}$ curves of the device under dark, and illuminated conditions with different lasers having different power densities from 50 to 994 W m$^{-2}$ (up to 100 W m$^{-2}$ for the 325 nm laser only). $\Delta$I is defined as the incremental photocurrent ($\Delta$I$_{Illuminated}$ - $\Delta$I$_{dark}$). We observed an increase in the $\Delta$I$_{ds}$ with illumination power density for every laser (325, 405, 532, 808, 980, and 1064 nm) (Fig. 4a–f). Under the same $\Delta$I$_{ds}$ scale the photoresponse at 405 nm was the highest. For comparison, we present the $\Delta$I$_{ds}$-V$_{ds}$ measurements on a similarly prepared individual MoS$_2$ device (without the UCNPs, ESI Fig. S4).

The dynamic photoresponse (I$_{ds}$-t), as a function of time (t), of both MoS$_2$ only, and MoS$_2$-UCNP nanocomposite device, was then measured under definite durations of ON-OFF cycles with V$_{ds}$ = 0.1 V (Fig. 5a–f).

The transient photocurrent stayed at the dark current value under illumination OFF, and increased (positive photoresponse) to reach a saturation with illumination ON after a certain rise time ($t_{rise}$). The

Fig. 1. Morphology, and structure of MoS$_2$-UCNP nanocomposites. (a) TEM image of a folded MoS$_2$ nanoflake. Inset in (a) shows HRTEM image of a MoS$_2$ nanoflake revealing the lattice spacing and well defined hexagonal arrangement of the atoms on the outermost layer. (b) TEM image of MoS$_2$-UCNP nanocomposite. UCNPs (encircled by yellow dash, or arrows) are attached on the surface of the MoS$_2$ nanoflakes (outlined by red dashed lines). Inset in (b) shows HRTEM image of a single UCNP with lattice spacing. (c) Cross-sectional HRTEM image of MoS$_2$-UCNP nanocomposite showing the interface between MoS$_2$ and UCNPs. (d) SAED pattern of MoS$_2$-UCNP nanocomposites. The marked planes are for MoS$_2$ (red) and UCNPs (yellow).
saturation or maximum photocurrent consistently increased with the power density of the irradiation. With illumination turned OFF the photocurrent returned to the value set by the dark current over a certain period of fall time ($\tau_{\text{off}}$) that we will calculate later. From the dynamic response, we noticed that our device, both MoS$_2$ and MoS$_2$-UCNPs, generated highest photocurrent under 405 nm illumination, which is up to 0.5 $\mu$A at 994 W m$^{-2}$ power density (Fig. 5b), and a minimum under 808 nm (Fig. 5d). Thereafter, the photocurrent again increased for the 980 (Fig. 5e), and 1064 nm (Fig. 5f) lasers in the IR. This is where the nanocomposite device has extended the spectral usability of the detector up to 1064 nm. To understand the stability of the MoS$_2$-UCNP nanocomposite, and the MoS$_2$ only PD devices, multi-cycle photoresponse is shown in Figs. S5 and S6 (ESI), respectively.

To understand the performance of our device, we have investigated several parameters such as Photoresponsivity ($R$), Gain ($\Gamma$), Normalized $\Gamma$, and Detectivity ($D^*$). The Photoresponsivity, $R$ (A W$^{-1}$), is a measure of photocurrent generation efficiency of a PD and is defined as the photocurrent ($I_p$) generated by the power ($P$) of light incident on an active area ($A$) of the device. Therefore, $R$ is generally written as:

$$R = \frac{I_p}{P}$$  \hspace{1cm} (1)

However, as the laser beam area ($A'$) exceeds the effective device area ($A$), the effective power incident on the device is estimated by $P \times (A'/A)$, where $P/A'$ is the laser power density [46]. Gain ($\Gamma$), indicates the circulating number of photocarriers moving through a photoconductor per unit time before recombination. Therefore, $\Gamma$ is defined as the ratio of carrier lifetime ($\tau$) to the transit time ($\tau_t$) between two electrodes, and is written as:

$$\Gamma = \frac{\tau}{\tau_t} = \frac{V}{P} \frac{1}{\mu}$$  \hspace{1cm} (2)

where $V$ is the bias voltage, $l$ is the electrode spacing equal to the channel length of the active device, and $\mu$ is the carrier mobility [45,47]. As $\Gamma$ has a linear relationship with $R$, and the photocurrent $I_p$, the $\Gamma$ value can be estimated according to the following equation:

$$\Gamma = \frac{E}{\eta} \frac{R}{e} \frac{I_p}{e \eta P}$$  \hspace{1cm} (3)

where $E$ is the photon energy, $e$ is the elementary charge, $\eta$ is the quantum efficiency [47]. As we cannot calculate the exact value of $\eta$ for our device, we underestimate the $\Gamma$ value by assuming $\eta = 1$.

$\Gamma_n$ is defined as the product of $\eta$, $\tau$, and $\mu$ [30,48]. In short, $\Gamma_n$ can be
calculated by the following equation 

\[ D = \frac{R/\eta}{\sqrt{2eI_d}} \]  

(4)

To calculate Detectivity (D*), we need to consider the dark current, \( I_d \), which contributes to the total noise current. D* is given by Ref. [49].

\[ D = \frac{R/\eta}{\sqrt{2eI_d}} \]  

(5)

where A is the effective area of PD device.

**Fig. 4.** Dark and photo current (I)-voltage (V) characteristics of the MoS\(_2\)-UCNP nanocomposite PD. Power dependent \( \Delta I_{ds} \) vs. \( V_{ds} \) (drain-source) characteristics of the device under dark (black), and different laser illumination (coloured) (a) 325, (b) 405, (c) 532, (d) 808, (e) 980, and (f) 1064 nm, respectively. \( \Delta I_{ds} \) represent (photo - dark) current data at each \( V_{ds} \). The laser power densities ranged from 0 to 100 W m\(^{-2}\) for (a), and 0-994 W m\(^{-2}\) for (b-f), demonstrating higher \( \Delta I_{ds} \) with increasing power density.

**Fig. 6** shows the comparison of the device parameters, including R (Fig. 6a), \( \Gamma \) (Fig. 6b), \( \Gamma_n \) (Fig. 6c), and D* (Fig. 6d) as a function of wavelength for the pure MoS\(_2\), and MoS\(_2\)-UCNP nanocomposite at the maximum available light power density (994 W m\(^{-2}\)), and so represents the minimum values of these parameters. These parameters display similar spectral dispersions. The results show a minimum, and maximum R of the nanocomposite device to be 38, and 109 A W\(^{-1}\) for 808 nm and 405 nm laser, respectively, at 0.1 V\(_{ds}\) and 994 W m\(^{-2}\) power density (Fig. 6a). The R @ V\(_{ds}\) 0.1 V for other lasers lie in between. For a better understanding, we also plot the device parameters as a function of power density (Fig. 6f, ESI). These numbers, apparently may not look impressive unless probed deeper. Most of the previously published R values are measured at very low power levels of Pico or Nano Watt [22,50], and sometime using V\(_{ds}\) values as high as 8 V [22]. The large change, in order of magnitude, in R originates from the power which appears at the denominator for the R calculation. We have used power densities in W m\(^{-2}\) values here. In addition, R is a function of V\(_{ds}\) also as \( I_d \) or V\(_{ds}\). Wu et al., noticed that increasing the V\(_{ds}\) by 10 times can increase R by about ten times [11]. In our case, V\(_{ds}\) 0.1 V only. From Fig. 5e, the calculated R value for 980 nm at V\(_{ds}\) 1 V is 1254 A W\(^{-1}\). This R value is the highest reported till date (at V\(_{ds}\) 1.0 V) for a MoS\(_2\)-UCNP based nanocomposite device at 980 nm.

Here, the MoS\(_2\)-UCNP PD is a two terminal device without any gate electrode or bias. In comparison, similar devices using 2D materials, such as reduced graphene oxide, showed R ~0.004 A W\(^{-1}\) only [51]. Again, a recently published literature utilizing UCNPs and graphene based PD shows a maximum R ~4 A W\(^{-1}\) at V\(_{ds}\) 0.1 V for 808 nm laser [23]. Zhou et al., reported R ~0.01 A W\(^{-1}\) at 1 V bias voltage for monolayer CVD grown MoS\(_2\) and UCNP based PD device [9]. When considering these R values, those of the current MoS\(_2\)-UCNP device is superior.

However, to better compare the PD devices, the external effects of V\(_{ds}\) and A (device area) needs to be excluded. The parameter \( \Gamma \) (Fig. 6b), and \( \Gamma_n \) (Fig. 6c), becomes important for a fair comparison of devices around the world [30,52]. The spectral variation of \( \Gamma \), and \( \Gamma_n \), are similar for individual MoS\(_2\), and MoS\(_2\)-UCNP device. Similar to R, and \( \Gamma_n \), the value for \( \Gamma \) is the highest, \( \Gamma_n \) 1.48 10 \(^{-4}\) cm\(^2\)V\(^{-1}\) for the 405 nm laser, and lowest \( \Gamma_n \) 2.8 10 \(^{-5}\) cm\(^2\)V\(^{-1}\) for the 808 nm laser. This value of \( \Gamma_n \) is higher by more than an order from the previous best of \( \Gamma_n \) 4.8 10 \(^{-6}\) cm\(^2\)V\(^{-1}\) for monolayer MoS\(_2\) [22], and graphene nanoribbon \( \Gamma_n \) 2.1 10 \(^{-7}\) based PDs [51]. A complete description of the
power and wavelength dependent device parameters can be found in Fig. S7, ESI.

Normally, R, Γ, and Π depend on the photocurrent (I_p) and don’t consider the dark current (I_d) that plays a major role towards the noise in the current measurement. To fully quantify the device performance and quality, the parameter D* has to be calculated that takes both I_p and I_d into account. The spectral dependence of D* for the MoS_2 only, and MoS_2-UCNP nanocomposite device is shown in Fig. 6d. The power dependence of D* for the MoS_2-UCNP nanocomposite device is shown in Fig. S8 (ESI). The value of D* is highest at 9.0 \times 10^{13} Jones for the 405 nm laser, and lowest at 3.4 \times 10^{11} Jones for the 808 nm laser. In comparison, PDs based on monolayer MoS_2 showed D* value of 2 \times 10^{12} Jones at 561 nm [22], and MoS_2 quantum dot hetero junction devices showed D* of 8 \times 10^{13} Jones [49]. To put these device parameters in context, a comparison of the published device parameters with the ones presented in this work is shown in Table 1.

Two features are identified from the plots in Fig. 6. First, the device parameters, and their spectral dependence is enhanced (in magnitude) for the nanocomposite with respect to the pure MoS_2 device. To explain such enhanced parameters over a broad band, optical absorption and absolute reflectance measurements of MoS_2 and UCNP-MoS_2 samples were done on quartz substrates (Fig. S9, ESI). The net absorption in the composite, with respect to MoS_2 only, is increased over the 300-1100 nm spectral range (Fig. S9a, ESI). This is intriguing as UCNPs don’t have absorption in the UV–Vis part of the spectrum. The angle dependent reflectance measurement showed ~50% reduction in absolute reflectance for the composites, with respect to pure MoS_2, over the 300–900 nm band (Figs. S9b–d, ESI). This may be due to multiple internal reflections resulting in light trapping in the layers of high refractive index transparent NaGdF_4 nanocrystals enhancing the optical absorption in MoS_2 (Fig. S9e, ESI) that supported the UCNPs. Layers of high refractive index nanostructures, such as silica, are commonly used as antireflection layers in solar cells [53-55].

Second, as the parameters for the pure MoS_2 device withers off to a minimum in the IR region, the nanocomposite device expresses a minimum at 808 nm and gains appreciably from 980 nm. This distinction is attributed to the presence of the NIR absorbing [26,56] UCNPs in the nanocomposite device. Although, the prominent absorption of the UCNPs is around 980 nm, researchers have shown additional UCNP absorption at longer (1523 nm) [57], and shorter (785, 905 nm) wavelengths [55], but still show photoreponse in the 1064, and 1342 nm wavelength [56]. Compared to the single layer MoS_2 device showing photoreponse below 700 nm [22], here, the photoreponse for multilayer MoS_2 device could be extended to higher wavelengths [11]. Multilayer MoS_2 have shown response beyond 700 nm [11,56]. The long band tail absorption in multilayer MoS_2 (down to 1.2 eV, ~1100 nm) [29,56] may also contribute to the increased absorption and photoreponse compared to the single layer MoS_2. In addition, the UCNPs can
upconvert a NIR photon to visible light which can be absorbed by the multilayer MoS\textsubscript{2} and, thus, produce a better photoresponse in the nanocomposite compared to the multilayer MoS\textsubscript{2} only device.

Another parameter for these PD devices is their response speed which is generally measured by the rise and fall time ($\tau_{\text{rise}}, \tau_{\text{fall}}$). The $\tau_{\text{rise}}$, and $\tau_{\text{fall}}$ are calculated from the dynamic photo response curves shown in Fig. 5. A simple definition of the $\tau_{\text{rise}}$ is the time required for the device to reach from 10 to 90\% of the saturation photocurrent when the illumination is turned on. Similarly, the definition of the $\tau_{\text{fall}}$ is the time required for the device to fall from 90 to 10\% of the saturation photocurrent when the illumination is turned off (Fig. S10, ESI). For the device under consideration the $\tau_{\text{rise}}$, and $\tau_{\text{fall}}$ are $\sim$10–20 s. This is not unusual as monolayer MoS\textsubscript{2} based devices have shown a response time of 15–20 s [58]. Even pure graphene PD devices have shown extremely long response times (50–100 s) [59]. Theoretically responsivity is linearly dependent on carrier lifetime. A long response time will generally result in high photocurrent and thus high responsivity.

As both the carrier transport speed, and transport mechanism will contribute to these response times, any adsorbed species or traps on the active surface of the device might influence the result. Fig. S11 shows the photoresponses measured in air, and in vacuum (~7 mTorr) under 405, 532, and 980 nm irradiation. The photoreponse times were between 10 and 20 s for the measurements in air, that increased to 40–60 s for those under vacuum (Table S1, ESI). Similar increase in response times, under vacuum, were also obtained before [58]. Interestingly, the photocurrent also increased under vacuum conditions (Table S1, ESI) that would result in even higher values for the device parameters. The observed changes, when in vacuum, is consistent with the oxygen-sensitized photoconduction (OSPC) mechanism [30,60]. Usually fast response time is required for high-frequency photodetectors.

### Table 1
Comparison of Responsivity (R), Normalized Gain ($\Gamma_{\text{r}}$), and Detectivity (D*) values for the different 2D material based PDs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$V_{\text{bi}}$ [V]</th>
<th>$V_{\text{g}}$ [V]</th>
<th>Power Density (W m\textsuperscript{-2})</th>
<th>R [A W\textsuperscript{-1}]</th>
<th>$\Gamma_{\text{r}}$ [$\times 10^{-7}$ cm\textsuperscript{2} V\textsuperscript{-1}]</th>
<th>D* [$\times 10^{12}$ Jones]</th>
<th>Wavelength [nm]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multilayer MoS\textsubscript{2}</td>
<td>0.1</td>
<td>0</td>
<td>35</td>
<td>$10^4$ (454 nm)</td>
<td>–</td>
<td>–</td>
<td>454-1550</td>
<td>[11]</td>
</tr>
<tr>
<td>Monolayer MoS\textsubscript{2}</td>
<td>8</td>
<td>70</td>
<td>150 pW</td>
<td>880 (563 nm)</td>
<td>48</td>
<td>2</td>
<td>400-800</td>
<td>[22]</td>
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<tr>
<td>Monolayer MoS\textsubscript{2}</td>
<td>1</td>
<td>50</td>
<td>1.3</td>
<td>780</td>
<td>–</td>
<td>–</td>
<td>532</td>
<td>[58]</td>
</tr>
<tr>
<td>Multilayer MoS\textsubscript{2}/UCNPs</td>
<td>1</td>
<td>8</td>
<td>20</td>
<td>342.6</td>
<td>–</td>
<td>–</td>
<td>532</td>
<td>[61]</td>
</tr>
<tr>
<td>Monolayer MoS\textsubscript{2}/UCNPs</td>
<td>1</td>
<td>0</td>
<td>6400</td>
<td>0.061</td>
<td>–</td>
<td>–</td>
<td>980</td>
<td>[9]</td>
</tr>
<tr>
<td>MoS\textsubscript{2}/UCNPs</td>
<td>2</td>
<td>0</td>
<td>20</td>
<td>10 pW</td>
<td>0.0001 (980 nm)</td>
<td>–</td>
<td>633-1342</td>
<td>[56]</td>
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<tr>
<td>UCNPs/perovskite hybrids</td>
<td>2</td>
<td>0</td>
<td>220</td>
<td>0.331</td>
<td>–</td>
<td>–</td>
<td>960</td>
<td>[27]</td>
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<tr>
<td>Graphene nanoribbon</td>
<td>2</td>
<td>0</td>
<td>800</td>
<td>1.21</td>
<td>–</td>
<td>–</td>
<td>1550</td>
<td>[51]</td>
</tr>
<tr>
<td>UCNPs/Graphene</td>
<td>0.1</td>
<td>4</td>
<td>4.5 pW</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>808</td>
<td>[23]</td>
</tr>
<tr>
<td>UCNPs/Graphene</td>
<td>1</td>
<td>0</td>
<td>0.31</td>
<td>2.7 $10^5$ (980 nm)</td>
<td>1100</td>
<td>8</td>
<td>405-1064</td>
<td>[12]</td>
</tr>
<tr>
<td>MoS\textsubscript{2}/UCNPs</td>
<td>0.1</td>
<td>0</td>
<td>50</td>
<td>192</td>
<td>3280</td>
<td>161</td>
<td>325</td>
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<td>2130</td>
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<td>81</td>
<td>840</td>
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<td>57</td>
<td>390</td>
<td>47.6</td>
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<td></td>
<td></td>
<td>85</td>
<td>480</td>
<td>71.4</td>
<td>980</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.5</td>
<td>650</td>
<td>105</td>
<td>1064</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1254</td>
<td>7120</td>
<td>1050</td>
<td>980</td>
<td></td>
</tr>
</tbody>
</table>

$V_{\text{bi}}$: bias voltage; $V_{\text{g}}$: gate voltage; - indicates values not reported. For refs. 22, 23, and 56 only power data is available.
However, for applications such as power meter, and optical switches broad band detection and high sensitivity are desirable than response speed.

The spectral dependence of the maximum R (at $V_{bias}$ 0.1 V) of the nanocomposite device is plotted along with the absorption of the individual MoS$_2$ nanoflakes, and the UCNPs to understand the contribution of each on the net R (Fig. 7). The high R in the UV region drops as we move into the visible, attaining a minimum at 808 nm, however, gaining again in the infrared part of the spectra. We observe that in the UV (325 and 405 nm) part of the spectrum, the R follows the absorption of the MoS$_2$, which implies that the device is dominated by the MoS$_2$. This is reasonable, as MoS$_2$ has a band gap around 1.83 eV above which the absorption increases. The visible part, 500–600 nm, of the spectrum shows a drop in R, compared to the UV part, owing to the drop in absorption in both the individual components. However, as the tail of MoS$_2$ absorption drops off in the IR region, the R actually gains with contribution from the UCNP absorbing around 980 nm (blue curve, Fig. 7). This additional absorption, over the negligible absorption of MoS$_2$, increases the R of the composite device in this region. Effectively, we obtain a broadband sensitivity, albeit, with variable R. To impart a flatter broadband response to the device, especially in the visible-NIR part where the R value decreased, a different absorber, Neodymium, in the UCNP may be tried which has absorption bands in the visible [25]. The loading ratio (UCNP:MoS$_2$) may also improve the IR absorption. To have increased control over the carrier transport, a transistor, instead of a diode, configuration may be tried for this class of device.

The PD device presented here could work as a ‘nano’ sensor for light emitted from domestic non-laser appliances including Na-Lamp (589 nm), mobile phone flash light (400–650 nm), and air-condition IR remote (930 nm, modulated at 30–50 kHz) shown in Fig. S12. The Na-Lamp, in the yellow band, yielded the highest photocurrent. Interestingly, the air-condition remote, modulated at 30 kHz, did not show signal modulation as the response time of this device was long. Devices with faster response times would be able to resolve the signal modulation in the air-condition remote [12]. A common mobile phone white flash light could also produce sufficient photocurrent for detection with the PD device. Evidently, radiation from a variety of sources could be detected using the MoS$_2$-UCNP based composite PD device.

4. Conclusion

A novel broadband PD made from a nanocomposite of chemically exfoliated MoS$_2$, and upconversion nanoparticle is presented that had unprecedented values of device parameters such as responsivity, normalized gain, and detectivity in this class of materials. The nanocomposite, as well as the individual components were extensively studied for their morphology, structure, composition, and optical properties using electron microscopy, fluorescence, UV–Vis absorption, and Raman spectroscopy. The fluorescence quenching of the UCNPs when electrostatically conjugated with MoS$_2$ (having opposite Zeta potentials) signaled the potential of the composite as a PD where the carrier transport would be dominated by the MoS$_2$, and the carrier generation would be contributed by the MoS$_2$ in the UV–Vis part, and by the UCNP in the NIR part of the spectrum. Single flake MoS$_2$ decorated with UCNPs (MoS$_2$-UCNP 1:10) were used to fabricate the PD device, and irradiated with 325, 405, 532, 785, 980, and 1064 nm laser, at different power density. Responsivities in excess of 100, with a maximum value of 192 A W$^{-1}$ for 325 nm laser at $V_{bias}$ 0.1 V, and R value of 1254 A W$^{-1}$ at $V_{bias}$ 1 V at 980 nm was obtained. Highest normalized Gain of 7.12 $10^{10}$ cm$^2$ V$^{-1}$, and Detectivity of 1.05 $10^{10}$ Jones (@980 nm, 1 V) was obtained for the nanocomposite. Dynamic photoresponse curves indicate good stability, and rise and fall times around ~10–20 s.

The photoresponsivity of the nanocomposite device followed the trends of the optical absorption of the nanocomposite over the broad spectral band, where the infrared segment was enhanced by the UCNPs, and the UV–Vis segment by the MoS$_2$. The UCNPs act as an antireflecting layer, possibly through multiple internal reflections, in the 300–900 nm range resulting in enhanced absorption in the nanocomposite (Fig. S9, ESI).

Fig. 7. Wavelength dependent Photoresponsivity of the device. Photoresponsivity (@ P 50 W m$^{-2}$ and $V_{bias}$ 0.1 V) of MoS$_2$-UCNP device at select wavelength of illumination (bottom axis). The line joining the data points is a guide to the eye only. Optical absorbance of MoS$_2$, and UCNPs (individually scaled on the right Y-axis) as a function of wavelength (top axis) is provided to understand the spectral variation of the photoresponsivity. The green arrows point to the MoS$_2$ absorption bands, and the blue arrow indicates the UCNP absorption at 980 nm.

Declaration of competing interest

The authors declare no financial competing interest.

Acknowledgements

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Appendix A. Supplementary data

The Electronic Supporting Information (ESI) contains the TEM images, Zeta potential, Raman spectra, optical absorption, and angle dependent absolute reflectance of UCNPs, MoS$_2$ nanoflakes, and MoS$_2$-UCNP nanocomposites. In addition, dynamic response of the device to domestic appliances, and I-V characteristics and calculation of device parameters, including response time, is also provided in the ESI.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.104258.

References

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