Graphene-Ta$_2$O$_5$ heterostructure enabled high performance, deep-ultraviolet to mid-infrared photodetection†

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Ultrafast, high sensitive, low cost photodetectors operating at room temperature sensitive from the deep-ultraviolet to mid-infrared region remain a significant challenge in optoelectronics. Achievements in traditional semiconductors using cryogenic operation and complicated growth processes prevent the cost-effective and practical application of broadband detectors. Alternative methods towards high-performance photodetectors, hybrid graphene-semiconductor colloidal quantum dots have been intensively explored. However, the operation of these photodetectors has been limited by the spectral bandwidth and response time. Here, we have demonstrated hybrid photodetectors operating from the deep-ultraviolet to the mid-infrared region with high sensitivity and ultrafast response by coupling graphene with a p-type semiconductor photosensitizer, nitrogen-doped Ta$_2$O$_5$ thin film. Photons with energy higher than the energy of the defect centers release holes from neutral acceptors. The holes are transferred into graphene, leaving behind ionized acceptors. Due to the advantage of two-dimensional heterostructure including homogeneous thickness, extending in a two-dimensional plane, large contact area between the N-Ta$_2$O$_5$ thin film and graphene, and the high mobility of carriers in graphene, holes are transferred rapidly to graphene and recirculated during the long lifetime of ionized acceptors. The photodetectors achieve a high photo-responsivity (up to $3.0 \times 10^6$ A W$^{-1}$), ultrafast rise time (faster than 20 ns), and a specific detectivity (up to $\sim 2.2 \times 10^{12}$ Jones). The work provides a method for achieving high-performance optoelectronics operating in the deep-ultraviolet to mid-infrared region.

Introduction

The capability to convert light into electrical signals over a broad spectral range with high sensitivity and low cost is central to many technological applications including video imaging, night-vision, security, optical communication, sensing, and spectroscopy. 1–3 Graphene has been exhibited as a potential optoelectronic material for broadband photodetectors from the deep-ultraviolet (UV) to the terahertz (THz) region.1–3 Unfortunately, due to the fast carrier recombination rate on the picosecond time-scale, 4 as well as the intrinsic low absorption of graphene, 5 photodetectors based on graphene suffer from poor detectivity as well as low photoresponsivity, preventing use in broadband applications. To enhance the light absorption, graphene is usually hybridized with other nanostructures for graphene-based photodetectors. 6,7 Among these nanostructures, the ultrahigh photoconductive gain was obtained in hybrid colloidal quantum dots (CQDs) on graphene, where graphene acts as an ultrafast carrier transport channel and CQDs are used as an ultrahigh photon absorbing material. In these hybrid nanoscale structures, charge carriers are generated from light-absorbing CQDs. Electrons or holes are trapped in the CQDs, while the oppositely charged carriers transfer to graphene and rapidly recirculate in the graphene channel controlled by a drain–source bias voltage, leading to a photogating effect. 8,9 Depending on CQDs, graphene hybrid photodetectors have shown a high sensitivity photodetection from the UV to near-infrared (NIR) region. However, graphene-CQD photodetectors face a limited spectral bandwidth due to the large energy of exciton peaks, 6,9 and a long response time in the sub-millisecond to second time-scale. 9–11

The ultrahigh photoconductive gain of graphene-CQD photodetectors originates from the long lifetime of trapped-charge carriers remaining in CQDs and the high carrier mobility ($\mu = 60,000$ cm$^2$ s$^{-1}$ V$^{-1}$) 12 of graphene sheet at room temperature on a substrate. The gain can be determined based on a simple approximation of the trapped-charge carrier lifetime, $\tau_{\text{trapped}}$, of electron or hole, and the transit time, $\tau_{\text{transit}}$
of the opposite type carrier given by \( G = \tau_{\text{trapped, carrier}}/\tau_{\text{transit}} \). For graphene-CQD photodetectors, the photo-responsivity is up to \( \sim 1 \times 10^{4} \, \text{A W}^{-1} \) in the visible region \( 400-510 \), while the response time is very slow (in the order of \( \sim 10 \, \text{ms} \) or longer) due to the long lifetime of carriers trapped in the CQDs. The ultrahigh gain has been observed in many types of hybrid structures including graphene-PbS, graphene-TiO\(_2\), graphene-ZnO, graphene-Si, and graphene-chlorophyll (biological material). The long lifetime of trapped-charge carriers provides an ultrahigh gain, but, leading to a slow response time of the photodetectors. The transfer time of carriers from CQDs to graphene strongly depends on the surface properties of CQDs, and the contact area between CQDs and graphene. Thus, to increase the operation speed in the graphene-CQD photodetectors, a reset voltage pulse applied to the back-gate has been used to purge charge carriers from CQDs.

To obtain an ultrahigh photoconductive gain as well as a fast operation time, including response and recovery time of graphene-based photodetectors, we have employed a two-dimensional (2D) light-absorbing layer, a p-type semiconductor photosensitizer, nitrogen-doped tantalum oxide (N-Ta\(_2\)O\(_5\)). The N-Ta\(_2\)O\(_5\) layer has a thickness of 10 nm grown by electron beam evaporation containing electron acceptor impurities atop graphene. Recently, this material has been used in a wide range of applications in solar energy conversion and microelectronics including photocatalytic materials, extending in a 2D plane, and large contact area between the N-Ta\(_2\)O\(_5\) and graphene. Thus, to increase the operation speed in the graphene-CQD photodetectors, a reset voltage pulse applied to the back-gate has been used to purge charge carriers from CQDs.

Results and discussion

The active area of the graphene-Ta\(_2\)O\(_5\) photodetectors consists of a graphene sheet and a 10 nm N-Ta\(_2\)O\(_5\) layer. Graphene acts as a carrier transport channel with the N-Ta\(_2\)O\(_5\) thin film and graphene, carriers are transferred rapidly and efficiently to graphene. Also, ionized acceptor impurities of the 2D light-absorbing layer will be neutralized quickly when the light source is turned off. The devices exhibit a significantly high photo-responsivity of \( \sim 3.0 \times 10^{4} \, \text{A W}^{-1} \) in the UV-to-NIR region, and \( \sim 7.2 \, \text{A W}^{-1} \) in the mid-infrared (MIR) region. A fast rise time of 20 ns or a high electrical bandwidth of \( \sim 50 \, \text{MHz} \) has been observed.

Now, let's focus on the long lifetime of carriers trapped in CQDs. The ultrahigh gain for the photodetectors, similar to the graphene-based photodetectors, we have employed a two-dimensional (2D) light-absorbing layer, a p-type semiconductor photosensitizer, nitrogen-doped tantalum oxide (N-Ta\(_2\)O\(_5\)). The active area is placed on top of a Si/SiO\(_2\) wafer as illustrated in Fig. 1a (see Materials and methods as well as ESIF† for details of the device fabrication). To compare with earlier findings for graphene-based photodetectors, where the photocurrent occurs with the presence of charges in CQDs changing the graphene sheet resistance, a decrease in the noise level, and is well protected from the top Al\(_2\)O\(_3\) layer. The Ta\(_2\)O\(_5\) layer was doped with nitrogen to form acceptor centers using the electron beam (e-beam) evaporation deposition. The device was transferred to an atomic layer deposition chamber to grow a 30 nm Al\(_2\)O\(_3\) layer on top. The N-Ta\(_2\)O\(_5\) layer contains acceptor centers with energy levels in the band gap of the material. Acceptor centers are ionized by absorbing photons with energy higher than the energy of the defect, resulting in hole generation. The holes are transferred rapidly into the graphene channel, leaving behind ionized acceptors (negative charges). Due to the high carrier mobility in graphene, holes are recirculated during the long lifetime of ionized acceptors. The graphene-Ta\(_2\)O\(_5\) heterostructure offers a large spectral sensitivity from the deep-UV to MIR region with very fast operation time.

Nitrogen incorporation into oxides is widely reported in the literature, and N-doped Ta\(_2\)O\(_5\) exhibits a dual functional modulation including band gap narrowing and p-type conduction. A number of studies including absorption experiments and X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and electrochemical techniques, time-resolved spectroscopic studies, and density-functional theory calculations have shown that Ta\(_2\)O\(_5\) phase changes to p-type in the nitrogen-doped Ta\(_2\)O\(_5\) material. Nitrogen doping in Ta\(_2\)O\(_5\) increases the number of defect states and produces multiple levels (or a band) above the valence band (VB) of \( \sim 1.25 \, \text{eV} \) from the N 2p orbital, and the oxygen sites are substituted by nitrogen atoms. The N 2p states form a band above the VB, resulting in band gap narrowing and p-type conduction. To verify the optical properties of the N-Ta\(_2\)O\(_5\) material, absorption spectra have been collected in the UV-visible as well as in the NIR to MIR regions (Fig. S5† in the ESI). For 100 nm N-Ta\(_2\)O\(_5\) layers. Note that to obtain better signals of absorption spectra in a large range of wavelengths (200 nm to 22 \( \mu \)m), 100 nm N-Ta\(_2\)O\(_5\) layers were grown on different substrates. For the visible region, a 100 nm N-Ta\(_2\)O\(_5\) layer was grown on a sapphire substrate, and for the infrared region this material was grown on a silicon substrate. The observation (Fig. S5†) is similar with previous reports in the literature. The band gap of the N-Ta\(_2\)O\(_5\) material becomes narrower (Fig. S5b†), and the infrared absorption spectrum (Fig. S5a†) shows a strong absorption in the infrared region with the maximum around 1 eV, and a long tail extending to the MIR region. The broad band of defect levels near the valence band of N-Ta\(_2\)O\(_5\) is supported by calculations of the density-functional theory (DFT), Several peaks at the long wavelength come from vibrational modes in the material (they are not electronic transitions), indicating the formation of the Ta\(_2\)O\(_5\) material (Fig. S5, ESI†).
The effect of light illumination on the graphene-Ta$_2$O$_5$ heterostructure photodetector with the gap between drain and source contacts (or the length), $L$, of 30 μm, and the width of the active area, $W$, of 30 μm ($W/L = 1$) is shown in the Fig. 1. Specifically, we have observed the drain–source current, $I_{DS}$, with and without illumination of a laser diode operating at 940 nm as a function of the back-gate voltage, $V_{BG}$. The power of the pump laser was varied from 300 fW to 7.5 nW. Fig. 1b shows transfer characteristic ($I$–$V$) curves of the device for the drain–source bias voltage, $V_{DS}$, of 0.5 V. A shift of the charge neutrality point (CNP) voltage ($V_{Dirac}$) of the transfer characteristic curves toward positive of the back-gate voltage, $V_{BG}$, has been observed with increasing illumination power. The photocurrent increases linearly with light intensity, and grows slowly at high illumination power. The photo-responsivity shows a constant value at low illumination power and reduces at high excitation power. The solid curves are the best fit to the data using the function in eqn (1).

By subtracting the dark-current from the illumination-current, we can determine the net photocurrent ($I_{ph} = I_{illumination} - I_{dark}$) of the device. The photocurrent curves under different illumination powers are plotted in Fig. 1c. A net photocurrent of $\sim$100 μA has been observed at $V_{BG} = 7$ V and $V_{DS} = 0.5$ V. The photocurrent curves demonstrate that the magnitude of the photocurrent increases with illumination power.

To gain insight into the characteristics of the graphene-Ta$_2$O$_5$ heterostructure, we carried out the power dependence of the photocurrent as a function of back-gate voltage. The power dependence of photocurrent at $V_{BG}$ = 7.0 V for three values of the drain–source bias voltage, $V_{DS}$, of 0.1, 0.5 V, and 1 V. The photocurrent increases linearly with light intensity, and grows slowly at high illumination power.

The photo-responsivity shows a constant value at low illumination power and reduces at high excitation power. The solid curves are the best fit to the data using the function in eqn (1).
the photocurrent (Fig. 1d) as well as determined the photo-
responsivity (Fig. 1e), $R_{ph} = I_{ph}/P$, of the photodetector under the
940 nm illumination, at $V_{BG} = 7.0$ V for three values of the
drain–source voltage, $V_{DS}$, of 0.1, 0.5, and 1 V. Under low illu-
mination power of 300 nW, the device shows a photo-responsi-
vity of $1.25 \times 10^5$ A W$^{-1}$, suggesting that graphene and Ta$_2$O$_5$
layers efficiently convert photon energy into a large electrical
current. The power dependence of the positive and negative photocurrent shows a similar behavior. The photocurrent increases linearly with illumination power from 300 nW to $\sim 2$
nW (almost four orders of magnitude) and grows slowly at high illumination power. In an equivalent way, the photo-
responsivity shows a constant value at low illumination power
and reduces after that (Fig. 1e). The photo-responsivity reduces from $1.25 \times 10^5$ to $5.85 \times 10^4$ A W$^{-1}$ when the exci-
tation power is higher than 2 nW. At low illumination power,
ionized acceptors in the N-Ta$_2$O$_5$ layer are well separated from
photon-generated holes, thus a high gain from the photogating
effect has been obtained. As we increase the illumination
power, a higher concentration of carriers (electrons and holes)
is introduced. Ionized acceptor centers (negative charges) can
be recombined with holes in the picosecond time-scale. These
holes will not take part in the charge transfer process,
and thus, the photo-responsivity reduces as well as the average
time of ionized acceptors is shortened at high illumination
power.

The photo-responsivity of photodetectors strongly depends
on the carrier dynamics. The carrier lifetime can be expressed
as a function of illumination power, $\tau_{carrier} = \frac{T_0}{1 + (P/P_0)^m}$, $T_0$ is the lifetime of trapped-charge carriers at low illumination
power ($P \rightarrow 0$), $P_0$ is the illumination power in which acceptor
centers are fully ionized, and $m$ is a phenomenological fitting
parameter ($m \approx 1$). Due to the high mobility of carriers in gra-
phene, holes will recirculate between drain and source elec-
trodes many times during the long lifetime of the ionized ac-
cceptors, resulting in a high photo-responsivity or a high gain.
The photocurrent can be defined as $I_{ph} = \alpha q N_{ph} \tau_{carrier} (L/V)$, where
$q$ is the elementary charge, $\alpha$ is the carrier transfer efficiency
from the N-Ta$_2$O$_5$ thin film to graphene, $\eta$ is the internal
quantum efficiency of the carrier photo-generation in the
N-Ta$_2$O$_5$ thin film layer, $N_{ph}$ is the number of photons
absorbed per unit time, and $V = \mu V_{DS} \lambda^{-1}$ is the carrier drift
velocity. For a device with $L = 30$ μm, $V_{DS} = 1.0$ V, and the carrier mobility, $\mu$, of $\sim 4850$ cm$^2$ V$^{-1}$ s$^{-1}$, the average
carrier transit time in the graphene channel, $T_t = (L/V)/2 = \mu^{-1} V_{DS}^{-1}$,$^1/2$, is estimated to be $\sim 0.93$ ns. The gain of this hybrid structure
can be determined, thusly:$^9,42$

$$G = \frac{N_{hole}}{N_{ph}} = \frac{I_{ph}/q}{P/h\nu} = R_{ph} \frac{h\nu}{q} = \alpha \left(\frac{T_0}{\tau_{carrier}}\right) \frac{1}{1 + (P/P_0)^m}.$$  

(1)

where $h\nu$ is the photon energy. The first term of eqn (1) is the expression for the gain, which is defined as the ratio of the
trapped-charge carrier lifetime at low illumination power to
the carrier transit time, and the second term regards for the
full ionization of acceptor centers at high illumination power.

The long lifetime of ionized acceptors combined with the fast
carrier transit time results in a high photo-responsivity $R_{ph} = 1.25 \times 10^5$ A W$^{-1}$ (or a gain of $1.65 \times 10^5$). The decrease of the gain at high illumination power is an indication of full ioniza-
tion. The solid lines are fitting curves to experimental data
with $P_0 = \sim 2.1$ nW and $m \sim 1.15$.

To examine the MIR response, experiments were conducted
with a CO$_2$ laser ($\lambda = 10.6$ μm, $V_{DS} = 0.5$ V, $V_{BG} = 7$ V). The photocurrent as a function of illumination power is shown in
Fig. 1f. A linear behavior of the photocurrent with the illumina-
tion power has been observed. From the results, the photo-
responsivity in the MIR region of 7.2 A W$^{-1}$ has been obtained.
In addition, the photocurrent shows a linear dependence on the
drain–source bias voltage, $V_{DS}$ (Fig. 1b, inset), suggesting that higher photo-responsivity can be readily obtained by
applying a higher bias voltage. As can be seen from Fig. 1d and e), with $V_{BG} = 7.0$ V, the photo-responsivity of the device at
$V_{DS} = 1.0$ V is higher than those from a lower voltage between
drain and source.

The photo-responsivity depends strongly on physical para-
eters of the devices. Specifically, the photo-responsivity
depends on the geometrical parameters including the length,
$L$, and the width, $W$, of the active area. A simple electrical
circuit has been developed for the graphene photodetectors:$^{43}$

$$I_{ph} = I_{illumination} - I_{dark} = \frac{V_{DS}}{R_0 + R_{illu}} - \frac{V_{DS}}{R_0 + R_D},$$  

(2)

where $R_0$, $R_{illu}$ and $R_D$ are the contact resistance, the resistance of the active area with and without light illumination, respect-
ively. The sheet resistance of the active area under the dark
condition can be calculated as:

$$R_D = \frac{L}{W} \frac{\eta \mu}{n},$$  

(3)

where $n$ is the carrier concentration in the graphene-Ta$_2$O$_5$
layer. Inset in Fig. 2a shows the dark current at the CNP (the minimum current of transfer characteristic curves) as a func-
tion of length, $L$, for $W/L = 2$. With $V_{DS} = 0.5$ V, the total resistance
under the dark condition, $R_{DS}$, is $\sim 2.7$ kΩ. The dark resistance
value is close with other reports.$^6,9,14$ When the device is
illuminated, a number of carriers are generated from the
N-Ta$_2$O$_5$ light-absorbing layer and transferred to electrodes. $\Delta n$
is the carrier concentration variation in the active area of the
device. The photocurrent for low illumination power is solved as:$^{43}$

$$I_{ph} = \frac{V_{DS}}{R_0 + \frac{W/L}{(n + \Delta n)\mu}} - \frac{V_{DS}}{R_0 + \frac{W/L}{n\mu}} + \frac{V_{DS}\Delta n\mu}{(R_0\eta\mu(W/L) + 1)^2(W/L)}.$$  

(4)

Fixing the ratio of the width and the length ($W/L$), the
photocurrent, $I_{ph}$, is proportional to the carrier concentration
variation, $\Delta n$. Thus, to increase the photo-responsivity of the
detector, reducing the active area will enhance the carrier con-
centration variation, $\Delta n$. Fig. 2a shows that for a fixed ratio of
For the best performance, optimal parameters are $W/W = 2$ and different lengths, $L$, as a function of illumination power. The solid curves are the best fit to the data using the function in eqn (1). Inset: The dark current at the charge neutrality point as a function of length, $L$. The dark current increases significantly when the length becomes shorter. (b) The measured photo-responsivity for $L = 10 \, \mu m$ with different ratios $W/L$ as a function of illumination power. Inset: The dark current at the charge neutrality point as a function of the ratio of $W/L$.

The thickness of the $N$-$Ta_2O_5$ layer plays an important factor for the performance of the grapheme-$Ta_2O_5$ devices. The photo-responsivity increases when the thickness of the $N$-$Ta_2O_5$ layer, $t$, increases from $5 \, nm$ to $10 \, nm$ (Fig. 3a), and then the photo-responsivity is lower when the thickness of the $N$-$Ta_2O_5$ layer is thicker ($t = 40 \, nm$). The effect of the thickness on the photo-responsivity can be attributed to the trade-off between the light absorption and the charge transfer efficiency. When we increase the thickness of the $N$-$Ta_2O_5$ layer, a high number of optical centers have been obtained, resulting in a higher photo-responsivity. However, as the thicknessness of the $N$-$Ta_2O_5$ layer is larger than the charge carrier diffusion length, the charge transfer to graphene is inefficient. Thus, the photo-responsivity for a device with the thickness of the $N$-$Ta_2O_5$ layer of $40 \, nm$ reduces. Furthermore, to have a thinner $N$-$Ta_2O_5$ layer, the graphene channel might degrade during a longer time of the growing process, and thus reducing the performance of the photodetectors.

To characterize the broadband photo-response of the devices, photo-responsivity as a function of illuminated photon energy was measured. The photo-responsivity shows a broadband spectrum from the MIR to deep-UV region (Fig. 3c). Specifically, the photo-responsivity at the MIR region ($10.6 \, \mu m$ or $0.12 \, eV$) is $7.2 \, A \, W^{-1}$, and is significantly sensitive in the range from the NLR ($1.53 \, \mu m$ or $0.81 \, eV$) to the deep-UV ($200 \, nm$ or $6.2 \, eV$) region on the order of $10^6 \, A \, W^{-1}$. The light sources used here include a monochromatic light extracted from a broadband deuterium/tungsten lamp ($0.19$–$2.6 \, \mu m$), laser diodes operating at $532$ and $940 \, nm$, a fiber laser lasing at $1.53 \, \mu m$, a quantum cascade laser lasing at $4.55 \, \mu m$, and a CO$_2$ laser operating at $10.6 \, \mu m$. The light source is expanded to a large beam and a pinhole has been used to obtain the photon flux. The spectral photo-responsivity of the device con-
taining a 10 nm N-Ta$_2$O$_5$ layer on graphene shows an onset at \( \sim 1 \) eV. As mentioned above, nitrogen doping in Ta$_2$O$_5$ contributes to the optical absorption of the material by two ways including increasing the number of defect states and producing energy levels above the valence band originated from the N 2p orbital. Photons with energy higher than the acceptor energy ionize the acceptor centers, resulting in hole generation. Holes transfer rapidly from the N-Ta$_2$O$_5$ layer into graphene channel, leaving behind negative charges (ionized acceptor centers). Furthermore, the N-Ta$_2$O$_5$ thin layer has an amorphous phase, the N 2p states create a broad band with the maximum of photon-ionization cross section at \( \sim 1 \) eV above the VB. The spectral photo-responsivity from the graphene-Ta$_2$O$_5$ heterostructure showed a maximum at \( \sim 1 \) eV and a long tail extending to the MIR region (Fig. 3c). Fig. 3d demonstrates a schematic diagram of energy band structures of graphene and N-Ta$_2$O$_5$ layers, and the tendency of charge transfer between layers. The blue dots present for the ionized acceptor centers, while hollow dots stand for holes.

To define the impact of a photodetector on the performance and speed, the rise time has been characterized. Rise time was measured using a low-noise current amplifier (DLPCA-200, FEMTO), and an oscilloscope to monitor the temporal dynamics of the photocurrent under different illumination power. To obtain the ultra-fast response, an acousto-optic modulators (AOM) using a TeO$_2$ crystal produced ultrafast laser pulses from a continuous-wave laser with the rise time of 20 ns. This is the limitation of our transient setup. The photo-

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**Fig. 3** Spectral sensitivity and detectivity of graphene-Ta$_2$O$_5$ heterostructure devices \((W \times L = 20 \times 10 \, \mu m^2)\). (a) The measured photo-responsivity of three devices with different thicknesses of the N-Ta$_2$O$_5$ layer under 940 nm excitation wavelength. (b) Power spectral density of 1/f noise in the dark for two devices of graphene-Ta$_2$O$_5$ heterostructure, and graphene only. The dashed line has the slope \(-1\) and shows “pure” 1/f noise. (c) Photo-responsivity of the device as a function of excitation photo-wavelength from 200 nm to 10.6 \( \mu m \) (or from 0.12 to 6.2 eV) under \( V_{DS} = 0.5 \) V and \( V_{BG} = 7 \) V. The blue diamonds are experimental data, and the orange line is a guide to the eye. Inset: Spectral dependence of the NEP and specific detectivity \((D^*)\) of the photodetector device at room temperature. (d) Schematic diagram of energy band structures of graphene and N-Ta$_2$O$_5$ together with the tendency of charge transfer between layers. The blue dots present for the ionized acceptor centers, while hollow dots stand for holes.
current appears periodically (Fig. 4a, inset) with the pulse duration of 6.3 μs under the 940 nm laser illumination, $V_{DS} = 0.5$ V, and $V_{BG} = -7$ V at room temperature. The temporal dynamics of the positive and negative photocurrent displays the same behavior. For the device with an active area of $W \times L = 20 \times 10 \, \mu m^2$, the rise time is estimated to be $\sim 125$ ns (from 10 to 90% of the peak photocurrent), while the recovery time is 41 μs (from 90 to 10% of the peak photocurrent). The signal in Fig. 4a shows an ultrafast rise time. The increasing of photocurrent with the illumination time can be fitted to an exponential function:

$$I_{ph} = I_0 - I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2),$$

in which $\tau_1 \sim 20$ ns, and $\tau_2$ is 325 ns. The short rise time, $\tau_1$, represents a fast transit time of holes to electrodes, whereas the longer time constant, $\tau_2$, corresponds to the hole transfer time from an acceptor center to graphene. Similarly, the decreasing of photocurrent with time when the light is turned off can be fitted to an exponential function:

$$I_{ph} = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$$

with two decay time constants, $\tau_3 = 500$ ns, and $\tau_4 = 45$ μs. The short decay time constant, $\tau_3$, can be attributed to the time for charge carriers transferring back to the N-Ta$_2$O$_5$ layer because it is similar to $\tau_2$. The slowest time $\tau_4$ may represent the lifetime of ionized acceptor centers. Using the e-beam evaporation to make the N-Ta$_2$O$_5$ light-absorbing layer, fast dynamics including the response and the recovery time of the photocurrent have been obtained. These values are orders of magnitude faster than those from previous reports.7,9–11,14,16 Extra reset gate-voltage pulses may be required for fast switching performance (faster than 45 μs) of these devices. Nevertheless, the speed reported here is more than sufficient for many imaging applications.

The rise time of the devices in the MIR is slower compared with those from the visible to NIR region (Fig. 4b). The rise time at 10.6 μm shows two components. The fast component is faster than 1 ms (limitation of the test system), and the longer component is 300 ms. The photo-responsivity of the devices strongly depends on the concentration of the acceptor centers. In the N-Ta$_2$O$_5$ thin layer, a broad band of defects is created with the maximum absorption at $\sim 0.9$ eV above the VB, and a long tail extending to the MIR region (Fig. S5, ESI†). The density of states of defects in the MIR region is lower than that in the NIR region. Thus, the electronic transport turns from a band-like regime at high carrier concentration in the NIR region to a hopping regime at low carrier concentration in the MIR region. As a result, the photo-responsivity at low acceptor density is slower in the MIR region, which is consistent with previous studies.45,46

To evaluate the capability of weak light detection of a photodetector, two key metrics including the specific detectivity ($D^*$) and the noise equivalent power (NEP) have been examined by considering the $1/f$ noise, shot noise, and thermal noise. The power spectral density of $1/f$ noise in the dark of the graphene-Ta$_2$O$_5$ heterostructure structure and graphene only is shown in Fig. 3b. The noise-power spectral density exhibits the $1/f$ behavior. The noise-power spectral density of the graphene-Ta$_2$O$_5$ heterostructure with an Al$_2$O$_3$ layer covered the entire surface is reduced by almost two orders of magnitude when compared to a device with only graphene (Fig. 3b). The improvement of the device is originated from the top Al$_2$O$_3$ layer which protects graphene as well as the N-Ta$_2$O$_5$ absorbing layer from moisture and other contaminations.47

A similar structure with an encapsulated Al$_2$O$_3$ layer in the literature also presented a significant improvement of the $1/f$ noise.48 A detail of the calculations for these noises is presented in the ESI† The frequency-dependence of the noise current for the photodetector at room temperature

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**Fig. 4** Photocurrent response of graphene-Ta$_2$O$_5$ photodetector ($W \times L = 20 \times 10 \, \mu m^2$) to on/off illumination. (a) The transient photo-response of the device for an illumination at wavelength of 940 nm under $V_{DS} = 0.5$ V and $V_{BG} = -7$ V. The photocurrent response shows fast response and recovery time. The red curves are the best fitting to the data with a bi-exponential function (left panel), and bi-exponential decay function (right panel). (b) The photocurrent response of the device for different illumination at wavelength of 1.53 μm (top panel), and at wavelength of 10.6 μm (bottom panel).
was measured under $V_{DS} = 0.5$ V and $V_{BG} = 7$ V at the modulation frequency of 1 Hz. The NEP values
\(\text{NEP} = \sqrt{S_{I}(1/f) + S_{I}(\text{shot}) + S_{I}(\text{thermal})/R}\) are achieved as low as $7.9 \times 10^{-16}$ and $2.2 \times 10^{-10}$ (W Hz$^{-1/2}$) in the UV-to-NIR region and the MIR region, respectively (Fig. 3c, inset). This yields specific detectivity values, $D^* = \sqrt{S_{I}/\text{NEP}}$, ($S_I$ is the area of the detector) in the order of $2.2 \times 10^{12}$ and $0.8 \times 10^{7}$ (Jones) for the UV-to-NIR and MIR regions, respectively (Fig. 3c, inset). The small values of NEP, or large values of $D^*$ indicate that graphene-Ta$_2$O$_5$ heterostructure photodetectors can be well used for weak light detection from deep-UV to MIR region.

Photo-responsivity and rise time for photodetectors based on 2D materials including graphene, black AsP, PtSe$_2$, black phosphorous are shown in Fig. 5. It is clear that the photo-responsivity of the graphene-Ta$_2$O$_5$ heterostructure is similar to the graphene-CQD photodetectors, but the rise time is orders of magnitude faster than other photodetectors based on 2D-materials.

Experimental section

Photodetector fabrication

The graphene-Ta$_2$O$_5$ heterostructure photodetectors were fabricated on a p-doped Si wafer (1–10 $\Omega$ cm). The surface of the Si wafer was covered by a 300 nm silicon dioxide and patterned with alignment marks. A metal back-gate directly contacting to the Si substrate was designed using photolithography, then a HF buffer etching solution was used to remove the SiO$_2$ area. Metal films of 10 nm Cr and 100 nm Au were deposited using e-beam evaporation. Metal source and drain contacts (Cr/Au with 10/100 nm thickness) for transport measurements were deposited directly onto the wafer by photolithography to form a field effect transistor.

The chemical vapor deposition (CVD) monolayer graphene film on a copper foil from Graphenea Inc. was transferred onto the Si/SiO$_2$ substrate. The CVD graphene on the Cu foil was spin-coated by poly-(methyl-methacrylate) (PMMA) solution. The Cu foil was removed by using 0.3 M ammonium persulfate solution for 2 hours. Graphene was rinsed with high purity deionized water and transferred onto the Si/SiO$_2$ wafer with metal contacts. The samples were stored in vacuum for 12 hours to ensure good adhesion. The sample was baked at 120 °C for 15 minutes, then the PMMA was cleaned with acetone for 1 hour. Photolithography and oxygen plasma etching were employed to fabricate graphene patterns between metal contacts. This process eliminates photoresist residue that cannot be removed completely during the lift-off steps. Next, a 10 nm N-Ta$_2$O$_5$ layer was deposited on the top of the CVD graphene by e-beam thermal evaporation with a rate of 0.1 Å per second. The device was covered with a 30 nm...
Al₂O₃ film using the atomic layer deposition method at 300 °C. The N-Ta₂O₅ and Al₂O₃ layers cover the entire surface, and photolithography was used to redefine source, drain, and back-gate contacts. These layers were then removed by SF₆ plasma dry-etching.

A schematic diagram of the graphene-Ta₂O₅ heterostructure photodetector is shown in Fig. 1a. The length, L, and width, W, of the active area have been varied. AFM and SEM images of our graphene-Ta₂O₅ heterostructure are shown in Fig. S1 and S3.†

### Photodetector characterization

The electrical and optical characteristics were examined by two Keithley 2400 source-meter units. The first unit, a Keithley 2400, is used to control the back-gate voltage, $V_{BG}$. The second unit, a Keithley 2450, is used to set a constant voltage between drain and source, $V_{DS}$, and to measure the drain current, $I_{DS}$. The electrical signal also is analyzed by a lock-in amplifier (SR830). Several light sources have been employed in the experiments. In the UV-to-NIR region, laser diodes operating at 190 nm to 2.6 μm (Edmund, deuterium/tungsten lamp, #87-300), and a fiber laser lasing at 1.53 μm have been used. A set of Edmunds bandpass filters with a narrow bandwidth is employed to select desired wavelengths from 200 nm to 1600 nm. For MIR experiments, a CO₂ laser operating at 10.6 μm and a quantum cascade laser lasing at 4.35 μm are used.

To obtain a low and precise power of the light sources on devices, a beam expander and a number of optical elements have been used (Fig. S7†). The beam expander increases the diameter of a collimated beam. A diaphragm with a 5 mm diameter is used to form uniformly the intensity distribution of the light source. The uniform intensity distribution has been verified using a photodetector with a 10 μm pinhole entrance on a two-dimensional stage. A half-wave plate and a polarizing beam-splitter are used to control the power of laser beams. To control the power of incoherent light sources, a number of neutral density filters have been employed. The light sources cover the entire graphene FET photodetector. By knowing the active size as well as photon flux, the power of the light incident upon the graphene-Ta₂O₅ heterostructure photodetectors can be estimated. We have checked polarization properties of the photodetectors by rotating the device. No polarization effect has been observed in the photodetectors. In addition to these experiments, the low-frequency noise spectra were acquired by a single-channel 100 kHz FFT spectrum analyzer (SR770).

### Conclusions

In summary, we have fabricated and demonstrated graphene-Ta₂O₅ heterostructure photodetectors with improved photoresponsivity and ultrafast response speed. The structure extends the photo-detection of graphene hybrid phototransistors from the UV-visible region into the MIR region. The current work has established the development of high-performance optoelectronic devices based on two-dimensional heterostructure, demonstrating for the first time the added value provided by merging of these two important materials – graphene for optoelectronic and Ta₂O₅ for microelectronics, photonics and solar energy applications.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

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