High-performance graphene-quantum-dot photodetectors

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Graphene quantum dots (GQDs) have received much attention due to their novel phenomena of charge transport and light absorption/emission. The optical transitions are known to be available up to \( \leq 2.8 \text{ eV} \) at full bandgap, \( \leq 1.4 \text{ eV} \) at half bandgap, and terahertz energies, which can make GQDs a particularly promising material for high gain photodetection in a broad wavelength range. Blue-luminescent GQDs in water have been shown to exhibit absorption spectra peaked at energies up to \( \leq 2.8 \text{ eV} \), especially useful for ultraviolet (UV) photodetectors (PDs).

PDs in optoelectronic integrated circuits (OEICs) usually have p-n or p-i-n junction diode structures or bipolar transistor structures fabricated using standard complementary metal oxide semiconductor (CMOS) technology, which requires many device-processing steps, thereby increasing the fabrication complexity and cost. The development of a simple PD structure is therefore highly desired not only for single-function PDs, but also for integrated PDs. Si is a good material as PDs for the visible and near infrared (VIS-NIR) wavelength range, but not useful for UV detection. Wide-bandgap compound semiconductors are currently used for UV detection, but require fabrication processes not compatible with Si technology. Compound-semiconductor quantum-dot PDs have recently emerged as top-surface detectors offering integration with circuit technologies due to the low cost and high sensitivity/tunability in the VIS and infrared regions, but their performance is limited by the relatively poor carrier mobility (\( \leq 10^{-2} \text{ cm}^2/\text{Vs} \)). Graphene, on the contrary, exhibits very high mobility reaching \( \leq 60,000 \text{ cm}^2/\text{Vs} \) on a BN substrate, and is a very thin, flexible, and durable material, suitable for transparent and foldable devices.

Previous studies have shown that photocurrent (PC) is generated in a graphene sheet near metallic contacts or at a graphene single-/bi-layer interface. The PC response was attributed to the presence of potential steps that act as transport barriers at the metal contacts and could be modulated by sweeping gate voltages. On the other hand, atomically thin heterostructures of two-dimensional semiconductors/graphene have presented strong light-matter interactions that can lead to large photon absorption and PC production. However, from all these studies, the magnitudes of PCs in graphene sheet were shown to be typically very weak compared to those in conventional semiconductor PDs. It is clear that if GQDs can be used as a PD material in a broad wavelength range including UV, it will not only significantly increase the capability of the current Si VIS-NIR PDs, but also...
add new functionalities to the OEICs. Here, we report a very simple GQD-based structure that works as a PD showing strong PC responsivity in the UV-VIS-NIR range. The structure is based on multiple layers of GQDs sandwiched between single-layer graphene sheets. The PD structures permit large PC flow by tunneling of charge carriers through the energy states in GQDs.

Results

Dark and photo I-V characteristics. Figure 1a shows a schematic diagram of a typical graphene/GQDs/graphene PD (see Supplementary Fig. S1 for the preparation details), composed of slightly p-type single-layer graphene sheets (Supplementary Figs. S2 and S3) and multiple layers of GQDs with a total thickness of ~45 nm, randomly distributed between the graphene sheets (Supplementary Fig. S4). The GQDs used in this sandwich device are estimated to be ~17 nm in average size and produce a photoluminescence (PL) spectrum similar to that of GQDs in DI water, as characterized in our previous work[13], whilst a control sample, the graphene/graphene sandwich structure and almost no structural alterations of GQDs occur with respect to the Ag electrode on lower graphene layer/dark current during the GQD PD fabrication.

The transport of electrons at the GQD layer may be induced by the thermionic emission above the barrier and the direct tunneling through the barrier. However, at low temperatures, we expect that the thermionic emission is very small and tunneling processes can dominate the transport. As an indication of the tunneling behavior[14], the local minimum of current arises at a point minimizing the available DOS when the measurement temperature (T) is lowered below ~200 K (Supplementary Fig. S7), possibly resulting from the reduced thermionic emission at lower T. The thermionic emission starts to be dominant above a threshold voltage that depends on T (~2.7 V at 78 K, ~1.7 V at 100 K, ~1.4 V at 150 K, and no tunneling behaviors are observed at temperatures ≥ 200 K). Such current minimum was not observed in the control sample (Supplementary Fig. S8). Since the tunneling process is seen at T ≥ 150 K, we estimate that the potential barrier between bottom graphene and GQD is ~2.2 V and that the barrier between top graphene and GQD is ~1.4 V (Supplementary Fig. S7), resulting in the asymmetric DC I-V characteristics of the device (Fig. 2a and Supplementary
Fig. 2d shows $R_i$ as a function of bias voltage at various T’s when for $V_{DC}$ (Supplementary Figs. S10 and S11). Fig. 2c shows responsivity the PC to DC ratio is strongly enhanced due to the sharp reduction of on/off ratio shows maximum intensities at bias voltages of around 1.6 depends on the photon wavelength. The ratio of PC to DC or the Photosensitivity and detectivity.

Almost not varied by using Au as electrode (Supplementary Fig. S9). I-V characteristics under dark as well as under illumination were hence, the tunneling current is not affected by the barriers. These observed slight enhancement of the total current under illumination can be understood from the carrier multiplication. At high voltages the total I-V curves become more symmetric, almost irrespective of incident light wavelength, as shown in Fig. 2a, because the kinetic energy of carriers exceed the potential barriers on both sides and hence, the tunneling current is not affected by the barriers. These I-V characteristics under dark as well as under illumination were almost not varied by using Au as electrode (Supplementary Fig. S9).

**Photosensitivity and detectivity.** The photoreponse strongly depends on the photon wavelength. The ratio of PC to DC or the on/off ratio shows maximum intensities at bias voltages of around 1.6 ∼ 2.1 V for various wavelengths ($\lambda$), as shown in Fig. 2b. At lower T, the PC to DC ratio is strongly enhanced due to the sharp reduction of DC (Supplementary Figs. S10 and S11). Fig. 2c shows responsivity (the electrical current response to the incident optical power, $R_\beta$), measured as a function of bias voltage for various $\lambda$. There are no big variations in $R_\beta$ from ∼2.5 to ∼5.5 V, irrespective of $\lambda$. $R_\beta$ at $\lambda$ ∼ 800 nm reaches ∼0.5 AW$^{-1}$ at 5.5 V. At 400 nm, $R_\beta$ is reduced to ∼0.2 AW$^{-1}$ because less light was absorbed by the device. These $R_\beta$ values are comparable to those reported for commercial Si and InGaAs PDs (∼0.5 and ∼0.9 A/W (4.2 K), respectively) [25,26]. Considerable values of $R_\beta$ are measured in certain ranges of $\lambda$ even for $V < 0$ due to the large absolute values of PC (Supplementary Fig. S12). Fig. 2d shows $R_\beta$ as a function of bias voltage at various T’s when the PC is excited at $\lambda = 532$ nm. The $R_\beta$ shows a big increase at T ∼ 200 K, especially when the bias voltage increases above ∼8 V. The DC gradually increases with increasing bias voltage at each temperature and converges to almost an identical value at 10 V, irrespective of temperature (Supplementary Fig. S7a). In contrast, the total current ($DC + PC$) under illumination almost saturates up to ∼8 V, but above ∼8 V it increases more rapidly than the DC does (Supplementary Fig. S10), resulting in such a big increase of $R_\beta$ (proportional to PC) above 8 V at low temperatures. Higher bias voltage will enhance the collection of the photoexcited carriers, thereby increasing PC.

Fig. 3 shows the spectral responsivity for voltages from 1 to 5 V. There are small variations in the spectral $R_\beta$ above 2 V. The quantum efficiency (QE) also gradually increases with increasing the bias above 2 V and is almost spectrally uniform with no clear peak in the visible range from 400 to 800 nm, as shown in Fig. 3b. By considering the spectral $R_\beta$ in Fig. 3a, it is noted that a strong enhancement is especially reflected in high-energy side of the QE, consistent with the fact that the absorption of the GQDs is strongly enhanced at high energies [4,12]. The QE reaches around 80% in the visible range under a bias of 5 V, which will be explained later in detail based on the transient PC data.

A key figure of merit of a PD is the noise equivalent power (NEP). This parameter is defined as the amount of incident light power that generates a PC equal to the noise current. NEP can be expressed as [ref. 34]: $NEP = \left(\frac{I_n^2}{\Delta f}\right)^{1/2} R_\beta$ where $I_n^2$ is the time-averaged square of the total noise current and can be estimated by integrating spectral density of noise power (Supplementary Fig. S13a). Then, NEP can be calculated by using the spectral $R_\beta$ data in Fig. 3a (Supplementary Fig. S13b). Another parameter used to characterize the performance of PDs is the detectivity ($D^*$), which is related to NEP by the expression: $D^* = (A\Delta f)^{1/2}/NEP$. Here, $A$ is the effective area (∼0.5 × 0.5 cm$^2$) of the detector in cm$^2$ and $\Delta f$ is the electrical bandwidth in Hz. With increasing the bias above 2 V, the $D^*$ decreases over almost full range of $\lambda$, as shown in Fig. 3c. The maximum $D^*$ at 2 V is closely related to the largest on/off ratio at 1.6 ∼ 2.1 V, as shown in Fig. 2b. The $D^*$ at 2 V remains high both in the VIS (1.1 × 10$^4$ cm Hz$^{0.5}$ W$^{-1}$ or Jones at 400 nm) and NIR (2.4 × 10$^4$ Jones at 900 nm) ranges due to its
Linearity and time response. The JPC increases with increasing the bias voltage. The JPC in the linear region quite-good spectral flatness. These values are comparable to those of imaging application of PDs. The LDR is expressed as 60 dB in imaging), in other words, more than 60 dB to about three orders of magnitude in intensity (conventionally the linear photo-generation of electron-hole pairs. However, at high powers the built-in electric field can be lowered due to a large accumulation of photogenerated carriers at the GQDs/graphene interfaces, which can easily expect $\tau_1$ and $\tau_2$ to be larger than the decay time in pristine graphene. These behaviors do not seem to be relevant to the RC time constant of the device, measured to be an order of ns (Supplementary Fig. S17b). From the C-V curve, the built-in potential between graphene and GQD is estimated to be ~1.3 V (Supplementary Fig. S17c), which is very close to the potential barrier (~1.4 V) obtained from the low-T dark I-V curves (Supplementary Fig. S7), as shown as above, the peak voltage (1.6 ~ 2.1 V) for the largest PC/DC ratio (Fig. 2b), and the threshold voltage (1 ~ 2 V) for inducing the PC decay with two characteristic times (Fig. 4d).

Discussion

It should be noted that the measured QEs are the effective ones, i.e., $\eta_{\text{eff}} = \eta G$, where $\eta$ and $G$ are the quantum efficiency and the internal gain of the device, respectively. Extremely-high gain is expected in the GQD PD devices because the gain is given by the ratio of the carrier lifetime (t) to the transient time ($\tau_0$) across the electrodes, $G \sim t/\tau_0$, and from the transient PC the lifetime of electron-hole pair is estimated to be several tens of $\mu$s ($t \sim (\tau_1 + \tau_2)$). Within several tens of ns ($\tau_0$) upon a light pulse, the electrons and holes are produced in GQDs and transit to the graphene sheets. Thus, the current gain in the PD can reach an order of $10^4$, resulting in effective QEs almost over 80% in the PD devices, as shown in Fig. 3b.

The achievement of the high-performance GQD PDs in this work suggests that GQDs can be employed in various kinds of transparent and foldable optoelectronic devices and will open exciting opportunities not only for the creation of single-function PDs in detecting optical signals in wide spectral range but also for the fabrication of a key component in high-resolution PD arrays for biomedical imaging, remote sensing, optical communication, and OEICs.

Methods

Preparation of GQDs. GQDs were fabricated by following processes. Graphene oxide (GO) sheets were obtained from natural graphite powder by a modified Hummers method. The GO sheets were subsequently dedeoxygenized in a tube furnace at 250 °C for 2 h under Ar ambient to prepare reduced graphene oxide powder, 0.05 g of which were then oxidized in concentrated 10-mL H2SO4 and 30-mL HNO3 for 20 h under mild ultrasonication. The mixture was then diluted with 250-mL.
deionized (DI) water and filtered through a 0.02-μm nanoporous membrane to remove the acids. The size-reduced/purified 0.2-g GO powder was re-dispersed in 40-ml DI water and the pH was tuned to 8 with NaOH. The suspension was transferred to a nitrogen-ambient furnace and heated at 230°C for 10 h. After cooling to room temperature, the resulting powder was re-dispersed in 40-ml DI water for 2 h under ultrasonication. Then, by filtering the resulting suspension through a 0.2-μm nanoporous membrane, a brown filter solution was separated. Since the colloidal solution contained large graphene nanoribbons, under weak blue fluorescence, it was further dialyzed in a dialysis bag of 3500 Da molecular weight overnight, thereby producing strongly fluorescent GQDs. The GQDs were separated as different sizes by using 1000, 25,000, and 50,000 Da dialysis bags and a 20-nm nanoporous membrane.

Fabrication of devices. Graphene layers were grown on 70-μm-thick Cu foils (Wacopa, 99.8 purity) in a graphite-heater-based chemical-vapour-deposition quartz tube furnace at a growth temperature of 1000°C with 10-sccm H2 and 20-sccm CH4 flowing at a pressure of 3 Torr. The graphene/Cu stack was spin-coated with poly(methyl methacrylate) (PMMA) and the Cu was then etched in a 1 M ammonium persulfate for 10 h. The graphene/PMMA stack was then placed in a He laser as the excitation source. During the measurements, the PDs were mounted in a dark, electrically-shielded, and thermally-isolated box, and the light was focused onto the PD devices with a spot size of 5 μm2. A 532-nm monochromatic light from a diode laser was used for studying the spectral response of the PDs. Emitted light was collected by a lens and then was sent to a low-noise current preamplifier (Stanford Research SR570) in the frequency range of 0.1–1 MHz.

Measurements. PL spectra were measured at room temperature using the 325 nm line of a He laser as the excitation source. Emitted light was collected by a lens and analyzed using a grating monochromator and a GaAs photomultiplier (PM) tube.

Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. The topographic image and height profile of graphene were obtained in a non-contact mode of atomic force microscope (Park system, model XE-100). Raman spectroscopy with an excitation wavelength of 532 nm was used to characterize the optical properties of graphene films. The transmittance of the sample was measured by UV–VIS–NIR optical spectrometer (Agilent Model Cary 5E). I-V measurements were performed to characterize the electrical behaviors of GQDs PDs. The device was in a 5V reverse bias and measured the forward current. The current density was calculated using the equation J = I/A, where I is the current and A is the device area. The device area is calculated by multiplying the length and width. The current density was calculated by dividing the current by the device area.

The average current density of the PD was obtained by measuring the current density of at least 10 devices and averaging the results. The average and standard deviation were calculated using the equations for the mean and standard deviation.

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**Author contributions**
J.H.K. and C.W.J. deposited graphene sheets by chemical vapour deposition. S.W.H. prepared GQDs with S.S.K. J.M.K. structurally characterized GQDs. K.W.L. carried out optical measurements. S.K. fabricated GQD PDs with D.H.S. C.O.K. characterized performances of GQD PDs. E.H. contributed to the theoretical interpretation of the results. S.-H.C. initiated, supervised the work, and wrote the paper. All authors discussed the results and commented on the manuscript.

**Additional information**
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**Competing financial interests:** S.-H.C., S.K., C.O.K. and D.H.S. have a Korea patent pending (10-2013-0053894) on the GQD PD production technology, reported in this paper.

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