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Towards Single Electron Transistor-Based Photon Detection with Microplasma-Enabled Graphene Quantum Dots

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ABSTRACT

Single-electron transistors (SETs) represent a new generation of electronic devices with high charge sensitivity, high switching speed, and low power consumption. Here a simple and controlled fabrication of graphene quantum dot (GQD)-based SETs for photon detectors has been demonstrated. The plasma-synthesized GQDs exhibit stable photoluminescence and are successfully used as the Coulomb islands between heteroepitaxial spherical-gold/platinum (HS-Au/Pt) nanogap electrodes. The as-fabricated GQD-SETs enable photon detection with 410 nm excitation owing to the ability of GQDs to generate photoluminescence emission.

Keywords: Transistor; Graphene Quantum Dots; Plasmas; Synthesis; Photon Detection

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Single-electron transistors (SETs) represent a new class of electronic devices and have been attracted a lot of attention due to their exceptional properties including low power consumption, high charge sensitivity, and multigate logic operation.^{1,2,3} The SETs have been shown promising potential for quantum computing, photon detectors, and nanooptoelectronics.^{1,2,3} In principle, the high charge sensitivity of SETs originates from the change in the offset charge (Q_0) on Coulomb island. When Q_0 changes from ne to $(n \pm 1/2)e$ (e : unit charge, n : integer), the current starts to flow owing to breaking Coulomb blockade condition. Moreover, as the bias voltage between the source and drain is increased, an electron can pass through the Coulomb island. If a photon excites the SETs consisting of Coulomb island and surrounding components, the surrounding components tends be charged, leading the change in Q_0 on Coulomb island to realize the photon detection by current owing to change in Coulomb blockade condition. Therefore, the materials of the Coulomb islands play a key role on the SET properties for photon detection. Recent studies demonstrate that graphene quantum dots (GQDs), a zero-dimensional (0D) graphene-like nanomaterials with lateral dimensions typically less than 10 nm, possess superior physical and chemical properties including large surface area, high electronic mobility, tunable bandgaps, stable photoluminescence and chemical stability.^{4,5} It has been shown that GQDs can be used as the Coulomb islands within the double-barrier tunneling junction in SETs and present high potential in SET fabrication.^{6,7} In addition, GQDs can act as an active materials for photon detectors with high photocurrents based on their unique optical properties.⁸ The development of fabrication for GQD-based SETs is important for fundamental study and applications.

In this letter, we report a simple fabrication of GQD-based SETs for photon detectors. Colloidal GQDs were initially synthesized from starch in liquid phase at ambient condition using microplasmas and then used as the active materials of Coulomb island to fabricate SETs for photon detector study. Microplasmas are gas discharges confined to electrode geometries less than 1mm and can be operated stably at ambient pressure, enabling its use for liquid phase processing at ambient conditions.^{9,10} When microplasmas interact with liquid solutions, energetic species including radicals, ions and electrons formed in the microplasma can initiate non-thermal chemical or electrochemical-related reactions in the solutions¹¹, leading colloidal nanomaterials synthesis.^{12,13} Recently, we have established fabrication processes of heteroepitaxial spherical-gold/platinum (HS-Au/Pt) nanogap electrodes with 5 nm in top radii and 0.7 nm in gap separation by using electron beam lithography (EBL, Elionix, ELS-500-EX)^{14,15} and our unique electroless-Au plating (ELGP)^{16,17}. Based on HS-Au/Pt nanogap electrodes, we have demonstrated single-molecule single-electron transistor operation.¹⁸ Here, we introduce a GQD between HS-Au/Pt nanogap electrodes, and demonstrate photon detecting properties of GQD-based

SETs. The GQD-based SETs show high potential in photon detection based on their exceptional optical properties.

GQD were synthesized in aqueous solutions using a direct current (dc) microplasma electrochemical reactor operated at ambient conditions.^{13,19-21} The synthesis details can be found in the Supporting Information. In brief, 6 mL of the solution mixed with starch (0.428 g), deionized water (15 mL), and 0.1 M aqueous solution of sodium hydroxide (2.5 mL) was used as the precursor. A flow of 25 sccm argon (Ar) was introduced in a hollow stainless steel capillary (i.d. = 180 μ m) to facilitate the formation of a microplasma with a constant current of 9.6 mA, and the process time was kept at 1 h. After the plasma synthesis, the solution was purified with 10 mL of ethanol for 10 min., and then vacuum filtrated with the filter membrane (polyvinylidene difluoride (PVDF) membrane filter; pore size: 0.2 μ m, diameter: 47 mm, Pall cooperation) to remove the unreacted starch. The filtered GQD solution was diluted to a concentration of 4 mg/mL by adding ethanol and used throughout the work. The morphology of as-synthesized GQDs was analyzed by transmission electron microscopy (TEM) as shown in **Fig. 1(a)-(c)**. TEM was performed using a cold-field emission Cs-corrected TEM (JEOL, ARM-200F) with an accelerating voltage of 200 kV. TEM samples were prepared from solution dry-casting of the colloidal solution on carbon-coated copper grids (300 mesh, Ted Pella Inc.). As revealed by TEM image shown in **Fig. 1(a)**, the GQDs exhibit spherical particle-like nanostructures with averaged diameter of 3.6 nm and a narrow size distribution (size histogram is shown as **Fig. S1**). High-resolution TEM (HRTEM) images further shows the as-synthesized GQDs were highly crystalline (**Fig. 1(b)**) and with 0.21 nm graphene lattice (**Fig. 1(c)**). The photoluminescence (PL) intensity of the synthesized GQDs as a function of excitation and emission was measurement by PL spectroscopy, and the obtained PL map shows one maximum PL intensity (shown in red) with 420 and 505 nm of excitation and emission (Supporting Information **Fig. S2**), respectively, which represents a radiative recombination center and presented excitation-dependent properties. The broad range of the radiative recombination center could be attributed to various energy levels induced by surface functional groups, defects and edges states.²²

To fabricate ultrafine Pt-based nanogap electrodes, electron-beam lithography (EBL) processes were used. Electron-beam (e-beam) resist was coated on a SiO₂/Si substrate through spin coating. Ultrafine electrode patterns with various nanogap designs and for different dose exposures were obtained by using EBL apparatus. After EBL resist development, titanium (Ti) and Pt were evaporated to form 3 and 10 nm thick layers, respectively, on the SiO₂/Si substrate by e-beam deposition. After a resist liftoff process, ultrafine Pt-based nanogap electrodes were obtained.¹⁴ Then, ELGP process was

introduced to prepare HS-Au/Pt nanogap electrodes.¹⁵⁻¹⁷ In brief, for removing the organic contaminants or residual resist on Pt surface, the Pt-based nanogap electrodes were first cleaned by immersing in an acetone/ethanol mixture followed by UV-ozone cleaning. To prepare ELGP solution, Au sheet (99.99%, 65 mg) was dissolved in 3 ml of the commonly used medical iodine tincture (I_2 and KI in ethanol) with ultrasonic agitation and then, L(+)-ascorbic acid was added as a reducing agent in the Au-dissolved iodine tincture solution until saturation. Finally, ELGP on the Pt surface was conducted by simply immersing cleaned Pt electrodes or Pt-based nanogap electrodes into the ELGP solution, which was diluted 1000 times by DI water (8 ml, 18.1 M Ω). After immersion for the plating, the ELGP Pt electrodes and ELGP Pt-based nanogap electrodes were rinsed in DI water and acetone/ethanol mixture for stopping Au plating. Fabrication of GQD-based SET devices is as follows: After chip cleaning, GQD solution was dropped 5 μ L each time onto the chip via naturally dry, then repeated 10, 20 and 60 times, respectively. Afterwards, electrical measurements were performed by using a semiconductor parameter analyzer (Agilent, B1500) and a probe station with He-refrigerator (Nagase Techno-Engineering, GRAIL 10-LOGOS01S) in a vacuum (10^{-5} Pa) at 9 K.¹⁻³ The SEM image is observed as shown in **Fig. 1(d)**. It presents the clear source, drain, side-gate 1, and side-gate 2 electrodes. In the other hand, the gap separation is less than 5 nm which is corresponding to the average size of GQD (3.6 nm), suggesting that the gap separation of device is suitable for the GQD particle. First, we put 20 drops of GQD solution to prepare the devices, and to prove the devices based on GQD are with SET characteristics. There are some identifications below.

The drain current–drain voltage (I_d – V_d) characteristics of a SET with 20 drops of GQD solution with varying a gate voltage (V_g) simultaneously applied from side gate 1, side gate 2 and Si back gate from -1.5 to 1.5 V as shown in **Fig. 2(a)**. The clear Coulomb blockade can be observed, suggesting that GQD particle can act as Coulomb island between drain and source electrodes. It notes that there was no current on the HS-Au/Pt nanogap before the 20 drops. The drain current–gate voltage (I_d – V_g) characteristics with different drain voltages (V_d) from -0.1 to 0.1 V are shown in **Fig. 2(b)**. I_d can be modulated with the varying V_g apparently, regarding that GQD particle works as the effective Coulomb island for current modulation. Note that the parallelogram shape of Coulomb diamonds demonstrates GQD working as a Coulomb island. The Coulomb oscillation is more obvious with increasing V_d , which indicated the Coulomb island based on GQD also works as the gate modulation. Based on the stability diagram in **Fig. 2(c)** and differential stability diagram in **Fig. 2(d)**, they are corresponding to the Coulomb gap in I_d – V_d characteristics (**Fig. 2(a)**) and I_d – V_g characteristics (**Fig. 2(b)**).

After the exploration of SET characterization, we study the relationship between the SET

characteristics and the density of GQDs. The density increased to 60 drops and decreased to 10 drops, as shown in I_d - V_d characteristics of **Fig. 3(a) and 3(c)**, respectively. Both of the I_d - V_d characteristics show the clear Coulomb blockade. I_d - V_g characteristics of the SETs with 60 and 10 drops are shown in **Fig. 3(b) and 3(d)**, respectively, which also present the Coulomb oscillation in each case. As I_d - V_g characteristics in **Figs. 3(b) and 3(d)** are not ideal Coulomb oscillation, these SETs should have multi-GQDs between the HS-Au/Pt nanogap electrodes. Based on the results, regardless of GQD density, the devices only present the SET characteristics, suggesting that it is a simple procedure to fabricate the SET devices based on GQD. Additionally, the yield of SET devices is from 6 % to 28% as the GQD density is from 10 drops to 60 drops, respectively. Note that increasing the GQD density can improve the yield efficiently.

Afterwards, the photon detector based on GQD-based SET devices is explored. Based on our PL result (Figure S2), GQDs present the maximum emission intensity under excitation 420 nm, thus, the LED (Lumileds) source of 410 nm is utilized. In addition, we utilized lock-in amplifier (NF, 5640) to obtain the change in current under intermittent photo irradiation at 520 Hz. We study on relationship between I_d and different parameters include I_{LED} and V_d . First, I_{LED} is adjusted from 2.8 to 352 mA, and the ΔI_d ($= I_d$ (with LED source) — I_d (without LED source)) – time dependence were measured under the application of $V_d = -2V$ as shown in **Fig. 4(a)**. The I_{LED} -dependent ΔI_d property under LED source is shown in **Fig. 4(b)**. ΔI_d increased with increasing I_{LED} , indicating that the higher photon flux density enhance the photo current. It is also suggested that once GQD particles detect stronger photon density, it would enhance the current directly. It notes that periodic noise with interval of 1 s in **Fig. 4(a)** comes from pumping of the He-refrigerator. The V_d -dependent ΔI_d property under LED source is also shown in **Fig. 4(c)**, and the clear linear relationship can be observed, suggesting that GQD-based SET devices show high potential and promising prospect in photon detection.

In summary, we have demonstrated that microplasma-synthesized GQDs can be utilized as Coulomb island in SETs, which present clear SET characteristics. In addition, the devices would only present the multi-GQDs SET characteristics regardless of GQD density, note that it is a simple procedure to fabricate the SET devices using GQD. Furthermore, the increasing density of GQDs can improve the yield efficiently. On the other hand, the photon detector based on GQD-based SET devices is also explored. We find superior sensitivity and linear relationship between ΔI_d and I_{LED} , and between ΔI_d and V_d , respectively. The GQD-based SET devices show high potential and promising prospect in photon detection. Our work provides an effective method for SET fabrication and open a new avenue

for SET fundamental study and applications.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Figure captions

Fig. 1. (a) Low-magnified TEM and (b) HRTEM images of as-synthesized GQDs using microplasmas. (c) HRTEM image of one GQD with 0.21 nm graphene lattice. (d) SEM image of GQD-based SET device.

Fig. 2. (a) I_d-V_d characteristics of a fabricated SET with 20 drops of GQD solution under different gate voltages, the solid and dashed lines are consecutive forward and backward drain voltage sweeps, respectively. (b) I_d-V_g characteristics of the SET with 20 drops of GQD solution under applying different drain voltage. the solid dashed lines are consecutive forward and backward tri-gate voltage sweeps, respectively. (c) Stability diagram. (d) Differential current stability diagram.

Fig. 3 (a) I_d-V_d characteristics of a fabricated SET with 10 drops of GQD solution, the solid and dashed lines are consecutive forward and backward drain voltage sweeps, respectively. (b) I_d-V_g characteristics of the SET with 10 drops of GQD solution. the solid dashed lines are consecutive forward and backward tri-gate voltage sweeps, respectively. (c) I_d-V_d characteristics of a fabricated SET with 60 drops of GQD solution. (d) I_d-V_g characteristics of the SET with 60 drops of GQD solution

Fig. 4. (a) ΔI_d - time characteristics of a fabricated SET with 20 drops of GQD solution under different I_{LED} . (b) $\Delta I_d - I_{LED}$ characteristic. (c) $\Delta I_d - |V_d|$ characteristic. ΔI_d are the average value of ΔI_d within 17 s.

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Figures

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