Electronic Supplementary Information

Dual N-type Doped Reduced Graphene Oxide Field Effect Transistors Controlled by Semiconductor Nanocrystals

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Methods

1. Experimental methods

1.1 Materials

Natural graphite (Bay Carbon, SP-1 graphite), sulfuric acid (95-97%), hydrogen peroxide (30 wt. %), potassium permanganate, sodium nitrate, hydriodic acid (57 wt. %), hydrazine monohydrate, sodium bicarbonate, and acetic acid were obtained from commercial sources and used as received. Cadmium acetylacetonate (Cd(acac)$_2$, 99.9%), 1,2-hexadecanediol (HDDO, 90%), 1-hexadecylamine (HDA, 90%), 1-octadecene (ODE, 90%), sulfur (S, reagent grade), selenium (Se, 99.99%), trioctylphosphine oxide (TOPO, 90%) and Trioctylphosphine (TOP, 90%) were purchased from Sigma Aldrich. Diisooctylphosphinic acid (DIPA, 90%) was purchased from Fluka.

1.2 Characterization

Raman spectroscopy measurements were taken using a micro-Raman system (Renishaw, RM1000-In Via) with an excitation energy of 2.41 eV (514 nm). All X-ray photoemission spectroscopy (XPS) measurements were made by a Sigma probe (ThermoVG, U.K.) with a monochromatic Al-K X-ray source at 100 W. All I-V curves were measured by a probe-station (Keithley, U.S) at room temperature after the devices were dried in a vacuum oven at 80 °C for more than 8 h.

1.3 Preparation of graphene oxide (GO)

GO was prepared from natural graphite powder by the modified Hummer’s and Offenman’s method using sulfuric acid, potassium permanganate, and sodium nitrate.¹
1.4 Synthesis of QDs

1.4.1. Synthesis of spherical CdSe seeds

Synthesis of monodispersed CdSe NCs proceeded based on a previously reported procedure with slight modifications\textsuperscript{2}. A mixture bath of 9 g TOPO (90%), 6 g HDA and 0.25 ml of DIPA was degassed at 100°C for 1.5 h. A precursor solution comprising of 317 mg Cd(acac)\textsubscript{2} and 567 mg HDDO in 6 mL of ODE was degassed at 120°C for 1.5 h, followed by addition of 4 mL of 1.5 M trioctylphosphine selenide at room temperature. The precursor solution was then rapidly injected into the bath at 360°C and allowed to cool to 80 °C. As-synthesized CdSe QDs were subsequently processed by 3-4 cycles of precipitation in a butanol/ methanol mixture and re-dispersion in hexane for further use.

1.4.2 Synthesis of CdSe/CdS Core/Shell Nanocrystals

Processed CdSe QDs were dispersed in a minimum amount of hexane and their concentration was determined by measuring their absorbance at 350 nm, whose molar absorption coefficient is known\textsuperscript{3}. For shell deposition, CdSe stock solutions were prepared at a concentration of 0.00015 M, and injected to a mixture bath of 9 g TOPO (90%), 6 g HDA which was degassed at 120°C for 0.5 h. A precursor solution comprising of 180 mg Cd(acac)\textsubscript{2} and 300 mg HDDO in 6 mL of ODE was degassed at 130°C for 1.5 h, and 18.6 mg S in 6 ml ODE was degassed at 160 °C for 1.5 h. For continuous shell deposition, both precursors were injected into the reaction RBF containing previously prepared CdSe core at 240°C. The injection rate is 0.1ml/min. A total of 4 monolayers was grown.

1.5 Fabrication of GO-FET device and substrate

A GO solution of a concentration of 0.5 mg/ml in DI water was sonicated in a Branson 1510 ultrasonic bath cleaner for 1 h and then shaken at 200 rpm for 1 h. After standing for 1h, the
resulting solution was dropped onto the device (substrate) surface with a spin-coating method.\textsuperscript{4}

1.6 Reduction of GO FET to rGO FET

In a typical procedure, GO FET device was placed on a device-stand in a closed jar that contains 2.0 ml of HI and 5.0 ml of acetic acid. The cover glass was sealed with vacuum grease and placed in an oil bath at 40 °C for 24 h. This product was rinsed with a saturated sodium bicarbonate solution, water and acetone, and then dried in vacuum oven prior to the next steps in the synthesis.\textsuperscript{5}

1.7 Concentration of the QD solution

The concentration of the QD solution was determined by measuring the weight of the QDs after drying the solution in glass vials. It was difficult to calculate the concentration from the UV-vis spectra since the ligand was added after synthesizing the QDs. After making a homogenous solution, the supernatant was used to determine the concentration. In our condition, CdSe/CdS solution was 1.015 mg/ml.

1.8 Deposition of quantum dots on rGO surface

A common spin-coating method was introduced to form a homogenous film on the rGO surface. The QD solution was allowed to slowly mix with the substrate at a rotational speed of 4000 rpm by a dropwise procedure.
2. Characterization data

Figure S1. Typical TEM image of CdSe/CdS core/shell nanocrystals with size distribution histogram (inset).

Raman spectroscopy is an effective tool for inspecting the structures of carbon materials, in particular CNT, graphene and rGO. After doping with QDs on the rGO channel, both the D and G bands were red shifted. There were no significant changes in the ID/IG ratio (Electronic Supplementary Information, Figure S2).

In surface analysis, X-ray photoelectron spectroscopy (XPS) not only detected elements but also distinguished various bonds between the atoms and the surface. In XPS spectra of the QD-rGO samples, the carbon peak was fitted onto three Lorentzian peaks at 284.5 eV, 286.6 eV and 288.4 eV, which were very similar to those of the bare rGO on the substrate (Supplementary Information, Fig. S3, S4). After surface doping with QD nanocrystals, Cd, Se, and S peaks appeared without any changes in the C peaks.

Considering the Raman and XPS data, it appeared that surface doping had taken place by physisorption on the rGO surface without any further breakage of the sp² carbon in the graphene internal plane. The removal of the surface dopants was tested for repeatability. The reappearance of the ambipolar type I-V curve indicated that surface doping occurred due to physisorption, while the doping amount of the physically adsorbed QDs could be controlled (Fig. S7).
**Figure S2** Raman spectra of QDs deposited on the rGO and the bare rGO\textsubscript{Hi}. a) With doped QDs, the D band was downshifted from 1357.97 to 1349.47 ($\Delta D = 8.50$ cm$^{-1}$). The G band was downshifted from 1598.01 to 1592.55 ($\Delta G = 5.46$ cm$^{-1}$); b) the whole Raman spectra.

**Figure S3.** XPS spectra of C 1s in a) GO, b) rGO.
**Figure S4.** XPS spectra of the QDs (CdSe@CdS) deposited on the rGO, a) C 1$s$ spectra, b) no nitrogen, N 1$s$, c) Cd 3$d$ spectra, d) Se 3$d$ spectra.

**Figure S5.** UV-Vis absorption and room-temperature photoluminescence (PL) spectra of CdSe/CdS core/shell nanocrystals.
**Figure S6.** Off-current characterization of QD-rGO FET. The current increased when the gate voltage increased from -40 V to 40 V with a constant drain-source bias.

**Figure S7.** Changes of the I-V curves a) bare, b) with and c) without QDs on the rGO surface.

**Figure S8.** Reproducibility of n-type QD-rGO device right after processing (left) and after 6 months in the air (right) (device 3, channel 50-5-3).
Table S1. Mobilities of bare rGO FET device and QD RGO FET device

<table>
<thead>
<tr>
<th>Mobility</th>
<th>Hole mobility 10^-3 (cm^2/(V·S))</th>
<th>Electron mobility 10^-3 (cm^2/(V·S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
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<tr>
<td>Bare</td>
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<td>100 µl</td>
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References