

Supporting Information

All-Printable ZnO Quantum Dots/Graphene van der Waals Heterostructures for Ultrasensitive Detection of Ultraviolet Light

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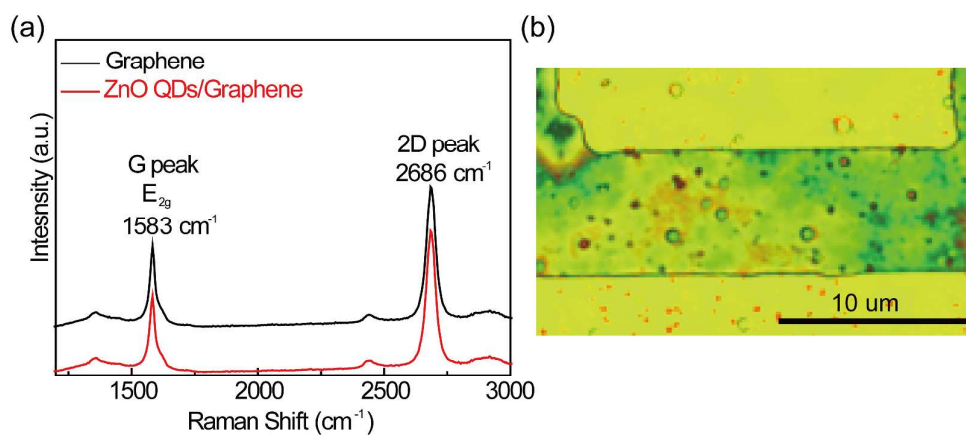


Figure S1. (a) Raman spectrum of the pristine monolayer graphene (black) and after ZnO QDs deposition; (b) Optical micrograph of the fabricated ZnO QDs/GFET device.

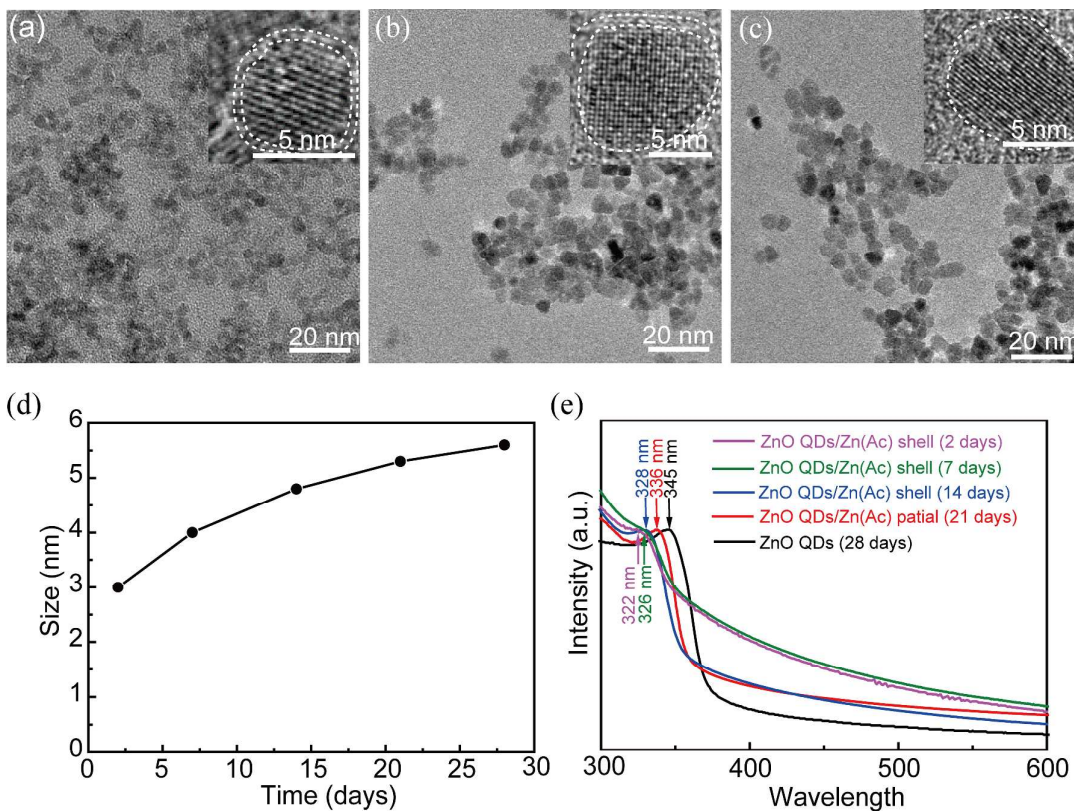
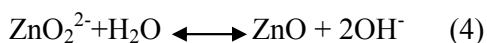
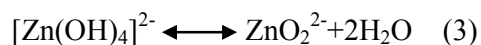
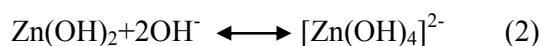
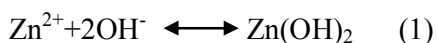


Figure S2. (a-c) The TEM images of ZnO QDs reaction at 4 °C for 14, 21 and 28 days of reaction or aging, respectively. The insets are high resolution TEM images on the corresponding samples, which indicate that the lattice fringes with spacing of 0.26 nm match the interspacing of (0002) planes of the wurtzite ZnO and illustrate high quality crystallinity obtained in all three ZnO QDs in the different aging stages. An amorphous shell (Zn(Ac)) on the ZnO QD was visible on samples at 14 days of aging, which becomes partial on the QD with 21 days of aging and invisible on the sample with 28 days of aging. (d) The size statistic of the ZnO QDs vs. the growth (aging) time. (e) The UV-abs spectrum of ZnO QDs corresponding to the different aging stages shown in (d).

The main reactions involved in the ZnO QDs growth:





At the very beginning, the Zn^{2+} and OH^- ions coordinate with each other, and then they form $\text{Zn}^{2+}-\text{O}^{2-}-\text{Zn}^{2+}$ bonds by dehydration, giving rise to an agglomerate of the form of $[\text{Zn}_x(\text{OH})_y]^{(2x-y)+}$ of octahedral geometry. In this dehydration process, H_2O was forming and migrating into the solution. These aggregates typically comprise fewer ions (<50), and the formation of O^{2-} ions implies dramatic changes within the aggregates. When the aggregates of ions reach an critical value ~ 150 ions, wurtzite type ZnO domains nucleated in the central region of the aggregates.¹ The central domains comprises Zn^{2+} and O^{2-} ions only, while the surfaces of these aggregates still consists of Zn^{2+} and OH^- ions. This study attested the unreacted $\text{Zn}(\text{Ac})$ and the intermediate $[\text{Zn}_x(\text{OH})_y]^{(2x-y)+}$ capped on the surface of small ZnO QDs and formed an insulating shell layer that blocks the charge transfer from ZnO QDs to graphene.

Fig. S2 (a-c) demonstrates the ZnO QDs evolution process. The hydrolysis of $\text{Zn}(\text{Ac})$ provides the nucleation and growth source of ZnO QDs, simultaneously, they absorb on the surface of the new nuclei crystals and seal the core (Fig. S2(a)). The aging time promotes the ZnO QDs growth and consume the $\text{Zn}(\text{Ac})$ source, and dramatically decrease this seal (Fig.S1(b)) until disappear (Fig.S2(c)). Fig. S2(d) records the size development of ZnO QDs vs the aging days. Fig. S2(c) depicts the transmission electron microscopy (TEM) images of the ZnO QDs for this work with a highly uniform rounded shape and an average dimension of 5.6 nm with a narrow size distribution as shown in Fig. S2(b). The inset of Fig. S2(c) is a high resolution TEM image of a ZnO QD. The lattice fringes with d-spacing of 0.26 nm match well the interspacing of (0002) planes of the wurtzite ZnO and illustrate high quality crystallinity in the ZnO QDs obtained. This is consistent with the sharp optical absorption band edge at about 345 nm, which corresponds to the bandgap of 3.59 eV in the absorption spectra of ZnO QDs in solution shown in Figure S2(e). The slight blue shift of the bandgap with respect to that of bulk ZnO at 3.35eV at room temperature is anticipated from the quantum confinement in ZnO QDs. Importantly, the absorption in visible spectrum is negligible, indicating minimal impurities and defects in the ZnO QDs. This is the key to

achieving wavelength selectivity in UV detection without visible interference.

During the growth of ZnO QDs it was noted that the hydrolysis of Zn(Ac) required long aging time under low temperature of 4 °C. The initial step in synthesis of ZnO QDs consisted of the creation of ZnO nucleus, which were suspended and encapsulated in the Zn(Ac) surroundings and grew by successive absorption and hydrolysis of Zn(Ac). Therefore, crystallinity selective precipitation of ZnO QDs was attempted. This process has up to now scarcely been described in detail, whereas it is demonstrated a useful way to improve the crystallinity and to reduce the surface insulator layer residues. Different aging times of precipitates were selected and the QDs were adequately washed by ethanol/hexane mixture solution after aging process finished. Fig. S2 demonstrates the characterization of ZnO QDs at different aging stages. After two weeks of aging time, the ZnO QDs were still sealed by an amorphous shell (Zn(Ac) as shown in Fig. S2(a). With the aging time of three weeks, this shell partially covered the ZnO QDs (Fig. S2(b)) and the four weeks aging time seemed adequate to completely remove the insulating shell as depicted in Fig. S2(c). Based on this analysis, representative ZnO QDs from these three stages were selected to study the optoelectronic properties in ZnO QD/GFET devices. It has been found the insulating residual shell on the surface of the QD dramatically influenced the charge transfer and therefore the performance of the device.

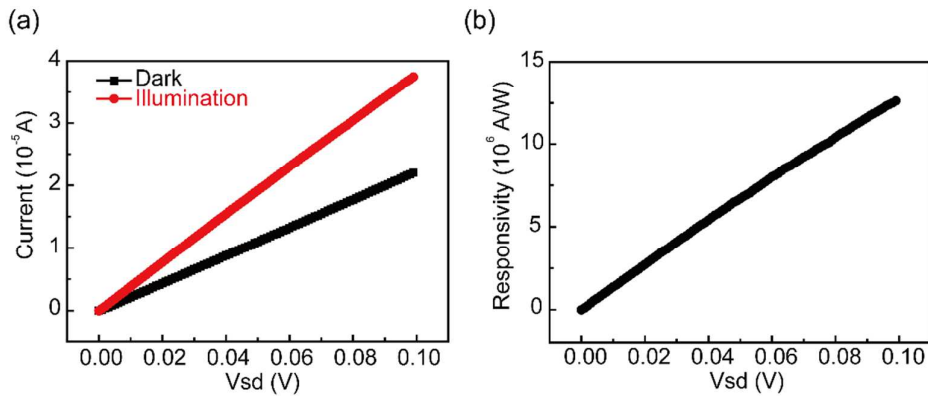


Figure S3. (a) I-V curves for ZnO QDs/GFET device under dark and illumination ($2.5 \mu\text{W}/\text{cm}^2$, 340 nm). The GFET channel size $4.3 \mu\text{m} \times 11.4 \mu\text{m}$. (b) Photoresponsivity as a function of bias voltage.

Reference

- (1) Xu, S.; Wang, Z. L. One-Dimensional ZnO Nanostructures: Solution Growth and Functional Properties. *Nano Res.* **2011**, *4*, 1013-1098.